A TALE OF FOUR CAVES

# A TALE OF FOUR CAVES: ESR DATING OF MOUSTERIAN LAYERS AT IBERIAN ARCHAEOLOGICAL SITES

 $\mathbf{B}\mathbf{Y}$ 

### VITO VOLTERRA, M. A.

A Thesis Submitted to the School of Graduate Studies In Partial Fulfillment of the Requirements For the Degree Doctorate of Philosophy

McMaster University

© Copyright by Vito Volterra, May, 2000

## DOCTORATE OF PHILOSOPHY (2000) (Anthropology)

McMaster University Hamilton, Ontario

- TITLE: A Tale of Four Caves: ESR Dating of Mousterian Layers at Iberian Archaeological Sites
- AUTHOR: Vito Volterra, M. A. (McMaster University)
- SUPERVISOR: Professor H. P. Schwarcz
- NUMBER OF PAGES: xviii, 250

## Abstract

This study was undertaken to provide supporting evidence for the late presence of Neanderthals in Iberia at the end of the Middle Paleolithic. This period is almost impossible to date accurately by the conventional radiocarbon method. Accordingly electron spin resonance (ESR) was used to obtain ages for four Spanish sites. They were El Pendo in the Cantabrian north, Carihuela in Andalusia and Gorham's and Vanguard caves at Gibraltar. The sites were chosen to allow the greatest variety in geographic settings, latitudes and sedimentation. They were either under excavation or had been excavated recently following modern techniques. A multidisciplinary approach to dating the archaeological contexts was being proposed for all the sites except El Pendo whose deposits had been already dated but only on the basis of sedimentological and faunal analyses. This was the first research program to apply ESR to such a variety of sites and compare its results with that of such a variety of other archaeometric dating techniques.

The variety allowed a further dimension to the research that is the opportunity of appraising first hand the applicability and advantages of a new dating technique and determining its accuracy as an archaeological dating method in comparison with other techniques.

Test samples for the research were collected at the sites as well as at the Museo de Ciencias Naturales in Madrid and the Gibraltar Museum.

The ESR results for El Pendo provide a terminus post quem of 31 Ka for the presence of the Neanderthal at the site. Those for Carihuela permit the Neanderthal skeletal remains found in layers V and VI to be dated between 45 ka and 74 ka and between 67 ka and 86 ka respectively. The data also confirm the late presence of the Neanderthals in Andalusia. The results for the Gibraltar final Mousterian layer also confirm the presence of Neanderthals in southern Spain at  $36.9 \pm 5$  to  $40.3 \pm 5$  ka.

While there are a number of secure dates for early Aurignacian deposits in Spain the results of the present research provide the first solid evidence of the late presence of *Homo* sapiens neanderthalensis in the Iberian Peninsula.

Furthermore, from the data collected it can also be concluded that the ESR method is accurate and eminently suitable for dating archaeological contexts.

I am very grateful for the guidance, understanding, continued warm support and empathy of the members of my committee Dr. Peter Ramsden, Dr. Jack Rink and especially of Dr. Henry Schwarcz and the Chair of the Department of Anthropology Dr. Ann Herring. In fact the entire Anthropology Department Faculty and staff (Janis Weir, Rosita Jordan and not to be forgotten Cookie Brymer) have made working with them a most interesting and enriching pleasurable experience. My thanks go also to Prof. E. Rinehardt for consenting to participate in my defense at such short notice. I wish also to acknowledge the assistance and warm empathy of Professor David Counts without whose support the project would not even have started.

My thanks are also extended to Jean Johnson whose patience, assistance and good advice proved invaluable. It was Jean that processed all the samples through INAA and prepared some of the Gorham's cave samples for irradiation. I am also grateful to Dr. Daniel Richter for his keen interest and cheerful comments and Dr. John Harvey for the extensive use of the Panasonic reader.

I would like to thank Dr. Nick Barton, Dr. Andy Currant, Dr. Clive Finlayson, Ramon Montes Barquino, Juan Sanguino Gonzales, Prof. Chris Stringer, Dr. Gerardo Vega Toscano and his wife Belen for their assistance with various aspects of the sample collection and for their generous hospitality at site. The free, open discussions and the interchange of ideas with them has proved a refreshing learning experience that has enriched my knowledge of the Neanderthal question and of the Paleolithic. I am equally indebted to the Museo de Ciencias Naturales of Madrid and the Gibraltar Museum for permitting me to use teeth from their permanent collections.

But foremost thanks go to my wife Gail who put up with my erratic work habits and my repeated travel to Spain as well as with extended hogging of the family computers

This research was funded with travel grants from the North Atlantic Treaty Organization to Dr., H. P. Schwarcz, in collaboration with Dr. W. J. Rink, Dr. V. Cabrera Valdes and Dr. F. Bernaldo de Quiros.

# Table of Contents

| ABSTRACTPage                                     | iii |
|--|-----|
| ACKNOWLEDGEMENTSPage                             | iv  |
| TABLE OF CONTENTSPage                            | v   |
| LIST OF TABLES                                   | xi  |
| LIST OF FIGURES                                  | xii |
| CHAPTER 1: INTRODUCTION                          |     |
| 1 - IntroductionPage                             | 1   |
| CHAPTER 2: THE EVOLUTION QUESTION                |     |
| 2 - The evolution questionPage                   | 5   |
| CHAPTER 3: DATING                                |     |
| 3 - DatingPage                                   | 12  |
| CHAPTER 4: ESR DATING                            |     |
| 4 - ESR datingPage                               | 15  |
| 4.1 Factors affecting ESR age determinationsPage | 29  |
| CHAPTER 5: CAVE ENVIRONMENTS                     |     |
| 5 - Cave environmentsPage                        | 32  |
| CHAPTER 6: TEETH                                 |     |
| 6 - TeethPage                                    | 33  |
| 6.1 Uranium uptake modelsPage                    | 35  |
| 6.2 Other considerationsPage                     | 38  |
| CHAPTER 7: EFFECTS OF SAMPLE PREPARATION         |     |
| 7 - Effects of sample preparationPage            | 40  |
| CHAPTER 8: ESR APPLICATIONS                      |     |
| 8 - ESR applicationsPage                         | 41  |

## **CHAPTER 9: PHYSICAL CONTEXT**

| 9 - Physical contextPage 4  | 47 |  |  |
|---|----|--|--|
| 9.1 GeneralPage 4   | 47 |  |  |
| 9.2 Geography and geologyPage 49                                      | 9  |  |  |
| 9.2.1 CantabriaPage 5   | 3  |  |  |
| 9.2.3 PenebeticaPage 56   | 6  |  |  |
| 9.2.4 GibraltarPage 60  | 0  |  |  |
| 9.3 Past ecologyPage 60   | 0  |  |  |
| CHAPTER 10: ARCHAEOLOGICAL CONTEXT                                    |    |  |  |
| 10 - Archaeological contextPage 6                                     | 6  |  |  |
| 10.1 Archaeological activitiesPage 6                                  | 66 |  |  |
| 10.1.1 The northern sitesPage 6                                       | 6  |  |  |
| 10.1.2 The southern sitesPage 7                                       | 2  |  |  |
| CHAPTER 11: ARCHAEOLOGICAL STRATA AND EXCAVATED MATERIAL              |    |  |  |
| 11 - Archaeological strata and excavated materialPage 8               | 34 |  |  |
| 11.1 Archaeological strataPage 8                                      | 34 |  |  |
| 11.1.1 El CastilloPage 8  | 84 |  |  |
| 11.1.2 El PendoPage 8   | 15 |  |  |
| 11.1.3 CarihuelaPage 82   | 7  |  |  |
| 11.1.4 Gorham's cavePage 9  | 3  |  |  |
| 11.1.5 Vanguard cavePage 9  | 9  |  |  |
| CHAPTER 12: PROCEDURES  |    |  |  |
| 12 - ProceduresPage 10  | 2  |  |  |
| 12.1 DosimetryPage 10   | )2 |  |  |
| 12.2 CaF <sub>2</sub> phosphorPage 10                                 | )3 |  |  |
| 12.3 Copper capsules for field dosimetry and their preparationPage 10 | 14 |  |  |
| 12.4 Emplacing and retrieving CaF <sub>2</sub> capsulesPage 10        | 6  |  |  |
| 12.5 Panasonic dosimetersPage 10                                      | 7  |  |  |

| 12.6 Emplacing Panasonic dosimeters in the fieldPage 107   |  |
|--|--|
| 12.7 Retrieving dosimeters from the fieldPage 110          |  |
| 12.8 Reading the $CaF_2$ dosimetersPage 110                |  |
| 12.9 Dose rate calculationsPage 111                        |  |
| 12.10 Sample collectionPage 114                            |  |
| 12.10.1 Field collectionPage 114                           |  |
| 12.10.1.1 Tooth and sediment collectionPage 114            |  |
| 12.10.1.2 Procedures for Recovery of In-Situ TeethPage 115 |  |
| 12.10.1.2.1 Recognition of teeth and locationPage 115      |  |
| 12.10.1.2.2 Recovery of teethPage 116                      |  |
| 12.10.1.2.3 General commentsPage 118                       |  |
| 12.10.1.3 Moisture samples collectionPage 119              |  |
| 12.10.2 Museum sample collectionPage 119                   |  |
| 12.10.2.1 SedimentsPage 120                                |  |
| 12.10.2.2 Preservatives and storage environmentPage 120    |  |
| CHAPTER 13: SAMPLE PREPARATION                             |  |
| 13 - Sample preparationPage 122                            |  |
| 13.1 Removal apparatusPage 122                             |  |
| 13.2 Tooth numbering and identificationPage 122            |  |
| 13.3 Tooth preparationPage 124                             |  |
| 13.3.1 Choosing and photographing samplesPage 127          |  |
| 13.4 Cutting samplesPage 128                               |  |

| 13.3 | Tooth preparationPage                           | 124  |
|------|---|------|
|      | 13.3.1 Choosing and photographing samplesPage   | 127  |
| 13.4 | Cutting samplesPage                             | 128  |
| 13.5 | Preparation of enamel, dentine and cementumPage | 128  |
| 13.6 | UGC analysisPage                                | 130  |
| 13.7 | IrradiationPage                                 | 133  |
| 13.8 | ESR spectrometryPage                            | 9133 |
|      | 13.8.1 Sample density vs. intensity signalPage  | 138  |
|      | 13.8.2 Effect of particle sizePage              | 140  |
|      |   |      |

|                    | 13.8.3 Effects of crystal orientation           | Page 141 |
|--------------------|---|----------|
|                    | 13.8.4 Effect of sample position within the     |          |
|                    | spectrometer cavity                             | Page 143 |
|                    | 13.8.5 Experimental repeatability               | Page 144 |
|                    | 13.8.6 D <sub>e</sub> Calculations              | Page 145 |
|                    | 13.8.7 Age determination                        | Page 145 |
| CHAPTER 14: THE FI | ELD WORK  |          |
| 14 - Field w       | ork and site visits                             | Page 149 |
| 14.1               | El Castillo Cave                                | Page 149 |
| 14.2               | El Pendo Cave                                   | Page 150 |
| 14.3               | Carihuela Cave                                  | Page 150 |
| 14.4               | Gorham's Cave                                   | Page 153 |
| 14.5               | Vanguard Cave                                   | Page 155 |
| CHAPTER 15: THE LA | BORATORY WORK                                   |          |
| 15 - Laborat       | ory work  | Page 158 |
| 15.1               | Dosimeters                                      | Page 158 |
|                    | 15.1.1 "Lumpy" and homogeneous sediments        | Page 159 |
| 15.2               | Tooth preparation                               | Page 161 |
| 15.3               | Sediments                                       | Page 162 |
| 15.4               | Determination of D,'s by Universal Growth Curve | Page 163 |
| 15.6               | Irradiation                                     |          |
| 15.7               | Spectrometer Measurement                        | Page 165 |
| CHAPTER 16: THE ES | RAGES   | Ũ        |
| 16 - ESR da        | tes   | Page 166 |
|                    | 16.1 El Pendo                                   | Page 166 |
|                    | 16.2 Carihuela                                  | Page 170 |
|                    | 16.3 Gorham's Cave                              | Page 173 |
|                    | 16.4 Vanguard Cave                              |          |
|                    | <b>v</b>  | 0        |

### **CHAPTER 17: CONCLUSIONS**

| 17 -       | - Conclusions   | Page 178 |
|------------|---|----------|
| APPENDICES |   |          |
| Ap         | pendix A  | Page 182 |
|            | Protocol for field gamma spectrometer readings              | Page 183 |
|            | Protocol for annealing CaF <sub>2</sub> phosphor            | Page 184 |
|            | Protocol for making CaF <sub>2</sub> dosimeters             | Page 186 |
|            | Protocol for preparing Panasonic dosimeters for the field   | Page 188 |
|            | Protocol for reading and zeroing Panasonic Dosimeters       | Page 189 |
|            | Protocol for preparing TL cupels                            | Page 191 |
|            | Protocol for establishing laboratory beta dose for          |          |
|            | CaF <sub>2</sub> dosimeters                                 | Page 193 |
|            | Detailed procedure for measuring TL phosphors               | Page 194 |
|            | Protocol for cleaning TL cupels                             | Page 199 |
|            | Reconciling measured dosimeter doses and doses              |          |
|            | calculated from sediments                                   | Page 200 |
|            | Collection of moisture samples and moisture measurement     | Page 205 |
|            | Teeth cutting   | Page 206 |
|            | Enamel, dentine and cementum prepration                     | Page 207 |
|            | Crushing dentine and cementum                               | Page 209 |
|            | Crushing enamel   | Page 210 |
|            | Protocol for UGC analysis                                   | Page 212 |
|            | Protocol for the operation of the ESR spectrometer          | Page 214 |
| Ap         | pendix B  | Page 219 |
|            | Gamma irradiation protocol: start-up procedure              | Page 220 |
|            | Protocol for obtaining the average doserate and calculating |          |
|            | the correction factor                                       | Page 221 |
|            | Protocol for irradiation of ESR samples                     | Page 224 |

•

| Appendix C   | Page 228 |
|--|----------|
| Levels of laboratory irradiation for each set of samples | Page 229 |
| U, Th, K levels in ESR samples                           | Page 230 |
| REFERENCES CITED   |          |

.

# List of Tables

| Table I . Effect of sample density on intensity signal                       | Page  | 140 |
|--|-------|-----|
| Table II . Effect of sample crystal size on $D_{_{e}}$                       | Page  | 141 |
| Table III .Effect of crystal orientation on measured intensity               | Page  | 142 |
| Table IV .Effect of sample position within the spectrometer cavity           | Page  | 143 |
| Table V . ESR spectrometer test repeatability                                | Page  | 144 |
| Table VI . γ ray field spectrometer reading at Gorham's cave                 | Page  | 154 |
| Table VII . Carihuela site - Comparison of ages based on radiation           |       |     |
| doses determined by sediment elemental analysis and by                       |       |     |
| site dosimetry   | Page  | 160 |
| Table VIII . Gorham's Cave - Comparison of ages based on radiation           |       |     |
| doses determined by sediment elemental analysis and by site                  |       |     |
| dosimetry  | Page  | 161 |
| Table IX . INAA Analyses results for typical sediments                       | Page  | 163 |
| Table X . Comparison of UGC $\mathrm{D_{e}}$ and measured $\mathrm{D_{e}}$   | Page  | 164 |
| Table XI . El Pendo cave - results of ESR analyses                           | .Page | 167 |
| Table XIIa . Carihuela cave - Results of ESR analyses                        | Page  | 170 |
| Table XIIb . Carihuela cave - Results of ESR analyses                        | .Page | 171 |
| Table XIII . Gorham's Cave - ESR ages for in-situ teeth                      | .Page | 173 |
| Table XIV . Gorham's Cave - ESR ages for the Samples from Gibraltar's Museum | Page  | 174 |
| Table XV . Vanguard Cave - ESR ages  | .Page | 176 |
| Table XVI . ESR ages of Mousterian layers at Iberian sites                   | Page  | 180 |
| Table XVII . Effect of moisture concentration on ESR dates                   | .Page | 181 |
| Table XVIII . Levels of laboratory irradiation for each set of samples       | Page  | 229 |
| Table XIX . U, Th, K levels in ESR samples                                   | Page  | 230 |

# List of Figures

| Figure 3.1:  | Comparison of Quaternary geochronological dating methods  | Page | 14 |
|--------------|---|------|----|
| Figure 4.1:  | Showing the mechanism of unpaired electron trapping in crystal lattices. (a) - Radiation displaces an electron from the valance |      |    |
|              | band moving it into the conduction band where, after a while,   |      |    |
|              | it drops into a trap. (b) - An alternative way at the phenomenon  |      |    |
|              | is that radiation imparts enough energy on an electron so that it   |      |    |
|              | can move around in the crystal lattice until it falls into a tran   | Page | 18 |
| Figure A 2.  | Illustration of the dimension of the regions which contribute   | идо  | 10 |
| rigute 4.2.  | significantly to the radiation does reaching a sample and of  |      |    |
|              | the processes and factors which control the decorate Only   |      |    |
|              | these or particles originating within a 25 m radius, these 8  |      |    |
|              | mose a particles originating within a 25 in radius, mose p  |      |    |
|              | particles within a 2 mm radius and $\gamma$ rays within a 30 cm radius  |      |    |
|              | will contribute to the dose absorbed by the sample. Cosmic rays   |      |    |
|              | also make a small contribution which is affected by latitude,   |      |    |
|              | altitude and burial depth.  | Page | 20 |
| Figuro 4.2   | Schematic display of homogeneous (a) and lumpy sodiments (b)  |      |    |
| r igute 4.5. | Note the impact of shouling on the 20 am effective range of a   |      |    |
|              | Note the impact of ebound on the 50 cm enective large of y  | Dees |    |
|              | radiation.  | Page | 22 |
| Figure 4.4:  | Schematic of an ESR spectrometer. The ESR sample is placed  |      |    |
| 0            | in the cavity between the magnets. The recorder captures the  |      |    |
|              | derivative of the intensity signal. The Bruker apparatus used   |      |    |
|              | for the tests is entirely computer controlled   | Page | 25 |
|              | for the total is enthery computer controlled.   |      | 20 |
| Figure 4.5:  | Typical ESR signal from tooth enamel. The vertical scale  |      |    |
| Ũ            | measures the ESR intensity signal in arbitrary units and the  |      |    |
|              | horizontal scale measures g value.  | Page | 26 |
|              | 0   | 0    |    |
| Figure 6.1:  | Types of mammal teeth - $A =$ human; $B =$ camel; $C =$ elephant.   |      |    |
|              | At archaeological sites enamel can be recovered from whole  |      |    |
|              | teeth or as individual pieces (D), as tooth parts (E), or as enamel   |      |    |
|              | within multiple layers of dentine (F). Note that individual pieces  |      |    |
|              | of enamel (D) would be recovered only in cases where extreme  |      |    |
|              | acidity dissolved all other organics.   | Page | 34 |
|              | J   |      |    |

| Figure 6.2: | Uranium uptake models. Uranium uptake in enamel, dentine<br>and cementum is a gradual process. The two limiting cases are<br>expressed by EU = early uptake and RU = recent uptake. Algebra-<br>ically this is expressed by the equation $u_t/U_T = (t/T)^{(P+1)}$ where:<br>$u_t$ is the uranium concentration at any time t; $U_T$ is the final<br>uranium concentration; T is the age of the ESR sample; P is a<br>parameter reflecting the rate of uptake at any time t. The linear<br>uptake model (LU), with a constant uptake, corresponds to the<br>value P=0. The limiting conditions are represented by P= -1<br>and P= $\infty$ for EU and RU respectively | 37 |
|-------------|---|----|
| Figure 8.1: | Ages determined by ESR for archaeological levels compare<br>quite favourably with those obtained through other scientific<br>dating methodsPage   | 42 |
| Figure 9.1: | Iberian Mousterian sites and sites of early Upper Paleolithic<br>occupation. A majority of Iberian Mousterian sites [indicated<br>with the symbol (=)] have been discovered inside caves located<br>on the periphery of the peninsulaPage   | 48 |
| Figure 9.2: | Outline of the dominant surface rocks in the Iberian peninsula<br>showing the extent of limestone deposits. Large areas of Iberia<br>display karstic phenomena rich in caves  | 50 |
| Figure 9.3: | Tectonic upheaval during the Tertiary period formed the<br>mountain ranges which include the Pyrenees and the Sierra<br>Nevada. The Mesa plateau which extends between these ranges<br>was protected from major folding during the Tertiary by the<br>massive underlying rocks of the ancient Hercynian continentPage   | 52 |
| Figure 9.4: | Map of the Iberian peninsula showing major river systems and elevations above 1000 mPage  | 54 |
| Figure 9.5: | Simplified relief map of Cantabrian Spain. The narrow coastal<br>plain is intersected by fast flowing streams from the Sierra<br>Cantabrica. During glacial maxima the shoreline would have<br>been displaced only 8-12 km to the north due to the deep<br>narrowness of the continental shelf  | 55 |
| Figure 9.6: | Late Middle early Upper Paleolithic sites in Cantabrian Spain:<br>8 = El Castillo; 9 = El Pendo; 10 = Cueva Morin. Access to<br>the area would have been along the Ebro river valley or through<br>the narrow gap between the Pyrenees and the sea east of the<br>Biderer eigen   |    |
|             | bidesoa river   | 57 |

| Figure 9.7:    | Geology of the Betic Cordillera showing the extensive deposits<br>of Triassic limestone. Carihuela cave, northeast of Granada,<br>and Gorham's and Vanguard caves, at Gibraltar, have been   |    |
|----------------|--|----|
|                | formed in Triassic limestone depositsPage  | 59 |
| Figure 9.8:    | The Rock of Gibraltar. Petrographic and stratigraphic analysis<br>has indicated that the uplifted limestone massif is part of a<br>lower Tertiary fold which extends south of the straight into<br>Jebel Sidi Musa in Morocco. Gorham's and Vanguard caves<br>are located on the eastern side of the peninsulaPage | 61 |
| Figure 9.9:    | Global sea level changes of the past 125,000 years. Sea level is<br>shown as below current datum. At the beginning of oxygen<br>isotope stage 5 the sea surface was approximately 10 m. below<br>the present level   | 64 |
| Figure 10.1: E | Castillo cave - above = plan; below stratigraphy. Lower<br>and Middle Paleolithic layers are shown in the section as<br>levels 20 to 26. Layer 18 is the basal Aurignacian   | ,  |
| Figure 10.2: T | he El Pendo cave, section showing the location from which<br>the ESR samples were collected. The well originally excavated<br>by Echegaray was expanded northward by Montes and Sanguino.<br>Horizontal scale = vertical scale   | 69 |
| Figure 10.3:   | The El Pendo cave plan, showing the location from which<br>the ESR samples were collected. Contour intervals are 1 m.<br>(descending 0 to 47)Page  | 70 |
| Figure 10.4:   | The El Pendo cave, showing the Echegaray stratigraphy and<br>the corresponding Montes/Sanguino layers. Montes and<br>Sanguino extended northward the well containing Echegaray's<br>levels XVI to XVIII and identified 8 separate layers A to H.<br>The ESP camples were recovered from the latter.                | 71 |
| Figure 10.5:   | Carihuela cave. Section showing the areas excavated by Spahni,<br>Washington State University and Vega ToscanoPage   | 73 |
| Figure 10.6:   | Carihuela cave plan showing the areas excavated by Spahni,<br>Washington State University and Vega Toscano. The ESR<br>samples came from the 2x2 m. excavations by Washington<br>State and Vega Toscano. Contours are 1 m. intervals   |    |
|                | [descending 0 to 4 m.]Page   | 74 |

•

,

| Figure 10.7:  | Carihuela cave, stratigraphy of the east wall of the Washington<br>State University excavation. The layers shown contain Mousterian<br>industries. All the ESR samples for level V came from this<br>area at the entrance to the cave. Sediments are light to dark<br>brown silty clay and eboulis is limestone                   | 75 |
|---------------|---|----|
| Figure 10.8:  | Carihuela cave. Stratigraphy of the north wall of the Vega<br>Toscano excavation. The levels contain Mousterian industries.<br>All ESR samples for level VII came from this area. Sediments<br>are light to dark brown silty clay and eboulis is limestonePage  | 77 |
| Figure 10.9:  | Carihuela cave. The cave contains 12 levels with rich lithic<br>industries ranging from Middle to Upper Paleolithic. What<br>makes this site important is not only the long archaeological<br>sequence but the fact that human remains have been recovered<br>from 5 living floors  | 78 |
| Figure 10.10: | Gorham's cave. Details of Waechter's excavation plan.<br>The lowest depth reached by the 1948-50 excavation was<br>level N. The excavation was amplified but not deepened<br>during the 1951-52 campaigns. Layer U was reached only<br>in the 1953-54 season. Contour intervals are 1 m. over sea levelPage                       | 79 |
| Figure 10.11: | Gorham's cave. Waechter's stratigraphy. The ESR museum<br>samples were tagged as prevenient from Waechter's layers<br>G, K, M, P, RPage   | 80 |
| Figure 10.12: | Gorham's cave, Stringer's excavation stratigraphy. Two areas<br>have been excavated by Stringer. Area I was cut into the<br>vertical face left by Waechter at the rear of the cave. Area II<br>was excavated further eastward in the cave interior through<br>what is assumed to coincide with the floor of Waechter's<br>level H | 81 |
| Figure 10.13: | Vanguard cave, Plan and stratigraphy. The original E-W<br>trench in Vanguard south intercepted two living floors which<br>were subsequently excavated. Sample ESR 7 was recovered<br>from the trench below level 105 at elevation -6.14 m   | 83 |
| Figure 11.1:  | El Pendo cave. Composite photograph of the north wall of<br>the Montes/Sanguino excavation. Levels A to H are clearly<br>visible  | 88 |

| Figure 11.2: | El Pendo cave. The Montes/Sanguino stratigraphy.<br>This excavation extends northward the original well dug by<br>Echegaray. The black dots indicate the location of the dosimetersPage   | 89  |
|--------------|---|-----|
| Figure 11.3: | Carihuela cave. View of the interior looking south. Visible is the south wall of Spahni's excavationPage  | 91  |
| Figure 11.4: | Carihuela cave. Proposed climatic sequence based on results<br>of floral and faunal analyses. From the period in which level<br>X started to be deposited the cave has been subjected mainly<br>to dry conditionsPage   | 92  |
| Figure 11.5: | Carihuela cave. View of the interior looking north. Visible<br>is the north wall of Spahni's excavation [at bottom of picture].<br>Washington State University's work was carried out north<br>of the area excavated by Spahni [visible at top of picture]Page  | 94  |
| Figure 11.6: | Gorham's cave, west wall of upper section of Area "A" . These<br>layers were assumed to correspond to E to J in the Waechter<br>stratigraphy. Gamma spectrometer readings were taken in<br>this area at locations shown as Gam 2 to Gam 6Page   | 96  |
| Figure 11.7: | Gorham's cave. West wall of lower section of area "A".<br>These layers were assumed to correspond with levels I to M<br>in the Waechter stratigraphy. One gamma spectrometer reading<br>was taken at the location shown as Gam 7. Dosimeter TLD 1<br>was emplaced in layer M  | 97  |
| Figure 11.8: | Vanguard cave. A = Vanguard South, plan of layer 106<br>showing the location of TLD 1. The excavation did not<br>extend to the cave walls; B = Vanguard North, plan of layer<br>1102 showing the location of the ibex tooth find and of<br>dosimeter TLD 4. The dosimeter was placed 2 m. from the<br>spot from which the tooth was recovered | 101 |
| Figure 12.1: | $CaF_2$ dosimeter capsules at various stages of processing. The copper tubing is crimped at one end and soldered. It is then filled with the phosphor and the open end is crimped and soldered. Page  | 105 |
| Figure 12.2: | Panasonic dosimeters. The frame containing the phosphor<br>(at right) is inserted in a plastic holder for normal laboratory<br>handling and storage (top and left)Page  | 108 |

| Figure 12.3:  | Panasonic dosimeters and their burial capsules. The frames<br>containing the phosphor are wrapped in plastic film and<br>placed inside copper tubing capsules. The latter are sealed<br>at both ends by means of copper caps secured with silicone  |      |     |
|---------------|---|------|-----|
|               | cement.   | Page | 109 |
| Figure 12.4:  | TL apparatus. The McMaster Quaternary Dating Laboratories'<br>Daybreak 1100 automated system utilising a Thorn EMI<br>electron tube type 923500.  | Page | 112 |
| Figure 13.1:  | Tools for enamel preparation. A dentist drill is armed with<br>a thin diamond saw blade (as shown) or with special grinding<br>bits (below the drill in the photograph).  | Page | 123 |
| Figure 13.2:  | Teeth master data sheet.  | Page | 125 |
| Figure 13.3:  | ESR tooth data sheet.   | Page | 126 |
| Figure 13.4:  | Tooth enamel after stripping of external and internal 40 $\mu$  | Page | 129 |
| Figure 13.5:  | ESR enamel aliquots after weighing and their storage vials  | Page | 131 |
| Figure 13.6:  | Universal growth curve.   | Page | 132 |
| Figure 13.7:  | Irradiation worksheet.  | Page | 134 |
| Figure 13.8a: | Typical ESR spectrum as printed by the spectrometer. Intensity<br>is measured peak-to-peak as shown but the measurement is<br>carried out directly on the apparatus monitor screen. When<br>the noise to signal ratio is high the reading is taken through<br>the middle of the signal at the peaks. Compare this printed<br>spectrum with the spectra as actually seen on the apparatus<br>monitor (Figure 13.8b). | Page | 136 |
| Figure 13.8b: | ESR intensity spectra as seen on the apparatus monitor screen.<br>The upper photograph represents a natural signal, the lower<br>photograph a signal after laboratory irradiation.  | Page | 137 |
| Figure 13.9:  | McMaster Quaternary Dating Laboratories' Bruker EMX EPR<br>spectrometer utilizing a Bruker ER 041XG microwave bridge<br>(x-Band) coupled to a Patriot M5100P processor.   | Page | 139 |
| Figure 13.10: | D <sub>e</sub> calculations. Output from the McMaster Quaternary Dating<br>Laboratories' Vfit program.  | Page | 146 |

| Figure 13.11a: | Age calculation. Printout from the McMaster Quaternary<br>Dating Laboratories' ROSY 1.3 program. All age calculations<br>were performed using this version of the ROSY program.<br>This figure shows the data input; for calculated ages see  |     |
|----------------|---|-----|
|                | Figure 13.11bPage   | 147 |
| Figure 13.11b: | Age calculation. Printout from the McMaster Quaternary<br>Dating Laboratories' ROSY 1.3 program. All age calculations<br>were performed using this version of the ROSY program.<br>This figure shows the ages calculated from the input shown |     |
|                | on Figure 13.11aPage  | 148 |

Subdiviser un cours d'événements continûment en évolution est assurément toujours un artifice. F. Bordes, 1968

### **CHAPTER 1. INTRODUCTION**

There is considerable uncertainty regarding all of prehistory. Particularly confusing appears to be the period from 200 kya to 30 kya which saw the emergence of modern humans. Their arrival on the European continent seems to have coincided with the extinguishing of the local population which preceded them. A better chronological analysis of sites which were occupied by Middle Paleolithic populations should assist in developing a clearer picture of human development. Much work has been done on dating European Paleolithic material and the results obtained are numerically large. However the information collected till now is qualitatively thin (Villa, 1991). In particular the chronologies developed for the Mousterian are not sufficient for a full study of this period and the one which immediately followed. The apparently rapid disappearance of the Neanderthals remains still an unexplained phenomenon.

It should be noted that Zubrow's 1989 demographic model demonstrated that, under competitive conditions, extinction could in fact take place as rapidly as within 30 generations or a millennium. However the model is based on the assumptions that: 1) the Neanderthals and moderns automatically occupied the ecological niches left empty by the other, 2) the two populations were exploiting the same resources, 3) each population occupied ecological niches at the exclusion of others, 4) population growth is independent of exploitable resource availability.

While Zubrow's model is consistent with prey/predator mathematics (Volterra, 1938), his assumptions relating to the exploitation of ecological niches are questionable because extant population densities were extremely low. Furthermore Neanderthals and moderns did not always exploit the same resources (Mellars, 1973; Chase, 1989; Soffer, 1989; Lewin, 1993).

Epidemics were not likely to be the source of the demise of the Neanderthal even though foreign ailments might have been imported by anatomically modern humans (AMH). As already indicated population densities were far too low. Even at the higher densities of the Middle Ages the plague did not eliminate the total extant population (Wolpoff et al., 1994). Anthropological thought regarding the appearance of modern humans is somewhat contentious with a number of hypotheses being proposed, none tested successfully and all challenged.

Some researchers support the proposition that modern humans constitute a separate new species. They base their hypothesis on the belief that speciation is not a continuous evolutionary process but rather it is concentrated in periods of substantial environmental change (Gould, 1994). They propose that such an event took place at about 200 kya probably in Africa, that is essentially concurrent with the first appearance of the Neanderthals in Europe. This is sometimes even extended to suggest that multiple waves of progressively more modern humans originated from a single region (Lahr and Foley 1994).

None of these supporters of a single Eve hypothesis appear to question the fact that both modern and Neanderthals evolved at the same time from a preceding archaic population derived from a common ancestor: *Homo erectus* (Demars and Hublin, 1989). However, all deny the possibility that other speciations may have occurred at the same time in different parts of the world, as for example in eastern Asia (Foley, 1989; Wolpoff, 1990). Yet there is nothing in evolution theory which would suggest that a multiple speciation event is not possible.

The African Eve hypothesis ignores the evidence that speciations normally seem to occur preferentially in peripheral zones (as Europe and eastern Asia would have been at the time) where population is small and "the mechanism of evolution acting on the genotype stands a better chance of becoming incorporated and fixed in the population" (Simmons, 1994).

Anthropologists who support instead a multiregional origin/gene-flow hypothesis of human progression interpret some of the fossil remains as providing clear evidence of in-situ evolution toward modernization of extant populations throughout the world. Their efforts are concentrated on explaining the genetic uniformity of the current human population as the result of extensive contacts between widely separated people, in spite of the evidence that even the world's current hybrid population is relatively small.

Research involving the study of mitochondrial DNA (MtDNA) has attempted to resolve the question of the emergence of modern humans and the disappearance of the Neanderthals. Many of the results have been widely questioned because of doubts on the validity of the premises on which the research is based.

A more recent and more appealing line of thought suggests that notwithstanding the apparent genetic differences between the two populations some hybridization did take place.

Some researchers even see archaic traits reflected in present day people (Brown, 1990; Wolpoff, 1989). Unfortunately the human fossils recovered to date are not adequate to confirm any of the hypotheses and remain too much open to subjective interpretations (Simmons, 1994).

However the archaeological record has allowed anthropologists to ascertain the fact that AMH and Neanderthals were contemporaries and that they occupied the same sites although at separate times. From the archaeological material some researchers also have inferred that the two populations maintained definite contacts over a relatively long period of time at least in parts of the European continent. What is not certain yet is how long this period was, what areas were so affected and whether the Neanderthals retreated progressively to avoid the impact of the new immigrants.

Part of the cause of such uncertainty is due to the paucity of absolute dates for the final occupations by Neanderthals of sites, particularly those located in the more peripheral regions of southwestern Europe.

Radiocarbon dating has been used extensively in archaeology. However the end of the Middle Paleolithic is at the extreme of this method's capability as it cannot be relied upon to provide secure dates beyond 35-40 kya. More secure dates are necessary to help in resolving or confirming some of the apparent problems and inconsistencies arising from the archaeological analyses of material recovered till now (Bailey 1983).

Accordingly my doctoral research was designed to provide new information for this very significant transitional period of human evolution. Specifically the questions to be addressed were dealing with how recent had been the Neanderthal occupation of Spain and what evidence existed for their progressive withdrawal southward in Iberia.

In Spain the final Neanderthal occupation is represented by Mousterian layers. There are a number of secure dates (mainly radiocarbon) for the early Aurignacian in this region, such as those by Cabrera and Bischoff for El Castillo (1989), Bischoff et al. for l'Arbreda (1989), Maure and Garcia for Cueva Millan (1990), etc. However, no secure ages have been obtained for final Mousterian layers anywhere in Spain, with the exception of a date for the deposits of Peña Miel (Utrilla, 1986) and two for the Waechter layers at Gorham's Cave (Garralda, 1978). Both were non-AMS radiocarbon dates and ranged between 40 and 47 ka.

The method to be employed for my research was the relatively new technology of electron spin resonance (ESR). ESR is not constrained as is radiocarbon by problems with contamination and calibra-

tion and can utilize amongst other material animal teeth which are essentially ubiquitous in sites of this period. Therefore it is a very suitable methodology for research involving archaeological material dating in the 30 to 50 kya range. ESR would be used to date what I believed would be terminal Mousterian layers at Spanish sites located north and south in the Peninsula. The sites involved were either under excavation or had been excavated recently following modern techniques. A multidisciplinary approach to dating the archaeological contexts was being proposed for all the sites except El Pendo whose deposits had been already dated but only on the basis of sedimentological and faunal analyses.

This allowed a further dimension to my research that is the opportunity of appraising first hand the applicability and advantages of a new dating technique and determining its accuracy as an archaeological dating method. Confirmation of the accuracy would come from comparison with a great variety of other techniques. These were: faunal and sedimentological analyses at El Pendo; palynological analysis, U-series, thermoluminescence and radiocarbon at Carihuela; radiocarbon and optically stimulated luminescence (OSL) at the Gibraltar sites. The choice of sites fit well with the research design and seemed to offer the most varied conditions for testing ESR. Due to geography and latitudes, environmental conditions at the time of cave utilization and during burial would have been different at each location and therefore sedimentation would have been different. The deposits at El Pendo in the north are highly intermixed with eboulis and therefore are "lumpy". So are those at Carihuela, while those at Gibraltar contain homogeneous sediments. Carihuela is located inland in Andalusia, while Gorham's and Vanguard are on the seashore. El Pendo is sufficiently inland not to be affected by marine deposits.

The latitudinal differences should have permitted me to verify whether the Neanderthal withdrawal in the face of ever encroaching moderns was occurring also in Spain. Thus the research would provide vital information regarding the demise of the Neanderthals in Europe and at the same time would permit to test the accuracy of a new dating technique as applied to archaeological material. This would have been the first research program that would apply ESR to such a variety of sites and compare its results with that of such a variety of other archaeometric dating techniques. The research would make a significant contribution not just to the understanding of the end of the Middle Paleolithic period in Iberia but also to the development of the application of a new technique to archaeological dating

#### CHAPTER 2. THE EVOLUTION QUESTION

Extensive anthropological studies of the physical remains of both Neanderthal and AMH populations have been undertaken to attempt to resolve the question of modern human evolution (Bräuer, 1984a; Kennedy, 1984; Smith, 1984; Stringer, 1984; Stringer et al., 1984; Wolpoff et al., 1984; Stringer, 1985; Dean et al., 1986; Stringer and Andrews, 1988; Arensburg, 1989; Bräuer, 1989; Gamble, 1989; Stringer, 1989; Wolpoff, 1989a, 1989b; Corrucini, 1990; Smith, 1991; Binford, 1992; Li and Etler, 1992; Wolpoff, 1992; Aiello, 1993; Bräuer, 1994; Anton, 1994; Etler and Tianyuan, 1994; Simmons, 1994; Wolpoff et al., 1994; Zollikofer et al., 1995; Pfeiffer, 1997). A number of prominent studies have also been carried out in the last decade utilizing genetic material (Vawter and Brown, 1986; Cann et al., 1987; Cavalli Sforza et al., 1988; Klein, 1989; Vigilante et al., 1991; Ruvolo et al., 1993; Cavalli Sforza et al., 1994; Relethford and Harpending, 1994; Wills, 1994; Gibbons, 1995a; Horai et al., 1995; Rogers and Jorde, 1995). Grand syntheses have been produced by Brown (1990), Stringer and Gamble (1993), Trinkaus and Shipman (1993), Bodmer and McKie (1994), Gamble (1994), Mellars (1996) and Stringer and McKie (1996).

Yet there are still so many gaps in the human fossil record that there is not sufficient information to tell whether evolution of AMH took place suddenly or slowly, and what their relationship to the Neanderthals might be (Jones, 1993). Neither is there sufficient genetic information to confirm a unique source of their origin and its location on the world map (Bodmer and McKie, 1994; Relethford and Harpending, 1994).

Some researchers suggest that human speciation did not occur globally but only in the mosaic environment of the tropics (Foley, 1989). However, the archaeological evidence indicates that around 250-300 kya there is a flourishing of new archaic yet modern human forms at least in Africa and in Europe. Archaic forms of fossils which can be interpreted as ancestral to either Neanderthals or moderns have been discovered and have been associated with periods of substantial environmental change which tend to magnify the effect of natural selection (De Lumley, 1973; Kingdon, 1993; Lewin, 1993 ; Calvin, 1994; Gould, 1994). At least in the old world something happened that fostered alterations in the composition of extant populations and mutations in their genetic material that transformed *erectus* into archaic modern forms.

In Europe the first evidence of trait differentiation from *Homo erectus* is found in the fossil record from terrestrial deposits correlated to oxygen isotope stage 7 as represented by the proto-Neanderthal forms discovered at Swanscombe, Steinheim, Mauer, Petralona and Tautavel. They seem to be transitional between late *erectus* and the more advanced Neanderthals (Stringer et al., 1984; Stringer and Andrews, 1989; Andrews and Stringer, 1993; Stringer and Gamble, 1993; Mellars, 1996). The latter appeared first in the period of the penultimate glacial and perhaps, in the case of the remains of Biache-Saint-Vaast, as early as 200-250 kya (Stringer and Gamble, 1993; Trinkaus and Shipman, 1993; Mellars, 1996). It was a cold-adapted human form whose skeletal morphology was perhaps due to a founder's effect resulting from a combination of climatic conditions and apparent isolation (Howell, 1952; Hublin, 1990; Anton, 1994; Mellars, 1996).

The African fossil and dating evidence is entirely consistent with that suggested by geneticists for an emerging AMH population. The archaic specimens which follow late *erectus* in Africa seem to have warm-adapted traits which anticipate the high forehead and the more gracile features of the moderns. Specimens from Florisbad, Kanjera I, Singa, Omo I (130 kya) and Klasies River Mouth (120-95kya) fall into this group (Butzer, 1978; Bräuer, 1984a, 1984b; Bräuer, 1993; Stringer, 1985; Stringer and Andrews, 1988; Stringer, 1989; Grün et al., 1990b; Kingdon, 1993). Although there are uncertainties regarding the dating of Omo I it appears to be older than the Levantine AMH (Bräuer, 1993).

In eastern Asia, according to Wolpoff, shovel tooth incisors and other typical Asian traits surfaced at about the same Middle to Upper Pleistocene period. These traits according to several researchers are still persisting in current eastern populations (Wolpoff, 1990; Wolpoff et al., 1994; contra: Habgood, 1990).

The archaeological record of succeeding events in modern evolution is relatively clearer in Europe and the Levant than in other regions. Modern forms appear in the Levant at approximately 100 kya (Schwarcz and Grün, 1992; Valladas et al., 1987; Valladas et al., 1988) and AMH seem to have moved westward some 50 k years later as suggested by the ages of the first Aurignacian sites discovered so far in Eastern Europe. Such migration would not be unusual. Fossil evidence indicates that human populations have migrated starting with *Homo erectus* (Gamble, 1986). Neanderthals moved eastward toward central Asia and reached the Levant, AMH probably followed the Danube into Europe and eventually Asians crossed the Bering land bridge into America.

Neanderthals and AMH over time came to occupy the same Eurasian territories but perhaps not contemporaneously, with the former apparently withdrawing progressively south-westward.

There were certainly contacts between the two populations as evidenced by the flourishing of the hybrid tool technologies of Chatelperronian, Aterian, Bohunician, Szeletian and Uluzzian (Stringer, 1984; Stringer, 1990). However, whether the two populations did interbreed is still questioned.

It is clear that a number of skeletal features distinguish the classical Neanderthals from AMH, beyond the nuchal buns, the chins and the basio-cranial differences (De Lumley, 1973; Hublin and Tillier, 1981; Olson, 1981; Bräuer, 1989; Zollikofer et al., 1995; Hublin et al., 1996). Dental eruption in the former is more advanced than in the latter (Dean et al., 1986; Zollikofer et al., 1995), while their supraorbital torus development, molar taurodontism and bone thickness are certainly more archaic (Stringer, 1993), and the bony ear labyrinth in the temporal is quite different in the two (Hublin et al., 1996).

The extent and significance of the morphological differences between Neanderthals and AMH strengthens the interpretation that a link between the two exists only through their respective ancestors and that biological separation is indeed a fact (Dean et al., 1986; Stringer, 1990; Rak et al., 1994; Zollikofer, 1995; Mellars, 1996).

The other evidence for suggesting a biological separation between Neanderthals and AMH is the persistence of their separate identities over a long period (Hublin et al., 1995; Gamble, 1996; Hublin et al., 1996). The radiometric dating of the remains from the Levant show that a Neanderthal population retained their distinct characteristics some 40 ka after the first presence of AMH in the region (Stringer, 1990; Kingdon, 1993; Lewin, 1993). However, there is no evidence of coexistence between AMH and Neanderthals in the Levant; the two populations most likely occu7

pied the same region in alternate periods as the result of migrations in response to fluctuating environmental conditions (Bar Yosef, 1994).

The adaptive morphological features of the Neanderthal appear to change in time as the environment changes (Howell, 1952; De Lumley, 1973; Trinkaus, 1981; Stringer et al., 1984; Smith, 1991; Anton, 1994; Jelínek, 1994; Simmons, 1994; Mellars, 1996). This being the case, it would seem at least possible that such features may disappear in hybrid offsprings of Neanderthals and moderns. The problem of course is that, given the small population extant at the time, the extremely poor recovery of human fossils remains from the Paleolithic period, and the rapid disappearance of the Neanderthal, it is statistically unlikely that remains of clearly hybrid individuals will be found. Nevertheless a number of European fossil specimens do appear to show traits that might suggest hybridization between Neanderthals and moderns (De Lumley, 1973; Smith, 1982; Smith, 1984; Stringer, 1984; Stringer et al., 1984; Arensburg, 1989; Bräuer, 1989; Gambier, 1989; Smith et al., 1989; Fryer, 1990; Andrews and Stringer, 1993; Leakey, 1994; Simmons, 1993; Mellars, 1996).

A number of researchers have interpreted traits present in human skeletal remains of the end of the Middle Paleolithic as providing evidence of in-situ evolution. Wolpoff and Thorne see continuity in Europe reflected in the current modern population. They maintain that the size of the nose and the configuration of the opening in the lower jaw into which the mandibular nerve runs are inherited Neanderthal traits (Wolpoff et al., 1984; Wolpoff et al., 1994).

Pfeiffer (1997) also found some relationship between European and African archaics. Her direct measurements of Border Cave and Broken Hill material showed that they fall in the same dimensional and robusticity ranges as do the Neanderthals. Bräuer (1984a; 1993) suggests that a comparison can be made between the Bodo and the Petralona specimens particularly when based on facial measurements. This of course does not confirm any direct linkage between the two populations except through a common ancestor as suggested by Stringer in his analysis of the Arago and Petralona skulls (1993). The latter skulls display Neanderthal-like traits but, in spite of their advanced character, they retain an overall robusticity which is greater than in either Neanderthals or moderns. Stringer includes them in the same archaic group as Bilzingsleben, Vertesszöllos, Broken Hill, Bodo and Dali (1985, 1989). Evidence for hybridization between Neanderthal and AMH does exist. Some of the human remains from European sites dated at approximately 40 kya appear to have both Neanderthal and modern traits. The prime example comes from Hahnöfersand (Stringer et al., 1984), while the La Ferrassie I, Guattari 3 and La Quina specimens exhibit also some mixed traits such as modern mental eminences associated with Neanderthal cranial features (Trinkaus, 1993).

The analyses of other fossils of this period by different anthropologists have produced different interpretations and some of the interpretations have been confusing. According to some, the mandibles from level G3 at Vindija have almost no retromolar spacing while the Vindija 261 frontal possesses a high forehead and hints at a high domed skull. Also all the facial remains from this site appear to show nasal breadths which are more than three standard deviations narrower than the western European Neanderthal mean and only one of the Vindija samples show evidence of occipital bunning. Therefore, these fossils should not be included in the count of the Neanderthals (Smith, 1982; Smith, 1991; Simmons, 1994). Furthermore the Vindija level G1 material could fit either in the Neanderthal or modern category, particularly when considering their teeth (Smith, 1982; Simmons, 1994). Also the Mladec samples show much reduced bunning and a greater skull vault curvature particularly sample 2 (Smith, 1982; Bräuer, 1989), while the Predmostí 3 has a small occipital bun while possessing projecting browridges (Bräuer, 1989).

At the same time, according to Smith (1982), although the mandibles of the Vindija level G3 show definite modern traits, the other skeletal and cranial material possess a definite Neanderthal appearance. Furthermore the Vindija layer G1 jaw and teeth and the Mladec crania 4, 5 and 6 and Predmostí 3, although seemingly modern, have traits that are reminiscent of a possible Neanderthal ancestry (Smith 1982; Bräuer, 1989; Stringer, 1989).

A number of researchers believe that all of the above fossil material suggests a certain degree of mixing between archaic and modern populations (Smith, 1982; Stringer, 1984; Bräuer, 1989; Smith et al., 1989; Fryer, 1990; Andrews and Stringer, 1993; Gamble, 1994; Leakey, 1994; Simmons, 1994) while others, such as Jelínek (1985) and Diamond (1992), do not support such an interpretation. In essence the apparent variability within the fossil sample of both Neanderthals and AMH recovered till now complicates a clear analysis of the evolution of our species. The problem of archaic/modern interpretation appears due mainly to a lack of agreement between researchers about which of the morphological complexes are primitive and which are derived and which are meaningful to resolve both the phylogenetic and the interbreeding issue (Clark and Lindly, 1989; Brace, 1994).

Attempts at resolving the problem of the evolution of modern humans have been made by geneticists. According to some researchers, the approach of the geneticists, although questionable in some aspects, does indeed provide an indication of both the geographical and the chronological origins of our modern ancestors.

The original work in this field was carried out by Wilson and Cann (Cann et al., 1987). Their success suggested that genetic material could be exploited to provide additional information on mankind's evolution (Bodner and McKie, 1994). Based on the fact that MtDNA is transferred only through maternal lines, and on the assumption of a constant genetic mutation rate, an age of original divergence at approximately 200 kya has been suggested (Bodmer and McKie, 1994; Cann et al., 1987).

Others have attempted to provide support for the findings of Wilson and Cann. Horai et al. (1995) analyzed the MtDNA of existing apes and modern Europeans, Africans and Asians. Based on the assumption of separation between the former and the latter, he suggested that the last *Homo erectus* common ancestor of modern humans existed 143 kya and originated in Africa. Ruvolo placed the divergence at 222 kya (Ruvolo et al., 1993). Cavalli Sforza et al. (1988) studied forty two human populations for one hundred and twenty alleles and, assuming constant genetic mutations, suggested that the oldest population had an African origin. Using the Qafzeh date of 92 kya for the separation between African and new non-African populations, he also derived reasonable dates for further splits into AMH Australians, Asians and Amerindians. A correlation using linguistic classification supported the dates proposed for the genetic splits (Cavalli Sforza et al., 1988). have taken place, some aspects still remain suspect (Bodmer and McKie, 1994; Wolpoff et al., 1994; Rogers and Jorde, 1995).

The basic validity of DNA genetic studies regarding the dating of human evolution has been challenged by a number of scholars (Friday, 1981; Pickford, 1991; Valencia and Ward, 1991; Ward, 1991; Hoelzer et al., 1992; Melnik and Hoelzer, 1992; Simmons, 1994; Brace, 1994; Corrucini, 1994; Wills, 1994). Furthermore, several researchers have questioned the proposition that genetic distances can be used to infer branching history in every condition. They believe this to be a reasonable assumption only when all extant population sizes are equal. They suggest that this was not so in the case of human evolution. They maintain instead that, if we assume sub-Sahara Africa to be the original source from which all AMH migrated, then the population size of this region would have been far greater than that of any other, particularly since conditions there were more supportive of humans (Friday, 1981; Relethford and Harpending, 1994; Relethford and Harpending, 1995; Rogers and Jorde, 1995).

A problem with the theory espoused by the more strict adherents to the out-of-Africa proposition is that they reject entirely the possibility of gradual change in evolutionary terms (Gould, 1994a). Also the time-span required for a speciation to occur is not known (Jones, 1993). Another problem is that they appear to follow an extreme interpretation of within-sample variation (Clark, 1988; Brace, 1989).

Currently an attempt is being made at sequencing DNA extracted from bone cut from the Neander Valley skeleton. The results obtained appear to indicate that there is no match between the DNA of the Neanderthals and that of the present population. But the sequence analysed so far is only a partial one and therefore the results can at best only be considered inconclusive . More importantly, the researchers are not carrying out a parallel study on AMH remains of for the matter of our common ancestor erectus. It could well be that sequencing of their DNA would also not produce a match with ours.

The uncertainty that still exists regarding the origins of AMH and the ambiguity presented by some fossil material enhances the proposition of multiregional in-situ evolution through a weak gene-flow mechanism, with no significant mutation producing key innovations. This would explain the disappearance of the Neanderthal (Wolpoff, 1989a; Lewin, 1993).

#### CHAPTER 3. DATING

The current widespread interest in the Middle Paleolithic and the evolution of modern humans has led to a renewed desire for absolute time frames to be established (Jelínek, 1994). The end of the Middle Paleolithic era has been, until recently, an awkward period to assess since it stretches beyond the practical range of the commonly used radiocarbon method of dating (Smith, 1982; Kozlowski, 1988; Straus, 1990; Grün et al., 1991; Julia and Bischoff, 1991; Bar-Yosef, 1992; Mellars, 1992b; Goebel and Aksenov, 1995; Morrel, 1995; Cabrera Valdes et al., 1996a, 1996b; Hedges et al., 1996; Mellars, 1996). As a result the fate of *Homo sapiens neanderthalensis* is still clouded by the uncertainty regarding the timing of their rapid disappearance and its potential coincidence with the arrival of modern humans on the European continent. (Clark and Lindly, 1989). While dates per-se will not explain the evolutionary process which led to the apparent displacement of Neanderthals by moderns, age determinations do provide an essential framework for research on this topic (Wolpoff, 1990; Dunnell, 1995).

A better chronological understanding of the material from this period must be achieved to assist in developing a clearer picture of how humans responded to the varying environment in the different regions of Europe and western Asia at the end of the Middle Paleolithic. More secure dates are necessary to help in resolving or confirming some of the problems of apparent cultural overlap between local archaic populations and potential alien modern humans such as the relationship between the Szeletian and the Aurignacian (Bailey 1983). Furthermore a greater number of independent scientific dates might resolve questions relating to rates of adaptive change during the transition from the Middle to the Upper Paleolithic as well as to differences in rates among regions and sub-regions. More precise dates would permit high-resolution comparisons between synchronic sites in different habitats and would support the reconstruction of more meaningful regional adaptive systems with greater degrees of confidence (Straus, 1992).

Until the introduction of new scientific dating methods, chronologies were based essentially on stratigraphic positioning, paleoclimate estimates based on biota and sediments, and the

attributes of artefacts recovered in site excavations. However, archaeological linkage between form and chronology is often arbitrary and cannot discriminate entirely between changes which are related to cultural-social developments or those that are strictly due to environmental constraints (Dunnell, 1986). In addition climatic events repeat and often cannot be distinguished.

New dating methods which involve scientific analyses of materials that are readily found at most archaeological sites have improved researchers' capacity to classify and establish chronologies. Their application to the search for and the interpretation of the past has been rapid and the increased level of current utilization of disparate methods at several archaeological sites allows for potential comparison of results obtained through different techniques (Masters, 1982; Valladas et al., 1987; Huxtable and Aitken, 1988; Valladas et al., 1988; Schwarcz et al., 1988; Bahain et al., 1989; Schwarcz et al., 1989; Stringer et al., 1989; Grün et al., 1991; Mellars and Grün, 1991; Schwarcz et al., 1991a; McDermott et al., 1993; Mercier et al., 1993; Brooks et al., 1995; Hublin et al., 1995; Boeda et al., 1996; Hedges et al., 1996, 1996a; Rink et al., 1996a). This multidisciplinary approach also permits testing and confirmation of the assumptions involved in the different scientific age determination techniques (Rink, 1997).

Although the <sup>14</sup>C dating method is considered highly reliable when dealing with material which is <35 kya, it is not unusual to seek supplemental evidence in support of radiocarbon dating because this method cannot be employed unquestioningly in all instances. Past fluctuations in cosmic ray emissions have resulted in varying <sup>14</sup>C concentrations in the atmosphere which lead to inaccuracy in <sup>14</sup>C measurements. Radiocarbon dates can also be influenced by the handling of recovered material, the storage and preparation of specimens and the contamination with modern carbon which may have taken place during their burial or recovery at archaeological sites. The latter is almost an unsurmountable problem particularly when material which dates beyond 35 kya is involved.

Accordingly over the last 40 years the focus of archaeometry has been the search for a technique of age determination which would transcend the 35-40 ka limit of <sup>14</sup>C (Grün, 1989; Porat and Schwarcz, 1991; Blackwell and Schwarcz, 1993; Grün and McDermott, 1994; Jonas et al., 1994; Klein, 1994) (Figure 3.1).



Comparison of Quaternary geochronological dating methods. The current actual limits of the age ranges depend on circumstances (e.g. state of sample preservation) (from M. J. Aitken, 1990)





#### **CHAPTER 4. ESR DATING**

One technique which has been used successfully to extend scientific chronologies beyond the range of <sup>14</sup>C dates is ESR. Natural mineral crystals are the clock exploited by ESR to measure when an event occurred through the phenomenon of electron and charge displacement by radiation (Robins et al., 1982; Grün, 1989; Aitken, 1990; Grün and Stringer, 1991; Rink, 1997).

This relatively new technique is now being applied to many fields of research including archaeology. ESR dating has a time range that offers significant opportunities for the study of human evolution (Rink, 1997). Age estimates from more than 2 million years to a few thousand years are theoretically possible. This renders it particularly well suited to the period which is critical in the study of the emergence of modern humans especially when dealing with contexts with suspected ages near or beyond the practical limit of radiocarbon dating (Schwarcz, 1985; Schwarcz et al., 1988b; Grün, 1989; Schwarcz et al., 1993; Rink et al., 1994; Rink et al., 1996b).

ESR age determinations, particularly using tooth enamel, are quite novel in comparison with radiocarbon, thermoluminescence and U-series dating. However its flexibility as a method has enhanced its application to archaeological sites, 54 of which had been dated by 1997 (Rink, 1997). Among these are some of prime importance to modern human evolution such as Qafzeh, Es Skuhl and Kebara (Schwarcz et al., 1988b; Schwarcz et al., 1989; Stringer et al., 1989). Results obtained for these sites have provided new chronological evidence which might suggest that anatomically modern humans co-existed with Neanderthals in the Middle East at around 100 ka.

There are currently over 50 laboratories worldwide involved in the application of ESR. However, though first suggested as a dating method by Zeller et al. in 1967, ESR has been applied extensively to geological, geomorphological and archaeological research only since the success in dating a stalactite from Akiyoshi Cave in Japan was reported by Ikeya (1975). A history of ESR development and details of the parameters and uncertainties that surround the method has been outlined comprehensively by Rink (1997). The ESR technique exploits the response of crystals to radiation which is similar to that associated with the thermoluminescence (TL) phenomenon (Ikeya and Miki, 1985; Nambi, 1985; Ikeya, 1986; Grün, 1989; Sales et al., 1989; Aitken, 1990; Grün and Stringer, 1991). One advantage over the latter is that no heating is involved in testing the specimens and therefore tests on the same sample can be repeated. Furthermore, it allows material such as mollusc shells and coral which are altered by heating to be dated (Goede and Hitchman, 1987; Schwarcz et al., 1991a; Brumby and Yoshida, 1994; Sherwood et al., 1994).

Materials tested include stalagmitic calcites (Ikeya, 1975; Ikeya, 1980; Hennig et al., 1981; Yokoyama et al., 1982a; Yokoyama et al., 1983; Falgueres et al., 1990), bone (Ikeya and Miki, 1981; Ikeya, 1982; Yokoyama et al., 1982b; Yokoyama et al., 1988; Sales et al., 1989; Abeyratne et al., 1997), burnt flints (Robins et al., 1982; Griffiths et al., 1983; Porat and Schwarcz, 1991; Monnier et al., 1994), mollusc shells (Ikeya and Ohmura, 1981; Hütt et al., 1985; Katzenberger and Grün, 1985; Radtke et al., 1985; Huang et al., 1989; Hütt and Jaek, 1989; Skinner, 1989; Molodkov, 1989; Imai and Shimokawa, 1993; Brumby and Yoshida, 1994; Abeyratne et al., 1997; Schellman and Radke, 1997) and teeth (Grün and Invernati, 1985; Schwarcz et al., 1988b; Schwarcz et al., 1989; Stringer et al., 1989; Grün et al., 1990a; Grün et al., 1990b; Grün et al., 1991; Bahain et al., 1992; Çetin et al., 1994; Chen et al., 1994; Rink et al., 1994; Rink and Schwarcz, 1994; Rink et al., 1995).

ESR has been utilized for provenancing studies (Warashina, 1992) as well as for extensive archaeological dating (Ikeya, 1975; Ikeya, 1980; Hennig et al., 1981; Ikeya and Miki, 1981; Yokoyama et al., 1983; Schwarcz et al., 1988a; Schwarcz et al., 1988b; Sales et al., 1989; Schwarcz et al., 1989; Grün et al., 1990b; Grün and Stringer, 1991; Grün et al., 1991; Porat and Schwarcz, 1991; Schwarcz et al., 1991a, 1991b; Schwarcz and Grün, 1993, 1993b; Çetin et al., 1994; Rink and Schwarcz, 1994a; Rink et al., 1994; Huang et al., 1995; Rink et al., 1995; Rink et al., 1996). Procedures and calculation methods for age determinations via ESR have been outlined in detail by Symons (1982), Nambi (1985), Grün et al. (1988), Grün (1989), Aitken (1990), Porat and Schwarcz (1991), Brumby, (1992), Blackwell and Schwarcz (1993), Porat et al. (1994), Rink and Schwarcz (1994), Brennan et al. (1997), Jonas (1997), and are outlined below.

Accuracy of ESR dates depends, as for TL, on the analytical uncertainties in the determination of the yearly dose of natural radiation absorbed by samples being analyzed. The potential error in determination is often the most significant factor in the age uncertainty and must be calculated precisely and accurately (Blackwell, 1994; Lau et al., 1997). Accuracy also depends on the appropriate choice of algorithm to fit the dose response of the dating signal and determination of a laboratory equivalent dose (Brumby, 1992; Grün, 1996; Rink and Schwarcz, 1995). The method is considered to provide a precision of approximately  $\pm 7 - 10\%$ . Accuracy of ESR ages can be determined best through comparison with the results obtained by other independent dating methods (Falgueres et al., 1990; Bahain et al., 1993; Grün and McDermott, 1994; Porat and Schwarcz, 1994; Rink et al., 1996b; Abeyratne et al., 1997; Zhou et al., 1997).

ESR spectroscopy is based on the fact that crystalline matter has charge defects in its lattice that can store free electrons temporarily (Schwarcz and Grün, 1993). When a crystal is formed all the electrons in the lattice are in a so called 'ground' state. With successive natural irradiation electrons and holes (charges) can be transferred to higher energy levels and become free to migrate through the lattice. Eventually some are trapped in natural charge defect sites, forming paramagnetic centres (Robins et al., 1982; Grün, 1989; Aitken, 1990; Grün and Stringer, 1991; Schwarcz and Grün, 1993; Rink, 1997) (Figure 4.1). The number of electrons so trapped is proportional to the radiation received by the crystal since the traps were formed.

All crystals possess some sites which are capable of trapping and retaining displaced charges. Most traps can retain these free charges because at ambient temperature the energy required for their release is very high and their thermal stability is in excess of 10<sup>7</sup> years (Yokoyama et al., 1983; Grün, 1989; Aitken, 1990; Schwarcz and Grün, 1992; Jonas, 1997).

Accumulation of trapped electrons takes place because in practice crystals are bombarded constantly by natural radiation from the decay of isotopes of U, Th and K present in the environment and the crystals themselves as well as by cosmic radiation. The sediments in which crystals become eventually buried contain varying amounts of natural radioisotopes. Isotopes can also be added or leached out when water infiltrates the sediments. Annual doses are dependent
Figure 4.1



Showing the mechanism of unpaired electron trapping in crystal lattices. (a) - Radiation displaces an electron from the valance band moving it into the conduction band where, after a while, it drops into a trap. (b) - An alternative way at the phenomenon is that radiation imparts enough energy on an electron so that it can move around in the crystal lattice until it falls into a trap. (from Grün, 1989; Ikeya and Zimmerman, 1993)

on the nature of the burial environment. They can range from 0.3 Gy/ka in limestone-rich sediments to 5 Gy/ka in open-air riverine sites or in volcanic terrains (Rink, 1997).

The crystals themselves can acquire amounts of uranium during burial as a result of leaching from the sediment or, as in the case of stalagmitic calcites, they can incorporate the uranium naturally dissolved in the water into their matrix during their formation. Details of uptake models are discussed below.

The net annual radiation dose absorbed by crystals is dependent on their temperature and temperature fluctuations. Thermal stability is optimal in caves and therefore it can be expected that the net rate of signal accumulation is steadier in crystals buried therein. This is significant when dealing with thermoluminescence but not for ESR since the traps responding to this technique are not heat sensitive.

The environmental dose rate can be determined either from *in-situ* dosimetry or from the chemical composition of the sediment which surrounded the sample. In general the use of chemical analysis of sediment to determine dose rates instead of in-situ dosimetry is discouraged because the distribution of  $\gamma$  dose sources in burial contexts is not always uniform. Since  $\gamma$  radiation often makes up the majority of the external dose rate large errors could result. Gamma rays penetrate about 30 cm through sediment therefore, where sediment is used to determine the level of external radiation component, it is paramount to be able to collect a homogenous representative sample of the sediment that surrounded the tooth up to 30 cm from the enamel. Since  $\beta$  particles have a limited range of travel, the exact 2 mm layer of sediment in contact with the enamel to be dated must also be collected separately for analysis (Figure 4.2). Where possible the use of bulk sediment samples which have been collected further than 30 cm from the samples being studied should be avoided (Rink et al., 1994; Rink et al. 1996b; Rink, 1997).

It should be noted that determination of ages by ESR is also affected by the homogeneity of the sediments from which samples are recovered since various components have different degrees of radioactivity. Limestone for example contains only about 1 ppm of uranium and essentially no thorium and potassium, and therefore is much less radioactive than typical

# Figure 4.2



Illustration of the dimension of the regions which contribute significantly to the radiation dose reaching a sample and of the processes and factors which control the doserate. Only those  $\alpha$  particles originating within a 25 m radius , those  $\beta$  particles within a 2 mm radius and  $\gamma$  rays within a 30 cm radius will contribute to the dose absorbed by the sample. Cosmic rays also make a small contribution which is affected by latitude, altitude and burial depth. (from Grün, 1989)

fine-grained sediment (Rink et al., 1996b). If the environment in which the samples are buried is not of uniform grain size but contains eboulis (i.e. it is a 'lumpy' site), as often occurs in caves, particularly when containing varying sizes of limestone blocks, it becomes difficult to ascribe precise gamma dose rates to which the testing samples have been exposed (Schwarcz, 1994; Schwarcz and Grün, 1993b; Rink et al. 1994; Rink et al., 1996; Brennan et al., 1997b; Jonas, 1997) (Figure 4.3). This is particularly important for teeth because in most cases the external gamma dose is a very large component of the total dose (Rink et al., 1994; Schwarcz, 1994; Rink, 1997). The level of lumpiness affects the overall radioactivity of the sedimentary contexts, so that results based on the chemical analysis of sediments in a lumpy environment will yield higher radiation doses than actual and therefore will yield age estimates which are lower than they would be based on direct dosimetry. (Blackwell et al., 1992; Blackwell, 1994; Lau et al., 1997; Rink, 1997).

As indicated above, alteration of the sediment through the burial life can also significantly affect the ESR results. The presence of ash in certain sites enriches the sediment with potassium while the presence of bone changes the uranium in the sediment (Schiegl et al., 1996; Rink, 1997). Uranium is often concentrated in transformation products of calcitic ash (Schiegl et al., 1996). Samples recovered within or below ash beds for example would be affected by water percolation, with their yearly dose rate changing with time; neither direct in-situ dosimetry nor chemical analysis can yield an indication of the correct yearly dosage under these conditions.

Furthermore, in the application of ESR to teeth, it should be noted that the organic fractions of teeth tend to absorb uranium which may be present in percolating water. This means that they themselves become a source of radiation which contributes an internal dose to the total dose absorbed by the enamel. Age determinations by ESR analysis of teeth are therefore dependent on the assumption of the rapidity with which the uranium uptake occurs (Grün and Invernati, 1985; Schwarcz, 1985; Grün et al., 1988; Aitken, 1990; Avery et al., 1997; Jonas, 1997; Rink, 1997). Details of uptake models and implications regarding age determinations are outlined below.

As indicated above, natural radiation is the result of the disintegration of isotopes present in the environment. Uranium, thorium and potassium isotopes, disintegrating naturally, bombard





Schematic display of homogeneous (a) and "lumpy" sediments (b). Note the impact of eboulis on the 30 cm effective range of  $\gamma$  radiation (from Schwarcz, 1994).

continuously any crystals in the environment with  $\alpha$ ,  $\beta$  and  $\gamma$  radiation. Part of this radiation is dissipated in the form of heat but some of the captive electrons present in the crystals become separated from their nuclei, setting up the pattern of migration and capture outlined above.

Uranium and thorium and their daughter isotopes each contribute different yearly doses of radiation due to  $\alpha$  and  $\beta$  particles and  $\gamma$  rays. Potassium-40 does not contribute any radiation due to  $\alpha$  particles and its radiation due to  $\beta$  particles and  $\gamma$  rays is also different from the two other isotopes. Typical values are quoted in the literature (Fleming, 1979; Aitken, 1985; Nambi and Aitken, 1986; Aitken, 1990). These theoretical dose rates must be modified by a number of assumptions dealing with the effect of sample size on radiation attenuation and with the radiation efficiency of  $\alpha$  and  $\beta$  particles and  $\gamma$  rays (Fleming, 1979; Aitken, 1990).

The amount of  $\alpha$  particle energy deposited in the crystal lattice is proportional to their track length and not their energy (Lyons and Brennan, 1989). The fraction of total  $\alpha$  energy deposited is also significantly lower than that caused by  $\beta$  and  $\gamma$  (typically 0.1 to 0.3). In principle the efficiencies of  $\beta$  and  $\gamma$  should also be considered individually but the difference is so small that it can be ignored in dating (Jonas, 1997).

Different paramagnetic centres for different materials have been identified as suitable for dating purposes (Griffiths et al., 1983; Porat and Schwarcz, 1991; Porat et al., 1994; Jonas, 1997). Each kind of trap has its own characteristic ESR signal. This in theory allows direct measurement of the trapped charges contained in each single specific trap type (Jonas, 1997).

There are three types of electron spins that contribute to the ESR signal. They originate from: transition metals with unpaired electrons on inner atomic shells, radicals (mostly organics, but also atomic hydrogen), and defects that trap single charges (electrons and holes). ESR measures these signals, if their g values agree they can be combined (Jonas, 1997).

At thermal equilibrium in a crystal the spins of free unpaired electrons parallel to a magnetic field H (N<sup> $\uparrow$ </sup>) and those antiparallel to H (N<sup> $\downarrow$ </sup>) have a Boltzmann distribution

## $N^{\uparrow}/N^{\downarrow} = e^{-\Delta E/KT}$

where E is the energy contribution of a free single electron spin and it can be in two orientations, T is absolute temperature and K is Boltzmann's constant. As the temperature increases,  $N \downarrow$  becomes equal to  $N^{\uparrow}$ . Since at thermal equilibrium this is a non-equilibrium state, energy must be absorbed in the crystal continuously up to a maximum which occurs when  $N^{\uparrow}=N\downarrow$ . At any lower temperature  $N^{\uparrow}$  is different from  $N\downarrow$  and we can observe transitions from the lower to the upper state. The energy of this transition corresponds to quanta of microwave radiation, so we can cause the spins to flip by irradiating with microwaves (Figure 4.4). The sample to be measured is placed in a magnetic field of intensity H, while being irradiated with microwaves of frequency v. Maximum absorption is obtained at a specific value of H corresponding to resonance between the energy of spin-flip and the microwaves, that is when:

 $hv = g\beta H$ 

where: h = Planck's constant

 $\beta$  = Bohr magneton

g = a constant characteristic of a specific trap site

ESR spectroscopy is based on measuring the power absorbed during this process which is proportional to the amount of free electrons in the crystal. Typically microwaves with frequencies v = 9.2 GHz are used, for which the corresponding values of H are of the order of a few hundred millitesla (a magnetic field of approximately 340 millitesla or 3400 Gauss).

When represented graphically, the total number of unpaired spins is proportional to the area under the absorption curve, that is, to its integral. The integral would be a very accurate means to determine the sensitivity, however it is often difficult or impossible to determine a good baseline for the curve. To avoid this problem, the derivative of the absorption function is utilised, although this does not allow all the components of the ESR signal to be distinguished (Jonas and Marseglia, 1997) (Figure 4.5).

Fossil and modern irradiated tooth enamels display a single strong ESR signal with a g value of 2.0018 (Figure 4.5). The peak to peak intensity of the g = 2.0018 signal is routinely used for ESR dating measurements. This was believed to arise from the anisotropic symmetry of a single defect site in carbonate hydroxyapatite crystals of tooth and bone mineral (Schwarcz, 1985; Jonas et al., 1994). The signal has been deconvoluted and found to be a combination of more

Figure 4.4



Schematic of an ESR spectrometer. The ESR sample is placed in the cavity between the magnets. The recorder captures the derivative of the intensity signal. The Bruker apparatus used for the tests is entirely computer controlled. (from Grün, 1989)





Typical ESR signal from tooth enamel. The vertical scale measures the ESR intensity signal in arbitrary units and the horizontal scale measures g value (from Schwarcz and Grün, 1992)

than one paramagnetic species and some researchers have suggested this approach as an alternative to the use of the derivative signal (Jonas et al., 1994; Jonas, 1995; Jonas 1997). The multiple signals identified by both these approaches might lead to incorrect ESR results in some cases (Rink, 1997). Superimposed noise perhaps originating from organics in the sample appears to interfere with the signal from specific paramagnetic centres in flint (Hennig et al., 1981; Porat and Schwarcz, 1991; Bahain et al., 1992; Jonas et al., 1994; Grün et al., 1997). This complicates the analysis but sometime the interference can be eliminated by testing at reduced temperature (Hennig et al., 1981; Griffiths et al., 1983). Porat and Schwarcz (1991) have indicated how superimposed signals can be subtracted from the main one to yield a pure dating signal (see also Jonas, 1997).

ESR allows the detection of the centres formed in crystals by ionizing radiation through the measurement of a signal proportional to the amount of electrons trapped which is, therefore, proportional to the total absorbed radiation over time (Grün, 1989; Aitken, 1990; Grün and Stringer, 1991). If the dose rate is known, the determination of the time elapsed since the start of irradiation can be derived from the relationship

$$D_{a}=\int_{0}^{T}D(t)dt,$$

where t is the time elapsed,  $D_e$  is the total dose absorbed and D is the dose rate. It should be noted that in general for tooth enamel D may not be constant over time (Grün, 1989). The equation can be solved for t if we can evaluate D(t). This depends on the varying intensities of  $\alpha$ ,  $\beta$ and  $\gamma$  activities through time in the tooth and its environment.

The above equation is of course valid if the following conditions are satisfied: - the sample being investigated was zeroed at the start of the period to be determined;

- the number of traps remained constant from then until the moment of measurement;

- the thermal life of the traps is much greater than the age to be determined;

- the sample preparation does not affect the electron spins or the properties and quantities of the traps.

Measuring the paleodose D<sub>e</sub> by ESR involves the determination of the sensitivity of the samples to radiation. This is achieved in practice by means of the additive dose method which involves

subjecting samples to increasing doses of artificial laboratory irradiation (Grün, 1989). The number of traps available for free electron accumulation in any crystal are limited. Thus the probability of electrons being trapped decreases as the traps become increasingly filled to eventual saturation. This behaviour is best represented by means of the single exponential saturation function:

$$I = I_o(1 - e^{(D/Dmax)})$$

where I is ESR spectrometer signal intensity. Such a function is employed in the calculations of ages for the additive dose method (Çetin et al., 1994; Brennan et al., 1997; Rink, 1997).

The annual dose rate is affected by attenuation of  $\alpha$ ,  $\beta$ , and  $\gamma$  particles by moisture content in the sediment in which the sample is buried, by the impact of cosmic rays, by the attenuation of internal  $\alpha$  and  $\beta$  particles and by the growth to equilibrium of uranium and its daughters present in the sample (Rink, 1997). Details of radiation uptake models are discussed below.

The upper range of dating achievable by means of ESR is mainly dependent on the thermal stability of the paramagnetic centres (Grün and Stringer, 1991). This is not a problem if the mean life of the electron in the traps is ten times higher than the age being measured. Annealing experiments show that the former is of the order of 10 to 100 ma (Schwarcz, 1985), therefore this phenomenon does not significantly affect dating of Paleolithic material.

As indicated above, the upper range is also affected by saturation in growth of the ESR signal (Grün, 1989; Grün and Stringer, 1991; Rink, 1997). This depends on crystal sensitivity, dose rate and time, and has not been found to be a problem in archaeological dating. Saturation appears to differ for different paramagnetic centres. For example for the E' centre in flint this occurs at relatively low doses limiting maximum dates to 200-600 ka, while the Al centre does not show any tendency to saturation (Porat and Schwarcz, 1991). It is to be noted that in most centres the saturation occurs at levels at least an order of magnitude higher than for TL, the former technique has potentially greater scope than the latter (Nambi, 1985).

At very high irradiation doses new traps can be formed in crystal lattices. However it should be noted that laboratory doses used for ESR age determinations are below such levels.

## 4.1 Factors affecting ESR age determinations

A number of complications apply to ESR dating which are similar to those encountered with TL. One of these is the impact of groundwater present in the soil in which the sample was buried on the amount of natural radiation absorbed by the sample itself (Fleming, 1970; Winter, 1971; Fleming, 1979; Carriveau and Harbottle, 1982; Aitken, 1990; Avery et al., 1997; Rink, 1997). Water in the soil reduces considerably the path length of radiation. In the case of  $\alpha$  particles, for example, the effectiveness of water in sediments in stopping radiation is close to 50 percent greater than that of dry clay or quartz (Fleming, 1979; Blackwell et al., 1992). The effect of water on radiation path lengths can be taken into consideration in the form of systematic error equivalent to 7 percent (Fleming, 1979) or attempts can be made at a closer determination of the loss (Carriveau and Harbottle, 1982).

As already mentioned, water can also leach out some of the radioisotopes both from the sample and from the burial sediment. In contrast, the absence of water will permit radioactive radon and thoron gas to escape (Fleming, 1979; Carriveau and Harbottle, 1982; Aitken, 1985; Aitken, 1990; Rink, 1997).

Radioactive radon and thoron are produced in the decay of uranium and thorium. Being gases, they tend to migrate away from their original locations. Such migrations are dependent on sediment density and permeability. When they are free to migrate, the total radiation absorbed by the crystals is reduced. For one hundred percent radon/thoron loss, typically 57 % of  $\alpha$ , 60 % of  $\beta$  and 95-97 % of  $\gamma$  energy associated with the entire decay chain is lost (Winter, 1971; Fleming, 1979; Carriveau and Harbottle, 1982; Lyons and Brennan, 1989; Lyons et al., 1993). Therefore loss of radon and thoron have an impact on the amount of yearly dose rates although in practice radiation decrease due to gas losses is considered to be < 5% and therefore has a minor effect on ESR ages (Rink, 1997). It should also be noted that cave environments are more likely to show a build-up of these gases in the cave atmosphere and therefore a plate-out of radon/thoron solid daughters is most likely to occur against the cave walls (Lyons et al., 1993). This complicates age determination when samples have been collected in these regions.

29

The problem associated with gas migration is complex and must be evaluated on a site by site basis (Carriveau and Harbottle, 1982; Volterra, 1994).

Another complication is due to the fact that, while the impact of cosmic radiation at various latitudes and elevations is well known, its uniformity during the past cannot be assessed although over long periods of time it is believed to fluctuate around an average value. Furthermore, cosmic radiation effects are much attenuated as sediment thickness increases and, if burial is deep or inside a cave, the impact of cosmic rays can become insignificant (Prescott and Stephan, 1982; Prescott and Hutton, 1988). Furthermore burial depth does change through burial history.

Electron accumulation in lattice defects of crystals under burial conditions is the result of excitation and migration of electrons into these lattice defects, while at the same time there is a loss of the trapped electrons due to the vibration of the lattice atoms. The net accumulation is steady only if the passage of energetic radiation is constant. At higher rates of energetic radiation passage the primary accumulation of the electrons in the traps is higher while the depletion by lattice atom vibration does not change. This is the case in instances of cave burials, since the environmental temperature remains quite constant over very long periods in spite of external environmental conditions. In this regard it should be noted that the artificial uniform laboratory irradiation that is used to determine the dose response of the samples may not parallel the actual field burial phenomenon. This can add to the error in age determination (Blackwell et al., 1992). Blackwell and Schwarcz proposed the isochron method to overcome this uncertainty (1993). The isochron method can also be applied to museum samples where in-situ sediments are no longer available and direct dosimetry is not possible. Since it requires the processing of multiple subsamples, this method can be applied only to teeth from which large samples can be extracted (Blackwell, 1994; Rink, 1997).

Other important considerations which affect archaeometric dating must always be kept in mind. Since the test material does not normally consist of human remains or their artefacts, dates measured represent only, and at best, the ages of the layers in which the test material was found. In fact it is sometimes difficult to correlate properly human remains or artefacts with the archaeological material which has been used for dating, as they can be separated vertically or horizontally and the human material may be intrusive. Furthermore it is possible that the layers might have been subject to selective redeposition. Thus not only could the test material be intrusive but the radiation to which it has been subjected might have changed considerably through time.

Disagreement between results obtained through the application of different methods of dating can often be ascribed to the paucity of sample or its fragmentation. At times discrepancies can be attributed to uncertain correlation of stratigraphic units excavated by different researchers or even to improper association of museum samples with field stratigraphy. Accordingly it should be noted that in certain cases even the results obtained by different scientific methods for the same Archaeological layers can appear very different (Huxtable and Aitken, 1988; Yokoyama, 1989). For example the contribution of anthropogenic sediment and the natural rearrangement of the accumulating deposits can result in what appear as sedimentary "events" totally unrelated to the external environment (Farrand, 1988; Barton and Clark, 1993). Downwashing of pollen in coarse textured sediment and the selective destruction of pollen taxa in alkaline environments also produces ambiguity in the palynological record (Mellars, 1996). Some climatic events which leave traces in the soil strata may have been too weak, too localized or too short to have made an impact on the regional vegetation which gave rise to the pollen record (Farrand, 1988).

Other complications arise when samples such as teeth are used for ESR measurements. These are covered in more detail below.

## **CHAPTER 5. CAVE ENVIRONMENTS**

Cave and shelter formation involves the natural enlargement of the cavity and the deposition of sediment. These physical processes present significant problems with regard to the estimation of dates by any technique.

The leaching of carbonates in karstic environment creates situations where large fluvial flows can occur. This allows for the removal of large portions of accumulations or alternatively for the collapse or shift of floors with subsequent redistribution of deposits. Mass wastings such as slumps and slides in caves and rock shelters, particularly at entrances, can alter previous depositions, and confuse the stratigraphic evidence. The presence of roofs and walls allows both for the exfoliation of limestone and also for significant collapses that can alter the contour of a context (Borziac et al., 1997). Alternating wetting and drying conditions can result in the cementing of horizons. Similar effects can occur because mass movements due to periglacial conditions such as gelifluction, solifluction and cryoturbation. Alteration of natural depositions also can be the result of bioturbation or voluntary and involuntary alterations effected by humans.

Furthermore, the physical parameters of caves create microenvironmental conditions which do not necessarily mirror the conditions in the surrounding landscape and, at even a short distance from the entrance, promote sediment deposition rates which differ from open environments. In effect cave geometry creates internal air movement patterns that are very difficult to reconstruct and therefore hinder the assessment of site taphonomy as well as potentially confusing the palynological evidence.

In spite of these complications, cave sites offer some positive conditions which assist in dating archaeological contexts. The moisture present in karstic caves is saturated with carbonate which renders the sediment deposits moderately alkaline. This favours the fossilization and preservation of tooth enamel (Michel et al., 1995) which is one of the principal materials utilized for ESR age determinations.

#### CHAPTER 6. TEETH

A special application of ESR is the dating of tooth enamel. This was first suggested by Ikeya (1982). Teeth are practically ubiquitous in archaeological sites and accordingly this dating technique has acquired increasing significance in Paleolithic research where ages being studied generally exceed the capability of radiocarbon (Schwarcz and Grün, 1992; Rink and Schwarcz, 1994; Rink et al., 1996a; Rink et al., 1996b).

Teeth contain three different tissues: enamel, dentine and cementum. Dentine forms the core of the teeth and is protected by an enamel layer. The latter is generally external, but it can be inter-layered. Cementum is the external tissue that binds teeth to the bone (Figure 6.1).

Dentine contains approximately 20% organic fraction, mainly collagen in 80% hydroxyapatite. By contrast, enamel consists of 99.5% inorganic crystals (Haskell et al., 1995). An ESR signal can be obtained from the dentine after the removal of the organics but it is a weaker signal than that of the enamel. Also the dentine signal appears to be generally less stable than in the enamel (Haskell et al., 1995).

Since tooth enamel consist mainly of crystalline hydroxyapatite it does not change mineral form during burial and is subject to minimal diagenesis (Michel et al., 1995; Rink and Schwarcz, 1995). Like all natural crystals, it is sensitive to radiation as photographic film is sensitive to x-rays and therefore it is well suited for dating by ESR (Grün et al., 1987; Rink and Schwarcz, 1994; Borziac et al., 1997). Tooth enamel contains 4.5 to 5.1 % by weight of carbonate and it is the carbonate ion which gives rise to the ESR signal (Gilinskaya et al., 1971; Cvec et al., 1972; Scott and Symons, 1974; Doi et al., 1979, 1980, 1981; Bacquet et al., 1981; Bouchez et al., 1984; Elliott et al., 1985; Geoffroy and Tochon-Danguy, 1985; Schwarcz, 1985; Callens et al., 1987; Rey at al., 1991; Poupeau and Rossi, 1992; Ikeya, et al., 1993; Rink and Schwarcz, 1995; Rink, 1997). Any mobility of the carbonate during burial would affect the sensitivity of the tooth enamel. While fossil bone contains significant amounts of diagenetic carbonates (Lee-Thorpe and Van der Merwe, 1987; Hedges and Millard, 1995; Wright and Schwarcz, 1996), it has been demonstrated that diagenetic processes which occur during burial do not affect the carbonate content of fossil enamel, perhaps because of the denser structure of this tissue (Rink and Schwarcz, 1995).



Types of mammal teeth - A = human; B = camel; C = elephant. At archaeological sites enamel can be recovered from whole teeth or as individual pieces (D), as tooth parts (E), or as enamel within multiple layers of dentine (F). Note that individual pieces of enamel (D) would be recovered only in cases where extreme acidity dissolved all other organics (from Grün et al., 1987)



There are some complications associated with obtaining results through the use of teeth for age determination by ESR. Of importance is the attenuation of the effects of  $\beta$  radiation. The cementum layers which are found on the external surface of teeth are very good absorbers of  $\beta$  particles. As they approach 2 mm in thickness, their absorption efficiency reaches 100%. Furthermore, the thickness of the tooth components (cementum, dentine and enamel) are of the same order of magnitude as the range of  $\beta$  particles. Thus attenuation models are important in age calculations (Grün, 1989; Brennan et al., 1997; Rink, 1997).

#### 6.1 Uranium uptake models

As indicated above, ESR ages calculated from enamel are dependent on the uptake of mobile uranium by the tooth tissue during burial Since it depends on environmental factors, in different contexts this phenomenon can vary significantly (Bahain et al., 1993; Borziac et al., 1997). Uranium uptake can be affected by proximity to eboulis or bones as well as by the action of bacterial decay and water percolation or the presence of ash or by soil pH and temperature (Grün et al., 1988). In addition, the process of accumulation of uranium in tooth tissue is associated with the decomposition of the organic components and the permeability of the tissue.

Fortunately the mineralized structure of the enamel renders it much less porous than dentine or cementum. As already mentioned, while all three tooth tissues contain organic matter, it is higher in the dentine and cementum and much lower in the enamel. Typical concentration is <100 ppm in the former two and <<10 ppm in the latter, although higher levels have been observed (Grün and McDermott, 1994; Chen et al., 1997). As a result cementum and dentine absorb more uranium during burial while enamel is often found free of this isotope (Falguéres et al., 1997).

When uranium is present in the teeth, there is an added source of radiation to augment the trapped electrons which generate the ESR signal. This internal radiation is in some cases controlling (Grün et al., 1988). Dental tissue with higher concentrations of uranium has produced anomalous ESR behaviour (Schwarcz and Grün, 1993; Chen et al., 1997). Where uranium concentrations are very high, as for example in the material from the *Homo erectus* site in Yunxian, some form of localized trap saturation is suspected to occur in portions of the enamel. This could be the result of very high levels of excitation along the paths of the  $\alpha$  particles (Chen et al., 1997).

Two models are usually assumed to represent the uranium absorption process: one involves a linear uptake (LU) and the other a rapid and early uptake (EU) (Figure 6.2). ESR ages are usually reported as LU and EU, each with individual uncertainties. Although attempts have been made at mathematical solutions for modelling theoretical intermediate uranium uptake histories, these are not usually considered (Schwarcz, 1985; Grün et al., 1988; Avery et al., 1997; Jonas, 1997; Rink, 1997). The degree of variance between the LU and EU ages is associated with the internal radiation resulting from uranium uptake by the sample. Normally the uranium uptake by dentine dominates the internal dose because the range of  $\beta$  particles is approximately 2 mm. However at an uptake level of < 0.2 ppm, the external radiation dominates and the EU and LU dates should coincide (Rink, 1997).

Rink (1997) states that in general the LU dates have shown better agreement with dates obtained by other independent methods (see also Grün et al., 1991). However no one model of uptake can be considered a preferable overall choice, and a single uptake model cannot be assumed to be valid for all material from any given site (Grün et al., 1988; Bahain et al., 1994; Grün and McDermott, 1994). In higher temperature environments water circulation can be expected to be correspondingly higher, resulting in optimum conditions for uranium mobilization and increasing uranium uptake by teeth. Therefore where uranium uptake is demonstrably higher in an upper rather than a lower layer, it is to be expected that EU ages will be more likely correct for the former contexts (Grün et al., 1991). It is also to be expected that, under the same environmental conditions, teeth with a thinner enamel layer will generally have a higher uptake than those with thicker enamel layers or enamel crowns (Grün et al., 1991).

A choice between uptake models can be made with reasonable confidence by calculating the closed-system U-series date for the sample and comparing it with the ESR ages. Rink (1997) details the effects of uranium uptake and suggests that when the closed-system U-series age is



Uranium uptake models. Uranium uptake in enamel, dentine and cementum is a gradual process. The two limiting cases are expressed by EU = early uptake and RU = recent uptake. Algebraically this is expressed by the equation  $u_t/U_T = (t/T)^{(P+1)}$  where:  $u_t$  is the uranium concentration at any time t;  $U_T$  is the final uranium concentration; T is the age of the ESR sample; P is a parameter reflecting the rate of uptake at any time t. The linear uptake model (LU), with a constant uptake, corresponds to the value P=0. The limiting conditions are represented by P=1 and P= $\infty$  for EU and RU respectively (after Rink, 1997)

equal to the EU age, then the latter is the correct uptake model to be used (see also Grün et al., 1988 and Bahain et al., 1993). When the U-series age < than the EU age then a linear uptake must be considered. A closed-system U-series age which is much less than the EU one would suggest a recent uptake model (Chen et al., 1997; Rink, 1997).

In practice uranium uptake can be sporadic and can be interspersed with periods of uranium loss (Brooks et al., 1995). These phenomena are difficult to ascertain in practice, but are generally associated with open air archaeological sites (Chen et al., 1994; Swisher et al., 1996).

## 6.2 Other considerations

There is an apparent difference in response behaviour to radiation from modern and from fossil tooth enamels. The former shows departure from a true saturation exponential dose response, but yields reasonable results with linear fitting in the order of  $\pm$  5-10% (Lee et al., 1997).

However, during burial there appear to be no diagenic changes that affect the ESR signal, so that the radiation sensitivity of all fossil tooth enamel is quite similar. This common behaviour permits the utilisation of a Universal Growth Curve (UGC) to estimate the equivalent dose for all teeth no matter what their age or provenance, which greatly simplifies and expedites analyses (Porat and Schwarcz, 1994; Rink and Schwarcz, 1994).

As indicated earlier, the intensity of the measured ESR signal may not yield correct age determinations if the material tested has reached trap saturation, has poor thermal stability or has been affected by crystal structure recombination. Thus each type of material tested must be evaluated for these parameters (Grün, 1996). One of the reasons that tooth enamel is particularly suitable for ESR dating is that it is not affected by the above constraints.

Trap saturation can be reached if exposure to radiation is very extensive, either because doses are very high or times of exposure are very long (Cheng et al., 1997). This can occur in the case of TL/OSL measurements of quartz for geological age determinations but is not likely to affect ESR when teeth are used in conjunction with archaeological contexts since in enamel spin trap saturation occurs near doses of 10,000 Gy. In low natural radiation environments this allows theoretical age determinations in excess of 2 million years (Grün, 1989; Porat and Schwarcz, 1994; Rink et al., 1994; Rink, 1997).

Anomalous fading due to thermal stability is not a problem, as already stated, if the mean life of the trapped electrons is at least ten times larger than the age to be determined (Grün, 1996; Chen et al, 1997). Tooth enamel has very good thermal stability (Schwarcz, 1994) and its ESR signals do not exhibit anomalous fading (Blackwell et al., 1991).

Transient irradiation induced ESR signals have been found to be present in tooth enamel, but they decay with time. The apparent increase in the dating signal in the enamel which is found when spectrometer readings are obtained immediately after laboratory irradiation would yield decreased D<sub>e</sub> values. This problem is overcome by waiting approximately a fortnight for measurement (Oduwole and Salas, 1994; Rink, 1997).

#### CHAPTER 7. EFFECTS OF SAMPLE PREPARATION

The intensity measurement in ESR depends on crystal orientation. This presents a problem of signal repeatability if solid enamel is analyzed. A sample powdered to a sufficiently small grain size can get around the problem of anisotropy.

Sensitivity of tooth enamel to irradiation is not affected by crushing during sample preparation but is dependant on grain size (Haskell et al., 1996), while intensity and width of signal each increase with decreasing grain size. This is likely due to the fact that smaller grains have undergone greater mechanical stress during preparation (Polyakov et al., 1995).

It should be noted that grinding does produce mechanically induced effects in certain materials. In enamel they appear to be similar to those due to ionizing radiation, possibly as the result of free radicals generated on the surface of the particles during grinding (Desrosiers et al., 1989; Polyakov et al., 1995; contra Haskell et al., 1995). One possibility, not yet investigated, is that, at least partly, the grinding-induced signal may be the result of reduced anisotropy as particle sizes become smaller. The induced signal is sensitive to radiation and occurs at about g = 2.0038 thus superimposing the apatite signal at g = 2.0018. Hand ground enamels display weaker signals. Hand grinding is recommended since it reduces pestle movements which would generate shear (Desrosiers et al., 1989). Minimizing the length of grinding is also suggested, since the intensity of the grinding signal appears to increase with the duration of crushing (Polyakov et al., 1995).

Using a rotating goniometer during measurements permits accurate measurements involving larger grain sizes since it overcomes the problem of orientation (Abrajain and Bleaney, 1986; Pilbrow, 1990; Jonas, 1997). This also permits the utilization of higher microwave power which enhances the measurement of the sensitivity to induced radiation (Haskell et al., 1997).

## **CHAPTER 8. ESR APPLICATIONS**

When materials recovered from archaeological excavations are used to date specific contexts, several problems are encountered. As already indicated one of the most troublesome is the relationship between the sample being analysed and the context itself. While this applies to all scientific dating techniques, some aspects can present particular problems for the application of ESR to teeth. Their relatively small size, density and durability makes them very liable to taphonomic displacement. Such displacements can involve multiple processes of redeposition. In particular this occurs where significant bioturbation has taken place or where teeth are recovered from fluvial or glacial sediments or contexts which have been subjected to frost heaving or tectonism. Caves are often subject to one or more of these phenomena particularly in karst system where limestone dissolution also present added dimensions of displacement (Blackwell, 1994). For example at Vanguard cave in Gibraltar bioturbation was evident both in the north contexts and in the upper layers of the south excavation. At the El Pendo cave in Cantabria the physical appearance of layers XVI to XVIII would seem to be evidence of secondary water-borne deposition. Thus the ages of the samples analysed are the ages of the teeth and not necessarily the ages of the artefacts recovered with them or the ages of the sediments in which they were buried.

Significant disagreement between ESR ages and ages obtained by other independent methods have been found at sites where uranium uptake appears to have been significant (Bahain et al., 1993; Rink, 1997). At times discrepancies can be attributed to uncertain correlation of stratigraphic units excavated by different researchers or even to improper association of museum samples with field stratigraphy. Like other techniques, ESR has not always been applied successfully (Bahain et al, 1993). However, results for several sites estimated at 40 k to 100 k years have found excellent agreement between ESR and other independent scientific dating methods (Rink, 1997) (Figure 8.1).

Age underestimations compared with geological determinations have been found at Stanton Harcourt (Zhou et al., 1997), Piegú and Vallonet (Bahain et al., 1993). Tests by Bahain et al. (1992) on *Elephas Antiquus* teeth from Isernia la Pineta in Italy produced dates which were





Ages determined by ESR for archaeological levels compare quite favourably with those obtained through other scientific dating methods.

● U-series O AMS uncalibrated □ Thermoluminescence

younger than racemization results obtained by Belluomini (1985) and Belluomini et al. (1987) on coeval bones and considerably younger than the K-Ar ages obtained by Delitala et al. (1983) for overlying volcanic deposits. The latter agree with the analysis of the faunal record. Bahain et al. (1992) attribute the discrepancy to interference of other signals at g = 2+. Other problems may also have contributed to the apparently erroneous results. The geometry of pachyderm teeth is not optimal for age determination by ESR. Furthermore the sediment from which the teeth were recovered was inhomogeneous and therefore there is uncertainty regarding the determination of gamma dose rate. In addition the layer contains a very significant amount of bone and its tendency to become enriched in isotopes might have affected the uranium uptake history of the teeth which were buried with them.

Also unsuccessful were the results obtained for burned flint from Yabrud Cave in Israel. Porat and Schwarcz measured ages which are about half of the results obtained by previous researchers both through ESR on teeth and TL on burnt flint (Porat and Schwarcz, 1991). The discrepancy is attributed to the values assumed for the efficiency of  $\alpha$  particles and to nonuniform distribution of the uranium in the flint.

Yokoyama et al. (1982b) could not obtain successful results for four samples of bone from the Caune de l'Arago. The ages determined decrease with depth as does the isotope disequilibrium. A most likely explanation for the results would appear to be that all samples have been affected by uranium leaching.

The ESR technique has had mixed success in the case of the Karaïn Cave in Turkey. Both Çetin et al. (1994) and Rink et al. (1994) obtained dates which were consistent with the Paleolithic cultural material recovered. The former tested teeth from levels AH-10, 11, 14, 17, 18 and the latter teeth from levels AH-16 to 27. The results both obtained for samples from layers 17 and 18 were in agreement. However, while the ages obtained by Çetin et al. were also consistent with stratigraphy, Rink et al. found no systematic increase in ages with sample depth. They attributed this to the uncertainty due to the inhomogeneous nature of the sediment surrounding the buried teeth.

The results obtained by Grün et al. in 1991 on 20 bovid teeth from Garrod's Tabun Cave collection are also uncertain. This is an important Middle Eastern site from which a number of

human remains have been recovered. In particular its layer C produced one of the most complete Neanderthal skeletons ever discovered. Since the cave has been fully excavated, no site dosimetry was possible and no sediment was available *in-situ*. Fortunately samples of soil had been retained in the museum archives and were analyzed by instrumented neutron activation analysis (INAA) to determine the external beta and gamma dose (in-situ gamma spectrometry of the cave actually yielded lower gamma values but the INAA data were used in the age estimation). The provenance of the teeth tested was known only by layer and therefore its relationship to any of the sediment was unknown. The ages for levels B to E show internal stratigraphic consistency, however they do not match previous dates assigned on stratigraphic bases nor do they correlate well with faunal material. The very high uranium content of the teeth produce EU and LU dates that diverge considerably and cause increased uncertainty.

The results obtained by Grün et al. (1990a) for Border Cave in South Africa are also confusing. In spite of good *in-situ* dosimetry and the lack of uncertainty regarding uranium mobilization and soil moisture content the results for two of the layers conflict with the stratigraphy. Other results instead appear satisfactory, in particular the date determined for the upper sequence 1BS matches a corrected <sup>14</sup>C date.

The results obtained by Hennig et al. (1981) for the controversial Petralona Man should be considered successful, though they have been contested by Poulianos and Ikeya (Poulianos, 1983; Ikeya and Miki, 1981) and Yokoyama et al. (1982a). Five sets of samples were analyzed including a thin calcite deposit adherent to the human skull and some skull bone fragments accidentally detached with the calcite. ESR was chosen because the samples were too small for U-series, because the high opacity of the material and clay inclusions would have hampered the use of TL and, in the case of the bone samples, because the date expected exceeded the capability of radiocarbon. *In-situ* dosimetry was carried out using calcium sulphate probes spiked with dysprosium. The results were consistent with the presumed stratigraphy. The age established for the bone fragments, though questionable because of possible diagenesis, was also consistent with the age of the calcite encrusted over it. Liritzis (1982) confirmed Hennig's dates with his own

results from U-series analysis. Furthermore, in 1992 Latham and Schwarcz (1992), upon retesting by U-series the material originally analyzed by Schwarcz et al. (1980a), derived ages similar to Hennig's own.

Schwarcz et al. (1988a) obtained acceptable ESR dates for four rhinoceros teeth from the fluvial travertine layer at Bilzingsleben in spite of the lack of *in-situ* dosimetry. While twice as old as U-series ages determined by Harmon et al. (1980) for this site, they were in agreement with two U-series dates obtained at the same time by Schwarcz et al. from calcite samples from the same levels and were consistent with U-series dates obtained by Brunnaker et al. in 1983 (Schwarcz et al., 1989a). The ages determined for the teeth and the calcite deposits were consistent with oxygen isotope stage 11. The faunal and floral assemblage recovered from this same layer are consistent with this interpretation since they appear to have been formed during an interglacial period.

The application of ESR to dating stalagmites from the Caune de l'Arago, the Grotte du Lazaret, the Abrí Pie Lombard and the Grotte du Vallonet by Yokoyama et al. (1983) was also very successful. The external dose was measured by in-situ gamma-ray spectrometry in all cases. The ESR signal measured was at g=2.0067 after annealing to 185 C. For the first three sites ESR ages were in agreement with U-series ages obtained at the same time for the same materials, and for the Grotte du Vallonet were also consistent with paleomagnetic results.

The Caune de l'Arago samples were obtained both at the centre and at the edge of the wall of the cave in the same layers. The U-series ages of the latter samples were much younger than the ESR ones and both are younger than for the central samples. This is probably due either to the radon plating phenomenon outlined above or to the fact that during rains a significant amount of water seeps through the walls and uranium is continuously added. This continuous addition would affect U-series more than ESR determinations since for the latter half of the annual dose would be external. The same phenomenon seemed to occur with one of the Grotte du Lazaret samples.

Schwarcz et al. (1988b) obtained good results for the Qafzeh sites on tooth enamel though the results did not show a gradient from the higher to the lower levels. This was probably because the layers appear to have been deposited very rapidly. Vandermeersch's study of the lithics found at Qafzeh supported this interpretation. Good *in-situ* dosimetry involved 13 calcium sulphate probes spiked with dysprosium. The EU age determined was consistent with TL dates obtained by Valladas et al. in 1988.

The efforts of Stringer et al. (1989) also were successful for the Es Skhul cave in Israel in spite of the fact that all the material analyzed came from the British Museum archives and no *in-situ* dosimetry was feasible. The age established for the layer B compared favourably with the ESR and TL dates obtained by others (Schwarcz et al., 1988b; Valladas et al., 1988) for layers at Qafzeh Cave considered coeval on the basis of archaeological material.

The results of ESR analysis of the two lower stalagmitic layers of the Fate Cave (Finale Ligure, Italy) by Yokoyama et al. (1988) were also successful. The ages calculated match ages obtained from U-Th and U-Pa dates obtained for bone on the same levels.

Porat and Schwarcz (1991) obtained successful results for two burned flint samples from Nahr Ibrahim in Israel. The ages determined were consistent with those derived from speleothems from the site and with archaeological estimates.

The results obtained by Schwarcz et al. (1991b) for samples retrieved from four sites in coastal Lazio in Italy also showed general agreement between U-series and ESR ages as well as consistency with stratigraphy, in spite of lack of appropriate dosimetry for some of the sites.

Successful ESR ages have also been obtained in studies of Australian deposits by Sherwood et al. (1994) where, for one of the sites analyzed, TL, racemization, radiocarbon and ESR techniques were used to date all sediment samples. Results showed a remarkable degree of concordance.

## **CHAPTER 9. PHYSICAL CONTEXT**

#### 9.1 General

The Iberian peninsula is perhaps one of the most important of the regions of Europe for the study of the Middle Paleolithic. Many of the locations so far excavated have yielded extensive and rich stratigraphies with evidence of repeated occupations over long periods (Straus, 1992; Vega Toscano, 1990; Waechter, 1951, 1964). Furthermore the proximity of many sites to one another and the indication of contemporaneity of occupation of neighbouring caves provide opportunities to study regional patterns of prehistoric culture.

The majority of Mousterian sites discovered in Iberia so far have been inside caves or shelters located on the periphery of the Peninsula (Butzer, 1981) (Figure 9.1). They were also all occupied after the Middle Paleolithic (Waechter, 1951; Vega Toscano, 1990; Straus, 1992). This in itself is quite different from the pattern of occupation in other parts of Europe, such as France, where mainly open air sites seem to have been utilized preferentially during the Middle Paleolithic, while caves and shelters were chosen more frequently in the Upper Paleolithic and sites are relatively evenly distributed on the landscape (Bordes 1968; Guichard, 1976; Bordes, 1984).

The difference in type and distribution of Middle Paleolithic sites between Spain and other European areas might possibly be better attributed to environmental factors rather than cultural choices. It is also possible that the evidence is biased by the limited archaeological activity that has taken place in Spain so far. In spite of the differences, from the evidence recovered till now it would seem that the Mousterian people that inhabited the peninsula adapted to the then prevailing environmental conditions on their own terms given their own physical, environmental and demographic limitations but in similar fashion to the other archaic population of Europe.





Iberian Mousterian sites and sites of early Upper Paleolithic occupation. A majority of Iberian Mousterian sites [indicated with the symbol (\*)]have been discovered inside caves located on the periphery of the peninsula. (from Straus, 1992)

## 9.2 Geography and geology

The geology of Europe results in a landscape which is extremely varied and offers different environments in which people have settled for millennia. In spite of succeeding glaciation episodes which affected fauna and flora, continental shorelines, access to individual eco-niches, and geographical features, the overall diversity of the environment was maintained. Wide river valleys and extensive plains have allowed the penetration of the continent by humans and animals and the exploitation of the land and its resources for at least the last 900,000 years.

Traces of land occupation by hominids have been discovered throughout the continent (Bordes, 1984; Gamble, 1986; Peretto, 1994). These consist of open air as well as cave sites. The latter are relatively frequent since the continent of Europe contains a karst of greater richness and diversity than perhaps any other area of similar size on earth (Middleton, 1986). The Iberian peninsula encompasses wide areas which display such geological phenomena (Haggett, 1994) (Figure 9.2).

The shape of Iberia contributes to its very low shoreline to surface ratio (1 km per 150 sq. km), in spite of its more than 4500 km of coast (Jones, 1986). Its geography is such that even in current times the population of the region beyond 10 km from the shoreline is only between 10 and 50 people per square kilometre. The large internal plateau of the Meseta covers 50% of the entire surface of Iberia and at an average elevation of 600 meters above current sea level it is the highest such highland in Europe. The only low altitude area, beside the narrow coastal band is the valley of the Guadalquivir in the south, a tectonically formed plain which in the Mesozoic was submerged.

The greater part of the crust of Iberia is strongly folded and partly metamorphosed with its oldest rock formations found mainly in the western part of Spain and northern Portugal (Ager, 1980). The peninsula was moulded out of fragments of the original Hercynian continent which formed in the Carboniferous and Permian periods (360-245 mya). During the Mesozoic era (245-65 mya) this land mass broke up and large segments sank below the sea level. In the Tertiary period (65-1.6 mya) marine deposits were crushed against one of the segments and the whole was uplifted by the northward movement of the African Plate. This tectonic upheaval formed mountain ranges





Outline of the dominant surface rocks in the Iberian peninsula showing the extent of limestone deposits. Large areas of Iberia display karstic phenomena rich in caves (from Enciclopedia del Gasso) which include the Pyrenees in the north and the Sierra Nevada in the south. The latter contains the highest peak in the peninsula at Malhacén (3478 meters above sea level). Between these ranges extends the vast Meseta Plateau which was protected from major folding by the massive underlying rocks of the ancient continent (Figure 9.3).

As a result of these geological happenings Iberia is, like Italy, isolated from the rest of the continent by a mountain range, the Pyrenees, which extends from the Mediterranean to the Atlantic coast uninterrupted. For most of their length the Pyrenees exceed 1500 meters in elevation and reach 3404 meters at the Pico de Aneto, their highest point. The passes are very few, at high elevation and in the past difficult to access even in summer. In fact one of the most important geographical facts pertaining to all of the Iberian peninsula is its mountainous terrain. which affects access as well as weather patterns and resource exploitation. The rich mineral deposits which began to be mined in the last few millennia would have not been of significant value to its Paleolithic inhabitants, while the mountain chains appears to have prevented the complete occupation of this area.

Mountain ranges are not confined to Pyrenees and Sierra Nevada. The Sierra Cantabrica, ranging from 1500 to 2500 m in elevation, separates the narrow fertile band along the Bay of Biscay from the interior. The ensemble of the Sierra de Guadarrama, the Sierra de Gredos, the Sierra de Gata and the Sierra de Estrela, reaching 2700 m above current sea levels, intersects the entire Meseta north of Madrid and Lisbon. The Sierra Morena, further south, parallels the Sierra Nevada. The latter joins a semi-continuous series of coastal mountain ranges that isolates the very narrow lowland strips which stretch along the length of the peninsula eastern coastline. These ranges rise to 500 m at about 15 km from the coast and eventually reach 1500 m above present sea level on average.

The average current rainfall at 50 cm/year is the lowest in Europe and becomes as low as 11.5 cm/year in the Almeria region in the southern interior. The north and the northwest are the only zones with adequate yearly precipitation. Elsewhere rivers bring life to parched generally narrow







Tectonic upheaval during the Tertiary period formed the mountain ranges which include the Pyrenees and the Sierra Nevada. The Mesa plateau which extends between these ranges was protected from major folding during the Tertiary by the massive underlying rocks of the ancient Hercynian continent (from Ager, 1980) valleys as well as devastating floods, since during the long dry spells the soil becomes baked and is not penetrated by sudden heavy rains.

The Ebro which runs parallel to the Pyrenees is the longest river in the Peninsula and is the only major water flowing eastward. The Duoro, the Tagus and the Guadiana, running parallel to the central Sierras and the Guadalquivir between the Sierra Morena and the Sierra Nevada, flow southwest. Outside of their valleys there is today a general lack of fertile soil. Soils in the north/northwest are mainly podzolized but in the south due the high evaporation and low rainfall they are salty pedocals.

The areas which are covered in this study include zones in the Cantabrian north, in the cordillera Penebetica of Andalusia and in the extreme south at Gibraltar (Figure 9.4)

## 9.2.1 Cantabria

Cantabria in the north is a 350 km long, 30 to 50 km wide karstic region of Mesozoic origin confined between the coastal Cantabrian mountains and the Atlantic ocean at the western end of the Pyrenees (Ager, 1980; Alvaredo, 1980). It is a narrow mountainous uplifted coastal strip traversed by frequent, fast flowing rivers which have carved deep valleys that provide excellent means of communication between the immediate hinterland and the sea. The height of the mountains however presents a significant natural barrier even in historic times to movement into the interior of the peninsula (Ager, 1980). The only reasonable approach into Cantabria from the east is along the Ebro and its tributaries and from the north through the narrow coastal gap immediately west of the Pyrenees (Figure 9.4).

A narrow coastal plain exists between the Sierra and the Bay of Biscay. The strip reaches its greatest width of 10 km at Santander where the El Castillo and El Pendo caves are located, while elsewhere mountains plunge directly into the sea (Figure 9.5). Due to the steep and narrow continental shelf at this edge of the peninsula, even during glacial maxima the shoreline would
Bay of Biscay



Map of the Iberian peninsula showing major river systems and elevations above 1000 m. NTS Elevation > 1000 m.







Simplified relief map of Cantabrian Spain. The narrow coastal plain is intersected by fast flowing streams from the Sierra Cantabrica. During glacial maxima the shoreline would have been displaced only 8 12 km to the north due to the deep narrowness of the continental shelf. (from Strauss, 1992) have been displaced no more than about 8-12 km to the north (Arija Rivares, 1972; Clark, 1983; Straus, 1992). The small gap between the western end of the Pyrenees and the sea would have allowed better access to the eastern shores of the Bay of Biscay and the wide plains of Guienne and therefore extended the exploitation range. It would have also provided an easy route for continuing contacts with other Paleolithic inhabitants of Gascony, the region of France just north of the Pyrenees (Figure 9.4, 9.6). The geography of Cantabria and Gascony is very similar in that both regions have high relief and precipitation and temperatures are more moderate than in the more continental areas north and south of the Pyrenees (Straus, 1986).

Due to its geographical location and its topography, Cantabria would have provided a very favourable microenvironment for humans with abundant precipitation and varied flora and fauna during glacial periods. All the components of the geography of this region would have combined to support a subsistence base that minimized effort and risk (Clark, 1983; Straus, 1992). This is particularly so in the region immediately south-west of Santander, where archaeological excavations have recovered evidence of the repeated occupation of the El Castillo and El Pendo caves over long periods. Such evidence would tend to confirm the general model developed for hunter-gatherer populations which indicates that those environments which allow for effort-risk minimization will be occupied as long as social and technical subsystems remain flexible and adaptation to climatic changes is feasible (Clark, 1983). As a result, the sites in this area have particular importance in research on human development through the Paleolithic.

### 9.2.3 Penebetica

The Penebetica area consists of the high mountain chains and the disconnected narrow valleys of south eastern Andalusia south of the Guadalquivir which developed during the Miocene and which form the western end of the great alpine chains of Europe (Way, 1962; Ager, 1980). The region consists of significant deposits of Jurassic and Triassic limestone. The Penebetica chain represents the major orographic system of the Iberian Peninsula. At 600 km in 56



Late Middle early Upper Paleolithic sites in Cantabrian Spain - 8 = El Castillo; 9 = El Pendo; 10 = Cueva Morin. Access to the area would have been along the Ebro river valley or through the narrow gap between the Pyrenees and the sea east of the Bidesoa river. (from Straus, 1992)

length and 100 km in width, they encompass mountain peaks which reach 1800 to 2400 m of elevation and are snow covered for at least seven months a year (Arija Rivares, 1972). The southern margin of the range is at least 100 km from the coast of the Mediterranean and isolated from the shore by the Sierra Nevada (Figure 9.7)

The only routes of easy access to the region are from the north from the Guadalquivir plain along the Guadalbullion river, between the Sierra Magina and the Sierra de la Pandera, or along a more complex route which follows the Guadiana Menor or Guenil rivers. Access from the south is feasible through the valley of the Lecrin between the Sierra Nevada, the Sierra de Guajares and the Sierra de Albuñuelas and past the Vega de Granada. Access from the west can be achieved from the delta marshes of the Guadalquivir across the valley of Utrera and north of the Sierra de Loja, and from the east from the Mediterranean along the complex course of the Sanganera river.

Except for the Guadalquivir in the north, most other watercourses are very small and some flow only intermittently. The coastal ranges effectively prevent this area from feeling the direct moderating impact of the Mediterranean, while weather patterns and high mountain ranges prevent any significant precipitation. Thus the land is generally arid, interspersed with steep limestone cliffs and the soil is agriculturally poor (Ager, 1980). The karstic cave of the Carihuela is located in this region at approximately 1200 m above sea level, overlooking a small valley and the river Piñar 200 m below.

In contrast with the northern area, past environmental conditions in this region would have been difficult except at the best of times and would have provided a harsh microenvironment during glacial periods due to its location and its topography. Nonetheless there is clear evidence of repeated occupation at the Carihuela site from the Lower Paleolithic period to modern times.



Geology of the Betic Cordillera showing the extensive deposits of Triassic limestone. Carihuela cave, northeast of Granada, and Gorham's and Vanguard caves, at Gibraltar, have been formed in Triassic limestone deposits. (from Ager, 1980)

Figure 9.7

## 9.2.4 Gibraltar

In the far south, Gibraltar has a unique location on the shore of the Mediterranean and in sight of Africa. The "Rock" is part of the Betic Cordilleras region which stretches far beyond the Strait. The 426 m high uplifted limestone massif stands isolated at the edge of the Mediterranean and is connected to the north by a short isthmus leading to a generally flat coastal plain south of the Sierra Bermeja (Figure 9.8). The geological origin of the entire Gibraltar zone is still being discussed, however the petrography and stratigraphic identity of the rock on both sides of the Strait shows that it is in fact a fold which occurred during the upper Tertiary era and continues south into Yebel Sidi Musa in Morocco (Arija Rivares, 1972; Ager, 1980; Alvaredo, 1980).

As at Carihuela, the area in which Gorham's Cave and Vanguard Cave are found is part of the calcareous Bethic Nappe formed during the Miocene period (Way, 1962). However the terrain is different and access to the sea is immediate. Furthermore the inland area beyond the "Rock" presents only minor rises over the present coastline and is relatively abundant in water resources. During the Middle Paleolithic this area would have provided a welcoming rich subsistence zone which minimized risk and effort.

# 9.3 Past ecology

During the Middle Paleolithic period significant environmental changes took place in continental Europe. Severe temperature and moisture fluctuations are recorded in the palynological and geological record of the continent (Raynal, 1988; Seret et al., 1990; Barton and Clark, 1993; Sanguino et al., 1993). Similar patterns apply to the Iberian peninsula although modified by the country's geography just as they are at present. The climate of Iberia today is the result of seasonal latitudinal shifts of the zone of global westerly air flows and their interaction with the subtropical high pressure zone lying over North Africa. There is no reason to believe that this pattern would have changed during the Quaternary. However, individual parts of the peninsula



The Rock of Gibraltar. Petrographic and stratigraphic analysis has indicated that the uplifted limestone massif is part of a lower Tertiary fold which extends south of the straight into Jebel Sidi Musa in Morocco. Gorham's and Vanguard caves are located on the eastern side of the peninsula. (from Arija Rivares, 1972) would have offered different micro-niches to flora and fauna affected by local geographical factors particularly during the smaller fluctuations which occurred periodically and frequently between major glaciations (Kerr, 1996; Van Andel, 1987a).

During the upper Pleistocene and the Holocene, in spite of its generally southerly location, Iberia also underwent very large climatic swings as a result of the massive changes in ocean water temperature (Gamble, 1986: Fig. 3-10). A number of studies have indicated that the climatic switches from interglacial to glacial conditions occurred in a space of only 100 years. This would have placed considerable stress on all organisms resulting in widespread shifts in biological zones (Butzer, 1971; Andrews, 1975). It can be certainly assumed that the Cantabrian Cordilleras and the Sierra Nevada would have been glaciated during the pleniglacials of oxygen isotope stages 4 and 2, but moraine remains indicate that glaciers extended only down to the 600 - 1000 m above sea level and to approximately 25 - 30 km from the existing coastline in the north (Straus, 1992). Therefore this would have left large exploitable areas accessible even under the most adverse conditions (Van Andel, 1985). This is confirmed by palynological data which show for example that the Cantabrian region appears to have sheltered an extensive variety of thermophile tree and plant taxa through the Upper Pleistocene (Butzer, 1981, 1986; Straus, 1986, 1992).

The glaciation of the Pyrenees and the lower elevation of the permanent snow line in the southern cordilleras would have influenced considerably local conditions. In the latter ranges the southern latitude and the influence of the Mediterranean would have resulted in warmer low temperatures and moister conditions than in the Cantabrian north with a corresponding greater yearly snow accumulations and lower snow lines in the middle of oxygen isotope stage 3 (Rossignol-Strick and Planchais, 1989; Seret et al., 1990; Sutherland, 1990). No data are available for the Pyrenees, but it has been estimated from evidence of changes in the regional snow lines that at the glacial maximum the region of the Alps, which is at approximately the same latitude,, would have had mean yearly temperatures reduced by 7.2 to 8.4 °C (Andrews, 1975). Mean temperature of the entire Iberian peninsula is estimated to have been some 2 to 6 °C lower than today (Van Andel, 1985). By comparison, at the peak of glaciation, the overall cooling effect world-wide would have resulted in a mean temperature reduction of 4 to 7 °C (Andrews, 1975).

Sea levels also fluctuated greatly over the last 125 ka due mainly to the effects of glaciations (Lumsden, 1992). Clear evidence of level changes is still shown by the raised beaches which exist at many locations along the Iberian coast such as at Gibraltar. Isostatic movements of land and sea floors apparently contributed very little to the change in the Iberian sea coasts (Deperet, 1918-1922; King, 1965; Andrews, 1975).

At the start of oxygen isotope stage 5 levels were approximately 10 m below current datum. The level fluctuated and then plunged by approximately 100 m around 70 kya to rise again in stage 3 to about 30 m below current datum (King, 1965; Andrews, 1975; Van Andel, 1985; 1987b) (Figure 9.9). In early isotope stage 5 sea waters would have been also much cooler than today. It has been estimated that the coastal waters of the Cantabrian coast were in the 10 °C range while those of the Atlantic coast around Cadiz would have been some 5 °C higher and those along the Mediterranean somewhat warmer still (Van Andel, 1985).

The Cantabrian coastal region has been identified as a region of moderate faunal and floral productivity with "a patchy distribution of densely populated, high diversity eco-niches which compensates to a certain extent for sparsely populated expanses of rocky, wave-stressed shorelines with low species diversity indices" (Clark 1983). The effects of topography would have been favourable to settlement by hunter-gatherers since the sharp gradient would have provided a wide range of resources over relatively short distances, and the natural barriers of the terrain could have been used to advantage by human populations in the prediction and control of animal movements (Bailey 1983).

In Middle Paleolithic faunal remains from the region there is evidence of the typical European long term trend toward the disappearance of archaic Pleistocene species as represented by mammoth, rhinoceros, giant deer, etc. (Straus, 1992). The presence of bison and horse remains until the onset of the most recent postglacial period indicates the existence of large tracts of grassland for most of the later period of occupation, while roe deer and boar, appearing only in the most recent deposits, would suggest a growth of wooded habitats (3 - 5 kya).

The oldest layers of the sites so far investigated in the Cantabrian region have been tentatively dated to oxygen isotope stage 5d or approximately 120 kya (Gamble, 1986; Straus, 1992).

.



Global sea level changes of the past 125,000 years. Sea level is shown as below current datum. At the beginning of oxygen isotope stage 5 the sea surface was approximately 10 m. below the present level. (from Van Andel and Sutton, 1987)

Thus the majority of finds represent occupations which existed under environmental conditions of the Penultimate Interglacial and the Last Glacial that is in the Upper Pleistocene.

The Carihuela site falls within the Mediterranean bio-climatic belt. The surrounding terrain is strongly continental and confined by surrounding tectonic masses in all directions. Unfortunately there has been very little paleobotanical work done on eastern Andalusia in which the site is located (Carrion, 1992). Thus one can only speculate on the paleoenvironment of the region.

The area is generally dry at present with a yearly rainfall below 15 cm and would probably also have been dry during oxygen isotope stages 3, and 4 although there is clear evidence of weathering of both roof and walls of the Carihuela cave indicating times of humid deteriorating environment. This is particularly evident in the Mousterian level VII. Conditions appear to have ameliorated during the deposition of level VI but they revert to harsh conditions during the genesis of level V. The lower half of level IV, the terminal Middle Paleolithic stratum, is capped by a calcite flow. The palynological analysis carried out by Carrion would seem to indicate that the environment in the area of Carihuela fluctuated between pine forest with essentially no underbrush and steppe conditions typical of western Europe (Carrion, 1992). Although not as rich as the Cantabrian environment, the region surrounding the Carihuela site would have still offered varied faunal resources for Middle Paleolithic hunter-gatherers.

Conditions at the Gibraltar sites in the Middle Paleolithic are entirely open to speculation. Palynological studies are currently underway and little is known of the prehistoric floral environment of the region. Proximity to the sea shore and a hinterland rich in water would have provided significant resources. The presence of large quantities of mollusc shells in the hearths of the upper Mousterian layer of Vanguard south cave is evidence of the exploitation of marine fauna alongside the more traditional hunting of cervids whose remains are also present in the sediments of both caves. The presence of purposefully cracked nut shells in the late Mousterian layer at Gorham's also attest to the gathering of plant derived foodstuff.

# CHAPTER 10. ARCHAEOLOGICAL CONTEXT

#### 10.1 Archaeological activities

### 10.1.1 The northern sites

Although not as extensive as in the rest of Europe, archaeological work in Spain has been progressing for over a century, since Sanz de Sautuola first discovered the cave art of Altamira in Cantabria in 1880. Indeed this region "was the cornerstone of the research program established by Prince Albert I of Monaco for his Institut de Palèontologie Humaine in Paris during the five years immediately preceding World War I" (Straus 1992). The research program carried out by Sautuola, Alcade del Rio, Sierra, Breuil, Teilhard de Chardin, Obermaier and others in the area adjacent to Santandèr revealed an extremely rich series of sites which had been occupied at intervals over a considerable time span.

The El Castillo site in particular proved to contain layers with a major culture-stratigraphic sequence, apparently dating from the lower Paleolithic to the Bronze Age (Figure 10.1). The material recovered by Breuil and Obermaier was instrumental in the development of the modern paleolithic chronological scheme still in use (Breuil and Obermaier 1912; 1913; 1914; Obermaier, 1924; Straus, 1992). The 26 superimposed layers found at El Castillo are particularly interesting for Paleolithic research; of these the four Mousterian and four Aurignacian levels have yielded material suited to research dealing with the Neanderthal/Modern transition.

The disruption created by the First World War prevented the detailed publication of the findings and at least part of the excavation records was lost. Work was restarted particularly at El Castillo after the war under the auspices of the Duke of Alba and the direction of Obermaier but it was again interrupted by the civil war. Archaeological research in Spain did not resume until the mid fifties, by which time significant advances had taken place in the Perigord region of France which had become the main focus of modern archaeologists.



Figure 10.1



El Castillo cave - above = plan (from Almargo, 1976; below = stratigraphy (from Straus, 1991). Lower and Middle Paleolithic layers are shown in the section as levels 20 to 26. Layer 18 is the basal Aurignacian. In 1970 Almagro Bash, then director of the Museo Arqueologico Nacionàl in Madrid, was able to make arrangements to repatriate the El Castillo material which had been archived with the Institut de Paléontologie Humaine. At the time a complete study of the cave, based on these data, was undertaken by Cabrera and eventually published in 1984.

Re-excavation of remnant stratigraphy was begun in 1989 (Cabrera and Bischoff; 1989) and is still underway. All archaeological layers have yielded significant amount of material which can be and has been dated chronologically by several scientific techniques (Bischoff et al. 1991, 1992; Cabrera and Bischoff, 1989; Rink et al., 1996). These are in general agreement with the faunal remains recovered (Cabrera, 1984). No attempt has been made to date material from El Castillo in this study. However the extensive stratigraphy identified in this cave and the dates already obtained by others for a number of archaeological layers (Cabrera and Bischoff, 1989; Rink et al., 1996b) provide a significant point of reference for any Iberian study.

The site of El Pendo was discovered by M. Sanz de Sautuola in 1878-1880. Cendrero started excavating the upper layers of the cave in 1914 but as at El Castillo the work was interrupted by the world war. Sautuola restarted in 1919 and continued the excavation until 1921 (Obermaier, 1924). After a period of abandonment the excavation was restarted by Gonzales Echegaray in the period 1953-1957 (Gonzales Echegaray et al., 1980) (Figure 10.2, 10.3).

The archaeological find consists of 18 main layers of which 16 were studied by Echegaray and Hoyos (Gonzales Echegaray et al., 1980; Hoyos and Laville, 1982). They included one Azilian, one Magdalenian, eight Aurignacian and nine Mousterian living floors which are as significant to the study of human evolution as those of El Castillo. Three layers extending through the lower area worked on by Echegaray were re-excavated by Ramon Montes and Juan Sanguino Gonzales (Figure 10.4). Results of their work have not yet been published and no dates have been reported yet for any of the archaeological material recovered by either Echegaray or by Montes/Sanguino.

Other significant archaeological work has also been carried out in the last four decades throughout Cantabria by Gonzales Echegaray and Freeman (1966, 1973, 19785, 1975a),



Location from which the ESR samples were collected

The El Pendo cave, section showing the location from which the ESR samples were collected. The well originally excavated by Echegaray was expanded northward by Montes and Sanguino. Horizontal scale = vertical scale (after Luque, 1994)





The El Pendo cave plan, showing the location from which the ESR samples were collected. Contour intervals are 1 m. (descending 0 to 47). (from Echegaray, 1980)

.

| Echegaray's stratigraphy |                |  |
|--------------------------|----------------|--|
| Level                    | Industry       |  |
| Ι                        | Azilian        |  |
| II                       | Magdalenian    |  |
| III - VIIIb              | Aurignacian    |  |
| VIIIc                    | Non-diagnostic |  |
| VIIId - XVI              | Mousterian     |  |

# Layers equivalence Montes/ Echegaray Sanguino's A-C XVI D XVII E-H XVIII

10

X

1X 11X 111X 71X 71X 71X

XVII

B-C

D

Е

F

G H The El Pendo cave, showing the Echegaray stratigraphy and the corresponding Montes/Sanguino layers. Montes and Sanguino extended northward the well containing Echegaray's levels XVI to XVIII and identified 8 separate layers A to H. The ESR samples were recovered from the latter. (after Echegaray, 1980)

411

VII

і п

)11

١¥

ambr.

10.4

3 m.

Cabrera (1978, 1984), Straus et al. (1981), Clark (1983, 1988), Altuna (1992), and others. These researchers have used modern collection and recording standards and have also employed multidisciplinary analyses to complement excavation and classification. However, except for the El Castillo and El Pendo sites, the archaeological evidence of Middle Paleolithic occupation of the Cantabrian region is relatively scarce, poorly dated and poorly contextualized (Straus, 1992). A number of radiocarbon dates have been obtained for Aurignacian occupations however they are often contradictory and have been put in question by some recent results obtained for El Castillo material (Bischoff et al., 1991, 1992; Straus, 1992; Rink et al., 1996).

## 10.1.2 The southern sites

Over 30 Middle Paleolithic sites have been discovered in southeast Spain. The presence of Mousterian and Upper Paleolithic artefacts in the region of Piñar were reported as early as 1924 by Obermaier (1924), however the Carihuela site was first excavated by Spahni only in 1954 (Figure 10.5, 10.6).

He worked in the central and east vestibule of the cave clearing the sediments entirely from the former in an area approximately 2 m by 8 m, leaving control faces still clearly visible today at both ends of the excavation. The first human remains were recovered during the 1955 field season (Savory, 1968; De Lumley-Woodyear, 1973). Pellicer Catalan worked in the cave in 1959-1960 continuing the excavation of Spahni along the Carihuela III gallery and on the external terrace. His excavation was limited to the postglacial layers (Vega Toscano, 1990).

In 1969-1970 the University of Madrid with the assistance of staff from Washington State University under the direction of Almargo Basch restarted the excavation concentrating in the entrance area (Gilman and Thornes, 1985) (Figures 10.6, 10.7). This campaign was carried out with extensive means and modern methodology and burnt flint samples recovered from the excavation were dated by thermoluminescence. Unfortunately, except for preliminary notes, no material has been published to date by this expedition and while the actual TL dates are known



Figure 10.5

Carihuela cave. Section showing the areas excavated by Spahni, Washington State University and Vega Toscano. (after Vega Toscano, 1988)



Excavated by Vega Toscano

Carihuela cave plan showing the areas excavated by Spahni, Washington State University and Vega Toscano. The ESR samples came from the 2x2 m. excavations by Washington State and Vega Toscano. Contours are 1 m. intervals [descending 0 to 4 m.]. (after Vega Toscano, 1988).



Carihuela cave, stratigraphy of the east wall of the Washington State University excavation. The layers shown contain Mousterian industries. All the ESR samples for level V came from this area at the entrance to the cave. Sediments are light to dark brown silty clay and eboulis is limestone. (from author's 1996 field sketches) they have not been correlated with the archaeological layers (Vega Toscano, 1990; Carrion, 1992; Vega Toscano et al., 1996; Gösku et al., 1974). A new program, still underway, involving extensive interdisciplinary research was initiated in 1979 and continues currently. In 1987 Vega Toscano excavated at the site to support his graduate dissertation (Vega Toscano, 1988) (Figures 10.6, 10.8).

The extensive stratigraphy of this site in 12 layers ranging from lower Middle Paleolithic to Upper Paleolithic is rich in lithics, faunal and palynological material (Figure 10.9). It has been used as the main reference for all other Paleolithic sites in the southern region of Spain (Vega Toscano et al., 1988; Vega Toscano, 1990; Carrion, 1992; Vega Toscano, 1993).

The human fossil remains discovered by Flint in 1848 at Forbes Quarry in Gibraltar were in fact those of a Neanderthal individual, although not recognized as such at the time. The archaeological potential of this area was ignored until the field work carried out by Garrod in 1925 with the excavation of the Devil's Tower site which had been identified by Breuil as early as 1917 (Breuil, 1922; Obermaier, 1924; Hoyos Sanz, 1963). In spite of the discovery of additional human remains by Garrod no further significant archaeological work was undertaken in Gibraltar until Waechter's excavation at Gorham's cave under the auspices of the British Museum of Natural History in the period 1948-1954. Trenches were dug in two sections, one at the back and one at the front of the cave, and 19 archaeological layers ranging from the Acheulean to the modern were identified. Results of the field work were only partially published (Waechter, 1951; Zeuner, 1953; Waechter, 1964; Zeuner and Sutcliffe, 1964) (Figure 10.10, 10.11).

After another long hiatus, work at Gorham's cave is currently proceeding under the direction of C. B. Stringer and the auspices of the British Museum of Natural History. The project involves a multi-disciplinary research approach with age determinations being attempted by means of ESR, OSL, <sup>14</sup>C and Palynological analysis. Excavation has been taking place inside the cave in the inner section originally worked in 1948. Several occupational layers ranging from Iron Age to Mousterian have been identified so far (Figure 10.12), however until now all attempts to recognize the stratigraphy proposed by Waechter have failed.





Carihuela cave. Stratigraphy of the north wall of the Vega Toscano excavation. The levels contain Mousterian industries. All ESR samples for level VII came from this area. Sediments are light to dark brown silty clay and eboulis is limestone. (from author's 1996 field sketches)

# Figure 10.9

| Levels | Industry          | Human remains          |
|--------|-------------------|------------------------|
| I      | Upper Paleolithic | _                      |
| II     | Upper Paleolithic | -                      |
| 111    | Magdalenian       | H. s. sapiens          |
| IV A   | Aurignacian       | H. s. sapiens          |
| IV B   | Mousterian        | -                      |
| V      | Mousterian        | H. s. neanderthalensis |
| VI     | Mousterian        | H. s. neanderthalensis |
| VII    | Mousterian        | -                      |
| VIII   | Mousterian        | H.S. neanderthalensis  |
| IX     | Mousterian        | -                      |
| Х      | Mousterian        | -                      |
| XI     | Mousterian        | -                      |
| XII    | Mousterian        | -                      |
|        |                   |                        |

Carihuela cave. The cave contains 12 levels with rich lithic industries ranging from Middle to Upper Paleolithic. What makes this site important is not only the long archaeological sequence but the fact that human remains have been recovered from 5 living floors. .

.



Gorham's cave. Details of Waechter's excavation plan. The lowest depth reached by the 1948-50 excavation was level N. The excavation was amplified but not deepened during the 1951-52 campaigns. Layer U was reached only in the 1953-54 season. Contour intervals are 1 m. [over sea level]. (after Waechter, 1951, 1964)





Gorham's cave. Waechter's stratigraphy. TheESR museum samples were tagged as provenant from Waechter's layers G, K, M, P, R. (from Waechter, 1964)



Gorham's cave, Stringer's excavation stratigraphy. Two areas have been excavated by Stringer. Area I was cut into the vertical face left by Waechter at the rear of the cave. Area II was excavated further eastward in the cave interior through what is assumed to coincide with the floor of Waechter's level H. (from author's 1996 field sketches)

Vanguard cave is adjacent to and approximately 300 m north of Gorham's. It consists of two chambers: a much larger south cave and a smaller shelter opening onto the north wall of the main cave (Figure 10.13). Excavation was first started in 1996 by the same group currently working at Gorham's and following the same approach. Two shallow Middle Paleolithic strata separated by a deep sterile layer have been identified in the main cave. Both contain hearths and several artefacts. Remains are indicative of short-lived occupation. In the north shelter three living floors contain remnants of charcoal but no artefacts have been found to alternate with remains of hyena. No dates for the remains from this site have been published yet.

Figure 10.13



Vanguard cave, Plan and stratigraphy. The original E-W trench in Vanguard south intercepted two living floors which were subsequently excavated. Sample ESR 7 was recovered from the trench below level 105 at elevation -6.14m. (from the author's 1997 field sketches)

# CHAPTER 11. ARCHAEOLOGICAL STRATA AND EXCAVATED MATERIAL

#### 11.1 Archaeological strata

### 11.1.1 El Castillo

The Monte Castillo is located 1 km south of the small town of Puente Viesgo in Cantabria. Its conical shape with steep sides rises 355 m above sea level. Five caves carved out of the Liassic limestone of the mount open at approximately the 200 m level. They appear to have been formed from the original Tertiary land surface in the Mio-Pliocene with little enlargement since (Butzer, 1981). The El Castillo cave faces north-east and it extends 190 m into the mountain. It consists of an ample outer vestibular area followed by a series of parallel chambers and of a longer inner gallery where cave paintings have been found (Almagro, 1973).

None of the occupational beds are developed beyond the vestibular area. Their bedding gradients show that the provenance of the deposits accumulated was external to the cave, except for the eboulis which suggest overhang collapses. This is particularly evident in the detritus accumulated outside the current cave opening. The sediments in the vestibule are approximately 20 m thick, are comprised of deposits from the Acheulean to the Bronze age and extend to bedrock (Obermaier, 1924; Cabrera Valdes, 1978; Butzer, 1981; Straus, 1992). Their pH ranges from 7.2 to 8.3 (Butzer, 1981). Archaeological material and fauna recovered have been described in detail by Cabrera Valdes (1978) and the geology of the sediments by Butzer (1981).

Butzer (1981) recognized 31 separate sedimentary layers encompassing the 26 separate archaeological levels identified by Obermaier and Cabrera Valdes (1978). Hearths were present in levels 6a, 6b, 8a and 8b. Sediments range from sandy clay to loam, some containing eboulis (Butzer, 1981).

A number of animal teeth together with samples of the appropriate sediment have been recovered *in-situ* from what were deemed to be the final Mousterian layers and were dated by Rink et al. (1996). Field dosimeters were also placed within 1 m of the location from which the tooth samples were recovered.

# 11.1.2 El Pendo

The cave of El Pendo is situated 2 km south of Escobedo and 11 km southwest of Santander. All this area of Cantabria consists of a hilly karst topography carved from Tertiary limestone with frequent sink holes 40-90 m deep. The area is also characterized by frequently appearing and disappearing water courses. The El Pendo cave opens to the south on a karstic depression. It is approximately 150 m long and 25 m wide at its largest point. Its entrance is approximately 85 m above sea level and some 5 m above the current elevation of the floor of the karstic uvala on which it opens (Figure 10.2, 10.3).

There is evidence of at least 5 distinct roof collapses inside the cave as well as of the collapse of the overhang at the front end. The cave was formed by a stream which drained the uvala. The stream now runs some 10 m below the Pleistocene deposits of the cave. According to Butzer (1980; 1981) it does not appear to have played any role in their accumulation while Hoyos Gomez and Laville (1982) believe it is a major contributor to the internal redeposition of sediments.

Butzer believes that the presence of considerable vegetation on the floor of the depression and in front of the cave and the height of the sill above the exterior ground level would suggest that internal deposits are due only to the natural environmental degradation of the cave itself and to human occupation. The latter is suggested by the high organic composition of the sediments (Butzer, 1980). However the presence of considerable algae growth inside as far as 15 m from the cave entrance drip line (Butzer, 1980) suggests a continuous water infiltration into the cave perhaps at least along the vertical rock face at the exterior. Hoyos Gomez and Laville point out that the uvala in front of the cave acts as a collection basin for atmospheric precipitation as demonstrated by the presence of dry arroyos on the uvala's floor. Furthermore the floor of the depression is much higher than the level of the archaeological zones excavated within the cave and therefore the stream draining it would flow through at least some part of the cave (Hoyos Gomez and Laville, 1982).

Fauna and pollen contained in the cave's sediments have been described by Gonzales Echegaray et al. (1980) and sediment geology by Butzer (1981) and Hoyos Gomez and Laville (1982). Echegaray recognized 18 archaeological levels (Figure 10.4) while Butzer identified 22 separate geological layers ranging from 7 to 120 cm in thickness. Hoyos Gomez and Laville identified 24 main levels. They encompass the eighteen archaeological levels identified by Gonzalez Echegaray, plus, in the case of Hoyos Gomez and Laville, two upper layers one of which contains remains from the Bronze Age. Levels I to VIII are visible starting from just inside the current sill of the cave, while levels IX to XVII are seen only further inside and level XVIII is found only at the bottom of the main excavation which occurs some 50 m from the entrance (Butzer, 1980). All levels tend to thin away from the cave entrance. The presence of hearths in layers II, V, VIII, X to XIV seem to suggest that the archaeological material in these units might not have been redeposited. Sediments consist mainly of silty clay loam, some containing eboulis and some showing a loess type texture ranging from 7.4 to 8.1 in pH (Butzer, 1980).

There is some disagreement between the analysis of Gonzales Echegaray and Butzer and that of Hoyos Gomez and Laville regarding layers VIII b and VIII d. The former assume the two layers to be different, the latter see level VIIId as the continuation of level VIIIb in another section of the excavation. Bernaldo de Quiros seems to support the latter (1978).

The archaeological material recovered by Echegaray ranges from Azilian to Mousterian. Light occupation is evident in layers XVII and XVIII but no diagnostic artefacts have been found in these levels. The Mousterian occupation appears first in Layer XVI and disappears after level VIIId (Butzer, 1980; Gonzalez Echegaray et al., 1980; Butzer, 1981). The sediments of these layers appear to indicate successive waves of longer cold periods interspersed with temperate conditions and varying degrees of moisture. The Mousterian levels are not separated by any sterile deposits. They display evidence of different durations of occupation but mainly moderate to heavy with very prominent hearths. Artefacts recovered are of the Typical and Denticulate kind without any apparent chronological order. Interestingly there does not appear to be the calcite layer between the terminal Mousterian and the early Aurignacian levels which is found in most other Iberian caves including those in the Cantabrian region.

The levels excavated by Gonzalez Echegaray did not reach bedrock. This was reached by R. Montes and J. Sanguino of the Universidad Complutense of Madrid who dug a 1.5 m x 0.3 m square 2.7 m into the heavy eboulis below level XV. Their excavation parallels and amplifies Gonzalez Echegaray's "well". They recognized 7 separate layers (named A to G; Figures 11.1, 11.2) in place of the levels XVI to XVIII identified by Gonzalez Echegaray and one additional layer (H) beyond them to bedrock.

The material recovered in their excavation resembled that recovered by Gonzalez Echegaray, consisting of Mousterian tools in the upper section and undiagnostic material in the lower levels. The upper four layers (A to D matching the old levels XVI and XVII) are greybrown and contain extensive voids with lack of fine sediments indicative of rapid accumulation. Layer B contains some dispersed charcoal. Eboulis and what appears to be angular spalls are mixed with significant amounts of splintered animal bones. Some eboulis and bones in the bottom quarter of layer D seem to be encrusted with calcite deposits. Layer E is yellowish brown with silty clay and is poorly sorted. Fewer bones mainly in the form of chips appear in this section. Layers F to G (corresponding to the old level XVIII) are similar in composition to the upper four but contain some charcoal and fewer voids, and layer H is yellowish-brown with silty loam and coarse spall with significant voids and concentrations of larger bones.

Dosimeters were inserted in the face of the Montes/Sanguino excavation: 3 units in layer B, 1 in layer D, 3 in layer F and 3 in layer H. Tooth and sediment samples were collected from layers B, D, F and H (Figure 11.2).

## 11.1.3 Carihuela

The cave of La Carihuela is just outside the town of Piñar in Andalusia, some 45 km north east of Granada. The cave opening is located at 1020 m above sea level and 170 m above the valley floor on the northern slope of Mount Castillo. The hill is formed from a highly fractured Lower Jurassic limestone forming part of the foothills of the Sierra Nevada. The limestone is traversed by a number of subterranean streams, some emerging as springs. One appears approximately 30 m below the Carihuela.

The cave is approximately 300 m long and is aligned in the N-S direction. Two parallel galleries forming 3 chambers extend southward from three main openings for some 20 m from



Et Pendo Gavo, Composite photograph of the north wall of the Montes/Sangumo excavation, Levels A to H are clearly visible.

:



Figure 11.2

El Pando cave. The Montes/Sanguino stratigraphy. This excavation extends northward the original well dug by Echegaray. The black dots indicate the location of the dosimeters.
the sill before joining (De Lumley, 1973; Carrion, 1992) (Figures 10.5, 10.6). It is in this section of the cave that most of the excavation has taken place. There is evidence of several roof collapses at the interior of the cave as well as of the collapse of the overhang which projected beyond the current sill. A chimney breached the largest and furthest chamber of the cave. The cave deposits reach a thickness of approximately 6 m (Vega Toscano et al., 1988) (Figure 11.3). Pollen analyses suggests that the sediment in the front chambers are derived from the entrance. The layers in fact dip strongly inward. Sediments in the central chamber instead show mixed origin apparently blended with material from the chimney (Carrion, 1992).

Twelve separate main archaeological layers containing artefacts ranging from the Mousterian to the Bronze Age have been identified in the cave; none reach bedrock (Vega Toscano 1990) and the upper 3 appear only as traces (Carrion, 1992). Sediments vary in composition from layer to layer and range from clayey silts containing organics to large eboulis. Blocks and large angular clasts are found extensively in layers X, VIIB and less frequently in levels IV and V. Levels VIIb and VIII as well as IVA and IVB are separated by a calcite flow. Above the last flow the material recovered belongs to the Upper Paleolithic and later periods. Below the flow, the material is all Mousterian. Levels II and IVA contained remains of *Homo sapiens sapiens* while Neanderthal remains were recovered from levels V, VI and VII (Vega Toscano, 1993).

The lowest deposits have been interpreted to suggest a humid and warm environment. Conditions appear to deteriorate in level XI with pronounced cooling in level X. A more temperate period occurred during the deposition of level VIII followed by harsher conditions during level VIIB and a moderating trend in level VIIA. After a period of marked erosion Level V marks a return to a very cold dry climate and was followed by a return to milder conditions in level IV (Figure 11.4).

The sedimentary sequence and the fauna contained therein have been described by Vega Toscano et al. (1988) and Carrion (1992), lithics by De Lumley (1969) and pollen sequences by Carrion (1992). Human remains have been discussed by Garcia-Sanchez (1960), De Lumley (1973) and Vega Toscano (1993). Figure 11.3



Carihuela cave. View of the interior looking south. Visible is the south wall of Spahni's excavation.

Figure 11.4

| Carihuela cave - climatic sequence |       |         |          |                |  |  |
|------------------------------------|-------|---------|----------|----------------|--|--|
|                                    | Tempe | erature | Humidity |                |  |  |
|                                    | + Hot | - Cold  | + Humid  | - D <b>r</b> y |  |  |
| Level I                            |       |         |          |                |  |  |
| Level II                           |       |         |          |                |  |  |
| Level III                          |       |         |          |                |  |  |
| Level IV                           | Γ     |         |          |                |  |  |
| Level V                            |       |         |          | ך              |  |  |
| Level VI                           |       |         |          |                |  |  |
| Level VII                          |       |         |          |                |  |  |
| Level VIII                         |       |         |          |                |  |  |
| Level IX                           |       |         |          |                |  |  |
| Level X                            |       |         |          |                |  |  |
| Level XI                           |       |         |          |                |  |  |
| Level XII                          |       |         |          |                |  |  |

Carihuela cave. Proposed climatic sequence based on results of floral and faunal analyses (after Vega Toscano, 1988). From the period in which level X started to be deposited the cave has been subjected mainly to dry conditions.

•

.

.

Twenty eight teeth for the Carihuela site were obtained from the collection of the Madrid Natural Sciences Museum, and eight were recovered in-situ. The museum material was identified as to the layers from which they had been retrieved (V, VI, VII, etc.), but no co-ordinates were given to indicate their actual position in the field. A number of sediment and moisture samples were collected in the field from the layers associated with the teeth. Unfortunately there is no way to determine the actual distance which may have separated sediment samples and museum teeth. The layers to be dated are clearly visible in the most westerly chamber of the cave both in the area excavated by Spahni and the two separate areas trenched by the University of Washington and by Vega Toscano (Figure 10.6, 11.5). The latter two are located further north than the Spahni excavation and immediately beyond the cave sill. The site dosimeters were placed in the exposed faces of the two trenches: 4 units were placed in level V, 3 in level VI and 3 in level VII.

Level V is comprised of angular clasts and sandy clay material of a grey/brown colour. The level contains 6 sub-units identified mainly by the relative coarseness of the deposits; the majority of the large eboulis is in the lowest of these. Level VI is composed of organic very silty clay of a slightly darker colour. It consists of 8 sub-units of relatively uniform composition identified by a slight variance in their colour (Figure 10.7). Level VIIA contains carbonate deposits in sparse sandy clay of light brown colour and level VIIB, comprised of 3 sub-units, contains limestone pebbles and blocks alternated with sandy clays of brown colour (Figure 10.8).

The cave conditions are currently extremely dry with no evidence of any floral growth. There is also no apparent evidence of any bioturbation in the levels studied.

### 11.1.4 Gorham's cave

Gorham's cave is one of several cut into Tertiary limestone at the base of the cliffs and on the east side of the Gibraltar peninsula. It is reached from above via a steep 342 step stairway built recently by the military. Only the narrow boulder and pebble Governor's Beach lies in front of the cave so that access to it via terra firma is not currently possible.



Carihuela cave. View of the interior looking north. Visible is the north wall of Vega Toscano's excavation (at bottom of picture). Washington State University's work was carried out north of the area excavated by Vega Toscano (visible at top of picture).

The entrance to the cave is approximately 10 m above the present sea level. It faces southeast and is comprised of a single chamber framed by an outer arch which is considerably higher than an inner one. It extends for 55 m and at its maximum girth it reaches approximately 9 m in height (Figure 10.10). The width of the cave opening exposes the interior to the elements and the moisture of the facing sea. The walls show evidence of continuing algae growth.

The interior is partly filled with aeolian sand. Sediments lie at a natural angle of repose, are generally uniform and include some calcite concretions fallen intermittently from the roof as well as organic material imported during periods of occupation. There is evidence of collapse of the outer portion of the cave overhang. Although there appears to be no percolation through the limestone roof at this time, the presence of stalagmites/stalactites in various sections of the cave attests to past periods of significant warmth and humidity.

Twenty three main levels, generally dipping toward the centre of the cave, were identified by Waechter (Figure 10.11). The lowest reached, layer U, was a fossil beach of sterile white sand. Occupational floors appear to start at level R; some are separated by sterile layers and others by calcite flows. The levels which show evidence of human occupation contained cultural material ranging from Mousterian to Punic. Upper Paleolithic material has been recovered from layer B to F. The site appears to have been abandoned by humans during the deposition of layers K and M as suggested by the presence of hyena coprolites and remains of juvenile hyenas.

Stringer's excavation so far has identified twenty two separate contexts which have not been correlated yet with Waechter's levels. The higher contexts have yielded Upper Paleolithic material and the lower ones Mousterian artefacts. Faunal remains have been far fewer than those recovered by Waechter in his excavation campaigns.

The presence of significant sand accumulations between calcite concretions suggests the alternating of low and high sea levels, the sand corresponding with the former. At low sea levels a shelf would have existed from which the sand would be blown and across which access to the cave by humans and animals would have been possible.

Tooth samples collected from the Gibraltar Museum were apparently recovered from levels G, K, M (Figure 11.6, 11.7) and also P and R (Figure 10.11). Site dosimeters were placed in



Gorham's cave, west wall of upper section of Area "A" (ref.: Figure 10.10). These layers were assumed to correspond to E to J in the Waechter stratigraphy. Gamma spectrometer readings were taken in this area at locations shown as Gam 2 to Gam 6. (from author's 1995 field sketches).

Figure 11.6





Gorham's cave. West wall of lower section of area "A" (ref.: Figure 10.10). These layers were assumed to correspond with levels I to M in the Waechter stratigraphy. One gamma spectrometer reading was taken at the location shown as Gam 7. Dosimeter TLD 1 was emplaced in layer M. (from author's 1995 field sketches)

what is believed to correspond to Waechter levels M (Figures 10.11, 11,6) and P (Figure 10.11). The sterile level N/O was the lowest layer reached during the 1948-50 campaign in a small trench on the south side of the cave. The sterile level H was the lowest reached in the main excavation. Above it, level G contained Mousterian flakes and some traces of charcoal in a "streaky and slightly sticky" matrix not further identified by Waechter. Level K also contained Mousterian material embedded in dark sand and is separated from the layer above it by a "thin hard crust" probably a layer of concreted sand about 1 cm thick (Waechter 1951; Waechter, 1964). Laver M is the third Mousterian laver. It contained flakes and charcoal embedded into a matrix very similar to that of level K. It was separated from the preceding levels by a layer of clean yellow sand containing a few bones and shells but no archaeological material. Excavation of layers P, Q, and R was begun in the 1953 season. Level P is a rather thin dark sand deposit rising toward the back of the cave. No hearths were found but several Mousterian implements and bones were recovered. Layer Q contained some bones and shells embedded in clean vellow sand. The bottom of the layer was horizontal. Layer R, the lowermost Mousterian level, consisted of yellow sand interspersed with "sticky dark patches" (Waechter, 1964). Several stalagmite pieces were found scattered within the sediments as well as pebbles coated in calcite. No hearths were discovered but charcoal, implements, bones and shells were all recovered.

The stratigraphy and artefacts of the layers uncovered in 1948-1954 have been described by Waechter (1951; 1964) (Figure 10.11) and by Zeuner (1953), *Mammalia* were discussed by Zeuner and Sutcliffe (1964), *Mollusca* by Baden-Powell (1964) and *Chelonia* by Delair (1964).

The first material obtained for Gorham's cave was culled from the Mousterian Waechter collection of the Gibraltar Museum. As at Carihuela, sediment samples were retrieved from layers supposedly associated with the teeth. The uncertainty regarding the Waechter stratigraphy however renders such association suspect.

Seven samples containing fourteen teeth in total were also obtained from the Stringer excavation from layer 22 (originally identified as context 106) in area II (Figure 10.12). Three of the samples were recovered in 1995, one in 1996 and three in 1997. The sediments of layer 22

consisted of coarse yellow sand. Appropriate moisture and sediment samples were collected from this context. Layer 22 yielded also pine seeds and flakes produced with clearly Middle Paleolithic technology.

One sample, a rhino tooth with some calcite still attached, was recovered in 1996 on the surface outside the cave toward the south wall approximately 10 m from the cave entrance.

## 11.1 5 Vanguard cave

Vanguard cave is located 100 m. north of Gorham's on Governor's Beach. The opening is formed by a single large arch facing eastward. The cave is not as deep as Gorham's, extending only approximately 30 m (Figure 10.13). As at Gorham's, only a narrow boulder and pebble beach lies in front of the cave and access via terra ferma in the past would have only been possible in periods of low sea levels.

The entrance to the cave is approximately 10 m above the present sea level. It is comprised of a southern chamber which narrows toward the interior and a much smaller northern chamber right beside the current cave opening. The width of the cave opening is much larger than Gorham's and the interiors of both chambers are entirely exposed to the elements and the moisture of the facing sea.

The interior of the southern chamber is partly filled with aeolian sand. When first discovered, the northern chamber was entirely filled with very damp deposits. Sediments lie at a natural angle of repose, are generally uniform and include some straw stalactites fallen intermittently from the roof as well as organic material imported during periods of occupation. There is evidence of collapse of the outer portion of the cave overhang. Although there appears to be no percolation through the limestone roof at this time, the presence of calcite flows on the walls of the cave suggest past periods of significant warmth and humidity.

Only two archaeological layers have been uncovered in the southern chamber. They are separated by thick deposits of sand. Mousterian artefacts, hearths, bones and shells have been recovered from both levels. One ibex mandible containing six teeth was recovered from the lower layer in 1997.

An artiodactyl jaw with two teeth was also recovered in 1996 from a shallow context below the lower layer. Dosimeters were placed at both locations and sediment and moisture samples were collected.

Four shallow archaeological layers have also been uncovered in the northern chamber. The uppermost contains scatters of charcoal but no lithics. The second contains hyena bones. An ibex jaw with a single tooth was recovered from this layer. The third layer contains a hearth but no lithics. The last contains hyena bones and coprolites. The evidence collected to date would seem to suggest that human occupation was of short duration. It also indicates that all the deposits in the northern chamber have been subjected to bioturbation. A dosimeter was placed in the second layer and moisture and sediment samples were collected from it (Figure 11.8).

Trace element analyses have shown that little or no uranium is present in any of the enamels of the teeth recovered so far at all the above five sites (Table XIX, Appendix C). In view of the absence of uranium contamination a comparison of ESR ages with results obtained by other methods will allow the confirmation of the basic algorithms used in ESR calculations since the distortion caused by diagenesis will be absent.



Vanguard cave. A = Vanguard South, plan of layer 106 showing the location of TLD 1. The excavation did not extend to the cave walls; B = Vanguard North, plan of layer 1102 showing the location of the ibex tooth find and of dosimeter TLD 4. The dosimeter was placed 2 m. from the spot from which the tooth was recovered. (from author's 1997 field sketches)

### CHAPTER 12. PROCEDURES

All the research work for this study was carried out at the Quaternary Dating Centre of McMaster University. Similar work had already been carried out by others at McMaster. However new procedures had to be developed for certain aspects of the research and a number of existing protocols were modified both when new equipment was brought on-stream and when our findings dictated changes which were more appropriate to current research.

#### 12.1 Dosimetry

Dating accuracy depends on the accuracy of the value of the radiation dose rate employed in the age calculations. The determination of the dose rate requires the measurement of the natural radiation in the burial environment. The fundamental uncertainty about environmental conditions in the burial context clouds all ESR results. Therefore, the accurate measurement of the natural radiation at a burial site is of paramount importance. Gamma radiation dominates the external component of the dose rate. This can be measured accurately by means of field gamma spectrometry utilizing portable instrumentation. The shortcoming of this procedure is that the readings taken are semi-instantaneous pictures of the environmental conditions and do not mirror seasonal fluctuations. Field spectrometry also will not mirror relevant long term fluctuations through the burial period. None the less field gamma spectrometry is useful as a confirmation of the  $\gamma$  dose actually measured by other means and as an indication of the natural radiation distribution throughout the burial site.

In general it is possible to determine the dose rate by collecting sediment and measuring the amount of naturally occurring radio isotopes present (Nambi and Aitken, 1986). Alternatively, the dose rate can be determined by emplacing field dosimeters for a number of months. The results of these analyses can usually be expected to be in agreement. This is normally the case when the burial deposits are homogeneous and the teeth to be analysed were recovered far from large rock

masses ("smooth" sites). In "lumpy sites" the results can be expected to be severely at variance, with those obtained from sediment yielding much higher values. In fact, as already mentioned, typically, fine-grained sediment contains much higher quantities of radio isotopes than a number of rock types, such as the limestone eboulis of caves (Schwarcz, 1994; Rink, 1997).

A field dosimeter placed as close as possible to the location where the tooth sample was recovered will yield results which account for the entire extant environmental conditions, such as proximity to cave walls, etc., which cannot be measured by utilizing sediment alone. It should be noted however that not even field dosimeters can account for the past history of the site. Changes in environmental conditions over long periods of time could have produced considerable changes in soil moisture, isotope migrations and other taphonomic phenomena. Accordingly for this study field dosimetry was always employed and, where feasible, appropriate sediment was collected and its isotopic content measured.

Two types of dosimeters were employed for this study. The first consisted of dysprosium spiked  $CaF_2$  phosphor enclosed in copper capsules. Panasonic type radiation monitor badges were utilized for the second type of dosimeter. Both dosimeters when emplaced in the field measure  $\gamma$  rays and cosmic radiation but do not measure either  $\alpha$  or  $\beta$  radiation.

#### 12.2 CaF, phosphor

There are several sources of  $CaF_2$ . The preferred material is of very high purity, particularly with respect to radioactive elements. The phosphor is highly sensitive to radiation and luminesces when heated after exposure. The photons emitted are proportional to the radiation absorbed. Basic dosimetric properties of  $CaF_2$  have been reported by Schayes et al. (1967) and Aitken (1968, 1990).

 $CaF_2$  requires careful preparation before use. The material is purchased commercially. It is normally received in powder form with a mixed grain size distribution. Only the 90-125  $\mu$ fraction is utilized for dosimetry, so that the material must be sieved. If insufficient yield is obtained the powder is gently ground in an agate mortar and then sieved again. Mechanical size reduction does not affect the performance of the phosphor.

The natural environmental dose of the  $CaF_2$  must be erased and its sensitivity to light must be reduced before the material can be used for dosimetry. This is achieved by annealing the powder at 600 °C. in a dry, oxygen-free atmosphere. The inert moisture-free atmosphere is necessary since the radiation sensitivity is impaired by the diffusion of oxygen and water vapour into the phosphor grains (Aitken, 1985). It should be noted that reduction in sensitivity occurs also if the  $CaF_2$  is not cooled rapidly while still under an inert atmosphere. Once this pre-treatment is carried out it need not be repeated unless there has been a significant exposure to radiation causing deep traps to be refilled (Aitken, 1985). In practice the procedure outlined in Appendix A as "Protocol for annealing  $CaF_2$  phosphor" is used.

 $CaF_2$  powder in the natural state has a thermoluminescence output several million times higher than other material being measured. Care must be taken at all times when handling the powder to ensure that laboratory equipment and surfaces connected with thermoluminescence analysis are not contaminated.

### 12.3 Copper capsules for field dosimetry and their preparation

For emplacement at archaeological sites, the  $CaF_2$  is housed inside a capsule made from high purity copper tubing (Figure 12.1). This not only allows proper handling and protection of the phosphor but permits its zeroing in the field by means of direct heating. After inserting a measured amount of  $CaF_2$  the container is rendered moisture proof by crimping and soldering both ends of the tubing. The silver used for soldering must be of high purity to ensure a low level of radioactivity from these materials. Detailed procedures are outlined in Appendix A as "Protocol for making  $CaF_2$  dosimeters".

.



Figure 12.1

CaF, desincter capsules at various stages of processing. The copper tubing is crimped at one end and soldered. It is then filled with the phosphor and the open end is crimped and soldered.

## 12.4 Emplacing and retrieving CaF<sub>2</sub> capsules

Prior to leaving the laboratory for emplacing in the field all dosimeter capsules are zeroed by heating to a cherry red colour. All units travel together to the archaeological site in a bundle to. ensure that their radiation history is common. At the archaeological site each capsule is emplaced as close as possible and in an environment similar to that from which the tooth was retrieved. When samples are obtained from museum collections and retrieval co-ordinates are not known, it is advisable to employ at least three capsules in each archaeological layer to be dated.

The dosimeters are inserted into an augered hole in the deposits to be dated. The hole should be at least 35 cm long. For ease of handling and retrieval, each capsule is placed in a 40 cm long plastic tube stoppered at both ends. The tube is then filled with sediment removed from the hole before emplacing.

Usually the burial period is approximately a year, but can be longer if necessary. In this study the dosimeters were buried for approximately one year. Shorter periods are not advisable since the capsules would not be then subject to sufficient seasonal variations in soil moisture. Three travel capsules are required in addition to the units to be emplaced in each archaeological site. The former are needed to determine the radiation dose received while the dosimeters are in transit between laboratory and site and back again.

The first of these units is zeroed before leaving the laboratory as indicated above. The second is zeroed at the site when the field capsules are emplaced. After emplacement these two travel units are returned to the laboratory, where they are stored together in a shielded lead pot to limit further exposure to  $\gamma$  rays from the surrounding building materials. The third unit is zeroed at the site when the field capsules are retrieved, travels back with them and is stored with them and the previous two travel units at the laboratory. The use of three travel units has been the traditional approach to site dosimetry. This is due to the fact that often it is impractical to heat the capsules at the actual excavation, and zeroing is carried out offsite. However only one . unit is necessary if all field dosimeters can be zeroed in the field before being emplaced, thus simplifying the procedure.

#### 12.5 Panasonic dosimeters

The Panasonic dosimeters are much easier to prepare and handle than  $CaF_2$  units. They can also be reused several times after zeroing, while instead in the process of reading the  $CaF_2$  dosimeters the capsules are destroyed. The Panasonic units consist of four sealed cells each containing phosphor (Figure 12.2). These phosphor cells are mounted on a rigid plastic frame which is inserted in a plastic sheath. Three of the cells are utilized for the actual dose measurement, while the fourth is a reference unit. The absorbed dose measurement for each emplacement location is thus averaged over three readings, improving accuracy. The units are ready to use as purchased from the manufacturer but must be zeroed before emplacement (Yamashita et al., 1972). They also must be protected against moisture before travelling to the field. To achieve this the frame mounted phosphor cells are placed in a reusable 1 cm diameter 5 cm long capsule of high purity copper (Figure 12.3).

The procedures for the preparation of Panasonic dosimeters are outlined in Appendix A as "Protocol for preparing Panasonic dosimeters for the field". Procedures for zeroing/reading the Panasonic dosimeters are described in Appendix A in "Protocol for reading and zeroing Panasonic dosimeters".

#### 12.6 Emplacing Panasonic dosimeters in the field

The procedure is the same as that already outlined for the  $CaF_2$  dosimeters. The plastic tubing used to house the dosimeter emplaced in the field must be of sufficient diameter to accommodate both  $CaF_2$  and Panasonic units when necessary. In some instances both types were emplaced in a single plastic tube as a confirmation check.

Apparatus to permit zeroing of the Panasonic units in the field has been developed recently by the McMaster Quaternary Dating Centre. However it was not yet available when the field work for this study was in progress. Therefore  $CaF_2$  dosimeters had to be used always to determine travel doses.



Figure 12.2

Panasonic dosimeters. The frame containing the phosphor (at right) is insorted in a plastic holder for normal laboratory handling and storage (top and left).

•



Papasonic dosineters and their burial capsules. The frames containing the phosphor are wrapped in plastic film and placed inside copper tubing capsules. The latter are sealed at both ends by means of copper caps secured with silicone cement.

109

## 12.7 Retrieving dosimeters from the field

Unfortunately many archaeological sites do not offer adequate security during the off-season. As a result it is not unusual to have a number of dosimeters stolen or displaced. It is also possible that excavated sections may slump or that cave roofs may collapse impeding the retrieval of dosimeters. Upon retrieval the units recovered must immediately be removed from their plastic tube containers and bundled together with a return travel dosimeter. The copper capsules containing the Panasonic units must be unsealed at one end and the cell frames must be unwrapped and checked for integrity upon receipt at the laboratory. The copper capsules should also be checked for moisture. If they are in good conditions the Panasonic elements are rewrapped and stored inside their copper capsules in the laboratory shielded lead pot pending testing.

## 12.8 Reading the CaF<sub>2</sub> dosimeters

 $CaF_2$  dosimeters retrieved from the field should be read as soon as feasible since, even when stored in lead pots, they tend to accumulate some natural background dose. Although generally very small, the amount can accumulate over time and eventually approaches the values of the travel dose. In the case of the storage facilities at McMaster this annual dose has been measured at 340  $\mu$ Gy/y.

The travel dosimeters and one dosimeter from each site must always be analyzed before any other units from the same site. The results of this preliminary analysis may reveal that there are some problems either due to original manufacture errors or field/travel contamination. If any damage is revealed it would not be profitable to proceed with more extensive work.

The copper capsules are retrieved from the storage lead pot and they are handled using the procedures included in Appendix A as "Protocol for preparing TL cupels".

The apparatus used for analyses of the dosimeter phosphors in this study was a Daybreak 1100 Automated TL System utilizing a Thorn EMI Electron Tube type 923500 coupled to a United processor (Figure 12.4). Procedures for operating the apparatus and processing the dosimeters are included in Appendix A as "Protocol for establishing laboratory beta dose for  $CaF_2$  dosimeters" and "Procedures for measuring TL phosphors".

Care must be taken to ensure that the dosimeter material does not contaminate anything else in the laboratory and that all work is always carried out under subdued orange light. Care also must be taken to maintain equipment cleanliness at all times. After use the cupels must be cleaned with MEK and then rinsed in acetone and air dried. The work bench on which the readied cupels were placed must be wiped clean and a check must be made that no phosphor grains have been left inside the reader. Cupels must be cleaned in a fume hood and outside the TL laboratory. Detailed procedures are outlined in Appendix A as "Protocol for cleaning cupels".

#### 12.9 Dose rate calculations

The dose rate measured through direct field dosimetry should be compared with that estimated via the isotopic composition of the sediments. The technique which permits the determination of the U, Th and K content in sediments is Instrumental Neutron Activation Analysis (NAA). The procedure relies on the transformation of the natural elemental nuclei in the sample fabric into radioactive ones allowing the subsequent measurement of the  $\gamma$  radiation which emanates from them. This permits the detection of concentrations down to  $10^{-6} \mu$ . grams. Neutron activation for quantitative elemental analysis was proposed as early as the 1930s. However practical applications were not possible until the advent of operational nuclear reactors in the 1950s. Currently the determination of provenance of materials through the identification of their trace elements composition is a well established procedure (Pavlish et al., 1985; Glascock et al., 1994; Volterra and Hancock, 1994; Volterra, 1994).



TL apparatus. The McMaster Quaternary Dating Laboratories' Daybreak 1100 automated system utilising a Thorn EMI electron tube type 923500. The United processor is not shown.

Neutron activation relies on the bombardment of samples with neutrons. In this case slow thermal neutrons, produced by an atomic reactor, are captured by the nuclei of stable isotopes present in the sample. The resulting compound nuclei have the same atomic numbers but a larger mass than before bombardment. This renders them unstable. These radioactive nuclids deexcite by emitting  $\beta$  particles followed by  $\gamma$  rays which have characteristic energy levels for each element contained in the sample. The amounts of  $\gamma$  ray decay products are proportional to the quantity of each element present. By measuring the former we can identify and quantify the elements composing the samples. The basic activity equation is:

$$\mathbf{A} = \mathbf{N}\mathbf{f}\sigma(\mathbf{1} \cdot \mathbf{e}^{-\lambda t})$$

where:

A = the number of disintegration per second

**N** = the number of atoms of the target element present in the sample

 $\mathbf{f}$  = the neutron flux of the reactor

 $\sigma$  = the cross section of the target sample

 $\lambda = \ln 2 / \text{half life of the isotope}$ 

t = the time duration of the bombardment

The original procedure involved a purely radiochemical analysis using Geiger or scintillation counters after separation of components into radio-chemically pure forms (Hoste et al., 1971). This presented considerable drawbacks since a large number of subsamples had to be analyzed serially. Such a procedure was very cumbersome particularly since short lived isotopes often cannot be separated readily after irradiation.

The current approach uses nuclear reactors with high, reliable neutron fluxes and advances in high resolution  $\gamma$  ray spectrometry, with detecting apparatus close-coupled to computer-driven counters run with sophisticated software. Such instrumented analysis permits the automatic conversion of the radiation spectra into meaningful digital results, making INAA a most productive archaeometric technique for the measurement of a wide array of trace element compositions when a large number of archaeological samples are involved. Another advantage is that only very small samples are required to obtain a positive identification and quantification of elemental compositions. However, it should be noted that detection limits are related to  $\gamma$  ray energy and radioactive half life as well as to sample mass, and can be seen to vary up to an order of magnitude depending on the properties of the isotopes used for analysis of each element (Hancock et al., 1991).

All the sediment and dental samples were analyzed using the facilities at the McMaster University atomic reactor.

The reconciliation between dose rates measured by dosimetry and those measured by isotopic analysis is achieved using the procedure included in Appendix A as "Reconciling measured dosimeter doses and doses calculated from sediments".

# 12.10 Sample collection

## 12.10.1 Field collection

# 12.10.1.1 Tooth and sediment collection

The reality of archaeological excavation creates a number of significant problems in the recovery of appropriate samples. Hopefully, most teeth will be found *in-situ*. In the case of teeth found under other conditions, such as those recovered by sieving, only partial recovery of the key doserate information available from the sediments is possible.

As mentioned above it is important that the correct portion of sediment related to the sample is collected. Preferably this should be the sediment closest to the side of the tooth that is going to be used for ESR testing. However at least 50% of the sediment is always removed before the sample is recovered (Mellars et al., 1997). Furthermore, depending on local conditions and type of sediment, the deposit may be so friable as to become readily separated from the tooth surface to which it originally adhered either at collection time or in transit or storage. Accordingly it is often not possible to meet the strict requirements of collection.

### 12.10.1.2 Procedures for Recovery of In-Situ Teeth

A tooth found partially exposed in a square or in a section is like the discovery of a watch ticking away in the archaeological deposit. Either it can be carefully extracted and eventually the time can be read or its hands can first be accidentally removed, so that the value of the discovery is lost. The need for proper collection of tooth and the associated sediment samples is dictated by the distances which are travelled by  $\beta$  and  $\gamma$  radiation as outlined above (Grün, 1989). The main problem in tooth collection is the need to preserve the source of the  $\beta$  irradiation. This is achieved by conserving the material found within 2 mm of the tooth surface separately from the rest of the sediment.

The longer travel of  $\gamma$  radiation means that a sample of sediment from a sphere 30 cm in diameter must be collected. The in-homogeneity ("lumpiness") of the sediment in which the tooth is buried is of concern. Therefore the latter sample must be as representative as possible of the layer in which the tooth was recovered.

## 12.10.1.2.1 Recognition of teeth and location:

It is important to become familiar with the appearance of a tooth emerging in a square or section being excavated. Ideally, when the first tooth is found at the beginning of a dig, all workers should be shown the partially excavated specimen so they can have some idea what to look for. Also one person should be selected to be in charge of teeth. From then on, whenever a tooth is identified, the person selected should be called, and the recovery should be done jointly with the digger of the square.

Detailed notes must be taken regarding the X,Y,Z coordinates of the find, the horizon in which it was found, and a description (ideally including a sketch) of the position of the tooth with respect to other objects in the square. All this information should be provided to the ESR laboratory along with the tooth. Normally a tooth is first revealed through gradual removal of the surrounding sediment, so that some sediment should be still left surrounding the tooth before removal (Mellars et al, 1997). The same rules apply to the recovery of tooth fragments as to whole teeth, with certain restrictions as noted below.

There are four possible conditions in which a tooth may be found. Detailed procedures are outlined below for each case.

A) Tooth found lying in dry/loose or wet/sticky sediment.

1 - sediment from areas of no interest (next to the occlusal surfaces, dentine and root) can be discarded.

2 - The sediment from 3 to 10 mm away from the tooth should be collected into a separate small bag; distance away from tooth that was sampled should be noted;

3 - After the tooth has been removed, the sediment directly in contact with the enamel (< 3 mm) should be scraped; it should be bagged separately and labelled.</li>
Objects, such as bone, present below the tooth may necessitate taking sediment at somewhat further distance. An accurate record of whatever was done should be kept.

4 - Total weight of 2 + 3 should be between 0.5 and 1 gram. If weight is less, then more sediment can be obtained from cavity beneath the tooth, labelling to indicate the source of the sediment.

5 - A larger sample of sediment (10 - 100 g) should also be collected from within the 30 cm radius sphere around the tooth. If the sediment appears to be very inhomogeneous, more than one sample of this weight and representative of the sediment should be collected If there is more than one enamel surface in contact with the ground (e.g. the upper and lower surfaces) the sediments related to each exposed enamel surface should be bagged separately; both the enamel surface and the sediment should be labelled accordingly, to facilitate later matching. The enamel surface can be identified with an indelible fine tipped marker. Ideally a sketch should be made of the tooth. In the case of teeth found in wet/sticky layers, generally there will be sufficient short-range sediment attached to the tooth to provide a sample; therefore there is no need to collect additional material from the post-removal cavity.

B) Teeth found in cemented sediment.

When the tooth is firmly encased in a cemented matrix, the latter should not be removed in the field. Rather the tooth should be left covered with sediment and this should be removed in the laboratory. The same sediments should be recovered as in (A) above if it is feasible. In addition, should the cemented material adhere only partly to the tooth, a portion of sediment from the removal cavity should be collected also to add to the < 3 mm portion. Teeth for ESR dating should not be soaked in acid to remove the coating sediment; rather, this should be carefully chipped off and preserved for analysis. Sediment from within a 30 cm radius is also collected as per (A) above.

C) Enamel fragments covered by dentine (Den) and cementum (Cem).

These teeth are less desirable for ESR analysis but may be the only samples available. The sampling procedures outlined above can be modified if the enamel is not in direct contact with sediment. Sediment from within a 30 cm radius is also collected as per (A) above.

D) Teeth found in washing or sieving

Unfortunately some teeth are unrecognized during excavation, especially where many similar objects such as bone fragments or stones are also present. If a tooth appears later in a sieve sample, then the siever should immediately notify the person working in the square from which the tooth came from (if the square is known), and the person in charge of tooth care.

If the tooth is surrounded by cemented matrix then the (B) procedure above is followed. If the tooth appears to be clean, an attempt should be made to recover sediment from as close to the tooth recovery site as possible; a notation should be put on the bag and in the field notes to indicate that the sample was found during sieving and that this sediment is not true *in-situ* sediment.

When the tooth is not found until after the square has been dug too far below the level at which the tooth was found, then one can attempt to collect sediment from a nearby baulk at a comparable stratigraphic level. This also applies to museum samples (see below). Dates obtained using such distantly related sediment samples are less reliable.

## 12.10.1.2.3 General comments

It should be remembered that ESR dates on teeth are often the best available estimators for the age of a site. Accordingly it is paramount to ensure that all the procedures, including tooth collection procedures, are followed closely.

Teeth needed for ESR dating are also required by zoo-archaeologists to study the fauna at a site. The procedures described above have been designed to allow for the collection of the sediment from adjacent to the teeth after which, if necessary, teeth can be studied by the zooarchaeologist before they are processed by the ESR laboratory.

Very few teeth appear in the field to be so badly preserved that they cannot be used for ESR dating. It is advisable to try to date all those found, rather than reject them at site on the basis of their appearance. Many teeth prove unsuitable for ESR analysis once cleaned in the laboratory, therefore it is preferable to collect too many samples than too few.

As discussed previously the various location from which the teeth are recovered are of considerable importance in the final outcome of the age determination as discussed previously as well as alteration of the burial environment through the burial life can affect the ESR results. For example the presence of ash enriches the sediment with potassium while the presence of bone changes the uranium in the sediment (Schiegl et al., 1996; Avery et al., 1997; Rink, 1997).

When a number of teeth are available for sampling then those which were recovered close to fires, ash deposits or bone concentration should be avoided.

The impact of cave environments on teeth has been discussed above (Lyons et al., 1993) and so has the burial proximity to eboulis (Schwarcz, 1994; Rink et al., 1996).

### 12.10.1.3 Moisture sample collection

The process of radiation absorption during the burial period is very much affected by the moisture content of the burial medium. This is particularly significant in cases where the uranium content of the teeth tissues is low since the ESR ages are almost entirely dependent on the external dose rate (Rink et al., 1996; Rink et al., 1996b). Unfortunately there is no direct way in which the past moisture regimes can be reconstructed with absolute certainty. However it is possible and advisable to collect sediment samples to determine the current moisture content of the various contexts. While not accurate they might give an indication of the tendency of the sediment to moisture retention.

Procedures for the collection and measuring of moisture samples are outlined in Appendix A as "Collection of moisture samples and moisture measurement".

### 12.10.2 Museum sample collection

Several problems that tend to increase the uncertainty of the dating results present themselves when museum samples are used for ESR analyses. It was unfortunate that for this study museum samples had to be used for the Carihuela site and partly for the Gorham's site.

#### 12.10.2.1 Sediments

In only a few cases do museum collections include some portion of excavated sediments. When they are available they generally are only "typical" of each excavated layer. To my knowledge there is no instance in which museum teeth collections include their related sediments. In addition there is often an uncertainty regarding the actual provenance of the teeth. This is sometimes due to the lack of find field co-ordinates but is sometimes also due to the mislabelling of the samples. Therefore, even if control baulks have been left at the excavation site, the measurement of the natural dose absorbed by the teeth can only be approximate. At best, dosimeters can only be placed in, and sediment collected from, somewhere in the layer from which the samples putatively originated.

In some cases it is possible to obtain museum samples with residual sediment still attached. Such teeth should be selected in preference to others since the particles that have remained attached to them are available for determination of radioactive component concentrations and therefore potentially of the natural dose rates during burial (Huang et al., 1995). The residual sediments should be recovered as indicated in the laboratory procedures below.

The results obtained from the analyses of such sediments should be used with caution. The sediment stuck to the teeth will generally be of smaller grain size and therefore not representative of the average of all sediment (Mellars et al., 1997). Sediment particle size is related in inverse proportion to the concentration of radionuclides. This can be explained by the greater absorption capacity of smaller particles (Osmond and Ivanovich, 1992). The measured radiation levels for these samples are therefore not representative of the burial context as a whole.

#### 12.10.2.2 Preservatives and storage environment

Most museum collections have been cleaned for zooarchaeological study and preservatives have been applied to the external surface of teeth. Often the material used for such operation is not known and thus it is not possible to determine whether it has added further radiation to the sample. Furthermore it is often not known what preservation procedures may have been used on museum material. This might by itself contribute to the measured doses both in the teeth and in the attached sediments.

## CHAPTER 13. SAMPLE PREPARATION

When they are received from the field the samples must be catalogued, cleaned and prepared for analysis. While not all teeth lend themselves to analysis, they should all be processed at least through the cleaning phase.

It is often expedient to avoid processing all the samples collected both because of the cost and time involved. It is therefore important to have in hand all the information which relates to the site stratigraphy and site conditions to permit an appropriate decision on the extent of the analysis to be carried out.

### 13.1 Removal apparatus

The equipment necessary for such work is not very sophisticated and can be found in any university laboratory. Surgical blades are used to remove residual sediment and brushes to clean the teeth. A standard dentist drill is required to cut the teeth and to separate enamel, dentine and cementum (Figure 13.1). Agate pestle and mortar are utilized to grind the separated teeth components and the sediment. A pedestal mounted photographic camera is used to record the teeth at various stages of processing.

### 13.2 Tooth numbering and identification

The first item of procedure is to assign a proper laboratory ID number to each tooth. This will accompany the sample throughout the preparation and analysis. The number should refer to the year the sample was collected from the site or the museum. The field collection bags are retagged with the laboratory ID number.



Tools for enamel preparation. A dentist drill is armed with a thin diamond saw blade (as shown) or with special grinding bits (below the drill in the photograph).

123

.

Teeth are then closely inspected and the animal species to which they belong is confirmed prior to preparation. All the data is then entered on the sample data sheets on which all the information collected during preparation is noted. This forms a permanent record for future reference (Figures 13.2, 13.3).

### 13.3 Tooth preparation

The first step is to remove and collect any sediment still remaining attached to the teeth. This is done with the help of dental picks and surgical blades. Work is carried out in an enclosed area under a very slight vacuum to ensure that dust is not dispersed.

The package containing the tooth is opened carefully over a clean paper sheet. The sediment from the root area of the tooth is removed and discarded. The remainder is collected on weighing paper and then stored in an appropriately tagged glass vials. Separate vials are used for buccal and lingual sediment portions since the part of tooth from which the sample will be taken has not been selected yet. The 2 mm sediment is collected and stored separately as already indicated. Sample numbers and the name of the archaeological site are written on the vials in indelible ink together with the sediment number (typically SED 1, SED 2, etc.) and its provenance (buccal/lingual/occlusal side). Provenance of the various portions of sediment is also recorded in the laboratory work book and on the tooth data sheet.

Notes are also kept in the laboratory work book and the tooth data sheet on the actual location at the archaeological site from which the sediment was collected. Tooth appearance and conditions are also recorded in both documents.

If the sediment is loose in the tooth package or is received in a separate container the procedure is slightly different. Foreign material clearly not represented evenly throughout the sediment is discarded. The sediment is then poured on thin hardboard (such as a file folder). Any large lumps present are evenly distributed in the pile which is then divided into quarters with the



# ELECTRON SPIN RESONANCE DATING LABORATORY

#### Sample Master Dating Worksbeet

| Catalogue Humber | Analysis Number    |
|------------------|--------------------|
| site             | Submitter          |
| Śquare           | Lavel              |
| X Y              | z z                |
| Analysis started | Analysis completed |

Photograph (pasta photo here or draw appropriate pictures) Ibdacata subsample Locations

۰.

| Subsamples | (List | subsamples | taken for  | various pro | cedures | 5)   |      |  |
|------------|-------|------------|------------|-------------|---------|------|------|--|
|            | ESR   | NAA        | <b>FRD</b> | Cathodol.   | SEH     | U/Th | Anac |  |
| Enamel     |       |            |            |             |         |      |      |  |
|            |       |            |            |             |         |      |      |  |
|            |       |            |            |             |         |      |      |  |
| Dentiae    |       |            |            |             |         |      |      |  |
|            |       |            |            |             |         |      |      |  |
| Sedmont    |       |            |            |             |         |      |      |  |
| odatime DC |       |            |            |             |         |      |      |  |
| Cement     |       |            |            |             |         |      |      |  |
|            |       |            |            |             |         |      |      |  |
| •          |       |            |            |             |         |      |      |  |
| FORe       |       |            |            |             |         |      |      |  |
|            |       |            |            |             |         |      |      |  |

125

Teeth master data sheet.
Figure 13.3

| Site                                     | Level                            |                     | Date 1                |                                       | ·Date 3              |   |
|--|----------------------------------|---------------------|-----------------------|---------------------------------------|----------------------|---|
| Sample Number                            | Square                           |                     | Water 1               |                                       | Water 3              |   |
| DE (Gy)+/-                               |                                  |                     | Cosmic<br>dose rate 1 |                                       | Cosmic<br>doserate 3 |   |
| U-Enamel (ppm)                           | U-Sediment[ppm]                  |                     | Eu. +/-<br>(Ka)       |                                       | Eu +/-<br>(Ka)       |   |
| U-Dentine [ppm]                          | Th-Sediment[ppm]                 |                     | Lu. +/-<br>(Ka)       |                                       | Lu =/-<br>(Ka)       |   |
| U-Dentine2 (ppm) or<br>U-Cementum(ppm)   | K-Sediment [%]                   |                     | Date 2                |                                       | Date 4               | · |
| H2O in<br>Dentine[wt. %]                 | H2O-Sediment [%]                 |                     | Water 2               |                                       | Water 4              |   |
| Original Thickness of<br>enamel(microns) | Bxternal Gamma<br>MicroGrays/Yr. |                     | Cosmic<br>dose rate 2 |                                       | Cosmic<br>doserate 4 |   |
| Sed. side removed<br>(microns)           | Depth for Cosmic                 |                     | Eu +/-<br>(Ka)        |                                       | Eu +/-<br>(Ka)       |   |
| Den. side removed<br>(microns)           |                                  |                     | Lu+/-(Ka)             |                                       | Lu +/-<br>(Ka)       |   |
| Source of sediment<br>for Beta           |                                  | cosmic<br>dose rate |                       |                                       |                      |   |
| Source of external gamma                 |                                  | method              | to estimate cosmic    |                                       |                      |   |
| cem + enam<br>thickness +                |                                  |                     |                       |                                       |                      |   |
| enam thickness =                         |                                  |                     |                       |                                       |                      |   |
| cem thickness =                          |                                  | [                   |                       |                                       |                      |   |
| outer rem, thickness =                   |                                  |                     |                       | · · · · · · · · · · · · · · · · · · · |                      |   |
| inner rem. thickness =                   |                                  |                     |                       |                                       |                      |   |
| amount outer rem. =                      |                                  |                     |                       |                                       |                      |   |
| amount inner rem. =                      |                                  |                     |                       |                                       |                      |   |

# ESR TOOTH DATA SHEET

l

i

\_

\_\_\_\_

ESR tooth data sheet.

126

.

.

help of a straight edge. One of the quarters is selected and the remainder is returned to the original container. The selected material is divided once more into four parts. One quarter is selected and stored into an appropriately tagged vial and the rest is returned to the original container. At least 5 g of sample should be collected.

Sediment is then prepared for INAA. The material collected is first processed through a 710  $\mu$  screen. The oversize fraction is then crushed in an agate mortar until it passes the screen mesh.

Once all remaining sediment has been removed the teeth are washed in running water with a brush and then air dried.

Care must be paid to ensure that the cementum layer is not disturbed in any way throughout the cleaning procedure. This is particularly important when cleaning cervid teeth whose cementum layer is quite fragile and equid teeth whose cementum is soft.

## 13.3.1 Choosing and photographing samples

Photographing is done after teeth have been dried. Buccal, lingual and occlusal views must be recorded. The set up will include labels indicating the sample number and the archaeological site of provenance to allow the photographs to be clearly identified for future reference. Photographs are attached to the sample data sheet discussed above. Teeth are then examined for suitability for ESR analysis. Discoloration, damage, etc. are often not clearly visible before cleaning.

The area selected is normally the part of the tooth closest to the crown, centred on the cusp, where the enamel thickness is most uniform and where the enamel is flattest allowing for the simplest geometry. This portion of the tooth can be expected to have received the most , uniform level of irradiation. In the case of bovid and cervid teeth the lingual side of the cusp of a molar or premolar should yield a suitable sample. The buccal side has normally thinner enamel but is sometime the only undamaged portion of a tooth.

If necessary the tooth will be examined under microscope to decide on sampling strategy. Photographs of the tooth are marked to show the location and size of the proposed cut for future reference.

Enamel samples are also photographed before crushing (Figure 13.4). The set up will include labels indicating the sample number and the archaeological site of provenance to allow the photographs to be clearly identified for future reference. Photographs are attached to the sample data sheet discussed above.

## 13.4 Cutting samples

A sufficiently large section of tooth must be cut to obtain an adequate amount of sample after final preparation. This should be in the order of 300+ mg. It should be noted that during the preparation steps some portions of the material are inevitably lost when handling samples.

If the final amount of sample is not sufficient, additional material can be cut from other parts of the same tooth assuming that the geometry is reasonable. Alternatively when a number of teeth are found still embedded in the bone additional samples can be taken from adjacent teeth. These different samples must be treated separately. Prior to proceeding the area to be cut is marked by pencil on the tooth.

Two teeth, one from the top and one from the bottom of the archaeological strata being dated will be processed first to determine a Universal Growth Curve (UGC) dose. This will permit the selection of the appropriate level of laboratory irradiation required for age determination. Teeth cutting is performed using the "Teeth cutting" procedure included in Appendix A.

## 13.5 Preparation of enamel, dentine and cementum

As enamel, dentine and cementum are separated, they are stored in appropriately labelled glass vials. The vials are marked with indelible ink to show site name, sample number and tooth component (enamel: EN, dentine: DEN and cementum: CEM).





Tooth enamel after stripping of external and internal  $40\,\mu_{\rm c}$ 

When enamel subsamples are necessary they are labelled and handled separately as EN 1, EN, 2, etc., and their dentine and cementum respectively as DEN 1, DEN 2, etc. and CEM 1, CEM 2, etc. If the dentine is removed in two layers then it must be identified as DEN 1 (far) and DEN 2 (near), etc.

In any crystal structure except the cubic, there is anisotropy. This phenomenon refers to the internal charge fields being different along the principal axes of the crystal because of atomic orientation. Thus if large pieces of tooth enamel were used for ESR analysis the intensity of the response to any radiation level would be different depending on the orientation of the sample in the microwave cavity. To overcome this problem the samples are reduced to powder sufficiently fine as to produce a truly random combined crystal orientation.

While dentine and cementum can be crushed using a mechanical grinder enamel must be processed in a hand held agate mortar and pestle (Refer to page 41: Effects of sample preparation). The crushed enamel is weighed and separated into 10 aliquots of equal size and placed in a small stoppered glass vial (Figure 13.5). Additional aliquots should also be collected for INAA determination of uranium content .

Tooth component preparations are outlined in Appendix A as "Enamel, dentine and cementum preparation", "Crushing dentine and cementum" and "Crushing enamel".

A glass fibre brush would prove very effective in the removal of dentine residues normally lodged in enamel crevices. This item is not used yet in tooth samples preparation but is utilized routinely by European restorers of ancient metal artefacts. Its two sides (hard and soft) are very effective in the rapid removal of tightly adhering oxides while not damaging to the metal substrata. Its use in tooth preparation should be investigated since it could produce better results involving less effort and time.

#### 13.6 UGC analysis

Aliquots from two teeth are chosen for UGC analysis preferably from the top and bottom of the context. They are processed through the ESR spectrometer and their intensity readings are normalized. The corresponding apparent dose is then read off from the UGC standard curve (Figure 13.6) and utilized to select the sample irradiation schedule. Procedures for the carrying out of UGC analysis are included in Appendix A as "Protocol for UGC analysis".



ESR enamel aliquots after weighing and their storage vials.

UNIVERSAL GROWTH CURVE #3

Normalized intensity 100 120 140 160 180 200 220 240 260 T 300 Grays

Universal growth curve (from McMaster Quaternary Dating Laboratories).

Figure 13.6

#### 13.7 Irradiation

The aliquots are irradiated using a <sup>60</sup>Co gamma source of known strength (the "hot cell") stored in the McMaster Nuclear Reactor building. Appropriate identification and irradiation badges must be worn at all times.

The maximum irradiation to be used should be approximately ten times the value of the UGC results. The lowest irradiation level should not be below the value "UGC dose/20". In practice ten steps are chosen, the lowest being equivalent to the value of the UGC result. The intermediate irradiation levels should increase from the lowest to the highest in exponential steps. Once these are chosen, each vial containing the aliquots should be marked with indelible ink to indicate which level of irradiation it received.

A number of detailed procedures must be followed when operating in the reactor building and when utilizing the hot cell used for irradiation. They are included in Appendix B as "Irradiation procedures".

To proceed with the irradiation it is necessary to obtain a calculator and a stopwatch, as well as writing implements, the irradiation work sheets (Figure 13.7) and the hot cell dosimeter. All the samples should also be at hand.

The first order of procedure is to measure the current cell dose rate and to determine the calibration ratios as detailed in the "Irradiation procedures" included in Appendix B.

The longest irradiation should be performed first. This ensures that any initial hesitancy in handling the cell or the length of the "up-time" and "down-time" will not be significant with respect to the total length of the irradiation.

#### 13.8 ESR spectrometry

ESR analysis is based on measuring microwave power absorbed by samples placed in a magnetic field. This power is proportional to the amount of free electrons in the crystal. The spectrometer

| Irradiation Operator: 2  | >c} [9' 9gDate Started:   | Roded: Wet 20 98  |
|--|---|---|
| Sample Series Positions:<br>1<br>2<br>3<br>4<br>5<br>8<br>8<br>9<br>8<br>9<br>10<br>10<br>10<br>10<br>10<br>10<br>10<br>10<br>10<br>10                 | 21 456<br>22 45<br>23 47<br>23 47<br>24<br>25<br>25<br>25<br>25<br>25<br>25<br>25<br>25<br>25<br>26<br>27<br>26<br>27<br>28<br>1 28<br>28<br>1 28<br>24<br>25<br>25<br>25<br>26<br>27<br>27<br>28<br>1 28<br>29<br>20<br>24<br>20<br>24<br>25<br>24<br>25<br>25<br>25<br>26<br>26<br>26<br>26<br>26<br>26<br>26<br>26<br>26<br>26<br>26<br>26<br>26 | 31 Doserati<br>32 10.08<br>33 CF<br>36 CF<br>37 1.467<br>39<br>40   |
| Desired Dose: 220 krad<br>Up Dose Time: 71 4seo<br>Stopwatch Time: 79 seo<br>Lag Time: 9 sec<br>Wall Clock Time: 10.18.12<br>Actual Time In: 10.18.15  | Desired Irradiation Time:<br>21810 sec = 3 min 36 sec<br>Actual Irradiation Time:<br>min sec = sec<br>Desired Time Out: 16 21 40<br>Actual Time Out: 5 unvo   | Source Rack Position: 1 2<br>Sample Rack Position: 1 2<br>Up Dose: (103.7) 152.13 rad<br>Down Dose: EST(31.7)465<br>rad<br>Av Dose Rate: 10:08 (ma.9)2<br>rad/s<br>Total Dose: 220.4 (1) ± krad |
| Desired Dose: 80 krad<br>Up Dose Time: 783 sec<br>Stopwatch Time: 94 sec<br>Lag Time: 11 sec<br>Vall Clock Time: 7.49,20<br>Actual Time In: 8:49:09    | Desired Irradiation Time:<br>7919, seo - Min /2 Sec<br>Actual Irradiation Time:<br>min sec - seo<br>Desired Time Out: 11:0/:07<br>Actual Time Out: 22002  | Source Rack Position: 1 2<br>Sample Rack Position: (1) 2<br>Up Dose: (117.6) 172.52 rad<br>Down Dose (32.9) 49.7 rad<br>Av Dose Rate: 0.08 rad/s<br>Total Dose: 800.00 t krad                   |
| Desired Dose: 40 krad<br>Up Dose Time: 78.2 sec<br>Stopwatch Time: 81 sec<br>Lag Time: 9 sec<br>Vall Clock Time: 11: (0:00<br>Actual Time In: 11:09:51 | Desired Irradiation Time:<br>3954 sec - 5 min 53 sec<br>Actual Irradiation Time:<br>min sec - sec<br>Desired Time Out: 12.15'44<br>Actual Time Out: 50000   | Source Rack Position: 1 (2)<br>Sample Rack Position: (1) 2<br>Up Dose: (101 3) 145 61 rad<br>Down Dose: (42) 618 (N9.95<br>Av Dose Rate: (008 rad/s<br>Total Dose: 10172 krad                   |
| Desired Dose: 20 krad<br>Up Dose Time: 11 sec<br>Stopwatch Time: 11 sec<br>Lag Time: 14 sec<br>Vall Clock Time: /320:40<br>Actual Time In: 3: 19:56    | Desired Irradiation Time:<br>HTD sec - 32min / sec<br>Actual Irradiation Time:<br>min sec - sec<br>Desired Time Out: /3:51:57<br>Actual Time Out: /2:51:57  | Source Rack Position: 1 (2)<br>Sample Rack Position: (1) 2<br>Up Dose (91.6) 143.2 rad<br>Down Dose: (31.2) 48.7 rad<br>Av Dose Rate: (2.0) rad/s<br>Total Dose: 2005 t krad                    |
| Desired Dose: bkradUp Dose Time:10secStopwatch Time:51secLag Time:11secVall Glock Time:1420112Actual Time In:13:59:21                                  | Desired Irradiation Time:<br>1574 Sec = 26 min 14 sec<br>Actual Irradiation Time:<br>min sec = sec<br>Desired Time Out: M. 2613<br>Actual Time Out: 4 2013  | Source Rack Position: 1 (2)<br>Sample Rack Position: (1) 2<br>Up Dose: (31.3) (31.30 rad<br>Down Dose: (31.3) 45.6 (rad<br>Av Dose Rate: (3.32 rad/5<br>Total Dose: 160.441 krad                |

88 8908.28

Irradiation worksheet.

output is displayed as a derivative of the absorption function and its peak-to-peak amplitude is used as the ESR measurement (Jonas, 1997) (Figures 4.5, 13.8a, 13.8b).

It has already been noted that the signal from a single defect would produce a perfect gaussian for the integrated curve (Jonas et al, 1994). However when an integral curve produced by any tooth sample is deconvoluted it shows that a best fit is obtained by a combination of three (Jonas and Grün, 1997) or four different curves (Jonas et al., 1994) of which two are isotropic. Thus it appears that different interfering signals are produced from separate crystal defects, each responding independently and to different degrees to irradiation (Jonas et al., 1994; Jonas and Grün, 1997). This occurs with signals obtained both before and after laboratory irradiation. Two of the curves have a narrow gaussian signal one coinciding with g = 2.0018 the other at g = 1.9977 and they are the main contributors to the overall peak to peak amplitude. Both curves seem to show the same sensitivity to radiation (Jonas et al., 1994)

Fortunately the response from the two other defects have very broad gaussian curves which have only a minor impact on the combined signal. It thus appears reasonable to use the standard derivative signal for determination of radiation sensitivity, as there does not appear to be a justification for the more cumbersome process of curve deconvolution.

A number of researchers have studied the effects of spectrometer settings on ESR spectra. Some settings appear to affect the results while some are irrelevant. For example, amplifier gain settings of most available commercial spectrometers are not accurately calibrated. Therefore the amplitude of the signals at different settings may not vary necessarily proportionately and thus it is important to measure all spectra at the same gain setting, and at times to accept some loss in resolution (Jonas, 1997).

Variations in measured absorbed doses in gamma irradiated samples also do not appear to be dependent on microwave power levels (Lyons et al., 1988). However results obtained for teeth samples irradiated with laboratory sources when measured at high microwave power appear to be more reliable than at lower power (Grün, 1996).

Overmodulating can smooth out some interfering signals. However while they are no longer visible, overmodulation does not suppress them and they may still affect the measured intensity levels and the shape of the spectrum (Jonas, 1997).

Figure 13.8a

WINEPR Acquisition

Date: 05/22/1997 Time: 09:06



Comment: EL PENDO 95072 UGC 48.4 GM



Typical ESR spectrum as printed by the spectrometer. Intensity is measured peak-to-peak as shown but the measurement is carried out directly on the apparatus monitor screen (Figure 13.9). When the noise to signal ratio is high the reading is taken through the middle of the signal at the peaks. Compare this printed spectrum with the spectra as actually seen on the apparatus monitor (Figure 13.8b). Figure 13.8b



ESR intensity spectrulas seen on the apparatus monitor screen. The upper photograph represents a natural signal, the lower photograph a signal after laboratory irradiation.

High signal to noise ratios are important to ESR measurements since with low ratios spectra are difficult to read. However with high ratios interfering signals may not be noticed (Jonas, 1997). Signal to noise ratios can be improved by accumulating consecutive runs at low ratios if the apparatus is stable. In my experiments all intensities are the result of accumulation of three consecutive runs.

Field sweeps speeds also affect the resolution of the spectra. If they are too slow the spectra shape may be distorted when the spectrometer system is not stable.

The spectrometer settings utilized for my ESR analyses are detailed in appendix A. The apparatus used for analyses was a Bruker EMX EPR Spectrometer utilizing a Bruker ER 041XG microwave bridge (X-Band) coupled to a Patriot M5100P processor (Figure 13.9). The analysis is carried out using the procedures included in appendix A as " Protocol for the operation of the ESR spectrometer".

## 13.8.1 Sample density vs. intensity signal

Three aliquots from a single tooth sample were chosen arbitrarily to test the relationship between crushed enamel density and spectrometer signal intensity. They were aliquots subjected to the natural and the highest laboratory dose as well as a dose which was approximately one half of the latter. Intensities were first measured just after pouring the sample into the test vial. Samples were then compacted by tapping against a table top ten times and the intensity measurement was repeated. The vial was then tapped again ten times for a total of twenty compactions and the intensity measurements were repeated. Twenty compactions are normally used as part of the standard procedures.

 $D_e$  was calculated using the McMaster VFit program on the basis of the intensities measured at the three irradiation levels. It is to be noted that the values of the natural dose as calculated varies inversely with the degree of compaction (Table I). The effect of compaction decreases as compaction increases and voids in the sample mass become filled. The result of ten compactions decreases the calculated  $D_e$  value by 3%. This would affect significantly the accuracy of the age determination. Uniform density of a sample "as poured" can never be ensured since it depends on several variables such as sample size, vial inclination, etc. Accordingly it is





MilM after Quaternary Dating Calebratorics. Braker EMX EPR spectrometer utilizing a Braker ER 04: XC and resource brage is Bradd coupled to a Patriot M5100P processor. necessary to provide uniform compaction. However, additional compactions beyond ten appear to reduce the value only marginally (0.15%). Yet, since little effort and time is involved in the compaction of the sample, it is felt that the use of twenty compactions as per current procedures is justifiable to ensure test repeatability by different operators. The change of I and  $D_e$  with changes in density confirms the findings of Regulla et al. (1985). The reduction in signal in the present experiment though is probably due to the fact these small samples with compaction become marginally less centred in the cavity.

| Sample#    | Wt. mg       | Dose Gy                         | Gain                         | Compactions             | Tot. Intensity |
|------------|--------------|---------------------------------|------------------------------|-------------------------|----------------|
| PEN ESR 32 | 17.8         | 100.6                           | 1.78x10 <sup>5</sup>         | 0                       | 39643.9        |
|            |              |                                 |                              | 10                      | 39604.5        |
|            |              |                                 |                              | 20                      | 40043.9        |
| PEN ESR 32 | 17.8         | 40.2                            | 1.78x10 <sup>5</sup>         | 0                       | 20967.4        |
|            |              |                                 |                              | 10                      | 20456.7        |
|            |              |                                 |                              | 20                      | 20431.7        |
| PEN ESR 32 | 17.4         | 0                               | 1.78x10 <sup>5</sup>         | 0                       | 6873.3         |
|            |              |                                 |                              | 10                      | 6663.1         |
|            |              |                                 |                              | 20                      | 6541.2         |
|            | Resultir     | ng D <sub>e</sub> s calculate   | ed from the ab               | ove data                |                |
|            | As po        | ured                            |                              | 20.69                   |                |
|            | 20 comp      | actions                         |                              | 20.05                   |                |
|            | Differen     | ce As poured/1                  | 0 Compaction                 | ns = 3.0%               |                |
|            | Difference 1 | ce As poured/2<br>0 Compactions | 0 Compaction<br>/20 Compacti | s = 3.1%<br>ons = 0.15% |                |

| - 11  | -  |
|-------|----|
| Tabla |    |
| Table | T. |

# 13.8.2 Effect of particle size

Aliquot sizes used in this experiment were comparable for all four samples averaging 29.5 mg and ranging from 28.3 mg to 30.1 mg with a standard deviation of 0.41. Analyzer gain values

were also different ranging from 1.12x10<sup>5</sup> to 1.59x10<sup>5</sup>. All data were normalized before D<sub>e</sub>'s were calculated.

Finer powders should have a more random crystal orientation and thus a larger D<sub>e</sub>. The results shown on Table II are instead inconsistent, indicating an increase in D<sub>a</sub> with crystal size in the case of sample PENESR 21 and the opposite in the case of sample PENESR 25. The results none the less appear to confirm that crystal orientation affects ESR intensity readings.

| Effect of sample crystal size on D <sub>e</sub> |                     |                 |              |
|---|---------------------|-----------------|--------------|
| Sample #  | Ave. Aliquot Wt. mg | Particle size µ | Calculated D |
| PENESR 21                                       | 29.6                | <150            | 8.68±0.4     |
|   | 29.8                | 150<250         | 9.59±0.3     |
| PENESR 25                                       | 29.6                | <150            | 14.24±0.9    |
|   | 28.8                | 150<250         | 13.44±0.7    |

|  | Т | ab | le . | Π |
|--|---|----|------|---|
|--|---|----|------|---|

#### 13.8.3 Effects of crystal orientation

The experiment was run to confirm that grinding the enamel samples to  $<150\mu$  would overcome anisotropy problems. The outer holding tube were marked to indicate degrees of rotation. First the outer tube was rotated for both samples VANESR 7 and VANESR 2F. Then the outer tube was fixed in the 0 degrees position and the sample vial for VANESR 2F was rotated by using the handling thread. It was not possible to measure accurately the degree of rotation achieved in the latter experiment. The standard was run before and after the experiment to confirm steady state conditions in the test apparatus. The difference in readings for the standard was 3.48%.

The results are difficult to justify since the powdered enamel samples should display a very random crystal orientation. The data obtained instead appear to indicate that orientation of the sample/vial/outer holding tube still affect the experimental precision and repeatability (Table III). Some of the difference could be attributed to the fact that the apparatus state was not as steady during the experiment as is normally expected.

The largest difference occurs when the outer holding tube is rotated, while instead, when only the sample vial is rotated, the difference is similar to the difference in standard readings at the start and end of the experiment. This would indicate it is possible that the apparent anisotropic effect may be attributable to properties of the holding tube. This suggests that the latter should be marked as to its orientation to ensure that it is repeatedly placed with the same orientation within the cavity.

| Effect of crystal orientation on measured intensity                      |  |  |
|--|--|--|
| Sample VANESR 7; weight 20.1 mg; spectrometer gain $1.26 \times 10^5$    |  |  |
| Outer tube rotation deg.   | Total intensity                              |  |
| 0  | 10660.58                                     |  |
| 90   | 9188.38                                      |  |
| 180  | 9323.01                                      |  |
| Sample VANESR 2F; weight 29.1 mg; spectrometer gain 1.26x10 <sup>5</sup> |  |  |
| Outer tube rotation deg.   | Total intensity                              |  |
| 0  | 13514.56                                     |  |
| 90   | 13268.47                                     |  |
| 180  | 15070.78                                     |  |
| Sample VANESR 2F; weight 29.   | 1 mg; spectrometer gain 1.26x10 <sup>5</sup> |  |
| Sample vial rotation deg.  | Total intensity                              |  |
| 0  | 13514.56                                     |  |
| 90   | 14121.17                                     |  |
| 180  | 12915.03                                     |  |

Table III

#### 13.8.4 Effect of sample position within the spectrometer cavity

Two aliquots of different mass but from the same site were chosen for this test. The outer sample holding tube has a collar which allows it to be centred consistently within the spectrometer cavity. This datum was taken as the zero position. A first set of readings was obtained with the outer tube in this position for sample VANESR 2F2. The outer tube was then lifted and the elevation above datum was measured with a pre-calibrated straight wedge or spacer. The next set of readings was then obtained. The process was repeated for sample VANESR 7. The standard was run before and after the experiment; the reading difference was 5%

It is clear that positioning the sample at the centre of the cavity is extremely important. Moving the larger aliquot did not significantly shift the bulk of its mass with respect to the cavity geometry. However the effect of the move on the aliquot which was 26% smaller was instead significant. The resulting larger intensity reading increases proportionately the measured D<sub>e</sub>.

The result of this experiment raises questions with respect to the appropriate positioning of aliquots which are much smaller than the standard 30 mg.

| Sample #   | Weight mg | Aliquot level mm | Total intensity | Max. difference of |
|------------|-----------|------------------|-----------------|--------------------|
| VANESR 2F2 | 25.1      | 0                | 11253.00        |                    |
|            |           | +0.5             | 11529.83        | 2.5                |
| VANESR 7   | 20.1      | 0                | 10660.58        |                    |
|            |           | +0.5             | 9342.72         | 14.1               |
|            |           | +1.0             | 10041.26        |                    |

| Та | hle | IV    |
|----|-----|-------|
| τa | DIC | 7 I V |

#### 13.8.5 Experimental repeatability

The natural dose aliquot of one sample was used for the test. Procedures and spectrometer settings were not altered and the sample aliquot was not moved during five successive runs at one minute interval. Each run consisted of three successive scans of the aliquot. The standard was run before and after the test runs to confirm steady state conditions in the apparatus. The difference in the readings for the standard was 0.08%.

The signal to noise ratio in the spectra of natural dose aliquots is consistently much lower than for the irradiated aliquots. As a result the curve displayed on the spectrometer screen is not smooth consisting of a consecutive series of secondary valleys and peaks. A spectrum typical of this phenomenon was used for the test. It was feared that this might affect the ability of the operator to measure repeatedly the correct  $\pm$  intensity peaks. The results would suggest that this is not the case and that in spite of the "dirty" signal the cursor can be placed with some degree of precision always in the same relative position.

| Run #                | Total intensity |
|----------------------|-----------------|
| 1                    | 1038.88         |
| 2                    | 1027.50         |
| 3                    | 1039.84         |
| 4                    | 1024.04         |
| 5                    | 1034.50         |
| Ave.                 | 1032.95         |
| Max. ave. difference | 0.8%            |

Table V

## 13.8.6 <u>D</u> <u>Calculations</u>

The spectrometer data were normalized using the computer program NORM.WB1. The normalized data were then fed into the McMaster Quaternary Dating Laboratories' VFit program. A typical printed output is shown on Figure 13.10. The Vfit program applies a single exponential saturation function of the type:

$$I = I_o(1 - e^{(D/Dmax)})$$

to fit the normalized intensity values of the different radiation levels obtained for each sample as discussed above (Brennan et al., 1997; Rink, 1997).

## 13.8.7 <u>Age determination</u>

The  $D_e$  are then used in the McMaster Quaternary Dating Laboratories' ROSY version 1.3 program to calculate the ages. The program takes into account the uranium level in the teeth to determine EU and LU dates. Age calculations are based on  $\gamma$  and cosmic radiation as measured by the field dosimeters and  $\beta$  dose based on the sediment composition. Typical program output is shown on Figure 13.11a and 13.11b.

#### File Name: GORESR1.dat

| UFIT Page | • 1 |
|-----------|-----|
|-----------|-----|

|            | Dose   | Experimental | Fitted   |
|------------|--------|--------------|----------|
|            |        |              |          |
| 1-         | 0.00   | 2692.70      | 2001.32  |
| 2 -        | 10.08  | 1121.50      | 4493.66  |
| J -        | 20.21  | 6314.30      | 6445.63  |
| 4 -        | 30.19  | 8390.90      | 8368.69  |
| 5-         | 10.19  | 10065.80     | 10295.41 |
| <b>6</b> - | 60.45  | 14185.50     | 14199.54 |
| 2-         | 90.54  | 19353.30     | 19070.71 |
| 8-         | 122.33 | 26846.70     | 26123.27 |
| 9-         | 140.51 | 33290.50     | 33490.21 |
| 10-        | 240.56 | 10338.00     | 40905.09 |



#### Chi\_sqr : 0.003008

D, calculations. Output from the McMaster Quaternary Dating Laboratories' Vfit program.

# Figure 13.11a

-----

| * * * | **************     | ******   | *******    | *****  | ****  | *******   | ******   | ******  | *******  |
|-------|--------------------|----------|------------|--------|-------|-----------|----------|---------|----------|
| N     | NAME OF F          | ILB:     | PEN74-     | DAT    |       |           |          |         |          |
| Q     | EQUIVALENT DOSE    | [Gy]:    | 14.24      | 1.     | 50    |           |          |         |          |
| С     | CALCULAT           | 'ING:    | Адеб       |        |       |           |          |         |          |
| R     | RATIO OF U234 TO L | 1238:    | 1.40       | Ο.     | 00    | Initial 1 | Ratio    |         |          |
| A     | ALPHA EFFICIE      | INCY :   | 0.15       | Ο.     | 00    | Varies w  | ith ener | gy, Ere | f=5.3MeV |
|       |                    | SEDI     | MENT       | CEME   | NTUM  | E         | NAMEL    | DEN     | TINE     |
| U     | U (ppm)            | 1.53     | 0.00       | 0,00   | 0.00  | 0.01      | 0.00     | 0.00    | 0.00     |
| Ť     | TH [ppm]           | 7.07     | 0.25       | 0.00   | 0.00  | 0.00      | 0.00     | 0.00    | 0.00     |
| K     | K [wt*]            | 0.43     | 0.18       | 0.00   | 0.00  | 0.00      | 0.00     | 0.00    | 0.00     |
| D     | DENSITY [g/cc]     | 2.00     | 0.00       | 1.70   | 0.00  | 2.95      | 0.00     | 1.90    | 0.00     |
| F     | FR. OF RADON       | 1.00     | 0.00       | 1.00   | 0.00  | 1.00      | 0.00     | 1.00    | 0.00     |
| W     | * WATER (Dry)      | 30.00    | 0.00       | 0.00   | 0.00  |           |          | 0.00    | 0.00     |
| н     | THICKNESS (microne | ;] -     |            | Ο.     | 0.    | 1000.     | 0.       | 2000.   | 0.       |
| Р     | UPTAKE 1=EARLY/2=1 | INEAR    |            |        | 2     |           | 1        |         | 2        |
| 0     | ENAMEL STRIPPED FF | IOM OUTS | SIDE [mic] | cons]: | 4     | 0.68      | 4.07     |         |          |
| I     | ENAMEL STRIPPED FF | IOM INSI | DE (mic)   | rons]: | 6     | 7.83      | 6.78     |         |          |
| G     | DEPTH & DENSITY FO | OR COSMI | [C [π.&.9  | g/cc]: | 3     | 0.00      | 0.00     | 2.13    | 0.00     |
| ***   | *****************  | ******   | *******    | *****  | ***** | *******   | ******   | ******* | *******  |

COMPOSITION OF MEDIA ("dry" weight fractions - water extra)

|    | BNAMEL   | DENTINE  | SEDIMENT | CEMENTUM |
|----|----------|----------|----------|----------|
| н  | 0.002222 | 0.047234 | 0.000000 | 0.047234 |
| С  | 0.005454 | 0.144330 | 0.00000  | 0.144330 |
| N  | 0.000000 | 0.041990 | 0.000000 | 0.041990 |
| 0  | 0.443324 | 0.446096 | 0.510240 | 0.446096 |
| Na | 0.007000 | 0.000000 | 0.00000  | 0.000000 |
| Mg | 0.004000 | 0.002200 | 0.000000 | 0.002200 |
| ΑĨ | 0.000000 | 0.000000 | 0.191209 | 0.000000 |
| Si | 0.000000 | 0.000000 | 0.298549 | 0.000000 |
| P  | 0.174000 | 0.104970 | 0.000000 | 0.104970 |
| S  | 0.000000 | 0.003150 | 0.000000 | 0.003150 |
| C1 | 0.003000 | 0.000000 | 0.000000 | 0.00000  |
| ĸ  | 0.003000 | 0.000000 | 0.000000 | 0.000000 |
| Ca | 0.358000 | 0.209930 | 0.000000 | 0.209930 |
| Fe | 0.000000 | 0.00000  | 0.000000 | 0.000000 |
| Zn | 0.000000 | 0.00000  | 0.000000 | 0.000000 |

Age calculation. Printout from the McMaster Quaternary Dating Laboratories' ROSY 1.3 program. All age calculations were performed using this version of the ROSY program. This figure shows the data input; for calculated ages see the following Figure.

Figure 13. 11b

\*\*\* EARLY UPTAKE \*\*\*

| Uranium   | h b <b>eta</b> | dose=  | 24.66     | microGy | r/a     |     |         |
|-----------|----------------|--------|-----------|---------|---------|-----|---------|
| Thorium   | a beta         | dose=  | 19.65     | microGy | r/a     |     |         |
| Potassium | h beta         | dose=  | 37.74     | microGy | /a      |     |         |
| Total     | beta           | dose≖  | 82.04     | microGy | /a      |     |         |
| Uranium   | alpha          | dose=  | 1.46      | microGy | /a      |     |         |
| Thorium   | alpha          | dose=  | 0.00      | microGy | /a      |     |         |
| Total     | alpha          | dose=  | 1.46      | microG  | //a     |     |         |
|           | Total          | dose-  | 83.51     | microGy | y/a     |     |         |
| Alpha     | Beta           |        | Gamma     | Cosm    | ic      |     |         |
| 1.4608    | 82.04          | 50     | 481.2668  | 1       | .8504   | mic | roGy/a  |
|           | Calcul         | ated I | Oose [Gy] | z       | 14.24   |     |         |
| Ĺ         | Age Es         | timate | (years)   | = 2     | 5131.35 | +/- | 2204.69 |

| *        | ** L    | INBAR  | UPTAKE         | ***          |         |         |
|----------|---------|--------|----------------|--------------|---------|---------|
| Uraniu   | m beta  | dose-  | = 24.41        | microGy/a    |         |         |
| Thoriu   | m beta  | dose:  | = 19.65        | microGy/a    |         |         |
| Potassiu | m beta  | dose   | = 37.74        | microGy/a    |         |         |
| Tota     | 1 beta  | dose   | = 81.80        | microGy/a    |         |         |
|          |         |        |                |              |         |         |
| Uranium  | alpha   | dose   | = 0.64         | microGy/a    |         |         |
| Thorium  | alpha   | dose   | = 0.00         | microGy/a    |         |         |
| Total    | alpha   | dose   | = 0.6 <b>4</b> | microGy/a    |         |         |
|          | Total   | dose   | = 82.44        | microGy/a    |         |         |
|          |         |        |                |              |         |         |
| Alpha    | Beta    |        | Gamma          | Cosmic       |         |         |
| 0.6448   | 81,79   | 77     | 481.2668       | 1.8504       | mic mic | roGy/a  |
|          | Calcula | ated I | Оове [Gy]      | <b>*</b> 14. | 24      |         |
|          | Age Es  | timate | e (years)      | = 25178.     | 60 +/-  | 2214.43 |
| ***      | COMB    | INATIC | ON UPTAKE      | ***          |         |         |
| Uraniu   | m beta  | dose:  | 24.66          | microGv/a    |         |         |
| Thoriu   | n beta  | dose-  | 19.65          | microGy/a    |         |         |
| Potassiu | n beta  | dose   | 37.74          | microGy/a    |         |         |
| Tota     | l beta  | dose.  | 82.04          | microGy/a    |         |         |
|          |         |        |                |              |         |         |
| Uranium  | alpha   | dose-  | 1.46           | microGy/a    |         |         |
| Thorium  | alpha   | dose-  | . 0.00         | microGy/a    |         |         |
| Total    | alpha   | dose=  | 1.46           | microGy/a    |         |         |
|          | -       |        |                |              |         |         |
|          | Total   | dose=  | 83.51          | microGy/a    |         |         |
| Aloha    | Beta    |        | Gamma          | Cosmic       |         |         |
| 1.4608   | B2.04   | 50     | 481.2668       | 1.8504       | mic     | roGv/a  |
|          |         |        |                |              |         |         |
| I        | Calcula | ated I | Dose [Gy]      | <b>=</b> 14. | 24      |         |
| i        | Age Bs  | timate | (years)        | = 25131.     | 35 +/-  | 2204.69 |

Age calculation. Printout from the McMaster Quaternary Dating Laboratories' ROSY 1.3 program. All age calculations were performed using this version of the ROSY program. This figure shows the ages calculated from the input shown on the preceding Figure

## CHAPTER 14. THE FIELD WORK

## 14.1 Field work and site visits

#### 14.1 El Castillo Cave

The first visits to the Iberian sites took place with Prof. W. J. Rink in August 1995 beginning at the cave of El Castillo in Cantabria. The El Castillo cave is secured, like the majority of archaeological sites in Iberia, by means of steel grating and locked gates. Access is strictly controlled and researchers must be accompanied by authorized personnel. The exposed face of the excavation is easily reached from the cave floor by means of long wooden ladders. Artificial illumination is provided to assist in the work since, in spite of the proximity to a wide entrance, sufficient natural light does not reach the area.

Several tooth samples from this location had already been collected by H. P. Schwarcz and W. J. Rink on previous visits and were stored at the McMaster Quaternary Dating Laboratories. In 1994 Rink had also retrieved twenty one Panasonic dosimeters which had been buried for 277 days on the main excavation face at the entrance to the cave. This is the same face which originally had been worked on by Breuil and Obermaier. The dosimeters had been embedded in the Mousterian levels 18C, 19, 20, 21 and 22.

The field work carried out during the 1995 visit included an in -situ study of the exposed stratigraphy. Four teeth from newly excavated levels 20d and 20f and associated sediment and moisture samples also were collected as well as nine moisture samples from the holes of the 1993 dosimeters. The visit was conducted under the guidance of the current excavators, Dr. V. Cabrera Valdes and Dr. F. Bernaldo dos Quiros of the Universidad Nacional de Educacion a Distanzia.

## 14.2 El Pendo Cave

The visit to the cave of El Pendo took place in September 1995 immediately after the visit to El Castillo. Access to the site and support for the work was provided by J. Sanguino and R. Montes of the Universidad Complutense of Madrid who are currently pursuing a program of excavation. Thirty five tooth samples from this location had already been collected by Dr. Rink on a previous visit and were stored at the McMaster laboratories.

The archaeological deposits at El Pendo are found at approximately 40 m from the entrance. It is quite unusual for a Middle Paleolithic living floor to be found so deep inside a cave and this raises the possibility that these strata may represent secondary depositions.

The samples for ESR dating were collected from the layers excavated by Sanguino and Montes. These supposedly Mousterian contexts are found at the bottom of the deposits originally excavated by Gomez Echegaray. A square well of 1.5 by 1.5 meters has been dug to a depth of approximately 3 meters to parallel the Echegaray "well". The exposed face is reached by ladder from the top. Artificial lighting is necessary since no natural light reaches this area.

Ten Panasonic dosimeters which had been embedded in 1994 in layers B, D, F and H were recovered during the visit (Figure 11.2). All units appeared to be in good conditions after a burial of 375 days. A phosphor travel dosimeter was fired at the time of the recovery of the field dosimeters and the lot was bundled for the return trip to Canada.

## 14.3 Carihuela Cave

Arrangements for the first trip to Carihuela were also made in September 1995 through the auspices of Dr. G. Vega Toscano and J. Sanguino of the Universidad Complutense of Madrid. The purpose was to make a quick study of the stratigraphy of the various sections then exposed. Samples of a calcite flow which appeared to be immediately below layer VII were retrieved from the western face of the trench excavated by the University of Washington in 1970 at the entrance to the cave. The material was submitted to the McMaster Laboratories for U-series dating.

As work was not in progress at the Mousterian layers of Carihuela, it was agreed that tooth samples for dating would be obtained from the Madrid Museo de Ciencias Naturales. This was carried out in the fall of 1996 with the assistance of Dr. G. Vega Toscano and J. Sanguino.

The material was to be selected from the many teeth in good conditions recovered during the 1954 campaign by Spanhi. The southern exposed face of his excavation (Figures 10.5, 10.6) showed the Mousterian layer very clearly and was easily accessible for TLD installation. During the winter 95/96 there had been a significant roof collapse and the resulting rubble obstructed access to this area. It was therefore decided to change the location to be studied to the area more recently excavated by Washington State University and by Prof. Vega Toscano. The intention was to obtain also some teeth from level IVb, which represents the terminal Mousterian at Carihuela, in order to be able to date a final Neanderthal layer. However no material was available at the Museum from this level. Suitable teeth were instead assembled from the material recovered from Mousterian levels V to IX.

The twenty eight teeth collected were catalogued, assigned ESR sample numbers and properly bagged in polyethylene containers.

Unfortunately the excavation logs do not give any coordinates for the teeth locations, although the layers and sub-layers were all marked on the individual museum storage bags and on the main catalogue. Furthermore no sediment samples had been retained by any of the excavators. However the trenches excavated by both the University of Washington and by Prof. Vega Toscano are relatively small (approximately 2 meters wide) and therefore the eventual collection of sediment on site and the placing of dosimeters should prove to be reasonably close to the original spot where the teeth had been uncovered originally.

After picking up the material in Madrid I travelled to the Carihuela site to attempt to emplace TL dosimeters, collect appropriate sediment and moisture samples and if possible also to gather additional *in-situ* tooth samples from the exposed trench walls. Prof. G. Vega Toscano accompanied me to the site and assisted in the correct identification of the appropriate archaeological levels. The dosimeters emplaced were Panasonics. One phosphor TLD was also added to the unit emplaced in layer V as a control.

The first 7 dosimeters were buried in the exposed face of the University of Washington excavation. This is at the very front of the cave, is illuminated by natural light and is easily accessible. The units were buried in layers V-1, V-2, V-5, V-6, VI-3, VI-6 and VI-8, corresponding to the levels from which museum teeth had been obtained.

The remaining 3 units were emplaced in the exposed face of the Vega Toscano trench in layers VIIB-1 and VIIB-2. They also corresponded to levels from which museum teeth were made available. The Vega Toscano trench is further from the cave entrance but it is also easily accessible although artificial light is necessary. Inside the Carihuela there exists an extensive system of illumination which is fed by a portable generator. Wooden ladders are available for access to all the sections of the cave.

During the emplacing of the dosimeters in this section eight teeth in layers V, VI, VII, VIII and IX were recovered *in-situ*. They were given field find numbers and properly bagged. Sediments associated with these samples were also collected, labelled and bagged in accordance with the collection procedures outlined above.

Some of the Carihuela archaeological layers contain a significant amount of eboulis and the preparation of holes to receive the dosimeters was sometime difficult. A long cold chisel and a heavy hammer were used for this purpose. Dosimeters were packed into the distal end of stoppered plastic tubes and the tubes were filled with sediment recovered from the dosimeter hole preparation.

Sediments and moisture samples were obtained from the dosimeter holes. The former were placed in polyethylene bags and appropriately labelled. The latter were enclosed in standard photographic film canisters, labelled and sealed with duct tape. A return dosimeter was fired when the units were emplaced and it was bundled with an unfired travel unit.

Dosimeters were retrieved in September 1997 after 360 days of burial. All were in good conditions except for the unit emplaced in layer VIIB-2 (TLD #9). The excavation face had collapsed between April and September 1997. The drop was approximately 1 meter and when recovered the TLD appeared to be still contained in the same sediment in which it had been originally buried.

Conditions at the cave are normally very dry as they are for the entire region. However the winter 96/97 had been very rainy. The distal end of TLD # 8, recovered from Level VIIB-1, was found to be entirely covered with free water. All other units were completely dry.

During the visit a sample of a calcite flow which appeared to be sandwiched between level IV-a and level IV-b was retrieved from deposits further inside the cave. This was intended to be dated by U-series at the McMaster Laboratories to act as a control for the ESR dates.

## 14.4 Gorham's Cave

The first visit to Gorham's cave was also carried out with Prof. W. J. Rink in September 1995. The work in progress was led by Prof. C. B. Stringer from the British Museum of Natural History in London. It should be noted that the archaeological layers being uncovered did not appear to ' match the stratigraphy reported by Waechter (1951).

Two TLDs were emplaced during the visit, one in a stratum assumed to correspond with Waechter's layer M and another in layer P. Their location was not in the same area of the Stringer excavation but in the lower outer section of the cave. Three other TLDs were also left with Dr. Stringer for emplacement at the end of the 1995 season. Two of the units were emplaced eventually by him in the section under current excavation while the other was buried at Vanguard cave. All the units were phosphor TLDs packed in plastic tubes.

Four luminescence (OSL) samples were also collected. One was from a stratum assumed to correspond with Waechter layers G, in the interior of the cave, and one from layer P in the outer part of the cave. One additional luminescence sample was collected in the area under excavation by Stringer.

Seven gamma spectrometer readings were also obtained using the procedure outlined in Appendix B as "Protocol for field gamma spectrometry". One in the area under current excavation and the others in the layers which supposedly corresponded to levels G to K of the Waechter stratigraphy. The readings were remarkably uniform throughout the cave and averaged 0.284 Gy/ka (Table VI).

| γ ray fiel     | ld spectromete | r reading at Gorha | m's cave     |  |
|----------------|----------------|--------------------|--------------|--|
| <u>Field #</u> | Tot. Count     | Cosmic count       | <u>Gy/ka</u> |  |
| Gam 1          | 5305           | 8                  | .2647        |  |
| Gam 2          | 5530           | 15                 | .2780        |  |
| Gam 3          | 7456           | 13                 | .3951        |  |
| Gam 4          | 5805           | 10                 | .2944        |  |
| Gam 5          | 5595           | 16                 | .2818        |  |
| Gam 6          | 4972           | 21                 | .2376        |  |
| Gam 7          | 4884           | 20                 | .2384        |  |
| Average        |                |                    | .2843        |  |

Table VI

Given the fact that the deposits contained mainly wind blown sea sand, the results are not surprising. This uniformity in environmental radiation was confirmed verbally later by P. Pettitt of the Oxford AMS Laboratories who also took gamma spectrometer readings in the cave the following year (= 0.285).

Eight samples were also collected for U-series analyses by the McMaster Laboratories. They consisted of small pieces of straw-sized stalactites which were recovered *in-situ* from sediments at various locations in the Waechter excavation (Figure 12.1, 12.2).

At the time of this visit no teeth had been found yet by the Stringer team. This contrasted with the abundant number of specimens which had been recovered by the Waechter expeditions of the 1950s. Accordingly it was necessary to obtain samples from the Waechter collection which were in storage at the Gibraltar Museum. Of these, forty one teeth from the original Waechter's layers G to R were eventually selected for ESR analysis. All had been assigned site numbers and layer identification by the original collectors but no location coordinates had been recorded. This was not considered a significant drawback in this instance given the apparent ent uniformity of radiation levels throughout the site. The ESR samples were properly bagged and tagged, some with amounts of sediment still attached. Portion of the sediments collected for the u-series and Luminescence analyses were used for INAA.

I returned to Gorham's cave in 1996 to retrieve the dosimeters buried in the previous year. Both the units I emplaced and the TLDs buried by Stringer were recovered. My units had remained buried for 375 days, those emplaced by Stringer 350. They all appeared to be in good condition. A travel TLD was fired at the time of the recovery of the buried units and the lot was bundled together for the return trip to the laboratory.

As the excavation progressed seven deer teeth and one rhino tooth were discovered. Three of the deer teeth were collected by me in the fall of 1997 with appropriate sediments. They were bagged and tagged and one new dosimeter was buried within 1 m from the find location. It was a Panasonic unit packed into a plastic tube. A travel dosimeter was fired at the time of the emplacement. In spite of the site remoteness and security, the site dosimeter was subsequently `• removed by vandals and was never recovered.

Sediment and humidity samples were collected from the bottom of the TLD hole. Humidity samples were also collected from other layers.

## 14.5 Vanguard Cave

No excavation had yet started at Vanguard cave when I first visited it in 1995 with Stringer and Rink. However a program of trenching parallel to the south wall of the cave was to start in the fall of that year. Accordingly I left a phosphor dosimeter to be buried by Stringer should a living floor were encountered during the final days of the excavation.

The dosimeter was in fact emplaced in late September 1995 in unit 107. A charcoal sample was also recovered from the same area by Pettitt for <sup>14</sup>C dating by the Oxford AMS Laboratories.

155

..

I returned to the site in 1996 and collected the dosimeter left with Stringer the previous year. It had been buried for 350 days and appeared to be in good condition. I also collected a cervid mandible with a single tooth still attached and a straw stalactite to be processed by McMaster Laboratories. This material had been recovered earlier by Stringer's team in the test trench the lower section. Appropriate samples of sediment were also collected, bagged and tagged. The buried dosimeter was bundled together with the units recovered from the nearby Gorham's site.

A Luminescence sample was later taken by Stringer in the same approximate area and was shipped separately to McMaster at the request of Prof. Rink.

My next visit to Vanguard cave took place in 1997. By then excavation had progressed considerably and two Mousterian living floors had been encountered and freed of overburden. The dosimeter collected in 1996 had in fact been buried by Stringer in what turned out to be the lower floor. The artiodactyl jaw mentioned above turned out to have been recovered from a humic deposit below this floor. Accordingly in 1997 two Panasonic dosimeters were buried within 1 m from the location of the find. A control phosphor TLD was buried with one of the Panasonic units.

Several straw stalactites were discovered on the uppermost level. They were collected with appropriate sediment samples, bagged and tagged for U-series dating at McMaster Laboratories. The excavation had also uncovered a large number of mollusc shells near a hearth at this level. Some were burnt and some showed obvious signs of forced prying, Samples of these were collected with associated sediments, bagged and tagged for possible future ESR dating. A cervid jaw with 6 teeth was also recovered with its associated sediment. A Panasonic dosimeter and a control phosphor TLD were buried within 1 m from the location of teeth, shells and stalactites (Figure 11.7).

An alcove opening on the north wall of the cave had also been discovered to contain Mousterian tools and hyena bones in alternating levels. In the second of these an ibex jaw with one tooth still attached was discovered. It was collected, bagged and tagged with an appropriate amount of sediment. A Panasonic dosimeter was buried in the same layer within one meter of the find (Figures 10.13, 11.7). Sediment and humidity samples were collected from the bottom of each of the TLD holes.

A travel TLD was fired when the dosimeters were emplaced and the it was bundled together with a control unit for the return trip to the laboratory. No TLDs have been recovered from Vanguard cave.

۰.

•

.

## **CHAPTER 15. THE LABORATORY WORK**

#### 15.1 Dosimeters

All the dosimeters collected at the sites were processed using the procedures outlined in appendix B. The Panasonic elements buried at El Castillo and El Pendo had been packed into their copper capsules before leaving the laboratory with powdered mineral hydroxyapatite. After examining the retrieved dosimeters, the use of hydroxyapatite was deemed not necessary and was not used for any other field unit.

After removal of the dosimeters from the storage lead pot, the cell frames were re-inserted into their own sheaths and were immediately read. The first group of dosimeters to be processed were accompanied from the lead pot to the reading apparatus by three control Panasonic units which had been previously zeroed. Readings of the latter confirmed that no extraneous radiation affected the units in transit.

There were no problems associated with the reading of the Panasonic units. The burial doses measured in all cases compared reasonably with doses calculated through associated sediments.

Three of the Panasonic units used at El Castillo and two of those used at El Pendo had laboratory radiation added to the third element to calculate a fading correction if necessary. The readings after burial indicated that essentially no fading had taken place and no correction was needed. The associated phosphor travel dosimeters were retrieved from the storage lead pot and were read in the TL apparatus at the same time that the Panasonic units were processed. The apparatus is shown in Figure 12.4.

Upon opening, one of the phosphor travel units used at El Pendo [#141] showed what appeared to be contamination by small black particles. However its luminescence curve appeared normal both for the natural and for the laboratory dose. Its measured value also fit with the other travel units and therefore it was used in the calculations. This also was the case with one of the travel dosimeters used for Carihuela [# 187]. The attempt at comparing results obtained by Panasonic dosimeters and phosphor TLDs buried at the same location unfortunately proved unsatisfactory. One of the control phosphor TLDs used at Carihuela [# 186] was discovered to be highly contaminated, the powder appearing entirely black once the capsule was opened. Accordingly it was discarded and not processed through the TL reader. The other phosphor unit buried as control with a Panasonic dosimeter showed no indication of contamination when opened. Its luminescence curves appeared normal both for the natural and the added dose cases. However, when calculated, its burial dose was found to be over twice as large as that determined through the Panasonic unit. The latter appeared consistent with the results of the other Panasonic units which in turn were consistent with doses calculated from the sediments. It is possible that these phosphor dosimeters were of defective manufacture.

The first return phosphor travel dosimeter from Carihuela also did not perform properly. Its measured dose turned out to be 40 % higher than that measured for the two way travel unit, which is obviously not possible. The dose of the final return dosimeter was measured at approximately half that obtained for the two way unit. This was as expected since there was no essential difference in travel patterns between the first and the second return trip. Accordingly the dose of the second return dosimeter was taken as applicable to both return travels. This should not add unduly to the uncertainty of the results.

## 15.1.1 "Lumpy" and homogeneous sediments

Ages based on radiation doses determined by site dosimetry are compared with those determined by INAA analysis of the sediments collected at the Carihuela site (Table VII). The archaeological deposits at this site are characterized by the significant inclusions of eboulis and are defined as "lumpy" (Schwarcz, 1994; Brennan et al., 1997b). A similar comparison is made for the Gorham's cave site where the sediment matrix is quite homogeneous consisting mainly of sand deposits (Table VIII).

Ċ

As already discussed, sediment collected in "lumpy" sites is never truly representative of the distribution of the material in archaeological layers. As shown below, ages based on these values for the "lumpy" Carihuela site were generally found to be considerably lower than the ages determined through site dosimetry. This is because the "lumps" present in the Carihuela deposits are pieces of Carboniferous limestone which has a much lower U, Th and K content than the windblown detritus that is analysed by INAA. The results for Gorham's Cave, whose sediments consist mainly of sand, indicate that the ages determined by elemental composition are also lower than the values obtained by direct site dosimetry, although the difference is only 7%. The results confirm that site dosimetry should always be considered the preferred technique for determining yearly radiation doses. This becomes of paramount importance when the archaeological layers at the site under investigation are characterized by the significant inclusions of eboulis.

| Sample #    | EU ka |             | INAA as % | LU   | INAA as %   |     |
|-------------|-------|-------------|-----------|------|-------------|-----|
|             | INAA  | Site dosim. |           | INAA | Site Dosim. |     |
| CAR ESR 9   | 57.3  | 45.2        | 127       | 72.6 | 53.7        | 135 |
| CAR ESR 14  | 65.9  | 56.0        | 118       | 74.0 | 61.5        | 120 |
| CAR ESR 5   | 41.9  | 70.5        | 59        | 43.3 | 74.9        | 59  |
| CAR ESR 10  | 40.4  | 58.5        | 69        | 46.8 | 74.4        | 63  |
| CAR ESR 11  | 54.4  | 74.3        | 73        | 64.0 | 95.6        | 67  |
| CAR ESR 7   | 66.2  | 118.3       | 56        | 76.2 | 126.4       | 60  |
| CAR ESR 20  | 54.7  | 79.6        | 69        | 55.3 | 81.0        | 68  |
| CAR ESR 17  | 65.0  | 79.7        | 82        | 69.7 | 87.4        | 80  |
| CAR ESR 28  | 54.5  | 68.4        | 80        | 56.3 | 71.5        | 79  |
| CAR ESR 33* | 70.8  | 87.8        | 81        | 71.7 | 89.3        | 80  |
| CAR ESR 34* | 68.9  | 87.5        | 79        | 70.3 | 90.1        | 78  |

| Table V | ΠV |  |
|---------|----|--|
|---------|----|--|

| Gorham's Cave - Comparison of ages based on radiation doses determined<br>by sediment elemental analysis and by site dosimetry |  |   |   |   |  |  |  |
|--|--|---|---|---|--|--|--|
| E  | U ka                                   | INAA as %   | I   | LU ka   | INAA as %  |  |  |
| INAA   | Site dosim.                            |   | INAA  | Site dosim.   |  |  |  |
| 36.7   | 39.6                                   | 93  | 44.4  | 47.9  | 93   |  |  |
| 30.9   | 33.3                                   | 93  | 36.6  | 39.4  | 93   |  |  |
| 30.9   | 33.3                                   | 93  | 36.1  | 38.9  | 93   |  |  |
|  | E<br>E<br>INAA<br>36.7<br>30.9<br>30.9 | Cave - Comparison of age<br>by sediment elemental andEU kaINAASite dosim.36.739.630.933.330.933.3 | Cave - Comparison of ages based on raby sediment elemental analysis and byEU kaINAA as %INAASite dosim.36.739.69330.933.39330.933.393 | Cave - Comparison of ages based on radiation d<br>by sediment elemental analysis and by site dosiEU kaINAA as %IINAASite dosim.INAA36.739.69344.430.933.39336.630.933.39336.1 | Cave - Comparison of ages based on radiation doses determine<br>by sediment elemental analysis and by site dosimetryEU kaINAA as %LU kaINAASite dosim.INAA36.739.69344.430.933.39336.630.933.39336.130.933.39336.1 |  |  |

Table VIII

#### 15.2 Tooth preparation

The teeth collected in the field and in the Museums were prepared following the procedures outlined in appendix A. No significant problems were encountered during this phase of the work.

Not all the teeth collected at any one site were processed through the full ESR dating sequence. After cleaning, some samples were found to contain insufficient dentine. Others had been badly burned or damaged, while some did not yield sufficient amounts of enamel to permit processing. Of the El Pendo samples only ten were processed and of the Carihuela museum ones only nine and two of the in-situ units. Twelve of Gorham's teeth from the Gibraltar museum and three of the field recovered samples were analysed. Only two of the teeth obtained from Vanguard cave were processed. This confirms the need to ensure that the collection of samples from any one site must be sufficiently large to permit an adequate number of teeth to be dated effectively.

In most of the cases, once the dentine and the cementum were removed, the enamel did fracture, sometimes into very small pieces. This made further processing difficult at times, particularly in the attempts to remove the external and internal 40  $\mu$ m layers. The amounts actually removed were not consistent and ranged from 45 to 100  $\mu$ m.
The amounts of enamel recovered for the fully tested samples ranged from 154.4 mg to 1116.8 mg.

Samples were ground to a <150  $\mu$  mesh size except for two units from the El Pendo site. Relatively large quantities of enamel were recovered from the latter, sufficient to yield two sets of aliquots each. Accordingly one half of these enamels was ground to <150  $\mu$  while the other half was ground to 150<250  $\mu$  mesh size. These samples were used to determine the effect of the crystal size on age determination. Results are reported above in paragraph 13.8.2.

All the powdered enamel samples were separated into aliquots. The weight of the individual aliquots ranged from 15.0 mg to 30.1 mg. This is within the acceptable range for ESR analysis (Aitken, 1990). The weight of the aliquots of any one sample did not vary beyond  $\pm 0.1$  mg.

#### 15.3 Sediments

Sediments were processed following the procedures outlined in Appendix A. No particular problems were encountered during this phase of the work.

Several of the teeth had still some sediment attached. In some cases this was the only sediment directly associated with the samples. In all cases this material was collected separately from other sediment and processed. The results of their analysis, as shown on Table IX, confirms Mellars' proposition that the material closest to the teeth should generally have higher levels of radioactivity (Mellars et al., 1997).

| Table IX     INAA Analyses results for typical sediments |                     |       |        |      |  |  |  |  |  |
|--|---------------------|-------|--------|------|--|--|--|--|--|
| Sample #   | Sediment provenance | U ppm | Th ppm | K %  |  |  |  |  |  |
|  | attached to tooth   | 2 00  | 7 1 4  | 995  |  |  |  |  |  |
| GORESR 42 SED 1<br>GORESR 42 SED 2                       | bulk                | 0.83  | 2.74   | .885 |  |  |  |  |  |
| GORESR 43 SED 1  | attached to tooth   | 0.66  | 1.83   | .286 |  |  |  |  |  |
| GORESR 43 SED 2  | bulk                | 0.49  | 1.90   | .271 |  |  |  |  |  |
| VANESR 7 SED 1   | bulk                | 0.72  | 2.58   | .400 |  |  |  |  |  |
| VANESR 7 SED 2   | attached to tooth   | 2.44  | 1.63   | .260 |  |  |  |  |  |

# 15.4 Determination of De's by Universal Growth Curve

Ground samples from each site were selected and a number of aliquots were processed through the ESR spectrometer. The intensities measured were normalized and the D<sub>e</sub>'s were determined using the Universal Growth Curve (UGC) developed by Porat and Schwarcz (1994) and Rink and Schwarcz (1994). The D<sub>e</sub>'s so determined were used to establish the levels of laboratory radiation to be employed for each aliquot.

 $D_{_{\!\!e}}\sp{s}$  calculated using the UGC are compared with the  $D_{_{\!\!e}}\sp{s}$  measured using the irradiated aliquots in Table X.

|           |            |       | D <sub>e</sub> |       |
|-----------|------------|-------|----------------|-------|
| Site      | Sample #   | UGC   | Measured       | Δ     |
| El Pendo  | PENESR 17  | 10.0  | 10.45          | -0.45 |
|           | PENESR 23  | 13.0  | 12.99          | +0.03 |
| Carihuela | CARESR 5   | 83.0  | 85.4           | -2.4  |
|           | CARESR 7   | 102.0 | 103.2          | -1.2  |
|           | CARESR 9   | 140.0 | 110.5          | +29.5 |
|           | CARESR 10  | 100.0 | 100.9          | -0.9  |
|           | CARESR 11  | 130.0 | 131.6          | -1.6  |
|           | CARESR 14  | 115.0 | 121.4          | -6.4  |
|           | CARESR 17  | 101.0 | 100.4          | +0.6  |
|           | CARESR 20  | 84.0  | 69.9           | +14.1 |
|           | CARESR 28  | 80.0  | 78.0           | +2.0  |
|           | CARESR 33  | 127.0 | 108.0          | +19.0 |
|           | CARESR 34  | 105.0 | 95.2           | -9.8  |
| Gorham's  | GORESR 45  | 10.0  | 12.5           | -2.5  |
|           | GORESR 45b | 11.5  | 13.2           | -1.7  |
|           | GORESR 49a | 12.5  | 14.4           | -1.9  |
| Vanguard  | VANESR 2F  | 28.0  | 35.05          | -7.05 |
|           | VANESR 2F2 | 28.0  | 36.17          | -8.17 |
|           | VANESR 7   | 28.0  | 36.6           | -8.6  |

Table X

The measured D<sub>e</sub>'s compare reasonably with the values obtained by using the UG curve. In most instances the UGC appears to underestimate slightly the actual absorbed dose.

#### 15.6 Irradiation

No problems were encountered with the laboratory irradiation of the aliquots. Irradiation levels are recorded in Appendix A.

## 15.7 Spectrometer Measurement

No significant problems were encountered when running the irradiated aliquots in the spectrometer. When operational the apparatus performed consistently under steady state conditions.

Some samples' spectra, particularly at low levels of radiation, displayed very "dirty" signals which could not be smoothed out in spite of attenuation.

As indicated above, a number of auxiliary experiments were carried out at the same time as the samples were analyzed. Results of these experiments were reported in Tables I to V.

#### CHAPTER 16. THE ESR AGES

Comparison between ages calculated on the basis of gamma doses determined by site dosimetry and those determined by INAA analysis of the collected sediments has already been shown on Tables VII and VIII. They cover results obtained both for sites where the matrix was inhomogeneous and sites where the sediments consisted mainly of sand deposits. As reported, ages determined on the basis of doserates calculated from of INAA of sediments are always more recent than those based on site dosimetry (with two exceptions). The ESR dates determined on the basis of site dosimetry only were used for purposes of discussion and conclusions in the following chapters. However, this does not apply to Vanguard cave since no dosimeters were recovered from the site. This is a "smooth" site and thus the use of INAA doserates are deemed acceptable.

Effects of moisture content in the site sediments on ESR ages is reported in Table XVII.

#### 16.1 El Pendo

Teeth were collected from levels B (7), D (10), F (8) and H (13) of the test pit which underlies layer XVI. Those from level B consisted of a mixture of bovids, cervids and equids. Those from level D were almost exclusively equids except for two bovid teeth. Those from level F were exclusively cervids while those from level H were cervids except for a single equid incisor. The scarce industry encountered was Mousterian. Only ten El Pendo samples were processed from eight teeth out of the thirty eight collected in the field.

The uranium content of the enamels was found to be very low, just as it was the case in the nearby El Castillo (Rink et al., 1996b). It ranged from 0 to 0.27 ppm and averaged <0.08 ppm. Uranium content of cementum and dentine was also low, ranging from 0.29 to 0.63 ppm and from 0 to 0.18 ppm respectively. The uranium content of sediments was found to be low as well, ranging from 1.02 to 2.56 ppm and averaging 1.5 ppm. Thorium ranged from 3.71 to 13.55 ppm and potassium from 0.27 to 0.65 %.

166

The layers studied appeared to be well drained but the cave environment is moist. For discussion purposes dates at 30% sediment moisture were used. While the moisture levels used for calculating the ages influence the final results, the choice of moisture levels does not affect the conclusions regarding the deposition of these archaeological layers (Table XVII). ESR dates are shown on Table XI.

|             | El Pendo cave - results of ESR analyses   |               |            |            |                  |                  |                |         |  |  |  |
|-------------|---|---------------|------------|------------|------------------|------------------|----------------|---------|--|--|--|
| Sample #    | Fauna   | Enamel        | Removed µm |            | De Gy            | EU ka            | LU ka          | Layer** |  |  |  |
| <u></u>     | ,   | Thick'ss µr   |            |            |                  |                  |                |         |  |  |  |
| 00          | л · 1   | 4005          |            |            | 40 40 4 4        | 01.0 1.0 7       | 04.0 1.0 1     | - 7     |  |  |  |
| PEN ESR 22  | Bovid   | 1097          | 96         | 76         | 16.10±1.1        | $31.0 \pm 0.7$   | $31.0 \pm 0.2$ | ИВ      |  |  |  |
| PEN ESR 23  | Bovid   | 1300          | 93         | 113        | 12.99±0.6        | $36.3 \pm 1.1$   | $36.7 \pm 1.2$ | 2 B     |  |  |  |
| PEN ESR 24  | Bovid   | 1119          | 83         | 136        | 12.15±0.7        | $21.6 \pm 0.4$   | $22.4 \pm 0.3$ | 5 B     |  |  |  |
| PEN ESR 25< | Equid   | 1098          | 41         | 68         | 14.24±0.9        | $25.4 \pm 2.2$   | $25.5 \pm 2.2$ | 2 B     |  |  |  |
| PEN ESR 25> | Equid   | 1098          | 41         | 68         | 13.44±0.7        | $24.0\pm2.1$     | $24.0 \pm 2.2$ | 1 B     |  |  |  |
| PEN ESR 26  | Equid   | 1165          | 96         | 150        | 18.07±0.7        | $54.1 \pm 1.6$   | $54.1 \pm 1.0$ | 6 B     |  |  |  |
| Ave         | erage laye  | r B*          |            |            |                  | $33.7\pm1.5$     | $33.9 \pm 1.0$ | 6       |  |  |  |
|             |   |               |            |            |                  |                  |                |         |  |  |  |
| PEN ESR 17  | Equid   | 1191          | 46         | 69         | 10.45±0.7        | $10.6\pm.02$     | $10.6 \pm 0.2$ | 2 D     |  |  |  |
| PEN ESR 21< | Bovid   | 1578          | 53         | 135        | $8.68\pm0.4$     | $17.9\pm0.3$     | $19.1 \pm 0.4$ | 4 D     |  |  |  |
| PEN ESR 21> | Bovid   | 1578          | 53         | 135        | 9.59±0.3         | $19.8\pm0.4$     | $21.1 \pm 0.4$ | 4 D     |  |  |  |
| Ave         | erage laye  | r D*          |            |            |                  | $15.3\pm0.4$     | $15.9 \pm 0.4$ | 4       |  |  |  |
| PEN ESR 32  | Equid   | 759           | 41         | 57         | 18.01±1.2        | $30.5\pm0.6$     | $30.5 \pm 0.0$ | 6 H     |  |  |  |
|             | De calculated using Vfit and dates by ROSY 1.3<br>All dates as calculated for sediments at 30% moisture |               |            |            |                  |                  |                |         |  |  |  |
|             | ** The sca  | arce industry | recovere   | d from the | ese layers was n | on-discriminatin | ng             |         |  |  |  |

Table XI

Based on his sediment analysis and on Shackleton and Opdyke's chronology (1973) Butzer suggested that overlaying layer XVI was deposited during isotope stages 5c-5b, that is approximately 100 ka ago (Butzer, 1981). The ESR dates obtained are instead considerably more recent (Table XI). In fact both EU and LU ages for layer D are too young to be associated with Mousterian material (Straus, 1992; Bischoff et al., 1989) and the others are too recent to be appropriate for the layers position in the El Pendo sedimentary sequence. As a comparison the basal Aurignacian layer at El Castillo has been ESR dated by Rink et al. (1996b) at  $39.9 \pm 4.6$  ka. Cabrera and Bischoff (1989) dated the same layer by uncalibrated <sup>14</sup>C at  $38.7 \pm 2$  ka. Straus (1983) reports the age of the flowstone capping the terminal Mousterian at La Flecha at  $31.6 \pm 1$  ka. Moure and Garcia (1990) reported an age of  $37.6 \pm 1$  ka by radiocarbon for the lowermost Aurignacian layer at Cueva Millan.

The ESR results appear to be reasonably precise since with few exceptions the dates for samples within the same archaeological layer fall within reasonable standard deviations. The fact that the ages are inconsistent with stratigraphy raises a question regarding the deposition of the layers, layer D being more recent than the rest of the sequence.

A possible explanation for the young dates obtained for the El Pendo material is that teeth of younger age may have become intermixed with Mousterian material as the result of transport from their primary deposition. This is supported by the fact that the ESR ages are inverted with respect to stratigraphy and therefore represent disturbed contexts. Since the units studied are exposed in a section that is some 40 m away from the cave entrance and at a significant lower elevation, it is likely that those deposits were created by water moving downslope after eroding younger deposits near the cave opening where people probably lived. The almost total absence of fines in the sediments of the basal layers is a clear indication of the effects of strong water movement. The material deposited in the well below Layer XV could have been deposited by the drainage system which exists now beneath the levels studied. The system has been discussed in detail by Gonzalez Echegaray et al. (1980), by Butzer (1981) and by Hoyos Gomez and Laville (1982). The low uranium content of the sediments also is possibly evidence of leaching consistent with downwashing of the archaeological layers.

Since the layers are in secondary deposition, the question arises as to whether it is possible to associate their sediments with the upper archaeological stratigraphy of the cave. Industries found in the strata dated by ESR are Mousterian but not diagnostic and might be intrusive. The significant element which may allow some comparison with upper layers must come from other analyses. For example, there is a significant difference in the faunal remains recovered from the different levels dated. In level B the faunal remains reflect a significant concentration of bovids with equids and cervids. In level D the majority of remains are equids. Level H contains essentially no other species but cervids.

Fuentes Vidarte (Gonzales Echegaray et al., 1980) studied in detail the El Pendo faunal material from the archaeological layers down to level XVI. His analysis shows that peak equid concentrations occurred in levels II, III, V and VII, while bovids were mainly found in level II. Layers IX- X contained mostly cervids, thus they appear to have the same faunal concentration as level H. Layers H and X also appeared to contain the same lithic industry.

Butzer (Gonzales Echegaray et al., 1980; Butzer, 1981) in his sedimentological analysis identified an abrupt and flat boundary between levels IX and X which could be an indication of erosional processes. Layer X is indeed thinner than most other layers. Butzer's sedimentological study also confirmed that the period which followed the deposition of level X appeared to have been temperate with moist summers. On the basis of his study Butzer placed the entire sequence between layers VIIId and XIVa in the approximate range of isotope stage 3. Also Leroi-Gourhan's palynological analysis of the same sediments confirmed that level IX appeared to have been deposited during a temperate period (Gonzales Echegaray et al., 1980). According to the records of the oxygen isotopes in marine cores, an interpleniglacial period occurred at the end of stage 3 at about 32 kya. This would lend support to Butzer's dating of layer X.

Based on the above evidence and the ESR ages, it would appear reasonable to suggest that the sediments found in the Montes/Sanguino level H were most likely deposited originally in the top portion of Echegaray level X.

Therefore, if we can assume with a degree of certainty that the sediments in layers H and X correspond, then the final Mousterian industries which are found in Echegaray levels VIIId and IX were deposited some time after 31 Kya (the apparent ESR age of level H). While Chatelperronian is accepted as the last industry employed by the Neanderthal, no such industry has been recovered at El Pendo. This is typical of Spanish sites. Chatelperronian points were recovered among Aurignacian material in the upper portion of layer VIII but, according to Echegaray and Freeman (Gonzales Echegaray et al., 1980), this is the characteristic of the Cantabrian archaic Aurignacian. Therefore level VIIId can be deemed to represent the last Neanderthal occupation at the site.

From these data we can conclude that the Neanderthal were present at El Pendo in very recent times. Furthermore we can confirm that the ESR technique produces accurate ages when compared to dating by sedimentological and faunal analyses.

# 16.2 Carihuela

Only eleven samples were processed out of the twenty eight collected from the Madrid museum and eight *in-situ* teeth. Detailed coordinates for the Museum samples were not available. However the trench from which they had been recovered was a 2 m x 2 m square (Figures 10.5, 10.6) so that site dosimeter and sediment sample locations could reasonably be expected always to be within 2 m from the actual teeth locations. ESR results are shown on tables XII a and XIIB

|   |             |           |              |              |              | .u                |                            |                            |        |
|---|-------------|-----------|--------------|--------------|--------------|-------------------|----------------------------|----------------------------|--------|
|   |             |           | Carihue      | la cave -    | Results      | of ESR analy      | 'ses                       |                            |        |
| - | Sample #    | Fauna     | Enamel       | Remov        | red µm       | De                | EU ka                      | LU ka                      | Layer  |
|   | <u></u>     |           | Thick'ss µn  | n <u>Out</u> | <u>In</u>    |                   |                            |                            |        |
|   |             |           | Calculate    | ed using     | in-situ      | dosimetry res     | ults                       |                            |        |
|   | CAR ESR 9   | Bovid     | 1037         | 49           | 68           | 59.43±1.6         | $45.2 \pm 2.0$             | $53.7 \pm 2.0$             | v-2    |
|   | CAR ESR 14  | Equid     | 1159         | 65           | 60           | 65.32±1.6         | $56.0 \pm 2.0$             | $61.5 \pm 2.0$             | V-3    |
|   | Avera       | ige layer | V-2/3        |              |              |                   | $50.6 \pm 2.8$             | $57.6\pm2.8$               |        |
|   | CARESR 5    | Equid     | 1191         | 119          | 113          | 45 92+1 0         | $70.5 \pm 1.0$             | 749+10                     | V-5    |
|   | CAR ESR 10  | Equid     | 1223         | 57           | 42           | 54 27+1 0         | $585 \pm 10$               | 747 + 10                   | V-5    |
|   | CAP ESP 11  | Fauid     | 750          | 48           | 80           | 70 81+2 1         | $743 \pm 20$               | $956 \pm 20$               | V-6    |
|   |             | ng lavore | V-5/6        | 40           | 00           | /0.0112.1         | $74.3 \pm 2.0$<br>678 ± 25 | $93.0 \pm 2.0$<br>917 ± 25 | V-0    |
|   | nvela       | ge layers | v-5/0        |              |              |                   | $07.0 \pm 2.0$             | 01.7 ± 2.5                 |        |
|   | CAR ESR 7   | Equid     | 1379         | 36           | 37           | 55.51±1.2         | $118.3 \pm 1.5$            | $126.4 \pm 1.3$            | VIIB-1 |
|   | CAR ESR 20  | Rhino     | 2428         | 50           | 48           | 37.59 <b>±0.7</b> | $79.6 \pm 1.2$             | $81.0 \pm 1.8$             | VIIB-1 |
|   | CAR ESR 17  | Equid     | 1401         | 48           | 60           | 54.03±4.4         | $79.7 \pm 5.0$             | 87.4 ±5.0                  | VIIB-2 |
|   | CAR ESR 28  | Equid     | 1606         | 75           | 108          | 41.98±1.3         | $68.4 \pm 1.1$             | $71.5 \pm 1.1$             | VIIB-2 |
|   | CAR ESR 33* | Cervid    | 1321         | 101          | 81           | 58.09±1.0         | $87.8 \pm 1.0$             | $89.3 \pm 1.0$             | VIIB-2 |
|   | CAR ESR 34* | Equid     | 1212         | 85           | 48           | 51.19±1.0         | $87.5 \pm 1.0$             | $90.1 \pm 1.0$             | VIIB-2 |
|   | Aver        | age layer | VIIB         |              |              |                   | $86.9 \pm 2.5$             | <b>91.0 ±2.5</b>           |        |
|   | <u> </u>    |           | De calcul    | ated usin    | g Vfit and   | dates by ROSY     | 1.3                        |                            | ·      |
|   |             |           | All dates as | calculated   | l for sedir  | nents at 10% mc   | oisture                    |                            |        |
|   |             |           |              | *Teeth       | recovered    | ł in-situ         |                            |                            |        |
|   |             |           | Recover      | ed indust    | ry in all la | ayers is Mousteri | ian                        |                            |        |
|   |             |           |              |              |              |                   |                            |                            |        |

Table XIIa

| Carihuela cave - Results of ESR analyses |        |              |            |              |                  |                |                |             |  |  |
|--|--------|--------------|------------|--------------|------------------|----------------|----------------|-------------|--|--|
| Sample #                                 | Fauna  | Enamel       | Remov      | ∕ed µm       | De               | EU ka          | LU ka          | Layer       |  |  |
|  | ,      | Thick'ss un  | n Out      | In           |                  |                |                |             |  |  |
|  |        |              |            |              |                  |                |                |             |  |  |
| Calculated using sediments INAA results  |        |              |            |              |                  |                |                |             |  |  |
| CAR ESR 9                                | Bovid  | 1037         | 49         | 68           | 59.43±1.6        | $57.3 \pm 2.2$ | $72.6 \pm 2.3$ | v-2         |  |  |
| CAR ESR 14                               | Equid  | 1159         | 65         | 60           | 65.32±1.6        | $65.9 \pm 2.4$ | $74.0 \pm 2.4$ | <b>V-</b> 3 |  |  |
|  | Aver   | age layer V  | /-2/3      |              |                  | $61.6 \pm 3.3$ | 73.3 ± 3.3     |             |  |  |
|  |        | 0 2          |            |              |                  |                |                |             |  |  |
| CAR ESR 5                                | Equid  | 1191         | 119        | 113          | 45.92±1.0        | $41.9 \pm 1.0$ | $43.3 \pm 1.0$ | V-5         |  |  |
| CAR ESR 10                               | Equid  | 1223         | 57         | 42           | 54.27±1.0        | $40.4 \pm 1.0$ | $46.8\pm1.0$   | V-5         |  |  |
| CAR ESR 11                               | Equid  | 750          | 48         | 80           | 70.81±2.1        | $54.4 \pm 1.6$ | $64.0 \pm 1.9$ | V-6         |  |  |
|  | Ave    | age layers   | V-5/6      |              |                  | $45.6\pm1.5$   | $51.4 \pm 1.7$ |             |  |  |
|  |        | 0            |            |              |                  |                |                |             |  |  |
| CAR ESR 7                                | Equid  | 1379         | 36         | 37           | 55.51±1.2        | $66.2 \pm 1.9$ | $76.2\pm1.9$   | VIIB-1      |  |  |
| CAR ESR 20                               | Rhino  | 2428         | 50         | 48           | 37.59±0.7        | $54.7 \pm 1.0$ | $55.3 \pm 1.0$ | VIIB-1      |  |  |
| CAR ESR 17                               | Equid  | 1401         | 48         | 60           | 54.03±4.4        | $65.0 \pm 5.1$ | $69.7 \pm 5.2$ | VIIB-2      |  |  |
| CAR ESR 28                               | Equid  | 1606         | 75         | 108          | 41.98±1.3        | $54.5 \pm 1.1$ | $56.3 \pm 1.1$ | VIIB-2      |  |  |
| CAR ESR 33*                              | Cervid | 1321         | 101        | 81           | 58.09±1.0        | $70.8 \pm 1.4$ | $71.7 \pm 1.5$ | VIIB-2      |  |  |
| CAR ESR 34*                              | Equid  | 1212         | 85         | 48           | 51.19±1.0        | $68.9 \pm 1.4$ | $70.3 \pm 1.4$ | VIIB-2      |  |  |
|  | Ave    | rage layer V | √IIB       |              |                  | $63.4 \pm 2.7$ | $66.6\pm2.8$   |             |  |  |
|  |        | De calcul    | ated usin  | g Vfit and   | dates by ROSY    | 1.3            |                |             |  |  |
|  |        | All dates as | calculated | d for sedir  | nents at 10% mo  | visture        |                |             |  |  |
|  |        |              | *Teeth     | recovered    | l in-situ        |                |                |             |  |  |
|  |        | Recover      | ed indust  | ry in all la | yers is Mousteri | an             |                |             |  |  |

Table XIIb

The uranium content of the enamels was found to be very low, ranging from 0 to 0.67 ppm and averaging 0.13 ppm. Uranium content of cementum and dentine varied considerably, ranging from 1.3 ppm to 13.35 ppm and 1.2 ppm to 19.58 ppm respectively. The uranium content of the sediments was generally lower than that of the teeth ranging from 1.5 ppm to 2.88 ppm and averaging 2.02 ppm. Thorium ranged from 7.12 ppm to 12.74 ppm and potassium from 0.39 % to 0.7 %.

Carihuela cave is extremely dry at the present time. This is confirmed by the moisture samples collected at the site. Moisture ranged from 0.5% to 14.6% and averaged at 8.6%. Accordingly, although the moisture history of the sediments cannot be estimated, the dates at 10% moisture were used for discussion purposes.

The ESR ages established for the layer V, the second Mousterian occupational floor, are somewhat older than the Würm III (32-20 kya) assigned by Carrión (1992) to the sediments of this level (Table XII). Carrion's date seems too recent even for a final Mousterian occupation. Based on the ESR EU dates, an age ranging between 45 and 70 ka for the entire layer V seems more appropriate. The EU date of  $45.2 \pm 2.0$  ka for layer V-2 is also considered consistent with an uncalibrated 40 ka obtained by radiocarbon for this level (Vega Toscano, 1988). An uncalibrated radiocarbon date of 46 ka has also been reported for the bottom of layer VI (Vega Toscano et al., 1996). However, as already discussed, the normal problem of potential contamination renders this date quite unreliable.

Extensive faunal and lithic analyses have concluded that all sites in southern Spain including Carihuela and Gorham's cave have the same archaeological sequences with several recognizable layers whose cultural contents coincide and are indeed deemed to be coeval. In particular Carihuela's upper layer IV is considered equivalent to the final Mousterian layer 22 at Gorham's cave (Vega Toscano, 1990, 1993). The ESR EU age for Carihuela's layer V-2/3 is certainly consistent with that obtained for the above level at Gorham's (see page 173).

Twenty burnt flint samples coming from the Washington State University excavation were dated by TL. The coordinates of the samples were never reported and the dates were never published except for those of a few flints that according to Gösku et al. (1974) were recovered from late Mousterian deposits only, most probably those of level IVB. The TL ages range from  $13.4 \pm 0.6$  ka to  $48.0 \pm 4.9$  ka and average  $44.0 \pm 4$  ka (Gösku et al., 1974). Accordingly they also support the ESR results for layer V.

Carrion (1992) reported some unpublished TL dates obtained by Fremlin for all the twenty Washington State University samples. The highest of these at 80 and 82.5 ka are comparable to the ESR EU age of  $86.9 \pm 2.5$  ka obtained for the tooth samples recovered from Level VIIB (Table XII). Also, Carrion (1992) suggests that the temperature optimum based on palynological data occurred in pollen zone R, corresponding to level VIIA. Zone S, corresponding to level VIIB, instead shows evidence of climatic severity. This is interpreted as placing Layer VIIB in the 85 to 90 ka range according to the oxygen isotope time scale, and matches the ESR EU date obtained for this layer. Additional support for the EU ESR age is provided by a 117 ka U-series date obtained by the University of Barcelona for the calcite layer which seals the bottom of level VIIB (Vega Toscano, 1996).

The results for the *in-situ* teeth yielded similar results to those of museum samples reportedly from the same layer. This adds additional weight to the dating results. While not associated with the final Mousterian the ESR age obtained for level V provides valuable information on the Neanderthal presence at Carihuela. In fact it yields a secure date for the Neanderthal remains discovered in this layer. Furthermore the Neanderthal remains recovered in layer VI can be dated between 60 and 90 ka based on the EU ESR ages for the straddling layers V and VIIB. In addition an EU age of  $45.2 \pm 2.0$  ka for the sublayer V-2 supports a possible date in the 30+ ka range for the final overlaying Mousterian layer IVB, thus suggesting the recent presence of the Neanderthals in Andalusia.

From the data obtained for this site we can also conclude that the ESR method yields accurate ages when compared with U-series, TL, radiocarbon and palynological dating.

# 16.3 Gorham's Cave

Only thirteen Gorham's samples were processed out of forty one museum teeth and three out of fourteen teeth collected *in-situ*.

ESR results are shown on Tables XIII and XIV.

| Gorham's Cave - ESR ages for in-situ teeth |        |            |         |          |                |              |              |                 |       |  |
|--|--------|------------|---------|----------|----------------|--------------|--------------|-----------------|-------|--|
| Sample #                                   | Fauna  | Enamel I   | Remo    | ved µ    | um De          | EU ka        | LU ka        | Other dates ka  | Layer |  |
|  |        | Thick's µm | Out     | In       |                |              |              |                 |       |  |
| GORESR 43                                  | Cervid | 739        | 44      | 51       | 15.82±3.6      | $35.7\pm4$   | $44.7\pm4$   |                 | 22    |  |
| GORESR 45                                  | Cervid | 788        | 37      | 52       | 12.48±1.5      | $35.3\pm4$   | $36.5 \pm 4$ |                 | 22    |  |
| GORESR 49                                  | Cervid | 631        | 40      | 38       | 14.38±2.1      | $39.7\pm4$   | $39.8 \pm 4$ |                 | 22    |  |
|  | Aver   | age        |         |          |                | $36.9\pm5$   | $40.3 \pm 5$ | 45.3±2 OxA 6075 | i     |  |
|  |        |            |         |          |                |              |              |                 |       |  |
|  |        | D          | e calci | ulated   | using Vfit and | d dates by R | OSY 1.3      |                 |       |  |
|  |        | All        | dates a | is calci | ulated for sed | iments at 5% | b moisture   |                 |       |  |

| Ta  | հեռ | VШ |
|-----|-----|----|
| 1.9 | DIG | лш |

|                  | Gorham's Cave - ESR ages for the Samples from Gibraltar's Museum |          |           |        |                    |                |                |            |       |  |
|------------------|--|----------|-----------|--------|--------------------|----------------|----------------|------------|-------|--|
| Sample #         | Fauna  | Enamel   | Remo      | ved    | um De              | EU             | LU             | Industry   | Layer |  |
| Thick's µmOut In |  |          |           |        |                    |                |                |            |       |  |
| GORESR 1         | Cervid   | 1029     | 84        | 88     | 11.78±1.6          | $29.7\pm4.4$   | $33.1 \pm 5.1$ | Mousterian | G     |  |
| GORESR 2         | Cervid   | 917      | 62        | 38     | 9.51 <b>±0</b> .3  | $23.6\pm1.9$   | $26.3 \pm 2.3$ | Mousterian | G     |  |
|                  |  | А        | verag     | e G    |                    | $26.7\pm5$     | $29.7\pm6$     |            |       |  |
| GORESR 5         | Bovid  | 1514     | 39        | 71     | 13.32±0.6          | $32.7 \pm 2.7$ | $36.2 \pm 2.3$ | Mousterian | K     |  |
| GORESR 6         | Caprid   | 712      | 47        | 42     | 15.67±1.0          | $36.4 \pm 3.4$ | $41.3 \pm 4.1$ | Mousterian | K     |  |
| GORESR 7         | Caprid   | 1005     | 69        | 75     | 14.04±2.8          | $32.5 \pm 6.7$ | 37.4 ± 7.9     | Mousterian | К     |  |
| GORESR 9         | Caprid   | 969      | 49        | 52     | 13.01 <b>±0</b> .5 | $32.8 \pm 2.8$ | $36.3 \pm 3.3$ | Mousterian | К     |  |
| GORESR15         | Caprid   | 794      | 37        | 50     | 17.61±1.0          | $34.8 \pm 3.0$ | $41.3 \pm 3.9$ | Mousterian | Μ     |  |
| GORESR18         | Caprid   | 809      | 38        | 38     | 14.43±0.7          | $29.5 \pm 2.6$ | $34.1 \pm 3.1$ | Mousterian | М     |  |
| GORESR 21        | Bovid  | 1113     | 37        | 49     | 12.31±0.9          | $29.0\pm2.9$   | $33.0 \pm 3.5$ | Mousterian | М     |  |
| GORESR 24        | Caprid   | 836      | 43        | 64     | 14.32±0.6          | $31.1 \pm 2.5$ | $36.1 \pm 3.1$ | Mousterian | Р     |  |
| GORESR 31        | Caprid   | 779      | 55        | 43     | 12.48±1.5          | $20.7 \pm 1.2$ | $25.9 \pm 1.7$ | Mousterian | Р     |  |
| GORESR33         | Caprid   | 795      | 35        | 43     | 15.48±1.4          | $27.5\pm2.9$   | $32.8\pm3.6$   | Mousterian | Р     |  |
|                  |  | Av       | erage     | K-P    |                    | 30.7±5         | $35.4\pm5$     |            |       |  |
| GORESR37         | Caprid   | 1181     | 58        | 67     | 23.89±1.3          | $56.5 \pm 4.9$ | $62.4 \pm 5.1$ | Mousterian | R     |  |
|                  | <u> </u>   | I        | De calc   | ulated | l using Vfit an    | d dates by RO  | SY 1.3         |            |       |  |
|                  |  | All date | es are in | n ka a | s calculated fo    | or sediments a | t 5% moisture  |            |       |  |

Table XIV

The uranium content of the enamels was found to be very low ranging from 0 ppm to 0.5 ppm and averaging 0.12 ppm. Uranium content of cementum and dentine varied considerably ranging from 0 ppm to 21.1 ppm (9.17 ppm ave.) and 0 ppm to 13.0 ppm (6.83 ppm ave.) respectively. The uranium content of the sediments ranged from 0.49 ppm to 0.71 ppm averaging 0.62 ppm. Thorium ranged from 1.83 ppm to 2.66 ppm and potassium from 2.7% to 3.0%.

The sediments at Gorham's cave consist almost entirely of wind blown sand. Samples collected showed that the current moisture levels ranged from 0.46% to 1.9% and averaged 0.33%. Given the nature of the sediments there is no reason to believe that their moisture content would have varied significantly over long periods. For discussion purposes the ESR ages at 5% moisture were used.

Presently layers 9 to 23 are being excavated at the interior of the cave. The upper levels have yielded Upper Paleolithic material while layer 22 is Mousterian and is separated from the upper contexts by a sterile partly cemented layer. Until now it has not been possible to reconcile exactly the newly excavated contexts with the original Waechter layers (for the location of the Waechter and the Stringer excavations see Figures 10.10 and 10.12 respectively). The provenance of the museum samples used for the present study was only indicated by layer. Accordingly dosimeters could only be placed at locations which likely only approximate the original spot of the teeth recovery. However, as discussed above, field  $\gamma$  spectrometry has indicated that the natural radiation levels in the cave are quite uniform. This is also confirmed by the uniformity of radioactive isotopes found in the sediments. Accordingly location of site dosimeters is not quite critical at this site.

There is very good agreement between the LU ages obtained for the *in-situ* samples from layer 22 and <sup>14</sup>C dates obtained from charcoal recovered from the same deposits (Table XIII), particularly since the latter are at the extreme limit of the capability of the radiocarbon method. There is also reasonable statistical agreement with the OSL date of  $35 \pm 7$  ka obtained by Rink et al. for the same level (1998) and with those reported for Gruta Nueva (Hublin et al., 1995) and Figuera Brava (Atunes, 1990) in Portugal for similar layers.

The average ESR ages obtained for the museum tooth samples reportedly recovered from the upper Waechter Mousterian level G are  $27 \pm 5$  ka EU and  $30 \pm 6$  ka LU (Table XIV). This is in sharp contrast with the date obtained for the *in-situ* samples from Stringer's upper Mousterian layer 22 (Table XIII), confirming that the two layers do not correspond. They are instead closer to the radiocarbon results obtained from material collected in Stringer's Upper Paleolithic layers 9 to 13 which average  $29.8 \pm 0.7$  ka (OxA 7074 to 7077 and OxA 7110). Furthermore, combining the ESR results obtained for all the museum samples labelled from layers K to P would yield average ages of  $30 \pm 5$  ka LU and  $35 \pm 5$  ka EU for all the Waechter Mousterian levels. With a range from 25 to 40 ka at the 1  $\sigma$  confidence level, this would suggest that the total length of

Mousterian occupation was extremely short which is unlikely and would not match the general stratigraphic sequence established for southern Spain. These results also do not agree with an OSL date of  $73 \pm 23$  ka reported by Rink et al. (1998) for what was assumed to correspond with Waechter's layer K. The ESR results would seem to suggest that all the museum samples used in this study were probably mislabelled. This is supported also by the radiocarbon date range of  $47 \pm ka$  to  $49.2 \pm ka$  reported for layer G by Garralda (1978), Bernaldo de Quiros and Moure-Romanello (1978).

From these data we can conclude that the Neanderthal occupation of Gorham's cave lasted until quite recently. Since layer 22 at this site corresponds with layer IVB at Carihuela and the final Mousterian at several other Andalusian sites these results also provide confirmation that the Neanderthals lived in southern Spain much more recently than they did in Eastern Europe.

Furthermore the results also confirm the accuracy of the ESR technique when compared with OSL and radiocarbon dating.

Last but not least, the ESR results confirm that the layers being excavated currently by Stringer do not match the dubious stratigraphy proposed originally by Waechter.

#### 16.4 Vanguard Cave

Two teeth were processed out of nine teeth from three finds collected in-situ in the Vanguard cave south area. ESR results are shown on Table XV.

|   |  |             | ١                  | Van            | guard Cave                          | - ESR age                     | :5                     |                          |       |  |
|---|--|-------------|--------------------|----------------|-------------------------------------|-------------------------------|------------------------|--------------------------|-------|--|
| Sample #  | Fauna  | Enamel I    | Remo               | ved            | µm De                               | EU ka                         | LU ka                  | Other dates ka           | Layer |  |
|   |  | Thick's µm  | Out                | In             |                                     |                               |                        |                          |       |  |
| VANESR 2f   | Caprid   | 981         | 72                 | 41             | 36.05±2.6                           | $58.5 \pm 4$                  | $67.2\pm5$             | 41.8 - 54.0 <sup>@</sup> | 158   |  |
| VANESR 7  | Caprid   | 1086        | 45                 | 71             | 36.60±2.2                           | $48.1\pm3$                    | $65.6 \pm 4$           | $> 40 \pm 66$            | *     |  |
| * Sample wa<br>@ (OxA 689<br>@@ (OxA. <sup>14</sup> | * Sample was recovered below the lower occupational level which has an estimated age of >40 ka - (OX. <sup>14</sup> C.)<br>@ (OxA 6891, 6892, 6998, 7127) - for layer 158, Upper Cave - C. Stringer, personal communication, February 1998<br>@@ (OxA. <sup>14</sup> C) - C. Stringer, personal communication, February 1998 |             |                    |                |                                     |                               |                        |                          |       |  |
|   |  | Di<br>All c | e calcu<br>dates a | ılate<br>s cal | d using Vfit an<br>lculated for sec | id dates by I<br>diments at 5 | ROSY 1.3<br>% moisture |                          |       |  |

Table XV

The uranium content of the enamels was below detection limits. Uranium content of dentine ranged from 10.99 ppm to 35.94 ppm. Only one sample had cementum attached with a uranium content of 11.1 ppm. The uranium content of the sediment ranged from 0.72 ppm to 2.44 ppm, thorium ranged from 1.63 ppm to 4.59 ppm and potassium from 0.26% to 0.68%.

As at Gorham's, the sediments at Vanguard cave consist almost entirely of wind-blown sand. Samples collected showed that the current moisture levels ranged from 2.6% to 3.8% and averaged at 3.1%. For discussion purposes the ESR ages at 5% moisture were used as for Gorham's.

Two occupational levels have been excavated in the Vanguard south area and four in the north alcove as well as a test trench extending from the outer to the inner portion of the cave.

The lower occupational layer in Vanguard South is approximately 1 m below datum and it contains a hearth. The LU ESR ages obtained for an ibex tooth recovered from this layer at  $67.2 \pm 5$  ka is compared with the radiocarbon AMS date of >40 ± ka obtained by Oxford from charcoal samples from the same area. The ESR age is in stratigraphic agreement with the <sup>14</sup>C dates obtained for the upper occupational layer. These ranged from 41.8 ± 1.4 ka to 54. 0 ± 3.3 ka (OxA 6891, 6892, 6998, 7127) and averaged 48.0 ± ka (Stringer, 1998).

Two teeth in a partial mandible were also recovered from humic sands at approximately 6.1 m below datum. The LU ESR age of  $65.6 \pm 4$  ka obtained for this sample would suggest that the mandible was discarded downslope by the occupiers of layer 158.

The ESR results for Vanguard cave do not allow us to draw any conclusions regarding the disappearance of the Neanderthal from Gibraltar. None the less they still provide valuable data regarding their presence in southern Spain in the Middle Paleolithic.

The radiocarbon dates obtained for Vanguard cave are also too old to be of value in assessing the accuracy of the ESR method . As stated previously radiocarbon results in this age range can only suggest an ante quem date. On this basis however they support the ESR ages proposed for layer 158.

#### CHAPTER 17. CONCLUSIONS

A number of conclusions can be drawn from the results of this research project.

1) - Great attention must be paid to the water content in archaeological contexts. In fact the impact of burial sediment moisture on ESR dates can be significant as can be seen from Table XVI.

For El Pendo a change from 10% to 50% moisture increases ESR ages by approximately 41%. The layers studied at this site appeared to be well drained even though the cave environment was moist. The sediments themselves are very coarse and would not retain free water. The use of the ESR ages calculated at 30% moisture is acceptable since the choice of moisture levels does not affect the conclusions regarding the deposition of the archaeological layers.

The Carihuela ESR results increase by approximately 34% (EU) to 37% (LU) over the same range of moisture change. The cave is extremely dry at present and there is no reason to believe that at any time their moisture content would have exceeded for long periods the measured average of 8.6%. Accordingly, in this instance the use of ESR ages calculated at a moisture level of 10% are considered acceptable.

The Gibraltar sites' ESR ages increase by a maximum of 2.7% when assumed moisture goes from 2 to 15%. Such change would not affect the conclusions regarding the dating of the layers. The sediments at these sites consist almost entirely of wind blown sand. Samples collected showed that the current moisture levels ranged from 0.46% to 1.9% and averaged 0.33%. Given the nature of the sediments there is no reason to believe that their moisture content would have varied significantly over long periods and would have exceeded the value of 5% used in the present calculations.

2) - The results from this research project confirm the necessity of utilizing direct site dosimetry in preference to sediment analysis particularly when dating "lumpy" contexts. Comparison of ESR results demonstrate the difference in ages which are obtained by using the two different methods (Tables VII, VIII). The data for Gorham's cave which contains homogeneous sediments also attest to the accuracy of the algorithms used to convert INAA results into radiation doses. 3)- We can conclude from the results of the tests run on the ESR spectrometer that the intensity signal repeatability is excellent regardless of operator capabilities and signal-to-noise ratios.

However the data obtained from tests carried out as part of this project to determine the impact of sample density and sample position within the spectrometer cavity on ESR results indicate that the utilization of small samples may present problems. It is suggested that further work be carried out to assess the effects of sample size and determine whether adjustments should be made when processing small samples in the spectrometer.

4) - It can be concluded from the data collected during the research that the ESR method is eminently suitable for dating archaeological contexts. The comparison with the many other archaeological dating methods as well as the variety in geography, latitudes and sedimentation of the sites studied confirm its reliability and accuracy regardless of location and nature of deposits encountered. No other previous research had allowed for such an extensive comparison between dating methods and utilizing such disparate archaeological contexts. This has permitted a significant contribution to the determination of the accuracy of this new technique to be made.

5) - What do the results of the ESR analyses of the teeth from the four Iberian sites tell about the survival of the Neanderthals? In fact quite a lot.

In spite of the fact that they are not consistent with the stratigraphy the El Pendo data provide quite useful information. A review of the work by Butzer, Hoyos Gomes and Laville and Fuentes Vidarte permitted the identification of the most likely origin of one of the contexts studied. Since this location is under the final Mousterian layer the age obtained by ESR provided at least a terminus post quem regarding the final Neanderthal occupation of the site.

The results at Carihuela were even more significant. Not only they provided secure dates for two of the three Neanderthal remains recovered at this site but also indicated the recent presence of the Neanderthals in Andalusia.

A further positive confirmation of the recent presence of Neanderthal in all of southern Spain comes from the ESR ages obtained for the final Mousterian layer at Gorham's cave. The questions which the research design was suggesting should be addressed by the thesis research have all been answered. Unfortunately the data collected did not yield any evidence of a continuous withdrawal of the Neandertals form north to south. However I was able to provide the first solid evidence of the late presence of Homo sapiens neanderthalensis in the Iberian peninsula. I was also able to confirm the adequacy, advantages and accuracy of the ESR technique in support of archaeological research.

As an archaeologist I try to pursue research in transitional period s. I am also very interested in the application of archaeometric techniques to archaeological research, Therefore I found extremely appealing the opportunity to work on a new dating technique and apply it to the study of a very significant transitional period in human evolution. It has thus been quite rewarding that my work was able to make a valid contribution to both fields of research.

| ESR ages of Mousterian layers at Iberian sites* |            |                              |                              |                               |  |  |  |  |  |
|---|------------|------------------------------|------------------------------|-------------------------------|--|--|--|--|--|
| Site  | Layer      | ESR a                        | Other dating results ka      |                               |  |  |  |  |  |
|   |            | EU                           | LU                           |                               |  |  |  |  |  |
| El Pendo##                                      | В          | $33.7 \pm 13$                | $33.9 \pm 12$                | O <sub>2</sub> isotope 5c (*) |  |  |  |  |  |
|   | D          | $14.3 \pm 7$                 | $14.9 \pm 7$                 | $O_2$ isotope 5c (*)          |  |  |  |  |  |
|   | Н          | $30.5 \pm 3$                 | 30.5 ± 3                     | $O_2$ isotope 5c (*)          |  |  |  |  |  |
| Carihuela**                                     | V2/3       | $50.6\pm8$                   | 57.6±6                       | Würm III (32-20) (**)         |  |  |  |  |  |
|   | V5/6       | $67.8 \pm 8$                 | 81.7 ± 12                    | Würm III (32-20) (**)         |  |  |  |  |  |
|   | VIIB       | $86.9 \pm 17$                | 91.0 ± 17                    | Würm II (75-32) (**)          |  |  |  |  |  |
| Gorham's cave***                                | 22         | $36.9 \pm 5$                 | $40.3 \pm 5$                 | 45.3±2 ®                      |  |  |  |  |  |
| Vanguard south***                               | 158<br>*** | $58.3 \pm 4$<br>$48.0 \pm 3$ | $66.8 \pm 5$<br>$65.4 \pm 4$ | 41.8 - 54.0 @@<br>> 40 ± @@@  |  |  |  |  |  |

Table XVI

# Individual sample results are detailed in Tables XI to XV. Calculated using ROSY 1.3

## Layer error calculated as deviation from mean

Butzer, 1981 - Oxygen isotope age assigned by Butzer on the basis of Shackleton and Opdyke, 1973.

\*\* Carrion, 1992 - Also a TL age of 44 ka by Göske et al. (1974) for layer IV and a 117 ka U-series date by Vega Toscano (1996) for the calcite layer sealing the bottom of layer VIIB

\*\*\* Sample was recovered below the lower occupational level which has an estimated age of >40 ka - (OX. 14C.)

@ (OxA 6075) - C. Stringer, personal communication, February 1998
@@ (OxA 6891, 6892, 6998, 7127) - for layer 158 south cave; C. Stringer, personal communication February 1998
@@@ (OxA. <sup>14</sup>C) - C. Stringer, personal communication, February 1998

<sup>###</sup> In-situ samples

| Ef             | fect of sedi  | ment moistu     | re concentra  | ation on ESF | R dates in ka   | k             |
|----------------|---------------|-----------------|---------------|--------------|-----------------|---------------|
|                |               |                 | Mois          | ture %       |                 |               |
|                | 1             | 0               | 30            |              | 5               | -<br>0        |
| Sample #       | EU            | LU              | EU            | LU           | EU              | LU            |
| FL PENDO CAVE  |               |                 |               |              |                 |               |
| PENESR 17      | 87            | 87              | 10.5          | 10.5         | 12 3            | 123           |
| DENESR 22      | 25.7          | 25.7            | 31.0          | 31.0         | 36.2            | 36.3          |
| PENESR 23      | 30.3          | 30.6            | 36.3          | 36.7         | 42.3            | 42 9          |
| PENESR 24      | 18.0          | 18.5            | 21.3          | 22.2         | 24.6            | 25.8          |
| PENESR 25      | 19.7          | 10.0            | 23 7          | 23.8         | 27.7            | 27.8          |
| PENESR 26      | 13.7<br>44 Q  | 13.7<br>14 Q    | 54 1          | 54 1         | 63.3            | 63.3          |
| DENESP 22      | 25.3          | 25.3            | 30.5          | 30.5         | 35.6            | 35.7          |
| CARIHIELA CAVE | 40.0          | 40.0            | 00.0          | 30.0         | 00.0            | 33.7          |
| CARESR 5       | <b>41 Q</b>   | 433             | 49.8          | 51 8         | 57 5            | 60.2          |
| CARESR 7       | 91.5<br>81.4  | 40.0<br>84 Q    | 96.4          | 101.8        | 110.8           | 117 7         |
| CARESR 10      | 40.4          | 46.8            | 45.8          | 54.6         | 50.6            | 61.8          |
| CAPESP 11      | 54 A          | 40.0<br>64.0    | -10.0<br>61 3 | 74.3         | 673             | 01.0<br>83 8  |
| CARESR 11      | 65 Q          | 74.0            | 75.8          | 870          | 84.6            | 00.0          |
| CARESR 14      | 65.0          | 60.7            | 75.0          | 07.0<br>97.0 | 04.0<br>86.1    | 99.2          |
| CARESR 17      | 54.7          | 55.2            | 70.0          | 66.5         | 76.4            | 90.4<br>77 7  |
| CARESR 20      | 54.5          | 56.2            | 64.7          | 67.4         | 70.4            | 79.4          |
| CARESR 22*     | 70.9          | 71 7            | 04.7<br>94.9  | 07.4<br>96.2 | 08.7            | 70.4<br>100.6 |
| CARESR 33      | 70.0<br>68.0  | 70.2            | 04.0          | 00.2<br>94 E | 90.7            | 100.0         |
| GARESR 34      | 06.9          | 70.3            | 04.3          | 04.3         | 95.4            | 96.4          |
|                |               |                 | Moist         | ure %        |                 |               |
|                |               | 2               |               | 5            | 15              |               |
| GORHAM"S CAVE* |               |                 |               |              |                 |               |
| GORESR43       | 35.5          | 44.5            | 35.7          | 44.7         | 36.2            | 45.4          |
| GORESR45       | 35.0          | 36.2            | 35.3          | 36.5         | 36.1            | 36.2          |
| GORESR49a      | 39.4          | 39.5            | 39.7          | 39.8         | 40.6            | 40.7          |
| VANGUARD CAVE* | :             |                 |               |              |                 |               |
| VANESR2f       | 58.3          | 66.8            | 58.5          | 67.2         | 59.3            | 68.2          |
| VANESR7        | 48.0          | 65.4            | 48.1          | 65.6         | 48.5            | 66.4          |
|                |               | Calcul          | ated using RO | SY 1.3       |                 |               |
| * I            | Based on U, T | h, K concentrat | ions in sedim | ents *       | *In-situ sample | s             |

Table XVII

# APPENDIX A

Operational protocols

#### PROTOCOL FOR FIELD GAMMA SPECTROMETER READINGS

(V. Volterra, McMaster Quaternary Geochronology Centre, 1997)

Field gamma spectrometer readings are taken using a Harwell Gamma Spectrometer operating in the γ scintillometer mode. The Apparatus consists of a portable multi-channel analyzer/counter with LDC display connected to a cylindrical probe. The latter is particularly fragile and must be handled with care.

1. With an appropriate coring tool bore into the sediments to produce a hole which will permit the full insertion of the spectrometer probe. It is advisable to collect some sediment sample from the hole for comparison purposes.

2. Connect the probe to the scanner. Turn spectrometer on and let stabilize for ten minutes. Check battery level. Check the spectrometer reading against the standard. Reading should be 13870.

3. Insert the probe entirely inside the bored hole into the sediments.

4. Select the Dis channel; this reads the total environmental radiation including the cosmic component. Set the time at one minute and start count. The final ten minute count should be of the same order of magnitude as this count. Record the one minute count.

5. With the Dis channel selected set the time at ten minutes and proceed with the count. Record the ten minutes count.

6. Select channel 3; this reads the cosmic radiation. Set the time at one minute and start count. The final ten minute count should be of the same order of magnitude as this count. Record the one minute count.

7. With channel 3 selected set the time at ten minutes and proceed with the count. Record the ten minutes count.

8. Confirm that the ten minute counts are of the same order of magnitude of the one minute counts.

9. Proceed to calculate the gamma radiation from the field readings using equation:

# {[a/10]-[b/10]-94}/1646

where: a = Total radiation = ten minute counts on the Dis channel

b = Cosmic radiation = ten minute counts on channel 3

.

#### PROTOCOL FOR ANNEALING CaF, PHOSPHOR

(V. Volterra, McMaster Quaternary Geochronology Centre, 1996 - Ref. Aitken, 1985)

1 - Secure a dry nitrogen cylinder with an appropriate bench clamp as close as possible to the annealing furnace. Install an appropriate pressure reducer/controller on the cylinder and connect flexible tubing to the controller outlet. Tubing length must be sufficient to permit reaching the furnace comfortably.

2 - Open the main cylinder valve and then the controller to confirm that the gas stream in gentle but positive.

3 - Place the powder to be annealed in a silica crucible.

4 - Purge the furnace through the top vent with the furnace door open.

5 - Place the crucible in the furnace while continuing to purge

6 - Continue to purge with the door open (1 minute) and then after closing the door slowly (2 minutes).

7 - Turn on the furnace controls and set temperature to 600 °C. Stop purging when the temperature reaches 50 °C. Turn off the nitrogen. Check that the furnace temperature is being controlled within  $\pm$  1 °C when it reaches the set temperature.

8 - After the furnace reaches the annealing temperature (approximately 5 minutes) maintain this temperature for 10 minutes.

9 - Turn on the nitrogen. Open the furnace and purge over the crucible. Remove the crucible with tongs always under a constant nitrogen stream and place on a metal plate on the bench top. Nitrogen must flow continuously over the crucible until the initial cooling is completed (2 minutes).

10 - Shut off the furnace and the nitrogen flow.

11 - Let the crucible and contents cool in air.

12 - After completing the procedure place the  $CaF_2$  powder in an appropriate labelled and stoppered container. The label must indicate the original material batch, the sieve fraction and the date of the annealing procedure.

#### PROTOCOL FOR MAKING CaF<sub>2</sub> DOSIMETERS

(V. Volterra, McMaster Quaternary Geochronology Centre, 1995)

Always wear eye protection when using soldering equipment. Ensure that all equipment is in proper working order and that the gas supply to the torch is open.

1 - Cut the 1/4 inch diameter 99.999% pure copper tubing into 45 mm lengths using a tubing cutter.

2 - Remove burrs at each end using an appropriate power driven pear-shaped burring tool

3 - Check for total burr removal under a microscope.

4 - Clean in 10% HCl for one hour and then rinse thoroughly in distilled water and air dry.

5 - Crimp one end of each tube.

6 - Place the "third hand" holder on the laboratory work bench over a carbon soldering block. The latter should be about 10 cm away from the edge of the working bench. Position the tube in the "third hand" holder, crimped end up, over the soldering block. Ensure that the tube is inclined away from you.

7 - Place sodium borate flux on the tube ensuring that the joint to be soldered is thoroughly covered. If the flux is not sufficiently liquid, add water.

8 - Cut the silver solder into 1 to 2 square mm pieces. Cut more than will probably be used immediately so that sufficient material is readily available. Place the cut solder on a carbon block.

9 - Place a few drops of flux over the cut solder.

10 - Light the soldering torch. Remember that the oxygen value is always the last to be opened and the first to be shut. Set the inner cone of the flame so that it is approximately 2.5 cm long.

11 - Heat the solder and pick up the solder bead with a carbon pencil. Slightly heating the pencil lead helps to pick up the bead.

12 - Heat all the copper tubing in the "third hand" starting from the bottom, until it becomes of dull red colour .

13 - Apply the solder to the crimped joint.

14 - Maintain the end of the tubing to be soldered to a cherry red colour ( approx. 800  $^{\circ}$ C) and melt the solder.

15 - Put the soldered piece down to cool.

16 - Repeat steps 6 to 15 for all the crimped tubes.

17 - Clean all tubes in 10% HCl.

18 - Rinse in distilled water and shake off excess water.

19 - File the soldered ends to clean the joint. Inspect the soldered joints under the microscope. If any joint is not completely sealed repeat steps 6 to 19.

20 - Allow the semi-finished units to dry thoroughly at a minimum of 60 °C. and at least overnight, using a drying cabinet. Place the units in a beaker together with a smaller beaker containing silica gel. Seal the larger beaker with "Saran" wrap and an elastic band prior to placing in the drying cabinet.

21 - Weigh sufficient CaF<sub>2</sub> aliquots of 100 mg each. Use the 90 to 125  $\mu$  sieved fraction.

22 - Fill each tube with an aliquot.

23 - Crimp close the tubing end still open.

24 - Repeat steps 6 to 15 for all units.

25 - Do not place in HCl at this stage. Instead repeat step 19. Make sure both ends are definitely sealed before proceeding.

26 - Reheat each unit to check that all joints are sealed.

27 - Repeat steps 17 to 18 for all the units.

28 - Obtain dosimeter numbers from the dosimeter log.

29 - Engrave the numbers sequentially on each capsule on opposite sides at each end.

30 - Write the dosimeter number again on each dosimeter in black indelible ink on the sides not engraved.

31 - Make notes in the dosimeter log: date the capsule were prepared, capsule number, contents (specifying the batch of phosphor used), location at which the capsule is to be emplaced. Eventually the date of emplacement must be also recorded in the dosimeter log.

### PROTOCOL FOR PREPARING PANASONIC DOSIMETERS FOR THE FIELD

(V. Volterra, McMaster Quaternary Geochronology Centre, 1995)

1 - Clean the copper capsules, ensuring that both ends and the end caps are free of debris.

- 2 Place one of the caps at one end of each capsule and seal with silicone. Let dry overnight.
- 3 Remove the cell frame from its plastic sheath.
- 4 Check that the frame number matches the sheath number.
- 5 Wrap the frame tightly with 'Saran' film.
- 6 Place the wrapped frame inside the copper capsule.

7 - Record the number of the frame and the number of the corresponding capsule in which it has been inserted in the dating notebook and the laboratory work book .

8 - Place the second cap at the open end of the copper capsule and seal with silicone. Let dry overnight.

Procedures for zeroing/reading the Panasonic dosimeters are described in Appendix B in "Protocol for reading and zeroing Panasonic dosimeters".

#### PROTOCOL FOR READING AND ZEROING PANASONIC DOSIMETERS

(V. Volterra, McMaster Quaternary Geochronology Centre, 1996)

1 - Turn on the Panasonic badge reader. Allow it to warm up and stabilize for at least 30 minutes.

2 - Turn on the printer. To do this press REQUEST, press 3, press ENTER, then press 1 (pressing 0 turns the printer off). Then in turn press ENTER, RETURN and RESET.

3 - Check the reader sensitivity. Turn the reader knob to SENSITIVITY. CAL displays on the display window. Then press READ. A sensitivity value will appear in the display. Repeat the procedure until the value is representative of the average reading.

4 - Turn the knob to ZERO.

5 - Place the dosimeter in the reader holder. The dosimeter can be inserted in one orientation only thus avoiding errors in reading. Proceed to read each of the three phosphor cells in the dosimeter by turning the knob progressively clockwise. Keep a separate written record of the readings for each dosimeter, even though each reading will be recorded on tape. Repeat the procedure for each unit.

6 - Repeat the sensitivity check every 50 dosimeters. The sensitivity should be above 0.9 at all times.

7 - Reading each unit releases the photons accumulated as the result of exposure to radiation and therefore by this action the dosimeter is automatically zeroed. Repeat the reading procedure for all the dosimeters to ensure that they have been properly zeroed.

8 - Turn the machine off.

9 - Some drift in cell efficiency has been found to occur after use. Accordingly, following the reading, the Panasonic units must be irradiated with a source of known strength and read again in order to check cell efficiency.

The amount of laboratory radiation required should yield readings similar to the average of the results for the units just read. To obtain the correct dose of radiation the current laboratory weak <sup>60</sup>Co source strength value is determined using the equation below and then the irradiation time required to yield a reading is calculated.

$$A = A_0^{(-\ln 2[t/T_{1/2}])}$$

where

 $A_o = \text{dose rate at a given } t_o$ t = the time elapsed since  $t_o$ 

 $T_{1/2}$  = half life of the <sup>60</sup>Co

or alternatively:

$$A = A_0^{(-\lambda t)}$$

where  $\lambda = \text{decay constant of}^{60}\text{Co}$ 

10 - Place the dosimeters in the appropriate rack in the irradiation room and proceed to irradiate them. Proper ID and radiation badges must be worn when using the source. When irradiation is completed, store the Panasonic dosimeters where they will not be subjected to further radiation.

11 - Wait for at least 24 hours after irradiation and then read the laboratory irradiated dosimeters repeating steps (1) to (8).

12 - The ratio of the new readings to the actual laboratory dose will yield the calculation factor to be used to normalize the results obtained in steps (1) to (7).

#### PROTOCOL FOR PREPARING TL CUPELS

(W. J. Rink; D. Richter, *Protocol for preparing TL cupels*, McMaster Quaternary Geochronology Centre, 1996; as edited by V. Volterra)

1 - From the moment the capsules are opened all the work must be carried out in subdued orange light as close as possible to the TL reader. Care must be taken to ensure that the phosphor does not contaminate anything in the laboratory. Spread clean paper over the working surface and label a clean Petri dish with the appropriate dosimeter number. Place the dish over the paper.

2 - Prepare 6 cupels for each capsule. Place all the cupels on the cupel holding basket and place the drilled spraying mask over them.

3 - Spray the cupels with 'Silko' silicone and remove the mask.

4 - Place the cupels on a glass tray next to the Petri dish.

5 - Holding the capsule at one end, tap it to ensure that all the phosphor falls to the bottom. Holding it vertically, open the capsule with a standard copper tubing cutter ensuring that no phosphor is lost.

6 - Place the piece of capsule containing the phosphor onto the labelled Petri dish.

7 - Using the calibrated measuring spoon collect the phosphor from the capsule and tip one measure into each cupel.

8 - Carefully tap the side of the cupel to spread the grains out and achieve an even layer.

9 - Inspect the phosphor to ensure it has not been contaminated with extraneous matter.

Note: when preparing cupels, never change the preparation technique whilst measuring. Any change may result in an increase in the overall procedure error.

# PROTOCOL FOR ESTABLISHING LABORATORY BETA DOSE FOR $CaF_2$ DOSIMETERS

(D. Richter, *Protocol for measuring CaF*<sub>2</sub> dosimeters, McMaster Quaternary Geochronology Centre, 1998; as modified by V. Volterra)

# A) Reader set up and parameters for dosimeters

1 - Samples must be heated to 400 °C. at a rate of 5 °C. per second.

2 - The weak beta source is used to obtain the proper irradiation. In the PARAMETER section select INTERNAL, TWO POSITIONS and BATCH IRRADIATION MODE.

3 - Use only a maximum of ten cupels per run, since there is no built-in shutter to the beta source.

4 - Use BG39 and the 7-59 filters

#### B) Laboratory beta dose estimation

Carry out a test run to estimate the beta dose required to match the natural signal level using one cupel from each capsule using the detailed instructions for running the apparatus as outlined in "Procedures for measuring TL phosphors" below.

1 - Get program file CAPS.PGM and then zero the program. Establish a new program file name (type "C" followed by the capsule number). Measure the natural and background radiation for each cupel (see "Run 1 - Procedures for measuring TL phosphors" below).

2 - When this is completed, place the source on the reader to irradiate the zeroed cupels from step (1) above (see "Run 2 - Procedures for measuring TL phosphors" below). If measuring a travel dosimeter the irradiation time should be set at 50 sec (for capsules which have been emplaced in the field irradiation time it should be 100-250 sec).

3 - Repeat step (1) above (see also "Run 3 - Procedures for measuring TL phosphors" below).

4 - Move the curves until the peaks obtained in steps (1) and (3) for each cupel coincide on the screen as detailed in the "Compare signals" section detailed below. Print out the integral around the peak, this occurs between 300 and 340 ℃.

5 - Calculate the actual irradiation time required to match the natural signal via the equa-

tion:

 $T = [peak 1/peak 3] \times t_{irr}$ (a)

where: peak 1 is the peak obtained in step (1) above

peak 3 is the peak obtained in step (3) above

 $t_{irr}$  is the irradiation time used in the step (2) above

6 - Re-irradiate each test cupel using the calculated time T above. Note that times will be different for each cupel and therefore this must be done individually based on the results of step (5) above.

7 - Confirm the irradiation length for each is correct by matching the peaks obtained from runs (1) and (6). If peaks still do not match repeat steps (5) to (7).

# C) Reading the dosimeters

1 - Place all the samples on the reader. Read all the five cupels remaining for each dosimeter applying the "Detailed procedures for measuring TL phosphors" detailed below.

2 - Measure both natural and background.

3 - Irradiate all the cupels using the irradiation times calculated in "B-5" above.

4 - Repeat step "1".

where:

The measured natural dose will be obtained from the equation:

Dn = [peak a/peak b] x [T] x [source dose rate]

peak a is the peak obtained in step (2) above

peak b is the peak obtained in step (4) above

T is the irradiation time as defined in equation (a), section (B) above.

Appropriate TL apparatus setting and operation are outlined in Appendix B as "Detailed procedures for measuring TL phosphors".

# DETAILED PROCEDURES FOR MEASURING TL PHOSPHORS

(D. Richter, *Procedures for measuring TL phosphors*, McMaster Quaternary Geochronology Centre. 1998; as edited by V. Volterra)

#### <u>Start-up</u>

1 - Turn on the computer.

2 - Turn off the main power to the reader.

3 - Remove the black and white wires at the top of the PM Tube and then unscrew carefully the tube from the reader base.

4 - Remove existing filters. Clean the filters removed and the filters to be installed with ethanol and dry.

5 - Place the 7-59 filter on top of the black 'O' ring in the filter housing. Next place the BG-39 filter and last add the white plastic 'O' ring.

6 - Screw the PM tube back onto the reader base and reconnect the wires.

7 - Remove the PM Tube together with the reader cover plate avoiding damage to the wires and place on a firm surface.

8 - Place the cupels to be read on the turntable starting at position '0'. Cupels must be handled with tweezers and must be placed at the edge of the turntable and so that they do not interfere with its operation.

9 - Replace the PM tube and reader cover plate.

<u>Run # 1</u>

Turn on the power to the reader apparatus. Proceed with Run # 1. This is the measurement of the natural dose absorbed by the dosimeter.

1 - In the computer select TAKE DATA

2 - Check the parameters for run 1, they should be:

Ramp rate =  $5 \, ^{\circ}C/sec;$ 

internal two-position [under "OTHER PARAMETERS"];

irradiator in place;

maximum temperature 400 °C;

limits for R.O.I. = 1;

directory name : DOSIMETER\

Press 'U'; this will update the parameters and will save them.

3 - Go to PROGRAM EDIT and select PROGRAM SELECT/GENERATE.

4 - Select GET PROGRAM FILE.

5 - Type "CAPS" (in capitals).

6 - At OPEN FOR EDIT select option YES.

7 - Delete ZERO PROGRAM.

8 - Select NEW DATA FILE.

9 - Choose CURRENT.

10 - Assign and type in a new file name ["C" followed by the capsule number].

11 - Hit RETURN, CONTINUE. This allows the preparation of a new spreadsheet.

12 - Select MODIFY PARAMETERS and check that AUTO BG has been selected.

13 - Choose SAME POSITION #. Notice that position "x" is already at the top of the spreadsheet.

14 - Select A: N [natural dose]. At the prompt [INFO O.K.] Select YES.

15 - At POSITION # CHANGE select CHANGE and type the cupel number.

16 - Repeat the procedure (21) to (23) to complete the spreadsheet.

17 - When the spreadsheet is complete select WRITE FILE to save the file. At the prompt SAVE AS CAPS select YES.

18 - Select CONTINUE. At the prompt SAVE TO FILE choose YES. The apparatus is now ready to proceed.

19 - Open the nitrogen bottle and ensure that the nitrogen flow is on by checking the flowmeter. Flow should be gentle but positive.

20 - Select GO. At the prompt START FROM THE BEGINNING choose YES. At the Prompt AUTO OPEN choose YES. The data acquisition screen will appear on the computer monitor.

21 - Turn on the vacuum.

22 - Select HV.

23 - Select V, this will open the reader to vacuum.

24 - Select P. This will operate the reader purge cycle. Pressing P again turns off the purge. Repeat this operation three times.

25 - Select V. This turns the vacuum off.

26 - Select G for the measurement to start.

27 - If the acquisition peak is too high [off-screen] reset the scale using the F10 button.

#### <u>Run # 2</u>

Proceed with Run # 2. This is the irradiation run for the cupels just read.

1 - In the main menu go to SELECT PARAMETERS. Change IRRADIATOR IN PLACE to BATCH IRRADIATION MODE. Select BETA=HIGH POSITION, and IRR TYPE = INTERNAL POSITION. Choose UPDATE and then exit. Choose UPDATE again and exit.

2 - Select PROGRAM EDIT.

3 - Select MODIFY PARMS and choose AUTO BG then EXIT.

4 - Select GET PROGRAM FILE.

5 - At the prompt, write DOSECAP. At the prompt OPEN FOR EDIT select YES.

6 - Select ZERO PROGRAM.

7 - Select NEW DATA FILE, then CURRENT then F(ILE), then write DOSECAP again.

8 - Select CONTINUE.

9 - Choose SAME POS#.

10 - Select E-BETA.

11 - Select ADD ITEM and the enter the time in seconds required to irradiate the cupels (see paragraph B-5 above). Note that the minimum irradiation time accepted by the apparatus is 10 seconds. After entering the time required click on it.

12 - Select YES.

13 - Select POSITION CHANGE and choose a cupel number.

14 - Repeat procedures (11) to (13) until the spread sheet is complete.

15 - When the spreadsheet has been completed select WRITE FILE and the CONTINUE.

16 - At the prompt SAVE EDITS TO FILE select FILE.

17 - At the prompt SAVE AS DOSECAP.PRG select YES.

18 - Remove the Beta irradiation source from storage and place it onto the shutter of the TL Reader. Make sure the cover is opened with the source facing away from the operator. Keep the free hand away from the front of the source holder.

19 - Select G for go/resume and click on the space bar. On the prompt PLACE ON IRRADIATOR the apparatus will start beeping, click on the space bar to indicate that the irradiating source is in place.

20 - Select C to continue and then G to start the irradiation.

21 - Once irradiation has been completed click on EXIT. Remove the Beta source ensuring that it points away from the operator at all times. Secure the source cover and store.

#### <u>Run # 3</u>

Proceed with Run # 3. This will measure the laboratory dose signal.

1 - Select CHANGE PARAMETERS, then IRRADIATOR IN PLACE, then BETA: EXTERNAL and then UPDATE

2 - Select program EDIT

3 - Select PROGRAM FILE

4 - Type in CAPS. The first file which was set up for Run #1 should appear. Select LEAVE AS IS to add to this file the Beta dose glow curve data.

5 - Select WRITE FILE. At the prompt SAVE AS CAPS? select YES.

6 - Select CONTINUE, then SAVE TO FILE. At the prompt SAVE AS CAPS select YES.

7 - Repeat sequence (19) to (27) for Run #1.

#### Compare signals

All data acquisition is now completed. Turn off the vacuum and the nitrogen supply, then proceed to compare the signals which were obtained for the natural and the laboratory irradiation doses.
1 - From the main computer menu select BREAK TO COMPUTE.

2 - Check that the file name which is now displayed is the correct one. Click CONTINUE.

3 - Click on the space bar to indicate acceptance of the data displayed on the screen.

4 - Select LOOK.

5 - Select SUBTRACTED.

6 - Highlight the two runs to be compared then select CONTINUE.

7 - The curves may not be properly aligned. To bring them into alignment click on TEMPSHIFT and then type in the degrees of shift necessary [+ or -].

8 - If more peaks are to be compared select ANOTHER. Repeat until all peaks have been selected and displayed then select EXIT.

9 - Select INTEGRALS/UTILITIES.

10 - If the peaks showed a normal graphic display choose INTEGRATE; if peaks are scrambled select RAW DATA and enter the run # and its background # for the messy peaks.

11 - For the remaining peaks select SUBTRACTED, then enter the natural peak # and the corresponding Beta dose run #.

12 - Select EXIT and continue to choose EXIT until the main menu on the computer is reached.

13 - Ensure that all results are recorded in a laboratory workbook.

14 - Copy all results to disk to ensure data are not lost accidentally.

### PROTOCOL FOR CLEANING TL CUPELS

(D. Richter, *Protocol for cleaning TL cupels*, McMaster Quaternary Geochronology Centre, 1998; as edited by V. Volterra)

1 - The spraying mask and the holding basket must be cleaned with soap and hot water immediately after use. Dry both units and store. Soak the cupels overnight in MEK in a covered beaker.

2 - Place the beaker containing the cupels and the solvent inside an ultrasonic bath.

3 - Decant the MEK into a waste container. Most of the phosphor grains will be removed with the waste MEK.

4 - Remove the cupels from the beaker and place into a clean beaker. Add more MEK and repeat steps (2) and (3).

5 - Rinse the cupels in the beaker with acetone. Place the beaker with the clean cupels in a drying cabinet overnight

6 - Wearing gloves examine the cupels under a microscope to ensure that all phosphor grains have been removed. Discard any cupels that show cracks or large imperfections. If material still remains inside the cupels:

a) Add to the beaker with the cupels a solution of 40 ml/l of "Deacon";

b) place into the ultrasonic bath;

c) rinse the cupels 4/5 times with distilled water;

d) rinse with acetone;

e) place in a drying cabinet overnight.

7 - Wearing gloves clean the cupels using acetone and a 'Q-tip'. When they are all clean give each cupel a final rinse with acetone and place cupels into a clean beaker. Place the beaker into a drying oven until the acetone evaporates.

8 - Store the dry cupels inside a covered glass container to minimize the risk of contamination.

199

# RECONCILING MEASURED DOSIMETER DOSES AND DOSES CALCULATED FROM SEDIMENTS

(V. Volterra, McMaster Quaternary Geochronology Centre, 1997)

## Travel dose

Dosimeters are subject and respond to radiation under normal conditions. Therefore they start accumulating doses even before they are placed at the site. This is related to the history of the dosimeters and is affected by such exposure to radiation as may occur during travel to and from the laboratory as the result of high altitude flying, security x-ray scanning, etc. The travel dose must be measured since it may account for a significant portion of the total dose absorbed by the dating dosimeters.

Three units are utilized to measure the dose which has been absorbed by dosimeters during their travels to and from site.

- Unit a: is zeroed at the laboratory. It travels outward with the bundle of site dosimeters and is returned to the laboratory after emplacement of the individual site dosimeters. It will record the radiation absorbed during the two-way trip.
- Unit b: is zeroed at site at the time of the emplacement of the site units. It returns to the laboratory and records the amount of return radiation to which it and unit 'a' have been exposed.
- Unit c: is zeroed at site when the dosimeters are retrieved and returns to the laboratory with the bundle. It records the amount of radiation to which it and the bundle have been exposed during the return trip as well as any subsequent radiation during storage and prior to processing in the laboratory.

The use of three travel units has been the traditional approach to site dosimetry. This is due to the fact that often it is impractical to heat the capsules at the actual excavation, and zeroing is carried out offsite. However units "a" and "b" are not necessary if all field dosimeters can be zeroed in the field before being emplaced, thus simplifying the procedure. When three units are used:

a - b = net radiation dose during travel to site

c = net radiation dose after retrieval from site (travel + storage)

and the total travel + storage dose is:

$$D_{TRAV} = a - b + c$$

### **Fading** correction

During storage some of the dose absorbed fades and this must be corrected for. The fading correction is calculated as follows:

$$D_{\text{TRAV CORR}} = (\mathbf{a} \cdot \mathbf{b}) \mathbf{f}^{n} + \mathbf{c} \mathbf{x} \mathbf{f}^{n}$$

where: f = yearly fading rate. For CaSO4 units this value is 1.05/year; for the CaF2 units this is 1.0/year (i.e. no fading occurs).

n = the actual storage time( which is different for a and b than it is for c).

Thus for the CaSO4 units:

 $D_{\text{TRAV CORR}} = (a - b) \ 1.05^n + c \ge 1.05^n$ 

and for the CaF2 units:

$$D_{\text{TRAV CORR}} = a - b + c$$

A similar fading correction must be applied to the Panasonic units. Their fading rate is 1.06/year. Accordingly for the Panasonics:

$$D_{APP CORR} = D_{APP} \times 1.05^{n}$$

where:  $D_{APP}$  = the total dose measured from the site dosimeter.

#### <u>*y* attenuation correction</u>

Phosphor and Panasonic dosimeters are encased in Cu containers made of electrolytically pure copper. This material attenuates the radiation emanating from the soil. Accordingly the actual dose rate which would impact on buried teeth at the same location would be somewhat higher than that measured by the dosimeters. This effect must be calculated using the guidelines outlined by Linde (1966).

Attenuation is characterized by the equation:

 $I = I_{O}e^{\mu\rho d}$ 

where:  $I_{O} = \gamma$  radiation received by the external surface of the container I = the actual radiation received by the phosphor =  $D_{APP \ CORR}$  for the Panasonics and  $D_{TRAV \ CORR}$  for the CaSO4/CaF2 units  $\mu = 5.72 \times 10^{-2} \ cm^{2}/g$  at  $\gamma$  radiation energy of 1.0 MeV for electrolytic copper  $\rho =$  density; 8.94 g/cm<sup>3</sup> for copper d = thickness of the Cu wall in cm: for the Panasonic units this is 0.158 mm and for the CaSO<sub>4</sub>/CaF<sub>2</sub> units it is 00.8 mm

The attenuated  $\gamma$  radiation absorbed by the phosphors is therefore:

for the Panasonic units  $D_{APP CORR} = I = I_0 e^{-(5.72x8.94x0.158)/100} = I_0 e^{-8.0796/100}$ and for the CaSO<sub>4</sub>/CaF<sub>2</sub> units  $D_{TRAV CORR} = I = I_0 e^{-(5.72x8.94x0.08)/100} = I_0 e^{-4.0909/100}$ 

The two equations above will allow the calculation of the presumed  $\gamma$  radiation dose absorbed by the phosphors, starting from the radiation calculated from soil composition. Conversely the actual value of the gross radiation due to the soil immediately surrounding the Cu container will be:

| for the Panasonic units  | $I_{O PAN} = D_{APP CORR} e^{(5.72x8.94x0.158)/100} =$ | $D_{APPCORR}e^{8.0796/100}$             |
|--------------------------|--|---|
| for the CaSO₄/CaF₂ units | $I_{O PHOS} = D_{TRAV CORR} e^{(5.72x8.94x0.08)/100}$  | $= D_{\text{TRAV CORR}} e^{4.0909/100}$ |

The latter two equations allow the calculation of the presumed  $\gamma$  dose absorbed by a buried object before any attenuation effect. This value should be equivalent to D<sub>N</sub> ( see page 204).

#### Cosmic radiation correction

Cosmic radiation must be added to that emanating from the soil to arrive at the total radiation which would have bombarded the dosimeters. Cosmic radiation is attenuated by the overburden above the burial location. This effect is calculated in accordance with Prescott and Hutton (1988). Burial attenuation is:

$$A = 0.21e^{(-0.07 + 0.0005x)x}$$

where: x =the effect of burial mass in hg/cm<sup>2</sup>.

For example in a limestone cave where the burial depth is a meters and the roof cover is b meters:

$$x = 2.6 b + 2 a$$

since the limestone density is 2.6 g/cm<sup>3</sup> and the soil density is assumed at 2.0 g/cm<sup>3</sup>.

Standard surface cosmic radiation at sea level is 22.2 mr/a (Prescott & Stephan, 1982 - TSL II-1: 22). Thus the actual attenuated dose due to cosmic radiation and affecting the dosimeter would be:

$$C_{\rm D} = 22.2 \text{ x A}$$

Note that beyond values of x of 70 hg/cm<sup>2</sup> the equation above yields nonsensical results and a different calculation must be made. Attenuation at 50 hg/cm<sup>2</sup> reduces the cosmic radiation to 2.2 mr/a (Prescott & Hutton, 1988: 247). Cosmic radiation attenuation between 50 and 180 hg/cm<sup>2</sup> is linear and at 180 hg/cm<sup>2</sup> it is down to 0.2 mr/a. Therefore, the attenuation rate between these two values is:

$$(2.2 - 0.2)/9180 - 50) = 0.0154 \text{ mr/hg/cm}^2$$

by interpolation. Thus at values above 50 hg/cm<sup>2</sup> the amount of the effective cosmic radiation is calculated as:

$$C_{\rm p} = 2.2 - [(x - 50) \times 0.0154]$$

where: x is the value calculated above.

The total natural dose which reaches the dosimeters is therefore:

$$D_{N} = D_{A} + C_{D}$$

This value should be equivalent to  $I_{\mbox{\tiny o}}$  above (see page 202).

## Comparison with dose resulting from soil elemental composition

The soil dose is directly related to its U, Th and K content and the moisture in the soil. Given the INAA results for the sediment sample, the total dose is calculated following Nambi and Aitken (1986) as:

 $D_s = U \ge 0.1136 + Th \ge 0.0521 + K \ge 0.2434$  (dry bases)

where:

U is the uranium concentration in ppm

Th is the Thorium concentration in ppm

K is the Potassium concentration in %.

The attenuation due to moisture is then calculated per Nambi and Aitken (1986) as:

 $D_A = D_S / (1 + 0.912 \text{ x m})$ 

where:

m = measured soil moisture in %/100.

# COLLECTION OF MOISTURE SAMPLES AND MOISTURE MEASUREMENT (V. Volterra, McMaster Quaternary Geochronology Centre, 1996)

1 - Approximately 10 g of sediment should be collected adjacent to the find. The material should be as representative as possible of the burial medium. This is sometimes difficult to achieve when significant amounts of eboulis is present.

2 - The sample should be stored in a rigid plastic container sealed tightly and labelled appropriately. Discarded cylindrical photographic film canisters lend themselves admirably to this use. After sample collection the lid must be sealed with duct tape.

3 - In the laboratory the duct tape is removed and each full container is weighed.

4 - The sample is removed from the container, placed in the aluminium pan and dried for 24 hours in an oven at 100  $^{\circ}$ C in the presence of silica gel. The container and its lid are air dried.

5 - After drying, container, lid and sample [in its aluminum pan] are weighed again separately. The sample is then removed and weighed . Containers and lids are weighed after drying to account for any moisture which might have been retained by them.

6 - The moisture content of the sediment on a dry basis is calculated from the equation:

$$M = (Ww - Wc) / (Ws \times 100)$$

where: M = moisture in %

Ww = original weight of full container before dryingWc = weight of empty, dry containerWs = dry weight of the sample, net of aluminum pan

### TEETH CUTTING

(H. P. Schwarcz and W. J. Rink - *Teeth cutting* - McMaster Quaternary Geochronology Centre, 1995; as edited by V. Volterra)

Throughout the preparation procedures eye protection and a surgical mask must be worn. Work is carried out in an enclosed area under a very slight vacuum to ensure that dust is not dispersed.

1 - Using a diamond cutting blade mounted on a dentist drill, the 2 mm closest to the occlusal surface are removed first. This portion of the tooth is often weathered and contaminated. In the case of the smaller teeth it might prove necessary to include a large portion of this section to ensure that sufficient sample is obtained. In this case the occlusal surface is partially ground off before cutting.

2 - The tooth surface is then cut following the pencilled lines. A vertical cut is also made behind the enamel to ensure that sufficient dentine is removed. The cutter must be held carefully since vibration in the blade may result in shattering of the sample.

3 - The dentine to be collected is that found within 2 mm from the inner surface of the enamel. After cutting the sample the dentine thickness is measured. The amount in excess of 2 mm is removed and stored separately in appropriately tagged vials. If the enamel becomes separated from the dentine during cutting sufficient amount of the latter must be harvested separately.

4 - Thickness, colour, consistency of the dentine should be recorded in the laboratory work book and on the tooth data sheet.

#### ENAMEL, DENTINE AND CEMENTUM PREPARATION

(H. P. Schwarcz, W. J. Rink, J. Johnson - *Enamel, dentine and cementum preparation* - McMaster Quaternary Geochronology Centre, 1995; as edited by V. Volterra)

1 - The first process involves separating the dentine from the enamel. Care must be taken to remove all of the dentine. This tissue contains approximately 20% organic fraction, mainly collagen in 80% hydroxyapatite. By contrast enamel consists of 99.5% hydroxyapatite (Haskell et al, 1995). The ESR signal in the former appears to be generally less stable than in the enamel. An admixture of the two tissues would yield lower estimates of equivalent doses and therefore would result in age underestimation (Haskell et al, 1995; Rink et al, 1996b).

During dentine removal, the integrity of the external cementum layer must be carefully maintained. Should some cementum become separated at this stage it must be handled carefully and stored separately to allow for measurement of its thickness.

The dentine is removed either using a surgical blade or, more likely, by grinding it away. A metal burr mounted on a dentist drill is used for this operation. Drill speed is kept relatively low to prevent shattering enamel and cementum. The operation takes place over weigh paper and the dentine being removed is collected and stored in appropriately labelled vials.

2 - When all the dentine appears to have been removed the enamel is examined under a microscope to determine areas still to be cleaned and any dark lines showing contamination or dentine inclusions. It may be necessary to cut along these lines to remove the contamination. Equid teeth are particularly bothersome in this respect. At this stage any dentine remaining is best removed using a surgical blade since the burr may not be able to reach interstices.

3 - After removal of all the dentine the enamel edges and any protuberances should be lightly ground prior to measurement.

4 - Using an electronic micrometer the thickness of each sample is measured and results are recorded on tape. This measurement includes both enamel and cementum. At least 100 measurements should be taken and averaged. Should the sample have broken into several pieces as is often the case a minimum of 20 measurements per piece should be taken and all readings averaged. 207

In some instances the external surface of the enamel is not covered with cementum and the next step is skipped.

5 - Cementum must be now removed from the enamel surface. This is achieved by means of a metal burr and surgical blade as for the dentine. Care must be taken to avoid splintering of the enamel which would make further processing very difficult. Equid teeth are particularly vulnerable at this stage

6 - When all the cementum appears to have been removed the enamel is examined under a microscope checking for areas still to be cleaned. As was done following the removal of all the dentine the enamel edges and any protuberances should be lightly ground prior to measurements.

7 - Using an electronic micrometer the thickness of the sample is measured again and results are recorded on tape. This measurement represents the net thickness of the enamel. Again at least 100 measurements should be taken and averaged. Should the sample have broken into several pieces as is often the case a minimum of 20 measurements per piece should be taken and all readings averaged.

The thickness of the cementum is determined by difference between the two measurements. Enamel and cementum thickness are recorded both in the laboratory work book and on the tooth data sheet.

8 - The outer surface of the enamel is then ground to remove a 40  $\mu$  layer using a diamond burr, since this material is harder than dentine and cementum. Care must be taken to ensure that a uniform stratum is removed. The ground enamel is measured again as suggested above and the measurement is recorded. The thickness of the stratum removed is determined by difference between this measurement and that of the net enamel. If less than 40  $\mu$  have been removed the procedure is repeated. The procedure is also repeated to remove 40  $\mu$  from the enamel surface which had been in contact with the dentine.

9 - The thickness of the strata removed from each side is recorded in the laboratory work book and on the tooth data sheet.

10 - The final enamel samples are photographed again. The set up will include labels indicating the sample number and the archaeological site of provenance to allow the photographs to be clearly identified for future reference. Photographs are also attached to the tooth sample data sheet.

#### CRUSHING DENTINE AND CEMENTUM

(H. P. Schwarcz, W. J. Rink - *Crushing dentine and cementum* - McMaster Quaternary Geochronology Centre, 1995; as edited by V. Volterra)

Dentines and cementa are processed in the same fashion but separately to avoid any contamination.

1 - The dentine and cementum collected should pass through a 250  $\mu$  sieve.

2 - Oversize material is then crushed in an agate mortar until it all passes the mesh. Ceramic mortars and pestles are to be avoided since their glazes are softer than tooth material and they contain amounts of potassium which would contaminate the samples. Gouges in the glaze would expose the ceramic matrix which would add to the contamination since it normally contains uranium, sodium and potassium. Gouges would also retain some portions of any sample resulting in cross-contamination.

3 - The sieve must be cleaned carefully with acetone and then with high pressure air when changing samples to avoid contamination. After each use the agate mortar and pestle are wiped with a paper towel and then washed with soap and water and then with dilute HCl followed by a further distilled water wash to prevent contamination between samples. Pestle and mortar are then air dried.

Dentines and cementa are now ready for determination of their uranium, thorium and potassium concentrations by INAA.

209

### CRUSHING OF ENAMEL

(J. Johnson - *Crushing enamel* - McMaster Quaternary Geochronology Centre, 1995: as edited by
V. Volterra)

In any crystal structure except the cubic, there is anisotropy. This phenomenon refers to the internal charge fields being different along the principal axes of the crystal because of atomic orientation. Thus if large pieces of teeth were used for ESR analysis the intensity of the response to any radiation level would be different depending on the orientation of the sample in the microwave cavity. To overcome this problem the samples are reduced to powder sufficiently fine as to produce a truly random combined crystal orientation.

While dentine and cementum can be crushed using a mechanical grinder enamel must be processed in a hand held agate mortar and pestle.

1 - The agate mortar should be placed inside a plastic bag with a hole cut for the pestle. This permits the collection of any small pieces which might fly away during the crushing. The enamel is then placed in the mortar and crushed gently by pressing with the pestle and rocking the pestle from side to side. A circular grinding motion must not be used to avoid friction heat being generated.

2 - The operation should be stopped frequently and the sample should be sieved using a 150  $\mu$  screen. The operation is repeated until it all passes the mesh (6 - 8 cycles are normal). The plastic bag should be checked for bits of enamel which might have escaped so that no sample is lost and the bag should be changed for each new sample.

3 - Screen, pestle and mortar should be cleaned using the same procedures suggested above for dentine and cementum.

4 - The prepared enamel is then weighed and separated into 10 aliquots of equal size. The difference in weight of each aliquot should not exceed  $\pm 0.1$  mg. In addition, crushed enamel aliquots for INAA determination of uranium content should also be collected from at least one tooth per archaeological layer. Each aliquot is placed in a small stoppered glass vial.

5 - Vials are marked with indelible ink to show sample number and aliquot size. After the irradiation schedule has been selected, each vial is marked to indicate the appropriate dose rate which has been received by the aliquot contained therein.

6 - The aliquots should be mounted on holding boards which facilitate their handling and avoid accidental intermixing of aliquot vials.

Once all the samples have been prepared the two chosen for UGC analysis are processed through the ESR spectrometer using the procedures detailed in this Appendix as "Protocol for UGC analysis. In addition to these, a sample whose natural dose is known is also processed for comparison purposes.

•

## PROTOCOL FOR UGC ANALYSIS

(W. J. Rink - *UGC analysis* - McMaster Quaternary Geochronology Centre, 1993; as edited by V. Volterra)

UGC analyses are carried out in accordance with the "Protocol for the operation of the ESR spectrometer" included in this Appendix. Departures from the protocol are outlined below.

1 - The following settings should be selected for the operation of the ESR spectrometer:

| Microwave Power:   | 20 dB               |  |  |
|--|---------------------|--|--|
| Mod. Amplitude:  | 5 x 10 <sup>1</sup> |  |  |
| Time Constant:   | 200 msec            |  |  |
| Sweep time:  | 200 sec             |  |  |
| Field Centre:  | 3480 gauss          |  |  |
| Scan range:  | 50 gauss            |  |  |
| Receiver frequency   | 9.75 GHz            |  |  |
| Set the gain so as to obtain a good readable signal on the screen. |                     |  |  |

2 - The chosen aliquot is placed into the ESR tube labelled "UGC" and inserted into the spectrometer cavity. After tuning, the signal height is recorded.

3 - The signal size is corrected by normalizing to a standard mass of 50 mg and a standard gain of 5 x  $10^4$  (50,000) using the following formula:

In = Io x (50/Wa) x (5 x  $10^{4}/Ga$ )

where: In = normalized signal

Io = actual signal measured

Wa = actual weight of the aliquot

Ga = actual gain

4 - Using the UGC standard curve, the apparent equivalent dose in krads for all the aliquots run which corresponds to the normalized signal is read off. As a check it is necessary to confirm that the result for the "known" aliquot matches the reading obtained previously for it.

5 - The procedure is repeated using an aliquot from a sample of known equivalent dose to confirm that the apparatus is in proper working order.

The dose determined by this analysis is utilized to select the sample irradiation schedule. The maximum irradiation to be used should be approximately ten times the value of the UGC results.

The lowest irradiation level should not be below the value "UGC dose/20". In practice ten steps are chosen, the lowest being equivalent to the value of the UGC result. The intermediate irradiation levels should increase from the lowest to the highest in exponential steps.

Once these are chosen, each vial containing the aliquots should be marked with indelibly ink to indicate which level of irradiation it received.

## PROTOCOL FOR THE OPERATION OF THE ESR SPECTROMETER

(V. Volterra, McMaster Quaternary Geochronology Centre, 1997)

1 - The cooling water, both supply and return valves, must be turned on to the open position.

2 - The spectrometer can then be turned on. A period of 30 minutes should be allowed for the apparatus to stabilize before starting analyses.

3 - Turn on the computer and select the "Acquisition Program".

4 - The "standard" run is the first and last step in the analysis. On the pull down menu select MW and confirm that the system is on stand-by.

5 - Select the Mn test tube from the tube set and insert it in the holder above the spectrometer cavity. The tube has a collar which positions it correctly in the centre of the cavity.

6 - On the pull down menu select OPEN FILE, then DATES, GEOLOGY, STANDARD. This will call up the spectrum for the standard. Select DUPLICATE, this will produce a copy of the standard spectrum on the computer screen and return the original to file; testing can then proceed without altering the original.

7 - On the pull down menu select EXPERIMENT PARAMETERS and check that the correct data are entered. They should be set as follows:

| Frequency:            | 9.450405 GHz         |
|-----------------------|----------------------|
| Attenuation:          | 20 dB                |
| Power:                | 2.007 MW             |
| Q value:              | 3000                 |
| Centre field:         | 3398.00 G            |
| Sweep width:          | 100.00 G             |
| Static field:         | 3488.968 G           |
| Step:                 | 1 dB                 |
| Receiver gain:        | 1.59x10 <sup>5</sup> |
| Modulation frequency: | 100.00 KHz           |

| Modulation amplitude: | 1.30 G      |
|-----------------------|-------------|
| Offset:               | 1.00%       |
| Time constant:        | 163.84 msec |
| Conversion time:      | 81.9 msec   |
| Sweep time:           | 83.89 secs  |
| Harmonic:             | 1           |
| Number of scans:      | 1           |

8 - Select again MW and set the attenuation at 20 Db.

9 - Select AUTOTUNE. When the spectrometer has stabilized click on FINE TUNE. When the iris has stabilized return to the spectrum.

10 - Select COMMENTS from the pull down menu. Record the operator's name, date and time and label the run as "run standard". Return to the spectrum.

11 - Select RUN from the pull down menu. The spectrometer will scan the field and a new spectrum will appear.

12 - When each run is complete, measure the (+) and (-) peaks by placing the arrow cursor at the top and the bottom of the spectrum and record them in the laboratory work book. When the top of the (+) peak of the spectrum is touched with the cursor, the peak value is displayed at the bottom right hand side of the screen. This is repeated for the (-) peak. The sum of the + and - values is the total intensity of the standard.

13 - From the pull down menu select SAVE. The spectrum will be saved on the computer databank. This spectrum will be used at the end of the total sample run when the standard total intensity must be checked again to confirm that the spectrometer has not drifted during operation.

14 - Select again MW and then STANDBY.

15 - The standard tube can now be removed from the cavity.

16 - The runs to determine the signal intensity of the individual aliquots of different irradiation levels can now begin. For each tooth sample the run is started with the aliquot which has been subjected to the highest irradiation dose. Then the aliquots of the same tooth sample are processed in descending order of laboratory irradiation until the aliquot with zero laboratory dose (i.e. with only the natural dose) has been analyzed. After all the aliquots for one tooth samples have been run the aliquots of the next tooth sample can be processed.

A "Spectrometer Results Table" should be set up in the laboratory work book on which to collect the results of the analyses. The columns should be headed : Sample number - Radiation level - Aliquot weight - Receiver gain - (+) intensity - (-) intensity - Total intensity - File name . Ten rows are required for each sample to record the information for each of the ten aliquots. Sample number, radiation level and weight of every aliquot should be recorded before starting the runs.

17 - Select the appropriate sample holding tube from the tube set, insert and secure it in the holder above the spectrometer cavity. The holding tube has a collar which positions it correctly in the centre of the cavity.

18 - On the pull down menu select OPEN FILE, DATES, GEOLOGY. The file of any suitable tooth sample aliquot run previously can now be chosen. Alternatively if previous runs have been recorded on a floppy disk the spectrum can be called up directly from the disk. When the spectrum appears on the screen, select DUPLICATE to produce a copy of it on the computer screen and return the original to file; the analysis can now proceed without altering the original spectrum.

19 - On the pull down menu click on EXPERIMENT PARAMETERS. They should be set as follows:

| Frequency:            | 9.448172 GHz   |
|-----------------------|--|
| Attenuation:          | 20 dB  |
| Power:                | 2.007 MW   |
| Q value:              | 3500   |
| Centre field:         | 3361.28 G  |
| Sweep width:          | 100.00 G   |
| Static field:         | 3488.968 G   |
| Step:                 | 1 dB   |
| Receiver gain:        | (to be selected for each tooth sample run. See below.) |
| Modulation frequency: | 100.00 KHz   |

| Modulation amplitude: | 5.09 G     |
|-----------------------|------------|
| Modulation phase      | 0 deg.     |
| Offset:               | 0%         |
| Time constant:        | 10.24 msec |
| Conversion time:      | 20.48 msec |
| Sweep time:           | 20.97 secs |
| Harmonic:             | 1          |
| Resolution in x       | 1024       |
| Number of scans:      | 3          |

20 - Select MW from the pull down menu and repeat step (9).

21 - Using a glass funnel the aliquot is transferred to the appropriate small quartz vial. The vial must be tapped gently at least 20 times to compact the aliquot. The same number of taps must be used every time to insure consistency of sample compacting.

22 - Lower carefully the small vial into the quartz holding tube already positioned in the cavity. Ensure that the vial has reached the bottom of the holding tube.

23 - Select MW again. Ensure that the attenuation is set at 20 Db. Select TUNE. When the spectrometer has stabilized, select FINE TUNE. When the iris has stabilized you can return to the spectrum.

24 - Select COMMENTS from the pull down menu. Record the operator's name, date, time and label the run with the sample number, the weight and the irradiation level of the aliquot and then return to the spectrum.

25 - Select RUN on the pull down menu. The spectrometer will scan the field three times and a new spectrum will appear. If the spectrum peak to peak amplitude exceeds the height of the screen window the run should be stopped and EXPERIMENT PARAMETERS should be selected, the receiver gain should be increased and the aliquot rerun. The receiver gain is adjusted until the spectrum appearing on the screen is adequate. If at first the spectrum appears too small then the receiver gain is reduced until the spectrum is adequate.

26 - Measure (+ ) peak of the spectrum by touching it with the cursor. Record the value on the "Spectrometer Results Table" and repeat the procedure for the (- ) peak.

27 - The (+) and (-) intensities are added to obtain the Total intensity. These values must be recorded for every aliquot together with the receiver gain value used as well as the file name under which the spectrum will be saved for ease of retrieval.

28 - From the pull down menu select SAVE AS, name the file at the prompt and then click OK.

29 - From the pull down menu select PRINT to obtain a hard copy of the spectrum. The copy should be stored together with the tooth data sheet.

30 - From the pull down menu select DUPLICATE, this will produce a copy of the above spectrum on the computer screen; testing can now proceed without altering the original.

31 - Select MW and then TUNE. The attenuation is changed to 40 Db.

32 - The small vial can now be removed and the aliquot returned to its stoppered container. The cork stopper should be marked to indicate that the aliquot has been analyzed. Prior to loading the next aliquot in the small vial both the funnel and the vial must be purged with dry nitrogen to remove any traces of the previous sample and avoid contamination.

33 - Select the next aliquot to be analysed and repeat steps 21 to 32 until all aliquots have been processed.

34 - When all aliquots have been processed select MW and then STANDBY.

35 - Repeat steps 4 and 5.

36 - From the pull down menu select OPEN FILE and then RUN STANDARD.

37 - Repeat steps 8 and 9 followed by steps 11 and 12.

38 - Measure the Total Intensity of the standard and confirm it has not changed during the analyses.

39 - Repeat steps 14 and 15.

40 - The acquisition program can now be closed.

41 - Shut down the spectrometer.

42 - Shut off the cooling water supply and return valves.

# APPENDIX B

# IRRADIATION PROCEDURES

.

### GAMMA IRRADIATION PROTOCOL - START UP PROCEDURES

(J. Johnson - *Gamma irradiation protocol, start-up procedures* - McMaster Quaternary Geochronology Centre, 1995; as edited by V. Volterra)

# **Precautions**

a - A portable irradiation monitor must be available and fully operational before approaching the access door to the hot cell room. Check its calibration. Turn the operating dial to "test " and verify that the meter is operational. When the irradiation procedure has been completed the meter must be returned to its proper storage place and must be plugged into a power source to ensure that the batteries are continuously charged.

b - The hot cell when not in use is stored in a safe position and the power supply to its operating apparatus is turned off and padlocked. The key to this lock is obtained from the reactor operating personnel who are its custodian when no irradiation is in progress. To ensure safety during irradiation the key must be kept by the person carrying out the irradiation and pocketed (even when leaving the reactor building), until the irradiation has been completed. Before leaving the window area for any reason the power supply must be padlocked.

c - When starting irradiation the window side of the hot cell area should always be approached first to check the status of the hot cell and confirm that it is all the way down in its storage well. The lights in the hot cell room should be turned on. A white tape wrapped around the wire from which the hot cell is suspended should be showing just above the storage well opening. The power to the hot cell handling system must be found turned off. Should the hot cell not be in the full down position or not locked report to the reactor operating staff. To proceed with the irradiation it is necessary to obtain a calculator and a stopwatch, as well as writing implements, the irradiation work sheets and the hot cell dosimeter (Figure 53). All the samples should also be at hand. The first order of procedure is to measure the current cell dose rate and to determine the calibration ratios as detailed in this Appendix as "Protocol for obtain-ing the average dose rate and calculating the correction factor".

# PROTOCOL FOR OBTAINING THE AVERAGE DOSERATE AND CALCULATING THE CORRECTION FACTOR

( J. Johnson, Average doserate and calibration ratio calculations, McMaster Quaternary Geochronology Centre, 1997; as edited by V. Volterra)

1 - Confirm that the radiation monitor is on, in Scale 11 and in audible mode. The monitor must be taken into the area of the hot cell door to monitor the cracks at left and right of door.

2 - The monitor must be left on and in place at about 30 cm from the hot cell door, with a dated note saying : "In use - do not remove". The monitor should be propped up so that the motion of its needle can be clearly seen.

3 - Unlock the hot cell door and open it. If the monitor alarm sounds or if its needle indicating presence of radiation is seen to move, the door should be let shut immediately and it should be locked. The operator must return to the hot cell window and re-check the position of the source. The operator must also report the incident immediately to the reactor supervisor whether the hot cell is up or down.

4 - If the monitor does not register any activity while the door is being opened, the door can be secured in the open position using the rope provided for this purpose.

5 - The monitor must be picked up and held in front of the body when the operator enters the hot cell room slowly, to ensure the area is safe. If the monitor register radiation the alarm procedure outlined in step 3 must be followed.

6 - If the area is found safe, the operation can proceed.

7 - The positions of the cell, sample and dosimeter racks can now be set as required for the irradiation. All the racks must be properly secured in place.

8 - The mirror is placed in position so as to permit viewing of the back of the cell when it is being placed into its holding rack.

9 - No obstructions must be left between cell and sample racks.

10 - The door must be closed reasonably slowly to avoid damaging the lock. The door is locked, the radiation monitor is turned off and left in place. The warning note 'In use - do not remove' must be left in plain view.

11 - Return to the window side and connect the dosimeter to the electronic counter with the cable provided for this purpose. Ensure that there are no knots or kinks in the wire before introducing the dosimeter into the conduit leading into the cell room. Push the dosimeter down until it starts appearing at the end of the conduit in the hot cell room.

12 - Turn the electronic counter switch to 'BATT' and check that the battery light shows green. If the light is red the batteries should be replaced with two D size units.

13 - Turn the electronic counter dial to '-10v'. The potential should read 10.25.

14 - When polarity stabilizes at 250.25, move to ON, setting the range dial to HIGH.

15 - Punch the CF button, and enter the value 0870 then hit ENTER and RESET.

16 - Unlock and raise the hot cell to test the dose rate. The cell must be handled carefully to ensure there is no damage to the pantographic arms and that it does not jam in the rack. The hot cell hoisting apparatus is operated from push-buttons on the window side of the hot cell room. They allow positioning of the cell over its holding rack and the pantographic arm is used to assist placing the hot cell within the rack.

17 - After the timer has been set on the electronic counter for 10 second, press SET TIME, 00 100, ENTER.

18 - Using the pantographic arms, place the dosimeter in the green dosimeter rack, measure for 10 sec and record the reading on the Irradiation Data sheet.

19 - The dosimeter is then removed from the rack, steps 17 and 18 are repeated and the average of the two readings is calculated.

20 - The dosimeter is then moved to Position 1 on the sample rack with the help of the pantographic arm, step 17 is repeated, and the dose is measured for 10 sec. The reading is recorded on the Irradiation data sheet.

21 - The dosimeter is then removed and step 17 and 20 are repeated.

22 - The dosimeter is moved to Position 2 on the sample rack with the help of the pantographic arm. Step 17 is repeated and the dose is measured for 10 sec. The reading is recorded on the Irradiation data sheet.

23 - The dosimeter is then removed and steps 17 and 22 are repeated. The average of the readings obtained in steps 20 to 23 is calculated.

24 - The dosimeter is removed and placed inside the conduit. The hot cell is lowered back into its storage position and its power supply is locked off.

25 - To calculate the "calibration ratio" or "correction factor", the average of the 4 reading from steps 20 to 23 are divided by the average from steps 18 and 19.

26 - The actual current hot cell "doserates" is calculated utilizing the following equations:

$$A = A_{o}^{(-\ln 2[t/T_{1/2}])}$$

where

A<sub>o</sub> = dose rate at a given t<sub>o</sub> t = the time elapsed since t<sub>o</sub>

 $T_{1/2}$  = half life of the cell

or alternatively:

$$A = A_0^{(-\lambda t)}$$

where  $\lambda = \text{decay constant of the cell}$ 

The "correction factor" must be calculated for each sample-rack/source-rack position combination. The "average doserate" and "correction factor" thus obtained should be used for the entire irradiation. However when starting a new set of samples the determination should be repeated even if it takes place on the same day.

27 - The dosimeter must now be prepared for the samples irradiation procedure. To do so clear the 10 sec time on the electronic counter and set the following instruction: SET TIME, CLEAR, CLEAR, RESET.

The longest irradiation should be performed first. This ensures that any initial hesitancy in handling cell or the length of the "up-time" and "down-time" will not be significant with respect to the total length of the irradiation. The irradiation of the samples is carried out using the "Protocol for irradiation of ESR samples" in this Appendix.

#### PROTOCOL FOR IRRADIATION OF ESR SAMPLES

(J. Johnson - *Protocol for irradiation of ESR samples* - McMaster Quaternary Geochronology Centre, 1995; as edited by V. Volterra)

1 - After obtaining the "average doserate" and the "calibration ratio", return to the door side of the hot cell room and turn the radiation detection meter on, in Scale 11 and in audible mode.

2 - The monitor is left on and placed at about 30 cm. from the door, with a dated note saying : "In use - do not remove" The monitor should be propped up so that the motion of its needle can be clearly seen.

3 - Unlock the hot cell door and open it. If the monitor alarm sounds or if its needle indicating presence of radiation is seen to move, the door should be let shut immediately and it should be locked. The operator must return to the hot cell window and re-check the position of the hot cell. The operator must also report the incident immediately to the reactor supervisor whether the hot cell is up or down.

4 - If the monitor does not register any activity while the door is being opened, the door can be secured in the open position using the rope provided for this purpose.

5 - The monitor must be picked up and held in front of the body when entering the hot cell room slowly, to ensure the area is safe. If the monitor register radiation the alarm procedure outlined in step 3 must be followed.

5 - If the monitor does not register any activity while opening door, the door can be secured in the open position using the rope provided for this purpose.

6 - Pick up the monitor and hold it in front of the body while entering the hot cell room slowly, to ensure the area is safe. If the monitor register radiation the alarm procedure outlined in step 3 must be followed.

7 - If the area is found safe proceed with placing the samples in the rack and the dosimeter in its holder. Record in the laboratory work book and on the Irradiation data sheets the position of each sample. 8 - The mirror must be placed in position so as to permit viewing the back of the cell when it is being placed into its holding rack.

9 - Check that there are no obstructions between cell and sample racks.

10 - Close the door reasonably slowly to avoid damaging the lock. The door is locked, the radiation monitor is turned off and left it in place with the warning note "**In use - do not remove**" in plan view.

11 - Return to the window side.

12 - Before proceeding further calculate the approximate duration time of each of the irradiations and record them in the irradiation data sheet. This is done by dividing the dose required by the "doserate" calculated above.

13 - Unlock the power supply to the hot cell hoist and make sure the stopwatch has been reset at zero. Start the stopwatch and electronic counter at the same time. Check that the LCD <sup>'</sup> display has been activated.

14 - The source can now be brought up and placed in the rack using the hoist and the pantographic arm.

15 - As soon as the source is in place immediately hit STOP on the electronic counter.

16 - Check that the cell is correctly positioned in the rack.

17 - Look at the clock and stop the stopwatch, and record the "wall clock time" and the "stopwatch time" on the Irradiation data sheet.

18 - Record (in brackets) on the Irradiation data sheet the dose showing on the electronic counter and multiply this figure by the "correction factor" calculated above to obtain the true "updose".

19 - Hit the READTIME button on the electronic counter to obtain "updose time" and record it on the Irradiation data sheet.

20 - The "lag time" ("stopwatch time" minus "updose time") can now be calculated and recorded on the Irradiation data sheet.

21 - The "actual time in" ("wall clock time" minus "lag-time") is then calculated and recorded on the Irradiation data sheet.

22 - If this was not done previously, the "average doserate" is recorded on the Irradiation data sheet. The dosimeter is removed from the rack and placed inside the conduit with the help of the pantographic arm.

23 - The desired irradiation time ("desired dose" minus "updose", divided by "average doserate") is calculated.

24 - The desired time at which the irradiation should be terminated (actual time in plus desired irradiation time) is calculated and recorded on the irradiation data sheet.

25 -Hit SET TIME, CLEAR, CLEAR, RESET on the electronic counter and clear the stopwatch to prepare for the "downdose" measurement. Switch off the electronic counter, lock the pantographic arms if leaving the premises and display the "Experiment in progress" sign on hot the cell room window. The power supply to the hot cell must be now locked in the "off" position.

26 - When the irradiation is almost completed, unlock the power supply to the hot cell and turn back on the electronic counter.

27 - Turn the electronic counter switch to BAT and check that the battery light shows green. If the light is red the batteries should be replaced with two D size units.

28 - The electronic counter dial is turned to -10V. The potential should read "10.25".

29 - When polarity stabilizes at "250.25" move the dial to ON and set the range dial to HIGH.

30 - Depress the CF button and enter the value 0870, then select ENTER and RESET are selected. Make sure that the 10 sec timer has been cleared.

31 - The dosimeter is placed on the rack using the pantographic arm one minute before the desired time for completion of the irradiation. The stopwatch is started.

32 - At the end of 1 minute, push the START button on the electronic counter check that the LCD is recording.

33 - The cell must be returned to its storage position as quickly as possible with the help of the hoist.

34 - The "downdose" shown on the counter is recorded (in brackets) on the Irradiation data sheet. This figure is multiplied by the "correction factor" to obtain the true "downdose".

35 - Push STOP. CLEAR. RESET immediately on the electronic counter.

36 - Turn off the power to the cell.

37 - Retrieve the samples just irradiated and proceed with the next irradiation repeating steps (1) to (36).

38 - Calculate the total dose received by the samples. This is:

[("actual irradiation time" in seconds) x ("average doserate")] + (true updose + downdose).

39 - When all the irradiations have been completed:

- retrieve the dosimeter and disconnect it from the electronic counter,

- turn off the power to the cell and then turn the cell room lights off,

- ensure that the radiation monitor is plugged in and its batteries are charging, and

- return the key to the reactor operating personnel.

Samples should be stored for approximately two weeks after irradiation before ESR analysis.

# APPENDIX C

Irradiation levels and U, Th, K content of ESR samples

|  |                  |                             | ·····                        |                 |
|--|------------------|-----------------------------|------------------------------|-----------------|
| Levels of laboratory irradiation for each set of samples |                  |                             |                              |                 |
| <u>El Pendo</u>  | <u>Carihuela</u> | <u>Gorham's - in-situ</u> ( | <del>Gorham's - museum</del> | <u>Vanguard</u> |
| Natural  | Natural          | Natural                     | Natural                      | Natural         |
| 0.5 krads  | 1.01 krads       | 1.01 krads                  | 1.01 krads                   | 1.01 krads      |
| 1.01 krads   | 2.02 krads       | 2.00 krads                  | 2.02 krads                   | 2.00 krads      |
| 2.02 krads   | 4.02 krads       | 4.05 krads                  | 3.02 krads                   | 4.05 krads      |
| 3.03 krads   | 8.02 krads       | 6.04 krads                  | 4.02 krads                   | 6.04 krads      |
| 4.02 krads   | 10.06 krads      | 8.11 krads                  | 6.05 krads                   | 8.11 krads      |
| 5.03 krads   | 20.06 krads      | 10.04 krads                 | 8.05 krads                   | 10.04 krads     |
| 6.02 krads   | 40.07 krads      | 12.05 krads                 | 12.23 krads                  | 20.01 krads     |
| 8.02 krads   | 80.06 krads      | 16.04 krads                 | 16.05 krads                  | 40.07 krads     |
| 10.06 krads  | 100.06 krads     | 20.05 krads                 | 24.06 krads                  | 80.05 krad      |
|  |                  |                             |                              |                 |

Table XVIII

| U, Th, K levels in ESR samples* |          |                  |           |           |            |         |
|---------------------------------|----------|------------------|-----------|-----------|------------|---------|
| SAMPLE#                         | U en ppm | U <b>den</b> ppm | U cem ppm | U sed ppm | Th sed ppm | K sed % |
| EL PENDO                        |          |                  |           |           |            |         |
| PENESR 17                       | nil      | 0.01             | 0.63      | 2.56      | 13.55      | 0.65    |
| PENESR 2                        | 0.27     | 0.05             | -         | 1.48      | 5.10       | 0.35    |
| PENESR 22                       | nil      | 0.12             | 0.39      | 1.26      | 7.08       | 0.37    |
| PENESR 23                       | 0.03     | 0.03             | 0.29      | 1.10      | 3.71       | 0.32    |
| PENESR 24                       | 0.21     | 0.13             | -         | 1.42      | 6.94       | 0.39    |
| PENESR 25                       | 0.01     | nil              | -         | 1.53      | 7.07       | 0.43    |
| PENESR 26                       | nil      | 0.02             | -         | 1.13      | 3.79       | 0.27    |
| PENESR 32                       | nil      | 0.18             | -         | 1.56      | 7.09       | 0.43    |
| CARIHUELA                       |          |                  |           |           |            |         |
| CARSER 5                        | nil      | 3.91             | 4.63      | 2.35      | 12.74      | 0.70    |
| CARESR 7                        | nil      | 10.09            | 10.64     | 1.92      | 7.12       | 0.45    |
| CARESR 9                        | 0.03     | 19.38            | 16.27     | 1.50      | 7.89       | 0.39    |
| CARESR10                        | 0.67     | 9.74             | 9.76      | 2.35      | 12.74      | 0.70    |
| CARESR 11                       | 0.41     | 2.65             | 12.00     | 2.88      | 8.56       | 0.64    |
| CARESR 14                       | nil      | 13.33            | 13.35     | 1.89      | 8.82       | 0.54    |
| CARESR 17                       | 0.20     | 3.06             | 2.42      | 1.86      | 8.20       | 0.60    |
| CARESR 20                       | 0.02     | 1.39             | 1.30      | 1.92      | 7.12       | 0.45    |
| CARESR 28                       | 0.10     | 1.20             | 1.68      | 1.86      | 8.20       | 0.60    |
| CARESR 33                       | nil      | 2.08             | 2.08      | 1.86      | 8.20       | 0.60    |
| CARESR 34                       | nil      | 1.26             | 1.58      | 1.86      | 8.20       | 0.60    |
| GORHAM'S                        |          |                  |           |           |            |         |
| GORESR 1                        | nil      | 7.62             | -         | 0.62      | 1.05       | 0.06    |
| GORESR 2                        | nil      | 7.47             | -         | 0.62      | 1.05       | 0.06    |
| GORESR 5                        | 0.06     | 7.58             | 6.57      | 1.16      | 3.60       | 0.19    |
| GORESR 6                        | nil      | 6.86             | -         | 0.78      | 1.35       | 0.07    |
| GORESR 7                        | nil      | 9.88             | 13.78     | 0.83      | 1.35       | 0.06    |
| GORESR 9                        | nil      | 6.40             | -         | 0.73      | 1.18       | 0.07    |
| GORESR 15                       | nil      | 11.11            | 13.58     | 1.71      | 1.71       | 0.09    |
| GORESR 18                       | nil      | 9.71             | -         | 1.98      | 1.36       | 0.10    |
| GORESR 21                       | nil      | 9.71             | -         | 0.85      | 1.82       | 0.08    |
| GORESR 24                       | nil      | 9.71             | -         | 1.11      | 1.44       | 0.08    |
| GORESR 31                       | 0.50     | 13.00            | 21.10     | 3.18      | 1.26       | 0.06    |
| GORESR 33                       | nil      | 13.74            | -         | 3.18      | 1.26       | 0.06    |
| GORESR 37                       | nil      | 7.07             | -         | 1.68      | 2.47       | 0.17    |
| GORESR 43                       | nil      | 12.08            | 16.23     | 0.49      | 1.90       | 0.27    |
| GORESR 45                       | nil      | 1.70             | 7.84      | 0.98      | 1.97       | 0.33    |
| GORESR 49                       | nil      | 0.07             | -         | 0.71      | 2.66       | 0.30    |
| VANGUARD                        |          |                  |           |           |            |         |
| VANESR 2F                       | nil      | 10.99            | 11.10     | 0.84      | 3.29       | 0.51    |
| VANESR 7                        | nil      | 35.94            | -         | 0.72      | 2.58       | 0.40    |
| * nil = below detection limits  |          |                  |           |           |            |         |

Table XIX

REFERENCES CITED

.

**`** 

231

# **REFERENCES CITED**

| Abeyratne, M.; Spooner, I | N. A.; Grün, R.; Head, J 1997 - Multidating studies of Batadomba cave,          |
|---------------------------|---|
| Sri                       | Lanka - Quaternary Geochronology, 16: 243-255                                   |
| Abrajain, A.; Bleaney, B. | - 1986 - Electron paramagnetic resonance of transition ions - Oxford            |
| Un                        | iversity Press, Oxford  |
| Ager, D. V 1980 - The g   | eology of Europe - John Wiley and Sons, N. Y.                                   |
| Aiello, L. C 1993 - The   | òssil evidence for modern human origins in Africa: a revised view -             |
| An                        | nerican Anthropologist, 95: 73-96   |
| Aitken, M. J 1968 - Low   | -level environmental radiation measurements using natural calcium               |
| flor                      | ride - Proceedings of the International Conference on Luminescence              |
| Do                        | <i>simetry</i> II, Gatlinburg, Tenn.  |
| Aitken, M. J 1985 - The   | ermoluminescence dating - Academic Press, London                                |
| Aitken, M. J 1990 - Scie  | nce-based dating in archaeology - Longman, New York                             |
| Almagro, M 1973 - Los     | omoplatos decorados de la Cueva de "El Castillo" - <i>Trabajos de</i>           |
| - Pre                     | historia, 33: 9-99  |
| Altuna, J 1992 - Le Pale  | eolithique Moyen de la region Cantabrique - <i>L'Anthropologie</i> , 96: 87-101 |
| Alvaredo, M 1980 - Esp    | agne - in: J. Dercourt (Ed), Geologie des pays Européens; Espagne, Gréce,       |
| Ita                       | ie, Portugal, Yougoslavie - Dunod, Paris: 1-54                                  |
| Andrews, J. T 1975 - Gl   | acial systems - Duxbury Press, North Scituate, Mass                             |
| Andrews, P.; Stringer, C. | B 1993 - The primates progress - in: S. J. Gould (ed.), The book of             |
| life                      | : 219-251   |
| Anton, S 1994 - Mechan    | ical and other perspectives on Neanderthal craniofacial morphology - in:        |
| R. 5                      | S. Coruccini and R. L. Ciochon (Eds.), Integrative paths to the past, Prentice  |
| Ha                        | ll, Englewood Cliffs, N. J.: 677-695  |
| Arensburg, B. 1989 - New  | skeletal evidence concerning the anatomy of Middle Paleolithic                  |
| po                        | oulations in the Middle East : the Kebara skeleton - in: P. Mellars:            |
| <b>Č</b> . 1              | 3. Stringer (Eds.), The human revolution: behavioural and biological            |
| per                       | spective on the origins of modern humans - Princeton University Press,          |
| Pri                       | nceton, N. J.: 164-171  |
| Arija Rivares, E 1972 -   | <i>Geografia de Espana</i> , Tomo I - Espasa-Calpe, Madrid                      |
| Atunes, M. T 1990 - O h   | iomen de gruta de Figueira Brava (ca. 30000 BP) - Memorias de la                |
| Ac                        | ademia Cientifica de Lisboa, 31: 487-535  |
| Avery, G.; Cruz-Uribe, K. | ; Goldberg, P.; Grine, F. E.; Klein, R. G.; Mareau, C. W.; Rink, W. J.;         |
| Scl                       | warcz, H. P.; Thackeray, A. I.; Wilson, M. L 1997 - The 1992-1993               |
| exc                       | avations at Die Kelders Middle and Late Stone Age cave site, South              |
| Afi                       | ica - Journal of Field Archaeology, 24: 263-291                                 |
| Baden- Powell, D. F. W    | 1964 - Gorham's cave, Gibraltar: report on the climatic equivalent of           |
| the                       | marine mollusca - in: J. d'A. Waechter (Ed.), The excavation of                 |
| Go                        | rham's cave, Gibraltar, Bulletin of the Institute of Archaeology ,              |
| 4:2                       | 216-218   |
|                           |   |

- Bahain, J. J.; Yokoyama, Y; Falguéres, C. 1992 ESR dating of tooth enamel: a comparison with K-Ar dating - *Quaternary Science Reviews*, 11: 245-250
- Bahain, J-J.; Sarcia, M. N.; Falguéres, C.; Yokoyama, Y. 1993 Attempt at ESR dating of tooth enamel of French Middle Pleistocene sites - *Applied Radiation and Isotopes*, 44: 267-272
- Bahain, J-J.; Yokoyama, Y.; Falguéres C,; Bibron, R. 1994 Choix du signal á utiliser lors de la datation par résonance paramagnétique électronique (RPE) de calcites stalagmitiques quaternaires *Comptes rendu de l'Academie des Sciences, Paris*, Ser. II, 318: 375-379
- Bailey, G. N. 1983 Hunter-gatherer economy in prehistory: a European perspective Cambridge University Press, Cambridge
- Barton, C. M.; Clark, G. A. 1993 Cultural and natural formation processes in late Quaternary cave and rockshelter sites of western Europe and the Near East - in: P. Goldberg; D. T. Nash; M. D. Petraglia (Eds.), Formation processes in archaeological context, Prehistory Press, Madison, Wis.: 33-52
- Bar-Yosef, O. 1992 The role of western Asia in modern human origins *Philosophical Trans* actions of the Royal Society, London, B, 337: 193-200
- Bar-Yosef, O. 1994 The contribution of southwest Asia to the study of modern humans in: M. H. Nitecki; D. V. Nitecki (Eds.), Origins of anatomically modern humans, Plenum Press, N. Y.: 3-17
- Belluomini, G. Delitala, L.; Poulianos A. N.; Polianos, N. A. 1987 The man of Petralona, an estimated age by amino acid racemization dating - *Anthropos*, 12: %9-64
- Bernaldo de Quiros, F. 1978 El Paleolítico Superior inicial en la region Cantabrica Doctoral Thesis, Universidad Complutense, Madrid
- Bernaldo de Quiros, F.; Moura-Romanello, A. 1978 Cronologia del Paleolitico y el Epipaleolitico peninsulares - *C-14 y Prehistoria de la Peninsula Iberica*, Fundacion Juan March, Madrid: 15-35
- Binford, L. R. 1992 Hard evidence Discover, Feb.: 44-51
- Bischoff, J. L.; Soler, M.; Maroto, J.; Julia, R. 1989 Abrupt Mousterian/Aurignacian boundary at c. 40 kabp: accellerator <sup>14</sup>C dates from l'Arbreda cave (Catalunya, Spain) -*Journal of Archaeological Science*, 16: 563-576
- Bischoff, J. L.; Garcia, J. F.; Straus L. G. 1991 Uranium-series Isochron dating at el Castillo cave (Cantabria, Spain): the "Acheulean/ Mousterian" question - Journal of Archaeological Science, 18
- Bischoff, J. L.; Garcia, J. F.; Straus L. G. 1992 Uranium-series Isochron dating at el Castillo cave (Cantabria, Spain) - *Journal of Archaeological Science*, 19: 49-62
- Blackwell, B. A. 1994 Problems associated with reworked teeth in electron spin resonance (ESR) dating - Quaternary Geochronology (Quaternary Science Review), 13: 651-660
- Blackwell, B. Porat, N. Schwarcz, H. P.; Debenath, A. 1991 ESR dating of tooth enamel -Quaternary Science Review, 10
- Blackwell, B. AS.; Porat, N.; Schwarcz, H. P. Debénath, A. 1992 ESR dating of tooth enamel: comparison with <sup>230</sup>Th/<sup>234</sup>U speleothem dates at la Chaise-de-Vouthon (Charente), France - *Quaternary Science Review*, 11: 231-244
Blackwell, B.; Schwarcz, H. P. - 1993 - ESR isochron dating for teeth: a brief demonstration in solving the external dose calculation problem - ESR Dosimetry and Applications: 243-252 Bodmer, W.; Mckie A. - 1994 - The book of man - Little Brown, London Boëda, E.; Corman, J.; Dessat, D.; Muhesen, S.; Mercier, N; Valladas, H.; Tisnérat, N. - 1996 - Bitumen as hafting material on Middle Paleolithic artefacts- Nature, 380: 336-338 Bordes, F. - 1968 - The Old Stone Age - McGraw-Hill Book Company Bordes, F. - 1984 - Lecons sur le Paléolithique - Centre National des Recherche Scientifique Borziac, I. A.; Allsworth-Jones, P.; French, C. A. I.; Meddyanik, S. I.; Rink, W. J.; Brace, C. L. -1989 - Medieval thinking and the paradigm of Paleoanthropology -American Anthropologist, 91: 442-445 Brace, C. L. -1994 - Review of the origins of modern humans and the impact of chronometric dating - Man, 29: 473-475 Bräuer, G. - 1984a - Craniological approach to the origins of anatomically modern Homo sapiens in Africa and implications for the appearance of modern Europeans, in : F. H. Smith and F. Spencer, The origins of modern humans : a world survey of fossil evidence, Alan R. Liss, New York: 327-410 Bräuer, G. - 1984b - The Afro-european sapiens hypothesis and hominid evolution in Asia during Middle and Upper Pleistocene - in: P. Andrews and G. Frazen (Eds.), The early evolution of man, Courier Forschungsinstitut Senckenberg, 69: 145-165 Bräuer, G. - 1989 - The evolution of modern humans: a comparison of the African and non-African evidence - in: P. Mellars; C. B. Stringer (Eds.), The human revolution: behavioural and biological perspective on the origins of modern humans -Princeton University Press, Princeton, N. J. Bräuer, G. - 1993 - The 'Afro-European sapiens hypothesis and hominid evolution in east Asia during the late Middle and Upper Pleistocene - in: R. L. Ciochon; J. G. Fleagle (Eds), The human evolution book, Prentice Hall, Englewood Cliffs, N. J.,: 446-460 Brennan, B. J.; Rink, W. J.; McGuirl, E. L.; Schwarcz, H. P.; Prestwick, W. V. - 1997 - Beta doses in tooth enamel by "One-group" theory and the ROSY ESR dating software - Radiation Measurements, 27: 307-314 Brennan, B. J., Schwarcz, H. P., and Rink, W. J. - 1997b - Simulation of the gamma radiation field in lumpy environments. Radiation Measurements, 27: 299-306 Breuil, H.; Obermaier, H. - 1912 - Les Premiers travaux de l'Institut de Paleontologie Humaine -L'Anthropologie - vol 23: 1-27 Breuil, H.; Obermaier, H. - 1913 - Travaux executes en 1912 - L'Anthropologie - Vol 24: 1-16 Breuil, H.; Obermaier, H. - 1914 - Travaux en Espagne - L'Anthropologie - vol 25: 233-253 Brooks, A.S.; Helgren, D. N.; Cramer, J. S.; Franklin, A.; Hornyak, W.; Keating, J. Brown, M. H. -1990 - The search for Eve - New York, Harper and Row Brumby, S. - 1992 - Regression analysis of ESR/TL dose-response data - Nuclear Tracks and Radiation Measurements, 20: 595-599 Brumby, S.; Yoshida, H. - 1994 - ESR dating of mollusc shell: investigations with modern shell of four species - Quaternary Geochronology, 13: 157-162

Butzer, K. W. - 1971 - Environment and Archaeology - Aldine - Atherton, Chicago

- Butzer, K. W. 1978 Sediment stratigraphy of the Middle Stone Ge sequence at Klasies River Mouth , Tsitsikama coast, South Africa - South African Archaeological Bulletin, 33: 141-151
- Butzer, K. W. -- 1980 Investigacion preliminar de la geologia de la cueva del Pendo in: J.Gonzales Echegaray et al., *El yacimiento de la cueva de "El Pendo"*, Consejo Superior de Investigaciones Científicas, Istituo Español de Prehistoria, Madrid: 200-213
- Butzer, K. W. -- 1981 Cave sediments, Upper Pleistocene stratigraphy and Mousterian facies in Cantabrian Spain - *Journal of Archaeological Science*8: 133-183
- Butzer, K. W. - 1986 Paleolithic adaptations and settlement in Cantabrian Spain Advances in World Archaeology, 5: 201 - 252
- Cabrera Valdes, V. 1978 La cueva del Castillo (Puente Viesgo, Santander): estudio y revision de los materiales y documentacion de ste yacimiento - Doctoral dissertation, Universidad Complutense, Madrid
- Cabrera Valdes, V. 1984 El yacimiento de la cueva de "el Castillo" Biblioteca Historica Hispania, Madrid
- Cabrera Valdez, V; Bischoff, J. L. 1989 Accellerator 14C dates for Early Upper Paleolithic (Basal Aurignacian) at El Castillo cave (Spain) - Journal of Archaeological Science, 16: 577-584
- Cann, R. L.; Stoneking, M.; Wilson, A. C. 1987 Mitochondrial DNA and human evolution *Nature*, 325: 31-36
- Carrion, J. S. 1992 Late Quaternary pollen sequence from Carihuela Cave, southeastern Spain - *Review Paleobotany and Palinology*, 71: 37-77
- Carriveau, G. W.; Harbottle, G. 1982 Radon and thoron emanation measurements and the effect of groundwater *PACT*, 6: 145-154
- Cavalli-Sforza, L; Menozzi, P.; Piazza, A. 1994 The history and geography of human genes -Princeton University Press
- Cavalli-Sforza, L.; Piazza, A.; Menozzi, P.; Mauntain, J. 1988 Reconstruction of human evolution: bringing together genetic, archaeological and linguistic data - *Preceedings of* the National Academy of Sciences USA,85: 6002-6006
- **Çetin, O.; Ozer, A. M.; Wieser, A. -** 1994 ESR dating of tooth enamel from Karaïn excavation, (Antalya, Turkey) *Quaternary Geochronology*, 13: 661-669
- Chase, P. G. 1989 How different was Middle Paleolithic subsistence? A zooarchaeological perspective on the Middle to Upper Paleolithic transition - in: P. Mellars; C. B. Stringer (Eds.), *The human revolution: behavioural and biological perspective on the origins of modern humans*, Princeton University Press, Princeton, N. J.: 321-337
- Chen, T-M.; Yang, Q.; En, W. 1994 Antiquity of Homo sapiens in China Nature, 368: 55-56
- Chen, T-M.; Yang, Q.; Hu, Y-Q.; Bao, W-B.; Li, T-Y. 1997 ESR dating of tooth enamel from Yunxian Homo erectus site, China - Quaternary Geochronology, Quaternary Science Review, 16: 455-458
- Clark, G. A. 1983 Boreal phase settlement/subsistence models for Cantabrian Spain in: G. N. Bailey. (Ed.), *Hunter-gatherer economy in prehistory: a European perspective*, Cambridge University Press: 96 - 110

Clark, G. A. - 1988 - Some thoughts on the Black Skull - American Anthropologist, 90: 357-371

Clark, G. A.; Lindly, J. M. - 1989 - The case for continuity: observations on the biocultural transition in Europe and western Asia - in: P. Mellars, C. B. Stringer (Eds.), *The human revolution: behavioural and biological perspective on the origins of modern humans*, Princeton University Press, Princeton, N. J.: 626-676

Corrucini, R. S. - 1990 - The forgotten Skhul crania and the "neo-sapiens" theory - American Journal of Physical Anthropology, 81: 209

Corrucini, R. S. - 1994 - Reganomics and the fate of the progressive Neandertals - in: R. S. Corrucini; R. L. Ciochon (Eds.), *Integrative paths to the past*, Prentice Hall, Englewood Cliffs, N. J.: 697-708

Dean, M. P.; Stringer, C. B.; Bromage, T. G. - 1986 - American Journal of Physical Anthropology, 70: 301-309

Delair, J. B. - 1964 - Gorham's cave, Gibraltar: report on the Chelonia - in: J. d'A. Waechter (Ed.), The excavation of Gorham's cave, Gibraltar, Bulletin of the Institute of Archaeology, 4: 218-219

Delitala, M. C.; Fornaseri, M.; Nicoletti, M. - 1983 - Datazioni argon-potassio sulla serie pleistocenica di Isernia La Pineta - in: C. Peretto (ed), *Isernia La Pineta:* un accampamento piú antico di 700.000 anni, Catalogo della mostra, Calderini Editore, Bologna: 65-66

**De Lumley, H. -** 1969 - Etude de l'outillage mousterien de la grotte de Cariguela (Piñar, Gredade) - Anthropologie, 73: 165-206, 325-364

De Lumley-Woodyear, M. A. - 1973 - Anténéandertaliens et Néandertaliens du bassin Mediterranée occidental Européen - Editions du Laboratoir de Paleontologie Humaine et de Prehistoire, Memoir 2: 247-309

Demans, P-y.; Hublin, J-J. - 1988 - La transition Néanderthaliens/hommes de Type moderne en Europe occidentale: aspects paléolontologiques et culturels - in:
 M. Otte (ed), L'homme de Neandertal: actes du colloque international de Liege (4-7 Dec. 1986) - Vol 7: L'extintion, Universite de Liege: 23-27

Deperét, C. - 1918-1922 - Essai de coordination chronologique des temps Quaternaires - *Compts Rendus de l'Academie de France, Paris,* 166: 480-486, 636-641, 884-889, 167: 418-422, 978-984; 168: 868-873

Desrosiers, M. F.; Simic, M. G.; Eichmiller, F. C.; Johnston, A. D.; Bowen, R. L. - 1989 -Mechanically-induced generation of radicals in tooth enamel -International Journal of Radiation and Applied Instrumentation, Ser. A, 40: 1195-1197

Diamond, J. - 1992 - The third Chimpanzee: the evolution and future of the human animal -Harper Collins, N. Y.

Dunnel, R. C. - 1986 - Methodological isues in Americanist artefact classification - in: M. B. Schiffer (ed.), Advances in archaeological method and theory - vol. 9

Dunnel, R. C. - 1995 - In search of Neanderthals - Nature: 376-397

Etler, D. A.; Tianyuan, L. - 1994 - New archaic human fossildiscoveries in China and their bearing on hominid species definition during the Middle Pleistocene - in:
 R. S. Corrucini and R. L. Cichon (Eds.), *Integrative paths to the past*, Prentice Hall, Englewood Cliffs, N. J.: 639-675

| Falgueres, C.; Yokoyama, Y.; Bibron, R 1990 - Electron spin resonance (ESR) dating of |
|---|
| hominid-bearing deposits in the Caverna delle Fate, Liguria, Italy -                  |
| Quaternary Research, 34: 121-128  |

- Falguéres, C.; Bahain, J-J.; Saleki, H. 1997 U-series and ESR dating of teeth from Acheulean and Mousterian levels at La Micoque (Dordogne, France) - *Journal of Archaeological Science*, 24: 537-545
- **Farrand, W. R.** 1988 Integration of late Quaternary climatic records from France and Greece in: H. L. Dibble; A. Martet-White (Eds.), Upper Pleistocene prehistory in western Eurasia, University of Pennsylvania, University Museum: 305-319
- Fleming, S. J. 1970 Thermoluminescent dating: refinement of the quartz inclusion method -Archaeometry, 12: 133-147

Fleming, S. J. - 1979 - Thermoluminescence techniques in Archaeology - Oxford

- Foley, R. 1989 The ecological conditions of speciation: a comparative approach ti the origins of anatomically-modern humans in: P. Mellars;
  C. B. Stringer (Eds.), The human revolution: behavioural and biological perspective on the origins of modern humans Princeton University Press, Princeton, N. J.: 298-318
- Freeman, L. G. 1966 The nature of Mousterian facies in Cantabrian Spain American Anthropologist, 68: 230-237
- Freeman, L. G. 1973 The significance of mammalian faunas from Paleolithic occupations in Cantabrian Spain - American Antiquity, 38: 3-44
- Freeman, L. G. 1975 Acheulean sites and stratigraphy in Iberia and the Maghreb in: W. K. Butzer; G. Ll. Isaac (Eds.): *After the Australopitecines*, The Hague: 661-743
- Freeman, L. G. 1975a The analysis of some occupation floor distributions from earlier and middle Paleolithic sites in Spain - in: - Views of the past - Freeman, L. G., The Hague: 57-116
- Freeman, L. G. 1980 Occupaciones Musterienses in: J.Gonzales Echegaray et al., *El yacimiento de la cueva de "El Pendo"*, Consejo Superior de Investigaciones Científicas, Istituo Español de Prehistoria, Madrid: 29-71
- Friday, A. E. 1981 Hominid evolution: the nature of biochemical evidence in: C. B. Stringer (Ed.), Aspects of human evolution, Taylor and Francis, London: 1-23
- Fuentes Vidarte, C. 1980 Estudio de la fauna de El Pendo in: J.Gonzales Echegarayet al., El yacimiento de la cueva de "El Pendo", Consejo Superior de Investigaciones Científicas, Istituo Español de Prehistoria, Madrid: 215-236
- Gambier, D. 1989 Fossil hominids from the early Upper Paleolithic (Aurignacian) of France in: P. Mellars; C. B. Stringer (Eds.), *The human revolution: behavioural and biological perspective on the origins of modern humans*-Princeton University Press, Princeton, N. J.: 194-211
- Gamble, C. 1986 The Paleolithic settlement of Europe Cambridge University Press, Cambridge
- Gamble, C. 1994 Timewalkers: the prehistory of colonial civilization Harvard University Press, Cambridge, Mass.
- Gamble, C. 1996 Society and mind Nature, 380: 119

Garcia -Sanchez, M. - 1960 - Restos humanos del Peleolitico Medio y Superior y del Neo-Eneolitico de Piñar (Granada) - Trabajos del Instituto Bernardino de Sahagun, Antropologia y Etnografia, 15: 17-72 Garralda, M. D. - 1978 - Datacion absoluta y restos humanos en la peninsula Iberica - C-14 y Prehistoria de la Peninsula Iberica, Fundacion Juan March, Madrid: 7-15 Gibbons, A. - 1995a - Out of Africa - at last? - Science, 267: 1272-1273 Gilman, A.; Thornes, J. B. - 1985 - Land-use and prehistory in southeast Spain - Allen and Unwin, Boston Goebel, T.; Aksenov, M. - 1995 - Accellerator radiocarbon dating of the initial Upper Paleolithic in southern Siberia - Antiquity, 69: 349-357 Goede, A.; Hitchman, M. A. - 1987 - Electron spin resonance analysis of marine gastropods from coastal archaeological sites in southern Africa - Archaeometry, 29: 163-174 Gonzales Echegaray, J; Freeman, L. G.; Barandiaran, I.; Apellanitz, J. M.; Butzer, K. W.; Fuentes Vidarte, C.; Madariaga, B.; Morales, G.; Leroi-Gourhan, A. - 1980 -El vacimiento de la cueva de "El Pendo", Consejo Superior de Investigaciones Cientificas, Istituo Español de Prehistoria, Madrid Gösku, H.Y.; Irwin, H.T.; Fryxell, R.-1974-Age determination of burned flint by a thermoluminescent method - Science, 2: 651-654 Gould, S. J. - 1994 - Lucy on the earth in stasis - Natural History, 9: 12-20 Gould, S. J. - 1994a - In the mind of the beholder - Natural History, Feb.: 14-23 Griffiths, D. R.; Seeley, N. J.; Chandra, H.; Symons, M. C. R. - 1983 - ESR dating of heated chert -PACT, 9: 399-409 Grün, R. - 1989 - Electron spin resonance (ESR) dating - Quaternary International, 1: 65-109 Grün, R. - 1996 - A re-analysis of electron spin resonance dating results associated with the Petralona hominid - Journal of Human Evolution, 30: 227-241 Grün, R.; Beaumont, P. B; Stringer, C. B. - 1990a - ESR dating evidence for early Modern Humans at Border Cave in South Africa - Nature, 344: 537-539 Grün, R.; Shackleton, N. J.; Deacon, H. - 1990b - Electron spin resonance dating of tooth enamel from Klasies River Mouth Cave - Current Anthropology, 31: 427-432 Grün, R.; Invernati, C. - 1985 - Uranium accumulations in teeth and its effects in ESR dating -Nuclear Tracks and Radiation Measurements, 10: 869-878 Grün, R.; Kohno, H.; Tani, A.; Yamanaka, C.; Ykeya, M.; Huang, H. P. - 1997 - Pulsed ESR measurements on fossil teeth - Radiation Measurements, 27: 425-432 Grün, R.; Mellars, P.; Laville, H. - 1991 - ESR chronology of a 1000 000 year archaeological sequence at Pech de l'Aze II, France - Antiquity, 65: 544-551 Grün, R.; McDermott, F. - 1994 - Open system modelling for u-series and ESR dating of teeth -Quaternary Geochronology, 13: 121-126 Grün, R.; Schwarcz, H. P.; Chadam, I. - 1988 - ESR dating of tooth enamel; coupled corrections for U-uptake and U-series disequilibrium - Nuclear Tracks, 14: 237-242 Grün, R.; Schwarcz, H. P.; Zymela, S. - 1987 - Electron spin resonance dating of tooth enamel -Canadian Journal of Earth Sciences, 24: 1022-1037 Grün, R.; Stringer, C. B. - 1991 - Electron spin resonance dating of the evolution of modern humans - Archaeometry, 33: 153-199 Grün, R.; Stringer, C. B.; Schwarcz, H. P. - 1991 - ESR dating of teeth from Garrod's Tabun cave collection - Journal of Human Evolution, 20: 231-248

Guichard, J. - 1976 - Les civilizations du Paléolithique moyen en Périgord - in: H. de Lumley (ed.), La Préhistoire Française, Paris Centre National de Récherche Scientifique: 1053-1069 Habgood, P. J. - 1990 - The origins of anatomically modern humans in East Asia - in: G. Bräuer and F. H. Smith (Eds.), Continuity or replacement in Homo sapiens evolution, Balkema, Rotterdam Haggett, P. (Ed.) - 1994 - Encyclopedia of world geography - Marshall Cavendish, North Bellmore, N. Y.:1302-1431 Hancock, R. G. V. - 1976 - Low Flux Multi-element Instrumental Neutron Activation Analysis in Archaeometry - Analytical Chemistry 48: 1443-1445 Harmon, R. S.; Glazek, J.; Novak, K. - 1980 - 230 Th/234U dating of travertine from Bilzingsleben archaeological site - Nature, 284: 132-135 Haskell, E. H.; Kenner, G. H.; Hayes, R. B. - 1995 - Electron paramagnetic resonance dosimetry of dentine following removal of organic material - Health Physics, 68: 579-584 Haskell, E. H.; Haves, R. B.; Kenner, G. H. - 1996 - Preparation-induced errors in EPR dosimetry of enamel: pre- and post-crushing sensitivity - Applied Radiation and Isotopes, 47: 1305-1310 Haskell, E. H.; Hayes, R. B.; Kenner, G. H. - 1997 - Improved accuracy of EPR dosimetry using a constant rotation goniometer - Radiation Measurements, 27: 325-329 Hedges, R. E. M.; Millard, A. R. - 1995 - Bones and groundwater: toward the modelling of diagenetic processes - Journal of Archaeological Science, 22: 155-164 Hedges, R. E. M.; Pettit, P. B.; Bronk-Ramsay, C.; van Klinken, G. J. - 1996 - Archaeometry datelist 22 - Archaeometry, 32,2: 391-415 Hennig, G. J.; Herr, W.; Weber, E.; Xirotiris, N. I. - 1981 - ESR dating of the fossil hominid from Petralona cave, Greece - Nature, 292: 533-536 Hoelzer, G.; Hoelzer, M.; Rosenbloom, L.; Melnick, D. - 1992 - A molecular phylogeny of Asian Macaque using mitochondrial DNA - American Journal of Physical Anthropology, Supplement 14:91 Horai, S.; Hayasaka, K.; Kondo, R.; Tsugane, K.; Takahata, N. - 1995 - Recent African origin of modern humans revealed by complete sequences of hominid mitochondrial DNAs - Proceedings of the National Academy of Sciences USA, 92, 2: 532-536 Howell, F. C. - 1952 - Pleistocene glacial ecology and the evolution of 'Classic Neandertal' Man,-Southwestern Journal of Anthropology, 8: 377-410 Hoyos Gomez, M; Laville, H. - 1982 - Nuevas aportaciones sobre la stratigrafia y sedimentologia de los depositos del Paleolitico Superior de la cueva de El Pendo (Santander): su implicaciones - Zephirus XXXV: 285-293 Hoyos Sainz de, L. - 1963 - Antropologia prehistorica Española - in: R. Mendez Pidal (Ed.), Historia de España, Espasia-Calpe, Madrid, Vol I: 97-241 Huang, P. H.; Liang, R. Y.; Jin, S. H.; Peng, Z. C.; Ritter, N. W. - 1989 - Study on accumulated dose in littoral shells of Argentina. Applied Radiation and Isotopes, 40: 1119-1122 Huang, W.; Ciochon, R.; Gu, Y.; Larick, K.; Fang, Q.; Schwarcz, H.; Yonge, C.; de Vos, J.; Rink, W. J. - 1995 - Early Homo and associated artefacts from Asia -Nature, 378: 275-278

- Hublin, J. J. 1992 Recent human evolution in northwestern Africa Philosophical Transac tions of the Royal Society, London, B, 337: 185-191
- Hublin, J-J.; Barroso Ruiz, C.; Medina Lara, P.; Fontugne, M.; Reyss, J. L. 1995 The Mousterian site of Zafarraya (Andalucia, Spain): dating and implications on the Paleolithic peopling process of western Europe - *Comptes Rendus de l' Academie des Sciences*, II, 321, 10: 931-937
- Hublin, J. J.; Spoor, F.; Braun. M.; Zonneveld, F.; Cardemi, S. 1996 A late Neanderthal associated with Upper Paleolithic artefacts *Nature*, 381: 224-226
- Hublin, J. J.; Tillier, A. M 1981 The Mousterian juvenile mandible from Irhoud (Morocco): a phylogenic interpretation in: C. B. Stringer (Ed.), Aspects of human evolution, Taylor and Francis, London: 167-185
- Huntley, D. J.; Godfrey-Smith, D. I.; Thelwalt, M. L. W. 1985 Optical dating of sediments -Nature, 313: 105-107
- Hütt, G.; Molodkov, A.; Kessel, H.; Raukas, A. 1985 ESR dating of subfossil Holocene shells in Estonia - Nuclear Tracks and Radiation Measurements, 10: 891-898
- Hütt, G.; Jaek, J. 1989 Dating accuracy from laboratory reconstruction of paleodose International Journal of Radiation and Applied Instrumentation, Part A, 40: 1057-1061
- Huxtable, J.; Aitken, M. J. 1988 Datation par luminescence in : Le gisement Paléolithique Moyen Biache-Saint-Vaast (Pas de Calais) - A. Tuffreau; J. Sommé (Eds), Editions du CNRS: 107-108
- Ikeya, M 1975 Dating a stalactite by electron paramagnetic resonance Nature, 255: 48-50
- Ikeya, M. 1980 ESR dating of carbonates at Petralona Cave Anthropos, 7: 143-150
- Ikeya, M. 1982 A model of linear uranium accumulation for ESR age of Hidelberg, Mauer and Tautevel bones - Japanese Journal of Applied Physics, 21: 1690- 1692
- Ikeya, M. 1986 Electron spin resonance in: M. R. Zimmerman; L. Angel (Eds.), Dating and age determination of biological material Croom Helm: 59-125
- Ikeya, M.; Miki, T. 1981 Electron spin resonance archaeological dose of Petralona and Choukoutien bones - Anthropos, 8: 95-104
- Ikeya, M.; Miki, T. (Eds.) 1985 ESR dating and dosimetry Proceedings of the first Interna tional symposium on ESR dating) - Ionics, Tokyo: 538
- Ikeya, M.; Ohmura, K. 1981 Dating of fossil shells with electron spin resonance *Journal of Geology*, 89: 247-251
- Ikeya, M.; Zimmerman, M. R.; Whitehead, N. 1993 New applications of electron spin resonance; dating, dosimetry and microscopy - World Scientific Press, Singapore
- Imai, M.; Shimokawa, K. 1993 ESR ages and trace elements in a fossil mollusc shell Applied Radiation and Isotopes, 44: 161-165
- Jelínek, A. J. 1994 Hominids, energy, environment, and behavior in the late Pleistocene in: M. H. Nitecki; D. V. Nitecki (Eds.), *Origins of anatomically modern humans*, Plenum Press, N. Y.: 67-92
- Jonas, M. 1995 Spectral deconvolution of the ESR dating signal in fossil tooth enamel -Quaternary Geochronology, 143: 431-438
- Jonas, M. 1997 Concepts and methods of ESR dating Radiation Measurements, 27: 943-973
- Jonas M.; Grün, R. 1997 Q-band ESR studies of fossil tooth enamel: implications for spectrum deconvolution and dating *Radiation Measurements*, 27: 49-58

Jonas, M.; Marseglia, E. - 1997 - The case for use of integrated spectrum devolution in ESR dating - a mechanically generated example - Radiation Measurements, 27: 359-363 Jonas, M.; Zhou, L. P.; Marseglia, E. A.; Mellars, P. - 1994 - New analysis of ESR spectra of fossil tooth enamel - Cambridge Archaeological Journal, 4: 139-146 Jones, E. (ed.) - 1986 - The Marshall Cavendish new illustrated Encyclopedia of the world and its people - Marshall Cavendish, Freeport, N. Y.: 1961-1973 Jones, J. L. - 1993 - The language of genes - Anchor Books, Doubleday, N. Y. Julia, R; Bischoff, J. L. - 1991 - Radiometric dating of Quaternary deposits and the hominid mandible of Lake Banyolas, Spain - Journal of Archaeological Science, 18:707-722 Katzenberger, O.; Grün, R. - 1985 - ESR dating of circumartic molluscs - Nuclear Tracks, 10:885-890 Kennedy, G. E. - 1984 - The emergence of Homo sapiens: the post cranial evidence - Man, 19:94-110 Kerr, R. A. - 1996 - Millennial climate oscillations spied - Science, 271: 146-147 King, C. A. M. - 1965 - Oceanography for geographers - Edward Arnold, London Kingdon, J. - 1993 - Self made man: human evolution from Eden to extition? - Wiley, N.Y. Klein, R. G. - 1989 - The human career: human biological and cultural origins - Chicago University Press, Chicago Klein, R. G. - 1994 - The problem of modern human origins - in: M. H. Nitecki; D. V. Nitecki (Eds.), Origins of anatomically modern humans, Plenum Press, N.Y.: 3-17 Kozlowski, J. K. - 1992: - The Balkans in the Middle and Upper Paleolithic: the gate to Europe or a cul de sac - Proceedings of the Prehistoric Society, 58: 1-20 Lahr, M.; Foley, R. - 1994 - Multiple dispersals and modern human origins - Evolutionary Anthropology, 3: 48-60 Latham, a.; Schwarcz, H. P. - 1992 - The Petralona hominid site: uranium-series re-analysis of 'Layer 10' calcite and associated paleomagnetic analyses - Archaeometry, 34: 135-140 Lau, B.; Blackwell, B. A. B.; Schwarcz, H. P.; Turk, I.; Blickstein, J. I. - 1997 - Dating a flautist: using ESR (electron spin resonance) in Mousterian cave deposits at Divje Babe I, Slovenia - Geoarchaeology, 12: 507-536 Leakey, R. - 1994 - The origin of humankind - Basic Books, N.Y. Lee, H-K.; Rink, W. J.; Schwarcz, H. P. - 1997 - Comparison of ESR signal dose responses in modern and fossil tooth enamel - Radiation Measurements, 27: 405-411 Lee-Thorpe, J. A.; Van Der Merwe, N. J. - 1987 - Carbon isotope analysis of fossil bone apatite -South African Journal of Science, 83: 712-715 Leroi-Gourhan, A. - 1980 - Analisis polinico de El Pendo- in: J.Gonzales Echegaray et al., El yacimiento de la cueva de "El Pendo", Consejo Superior de Investigaciones Científicas, Istituo Español de Prehistoria, Madrid: 263-264 Lewin, R. - 1993 - The origin of modern humans - Scientific American Library, N.Y. Li, T.; Etler, D. A. - 1992 - New Middle Pleistocene hominid crania from Yunxian in China - Nature, 357: 404-407

241

Linde, D. R. - 1966 - CRC Handbook of Chemistry and Physics - 76th Edition: 10-284.

Liritzis, Y. - 1982 - Letter to Nature, 299: 282

- Lumsden, G. I. 1992 Geology and the environment of western Europe Clarendon Press, Oxford
- Lyons, R. G.; Bowmaker, G. A.; O'Connor, C. J. 1988 Dependence of accumulated dose in ESR dating on microwave power: a contra-indication to the routine use of low, power levels - *Nuclear Tracks and Radiation Measurements*, 14: 243-251
- Lyons, R. G.; Brennan, B. J. 1989 Alpha-particle effectiveness in ESR dating: energy dependence and implications for dose rate calculations Applied Radiation and Isotopes, 40: 1063-1070
- Lyons, R. G.; Brennan, B. J.; Readhead, M. 1993 Games with gammas: problems in environmental gamma dose determinations - *Applied Radiation and Isotopes*, 44: 131-137
- Masters, P. M. 1982 An aminoacid racemization chronology for Tabun in: A. Ronen (Ed.), The transition from Lower to Middle Paleolithic and the origin of modern man, BAR International Series151: 43-56
- McDermott, H. F.; Grün, R.; Stringer, C. B.; Hawkesworth, C. J. 1993 Mass-spectrometric u-series dates for Israeli Neanderthal/ early modern hominid sites *Nature*, 363: 252-255
- Mellars, P. 1973- The character of the middle-upper palaeolithic transition in south western France - in: A.C. Renfrew (ed.), *The explanation of Culture change* - Duckworth, London: 255-276
- Mellars, P. 1992b Archaeology and the population-dispersal hypothesis of modern huma origins in Europe - *Philosophical Transactions of the Royal Society*, London, B, 337: 225-234
- Mellars, P. 1996 The Neanderthal legacy: an archaeological perspective from western Europe - Princeton University Press, Princeton, N. J
- Mellars, P. A.; Grün, R. 1991 A comparison of the electron spin resonance and thermolumi nescence dating methods: the results of ESR dating at le Moustier (France) - Cambridge Archaeological Journal, 1: 269-276
- Mellars, P. A.; Zhou, L. P.; Marseglia, E. A. 1997 Compositional inhomogeneity of sediments and its potential effects on dose rate estimation for electron spin reso nance dating of tooth enamel - *Archaeometry*, 39: 169-176
- Melnick, D.; Hoelzer, G. 1992 What in the study of primate evolution is mt DNA good for? -American Journal of Physical Anthropology, Supplement 14: 122
- Mercier, N.; Valladas, H.; Bar Yosef, O.; Vandermeersch, B.; Stringer, C.; Joron, J-L. 1993 -Thermoluminescence date of the Mousterian burial site of Es-Skhul, Mt. Carmel -Journal of Archaeological Science, 20: 169-174
- Michel, V.; Ildefonse, P.; Morin, G. 1995 Chemical and structural changes in *Cervus elephas* tooth enamels during fossilization (Lazaret cave): a combined IR and XRD Rietveld analysis - *Applied Geochemistry*, 10: 145-159
- Middleton, J. 1986 The underground atlas Robert Hale, Bury St. Edmonds
- Molodkov, A. 1989 The problem of long-term fading of absorbed paleodose on ESR-dating of quaternary mollusc shells - International Journal of Radiation and Applied Instrumentation, Part A, 40: 1087-1093

| Monnier, J. L.; Hallégouët, B.; Hinguant, S.; Laurent, M.; Auguste, P.; Bahain, J-J.; Falguéres, C.;<br>Gebbardt, A.: Marguerie, D.: Molines, N.: Morzadec, H.: Yokovama, Y                                  |  |
|--|--|
| 1994 - A new regional group of Lower Paleolithic in Brittany (France),<br>recently dated by electron spin resonance - <i>Compt rendu de l'Academie</i><br><i>des Sciences</i> , Paris, Ser. II, 319: 155-160 |  |
| Morell, V 1995 - Siberia: surprising home for early modern humans - <i>Science</i> , 268: 1279   |  |
| Moure and Carcia - 1990 - see Straus I. G - 1990 - The Early Upper Paleolithic of southwest  |  |
| Europe: Cro-Magnon adaptation in the Iberian peripheries 40000 - 20000 BP  |  |
| in P. Mellers (Ed.) The emergence of modern humans: an   |  |
| archaeological perspective - Edimburgh University Press: 276-302   |  |
| Nambi K S V $= 1085$ - Scope of FSR studies in thermally stimulated luminescence studies and   |  |
| chronological applications - Nuclear Tracks and Radiation Measure  |  |
| monte 10: 112-121  |  |
| Nambi K S V · Aitkon M I - 1086 - Annual dose conversion factors for TL and ESR dating -   |  |
| Archaeometry 28: 202-205   |  |
| Nitecki MH·D V Nitecki - 1994 - Origins of anatomically modern humans - Plenum Press New   |  |
| York 1994  |  |
| <b>Obermaier</b> , H. 1924 - Fossil Man - Yale University Press  |  |
| Oduwole, A. D.: Sales, K. D.: Dennison, K. L Some ESR observations on hone, tooth enamel and   |  |
| eggshell - Applied Badiation and Isotopes, 44, 1993: 261-266   |  |
| Oduwole, A. D.: Sales, K. D 1994 - Transient ESR signals induced by v-irradiation in tooth   |  |
| enamel and in bone - Ougternary Chronology, 13: 647-650  |  |
| <b>Olson. T. R</b> 1981 - Basicranial morphology of the extant hominids and Pliocene hominids - in:  |  |
| C. B. Stringer (Ed.), Aspects of human evolution, Taylor and Francis,<br>London: 99-128  |  |
| Osmond, J. K.; Ivanovich, M 1992 - Uranium-series mobilization and surface hydrology -   |  |
| in: M. Ivanovich, R. S. Harmon (Eds.), Uranium series disequilibrium:  |  |
| applications to earth, marine and environmental sources, Clarendon   |  |
| Press, Oxford: 513-552   |  |
| Otte, M 1981 - Le Gravettien en Europe céntral - Dissertationes Archaeologicae Gandenses,  |  |
| Brugge, 20   |  |
| Peretto, C 1994 - Le industrie litiche del giacimento paleolitico di Isernia la Pineta - Cosmo Iannone   |  |
| Editore, Isernia   |  |
| Pettitt, P - 1997 - Personal communication   |  |
| Pettitt, P.; Stringer, C. B.; Barton, N (in press) - Radiocarbon dates for Gorham's cave   |  |
| Pfeiffer, J. E 1978 - The emergence of man - Harper and Row  |  |
| Pfeiffer, S 1997 - Personal communication  |  |
| Pickford, M 1991 - Paradise lost: mitochondrial Eve refuted - Human Evolution, 6: 263-268  |  |
| Pilbrow, J 1990 - Transition ion electron paramagnetic resonance - Oxford University Press,<br>Oxford  |  |
| Polyakov, V.; Haskell, E.; Huett, G.; Hayes, R.; - 1995 - Effect of mechanical and induced   |  |
| background signal on EPR dosimetry of tooth enamel - Radiation   |  |
| Measurements, 24: 249-254  |  |
| <b>Porat, N.; Schwarcz, H. P.</b> - 1991 - Use of signal subtraction methods in ESR dating of burned flint - <i>Nuclear Tracks and Radiation Measurements</i> . 18: 203-212                                  |  |
|  |  |

Porat, N.; Schwarcz, H. P. - 1994 - ESR dating of tooth enamel: A universal growth curve - in: R. Corrucini; R. Ciochon (Eds), Integrative paths to the past: Paleoanthropological advances in Honour of F.C. Howell, Prentice-Hall, Englewood Cliffs: 521-530

- Porat, N.; Schwarcz, P. H.; Valladas, H.; Bar-Yosef, O.; Vandermeersch, B. 1994 Electron spin resonance dating of burned flint from Kebara Cave, Israel -*Geoarchaeology*, 9; 393-407
- Poulianos, A. N. 1983 On the stratigraphy and dating of the Petralona Man Anthropos, 10: 49-52
- Prescott, J. R.; Hutton, J. T. 1988 Cosmic ray and gamma ray dosimetry for TL and ESR -Nuclear Tracks and Radiation Measurements, 14: 223-227
- Prescott, J. R.; Stephan, L. G. 1982 Contribution of cosmic radiation to environmental dose -PACT, 6: 17-25
- Radke, U.; Mangini, A.; Grün, R. 1985 ESR dating of marine fossil shells Nuclear Tracks, 10: 879-884
- Rak, Y.; Kimbell, W.; Hovers, E. A Neanderthal infant from Amud Cave Journal of Human Evolution, 26, 1994: 313-324
- Raynal, J-P. 1988 Paléoenvironnéments et chronostratigraphie du Paléolithique Moyen dans le Massif Central Français. Implications culturelles - in: M. Otte (Ed.), *L'Homme de Néandertal*, Liege, 2: 113-145
- Relethford, J.; Harpending, H. 1994 Craniometric variation, genetic theory, and modern human origin American Journal of Physical Anthropology, 95: 249-270
- Relethford, J.; Harpending, H. 1995 Ancient differences in population size can mimic a recent African origin of modern humans - American Journal of Physical Anthropology, Supplement 20: 364
- Rink, W. J. 1997 Electron Spin Resonance (ESR) dating and ESR applications in Quaternary science and Archaeometry *Radiation Measurements*, 27: 975-1025
- Rink, W. J.; Grün, R.; Yalcinkaya, I.; Otte, M.; Taskiran, H.; Valladas, H.; Mercier, N.; Schwarcz, H. P. - 1994 - ESR dating of the last interglacial Mousterian at Karaïn Cave, southern Turkey - *Journal of Archaeological Science*, 21: 839-849
- Rink, W. J.; Schwarcz, H. P. 1994 Dose response of ESR signals in Tooth enamel Radiation Measurements, 23: 481-484
- Rink, W. J.; Schwarcz, H. P. 1995 Tests for diagenesis in tooth enamel: ESR dating signals and carbonate contents *Journal of Archaelogical Science*, 22: 251-255
- Rink, W. J.; Schwarcz, H. P.; Smith, F. H.; Radovcic, J. 1995 ESR dating of Neanderthals and Modern humans from the site of Krapina, Croatia - *Nature*
- Rink, W. J.; Schwarcz, H. P.; Valoch, K.; Seitl, L.; Stringer, C. B. 1996 ESR dating of Micoquian industry and Neanderthal remains at Kulna, Czech Republic - *Journal of Archaeological Science*, 23: 889-901
- Rink, W. J.; Schwarcz, H. P.; Stuart, A. J.; Lister, A. M.; Marseglia, E.; Brennan, B. J. 1996a ESR dating of the type Chromerian freshwater bed at West Runton, UK *Quaternary Sciences Review*, 15: 727-738
- Rink, W. J.; Schwarcz, H. P.; Lee, H-K.; Cabrera Valdes, V.; Bernaldo de Quiros, F.; Hoyos, M. 1996b - ESR dating of tooth enamel: comparison with AMS <sup>14</sup>C at El Castillo Cave, Spain - Journal of Archaeological Science, 23: 945-951

- Rink,W.J.; Rees-Jones, J.; Volterra, V.; Schwarcz, H. P. 1998 Optical luminescence dating of cave sands and U-series dating of crystalline calcite at Gorham's cave, Gibraltar -*Proceedings of the Gibraltar 1997 Conference*, in print
- Robins, G. V.; Seeley, N. J.; Symons, M. C. R.; Bowman, S.G.E. 1982 The Institute of Archaeology (London) ESR flint project - *PACT*, 6: 322-332
- Rogers, A.; Jorde, J. 1995 Genetic evidence on modern human origins Human Biology, 67: 1-36
- Rossignol-Strick, M; Planchais, N. 1989 Climate patterns revealed by pollen and oxygen isotope records of a tyrrhenian sea core *Science*, 342: 413-416
- Ruvolo, M.; Zehr, S.; Van Dornum, M.; Pan, D.; Chang, B.; Lin, J. 1993 Mitochondrial COII sequences and modern human origins - *Molecular Biology and Evolution*, 10: 1115-1135
- Sanguino Gonzales, J.; Montes Barquin, R.; Muños Fernandez, E. 1993 Consideraciones en torno a las alteraciones postdeposicionales en cavidades karsticas: el caso de la cueva de "El Linar" (Alfoz de Lloredo, Cantabria) - Arqueologia Espacial, *Seminario de Arqueologia y Etnologia Turolense*, Clegio Universitario de Teruel,16-17: 143-155
- Sales, K. D.; Robins, G. V.; Oduwole, D. 1989 Study of bone from the Paleolithic site at Zhoukoudian - in: R. O. Allen (Ed) *Archaeological Chemistry IV*, American Chemical Society, Washington
- Savory, H. N. 1968 Spain and Portugal, the prehistory of the Iberian peninsula Thames and Hudson, London
- Schellman, G.; Radke, U. 1997 Electron spin resonance (ESR) techniques applied to mollusc shells from South America (Chile, Argentina) and implications for Paleo sea-level curve - *Quaternary Geochronology*, 16: 465-475
- Schiegl, S.; Goldberg, P.; Bar-Yosef, O.; Weiner, S. 1996 Ash deposits in Hayonim and Kebara caves, Israel: macroscopic, microscopic and mineralogical observations, and their archaeological implications - *Journal of Archaeological Science*, 23: 763-781
- Schayes, R.; Brooke, C. J.; Kozlowitz, I.; Lheureux, M. 1967 Luminescence Dosimetry in: F. H. Attix (Ed.), *Luminescence Dosimetry*, USA EC, CONF 650637: 138
- Schwarcz, H. P. 1985 ESR studies of tooth enamel Nuclear Tracks, 10: 865-867
- Schwarcz, H. P. 1994 Current challenges in ESR dating Quaternary Geochroology, 13: 601-605
- Schwarcz, H. P.; Bietti, B.; Buhay, W. M.; Stiner, M. C.; Segre, A. 1991a On the reexamination of Grotta Guattari: Uranium-series an electron-spin-resonance dates - *Current Anthropology*, 32: 313-316
- Schwarcz, H. P.; Buhay, W. M.; Grün, R.; Valladas, H.; Tchernov, E.; Bar Yosef, O.; Vandermeersch, B. - 1989 - ESR dates for the Neanderthal site of Kebara, Israel - Journal of Archaeological Science, 16: 653-661
- Schwarcz, H. P.; Grün, R. 1992 Electron spin resonance (ESR) dating of the origin of modern man -Philosophical Transactions of the Royal Society, London, B: 145-148
- Schwarcz, H. P.; Grün, R. 1993 Electron spin resonance dating of tooth enamel from Bir Tarfani - in: F. Wendorf; R. Schild; A. E. Close (Eds.), *Egypt during the last interglacial*, Plenum Press, New York: 234-237

Schwarcz, H. P.; Grün, R. - 1993b - Electron spin resonance (ESR) dating of the lower industry in: R. Singer; B. G. Gladfelter; J. J. Wymer (Eds.), *The lowe Paleolithic site at Hoxne, England*, University of Chicago Press, Chicago: 210-213

- Schwarcz, H. P.; Grün, R.; Latham, A. G.; Mania, D.; Brunnaker, K. 1988a The Bilzingsleben archaeological site: new dating evidence - *Archaeometry*, 30: 5-17
- Schwarcz, H. P.; Grün, R.; Tobias, P. V. 1993 ESR dating studies of the Australopitecine site of Sterkfontein, South Africa Journal of Human Evolution, 26: 175-181
- Schwarcz, H. P.; Grün, R.; Mania, A. G.; Brunnaker, K. 1988 New evidence for the age of the Bilzingsleben archaeological site - *Archaeometry*, 30: 5-18
- Schwarcz, H. P.; Grün, R.; Vandermeersch, B.; Bar-Yosef, O.; Valladas, H.; Tchernov, E. 1988b - ESR dates for the hominid burial site of Qafzeh in Israel - *Journal of Human Evolution*, 17: 733-737
- Schwarcz, H. P.; Grün, R.; Vandermeersch, B.; Bar-Yosef, O; Valladas, H; Tchernov, E. 1989 -ESR dates for the hominid burial site of Qafzeh in Israel - *Journal of Archaeological Science*, 16: 653-661
- Schwarcz, H. P.; Liritzis, Y.; Dixon, A. 1980a Absolute dating of travertines from Petralona cave, Khalkidiki peninsula, Greece - Anthropos , 7: 152-173
- Seret, G.; Dricot, E.; Wansard, G. 1990 Evidence for an early glacial maximum in the French Vosges during the last glacial cycle *Nature*, 346: 453-456
- Shackleton, N. J.; Opdyke, N. 1973 Oxygen isotope and paleomagnetic stratigraphy of Equatorial Pacific core V28-238 - *Quaternary Research*, 3: 39-55
- Sherwood, J.; Barbetti, M.; Ditchburn, R.; Kimber, R. W. L.; McCabe, W.; Murray-Wallace, C. V. - 1994 - A comparative study of quaternary dating techniques applied to sedimentary deposits in southwest Victoria, Australia - Quaternary Geochronology, 13: 95-105
- Simmons, T. 1994 Archaic and modern Homo sapiens in the contact zones: evolutionary schematics and model predictions in: M. H. Nitecki, D. V. Nitecki (Eds.), Origins of anatomically modern humans, Plenum Press, N. Y.: 201-225
- Skinner A. F. 1989 ESR dosimetry and dating in aragonitic molluscs International Journal of Radiation and Applied Instrumentation, Part A, 40: 1081-1085
- Smith, F. H.- 1982 Upper Pleistocene hominid evolution in south-central Europe: a review of the evidence and analysis of trends - *Current Anthropology*, 23: 667-686
- Smith, F. H. 1984 Fossil hominids from the later Pleistocene of central Europe and the origins of modern Europeans - in: F. H. Smith (ed.), The origins of modern humans: a world survey of the fossil evidence, Alan R, Liss, New York: 1347-209
- Smith, F. H. 1991 The Neanderthals: evolutionary dead ends or ancestors to modern people? -Journal of Anthropological Research, 47: 219-238
- Smith, F. H.; Falsetti, A. B.; Donnelly, S. M. 1989 Modern human origins Yearbook of Physical Anthropology, 32: 35-68
- Smith, F. H.; Simek, J. F.; Harrill, H. S. 1989 Geographic variation in supraorbital torus reduction during the later Pleistocene (c. 80,000-15,000 BP) in: P. Mellars;
  C. B. Stringer (Eds.), The human revolution: behavioural and biological perspective on the origins of modern humans Princeton University Press, Princeton, N. J.: 172-193

- Soffer, O. 1989 The Middle to Upper Paleolithic transition on the Russian plain in: P. Mellars; C. B. Stringer (Eds.), *The human revolution: behavioural and biological perspective on the origins of modern humans*, Princeton University Press, Princeton, N. J.: 714-742
- Straus, L. G. 1983 From Mousterian to Magdalenian: cultural evolution viewed from Vasco-Cantabrian Spain and Pyrenean France - in: E. Trinkaus (ed.), *The Mousterian legacy*, BAR, 164: 73- 111
- Straus, L. G. 1986 The end of the palaeolithic in the old world BAR, Oxford
- Straus, L. G. 1990 The early Upper Paleolithic of southwest Europe Cro-Magnon adaptation in the Iberian peripheries, 40,000 -20,000 BP - in: The emergence of modern humans, an archaeological perspective-P. A. Mellars (ed), Cornell University Press, Ithaca, N. Y.: 276-302
- Straus, L. G. 1992 Iberia before the Iberians University of New Mexico Press, Albuquerque, 1992
- Straus, L.; Altuna, J.; Clark, G.; Gonzalesa, M.; Laville, H.; Leroi-Gourhan, A.; Mendez, M.; Otera, J. - 1981 - Paleoecology at La Riera (Asturias, Spain) - *Current Anthropology*, 22 (4): 655-682
- Stringer, C. B. 1982a Towards a solution to the Neanderthal problem Journal of Human Evolution, 11: 431-438
- Stringer, C. B. 1984 Ancestors: fate of the Neanderthal Natural History, 93: 6-12
- Stringer, C. B. 1985 Middle Pleistocene hominid variability and the origin of late Pleistocene humans in: E. Delson (Ed.), Ancestors, the hard evidence , Liss, N. Y.: 289-295
- Stringer, C. B. 1989 The origin of early humans : a comparison of the European and non-European evidence - in: P. Mellars, C. B. Stringer (Eds.), The human revolution: behavioural and biological perspective on the origins of modern humans -Princeton University Press, Princeton, N. J., 1989: 232-244
- Stringer, C. B. 1989 Documenting the origin of modern humans in: E. Trinkaus (ed.), *The* emergence of modern humans, Cambridge University Press, Cambridge: 670-696
- Stringer, C. B. 1990 The emergence of modern humans Scientific American (12)
- Stringer, C. B. 1998 Personal communication
- Stringer, C. B. 1993 Reconstructing recent human evolution in: M. Aitken; C. B. Stringer; P. Mellars (Eds.), The origin of modern humans and the impact of chronometric dating, Princeton University Press, Princeton, N. J.: 179-195
- Stringer, C. B.; Andrews, P. 1988 Genetic and fossil evidence for the origins of modern humans - *Science*, 239: 1263-1268
- Stringer, C. B.; Hublin, J. J.; Vandermeersch, B. 1984 The origins of anatomically modern humans in western Europe - in: F. H. Smith and F. Spencer (Eds.), The origins of modern humans, Liss, N. Y.: 51-135
- Stringer, C. B.; Gamble, C. 1993 In search of Neanderthals Thames and Hudson, London
- Stringer, C. B.; Grun, R.; Schwarcz, H.P.; Goldberg, P. 1989 ESR dates for the hominid burial site of Es Skhul in Israel *Nature*, 338: 756-758
- Stringer, C. B.; McKie, R. 1996 African Exodus Johnathan Cape, London
- Sutherland, D. G. 1990 Ice masses on the move Science, 346: 410

| Swisher, C. C. III; Rink, W. J.; Antón, S. C.; Schwarcz, H. P.; Curtis, G. H.; Symons, M. C. R.        |          |
|--|----------|
| - 1982 - Electron spin resonance as tool in archaeological dating -                                    |          |
| <i>PACT</i> , 6: 302-313   |          |
| Trinkhaus, E 1981 - Neandertal limb proportions and cold adaptation - in: C. B. Stringer (Ed.)         | ,        |
| Aspects of human evolution, Taylor and Francis, London: 187-224  |          |
| Trinkaus, E 1993 - Comments to: D. E. Lieberman, The rise and fall of seasonal mobility                |          |
| among hunter-gatherers: the case of the southern Levant, <i>Current</i>                                |          |
| Anthropology, 34 (5): 620-622  |          |
| Trinkaus, E.; Shipman, P 1993 - The Neanderthals: changing the image of mankind                        |          |
| Knopff, New York   |          |
| Utrilla, F 1986 - Nuevos datos sobre el Paleolítico Inferior y Medio de la Rioja - <i>Quadernos de</i> | <b>)</b> |
| Investigacion Historica, 12: 171-192   |          |
| Valencia, D.; Ward, R. H 1991 Using mitochondrial sequence data to stimate evolutionary                |          |
| distance - American Journal of Physical Anthropology, Supplement                                       |          |
| 12: 167-177  |          |
| Valladas, H.; Geneste, J. M.; Joron, J-L.; Chadelle, J. P 1986 - Thermoluminescence dating of          |          |
| Le Moustier (Dordogne, France) - <i>Nature</i> , 322: 452-454  |          |
| Valladas, H.; Joron, J. L.; Valladas,G.; Arensburg, B.; Bar-Yosef,O.; Belfer-Cohen, A.;                |          |
| Goldbertg, P.; Laville, H.; Meignen, L.; Rak,Y.; Tchernov, E.; Tillier, A.                             |          |
| M.; Vandermeersch, B 1987 - Thermoluminescence dates for the   |          |
| Neanderthal burial site at Kebara in Israel - Nature, 330: 159-160                                     |          |
| Valladas, H.; Reyss, J. L.; Joron, J. L.; Valladas, G.; Bar-Yosef, O.; Van Andel, T. H 1985 -          |          |
| New views n an old planet - Cambridge University Press, Cambridge                                      |          |
| Van Andel, T. H 1987a - The modern climate - in: T. H. Van Andel; S. B. Sutton (Eds), Land             |          |
| scape and people of the Franchthi region, Indiana University Press,                                    |          |
| Indianapolis: 3-20   |          |
| Van Andel, T. H 1987b - The adjacent area - in: T. H. Van Andel; S. B. Sutton (Eds), Landscap          | )e       |
| and people of the Franchthi region, Indiana University Press,  |          |
| Indianapolis: 31-54  |          |
| Van Andel, T. H.; Sutton, S. B 1987 - Landscape and people of the Francthi region - Indiana            |          |
| University Press, Indianapolis   |          |
| Vawter, L.; Brown, W Nuclear and mitochondrial DNA comparisons reveal extreme variations               | ın       |
| the molecular clock - <i>Science</i> , 234, 1986: 194-196  |          |
| Vega Toscano, L. G 1988 - El Paleolítico Medio del sureste Español y Andalucia oriental -              |          |
| Unpublished thesis, Universidad Complutense, Madrid  |          |
| Vega Toscano, L. G 1990 - La fin du Paléolithique Moyen oau sud de l'Espagne - Memoirs de              |          |
| Musee de Prehistoire de l'Ile-de-France, 3   |          |
| Vega Ioscano, L. G.; Losano, P.; Villar, A., Escarpa, U.; Kojas, I 1996 - Las industrias de la         |          |
| intertase Pleistoceno Medio-Superior en la cueva de la Carinuela (Pinar,                               |          |
| Granada) - Actos del Il Congreso de Arquelogia Peninsular, Lamora:1-14                                 |          |
| Vega Toscano, L. G.; Hoyos, M.; Kuiz Bustos, A.; Laville, H 1988 - La s quence de la grotte de         |          |
| Carinueia (Pinar, Grenade): Chronostratigraphie et Paleoecologie du                                    | ,        |
| Pleistocene superieur au sud de la penínsule iberique - in: M. Otte (ed), L                            | ,        |
| nomme de Neandertal, Actes du Colloque International de Liege,   |          |
| Universite de Liege, Vol 7: 169-180  |          |
|  |          |

-----

-----

Vega Toscano, G. - 1993 - El transito del Peleolitico mediom al Paleolitico Superior en el Sur de la peninsola Iberica - in: V. Cabrera (Ed.), El origen del hombre moderno en el suroeste de Europa, U. N. E. D.: 147-170 Vigilant, L; Stoneking, M.; Harpending, H.; Wilson, A. - 1991 - African populations and the evolution of human mitochondrial DNA - Science, 253: 1503-1507 Villa, P. - 1991 - Middle Pleistocene prehistory in Southwestern Europe: the state of our knowledge and ignorance - Journal of Anthroplogical Research, 47: 193-217 Volterra, V. - 1938 - Population growth, equilibria and extinction under specified breeding conditions - Human Biology, 10: 1-11 Volterra, V. - 1994 - Dating and provenancing of sherds from five Balsam Lake area sites -Unpublished Master's degree thesis, McMaster University Volterra, V.; Hancock, R. G. V. - 1994 - Provenancing of ancient Roman millstones -Journal of Radioanalytical and Nuclear Chemistry, 180, (1),: 37 - 44 Waechter, J. d'A. - 1951 - Excavations at Gorham's cave, Gibraltar - Proceedings of the Historical Society, 17: 83-92 Waechter, J. d'A. - 1964 - The excavation of Gorham's cave, Gibraltar, 1951-54 - Bulletin of the Institute of Archaeology, University of London, 4:189-221 Warashina, T. - 1992 - Allocation of jasper archaeological implements by means of ESR and XRF - Journal of Archaeological Science, 19: 357-373 Ward, R. H. - 1991 - On the age of our mitochondrial ancestors: evidence for deep lineage in "mongoloid populations" - American Journal of Physical Anthropology, Supplement 12 : 180-181 Way, R. - 1962 - A geography of Spain and Portugal - Methuen and Co., London Wills, C. - 1994 - Putting human genes on the map - Natural History, June 1994: 82-85 Winter, J. - 1971 - Thermoluminescence - in: F. Rainey (Ed.), Dating techniques for the archaeologist, Wolpoff, M. H. - 1985 - Human evolution at the peripheries: the pattern at the eastern edge - in: P. V. Tobias (ed.), Hominid evolution: past, present and future, Alan R. Liss, New York: 355-365 **Wolpoff**, M. H. - 1989a - Multiregional evolution: the fossil alternative to Eden - in : P. Mellars; C. B. Stringer (Eds.), The origins of modern humans: behavioural and biological perspective, Edinburgh University Press, Edinburgh Wolpoff, M. H. - 1989b - The place of the Neanderthals in human evolution - in: E. Trinkaus (Ed.), The emergence of modern humans: biological adaptations in the later Pleistocene, Cambridge University Press, Cambridge: 97-141 Wolpoff, M. H. - 1990- Theories of modern human origins, in: G. Bräuer and F. Smith (eds), Continuity or replacement : controversies in Homo sapiens evolution, Balkema, Rotterdam Wolpoff, M.; Wu, X.; Thorne, A. G. - 1984 - Modern Homo sapiens origins: a general theory of hominid evolution involving the fossil evidence from east Asia, in: F. H. Smith and F. Spencer (Eds.), *The origins of modern humans:* a world survey of fossil evidence, Alan R. Liss, N. Y.: 411-414 Wolpoff, M. H.; Spuhler, J. N.; Smith, F. H.; Radovcic, J.; Pope, G.; Frayer, D. W.; Eckhardt, R.; Clark, G. - 1988 - Modern human origins - Science, 241: 772-773

- Wolpoff, M. H.; Thorne, A.G.; Smith, F. H.; Frayer, D. W.; Pope, G. G. 1994 Multiregional evolution: a world-wide source for modern human population - in: M. H. Nitecki and D. V. Nitecki (Eds.), Origins of anatomically modern humans, Plenum Press, N. Y.: 175-199
- Wright, L. E.; Schwarcz, H. P. 1996 Infrared and isotopic evidence for diagenesis of bone apatite at Dos Pilas, Guatemala: paleodietary implications - *Journal of Archaeological Science*, 23: 933-944
- Yamashita, T.; Ohnishi, H.; Yasuno, Y.; Takenaga, M.; Yamamoto, O. 1972 Thermoluminescent dosimeter (TLD)II. Construction and characteristics of CaSO<sub>4</sub>:Tm TLD -Matsushita Electric Industrial Co. Ltd., Technical Report 18, 2
- Yokoyama, Y.-1989-Direct gamma-ray spectrometric dating of Anteneandertalian and Neandertalian human remains - in: *Hominidae* - G. Giacomini (ed), Preceedings of the 2nd International Congress of Human Paleontology, Turin
- Yokoyama, Y.; Quaegebeur, J-P; Bibron, R.; Leger, C.; Zouridakis, N. M.; Shen, G-J. 1982a -Electron spin resonance and U/Th dating of Petralona Man site -Anthropos, 9, 11-12
- Yokoyama, Y.; Nguyen, H-V; Quaegebeur, J. P.; Poupeau, G. 1982b Some problems encoun tered in the evaluation of annual dose rate in the electron spin resonance dating of fossil bones *PACT*, 6: 103-115
- Yokoyama, Y.; Quaegebeur, J-P; Bibron, R.; Leger, C.; Chappasz, N; Michelot, C.; Shen, J-G.; Nguyen, H-V - 1983 - ESR dating of stalagmites of the Caune de l'Arago, the Grotte du Lazaret, the Grotte du Vallonet and the Abrie Pie Lombard: a comparison with the U-Th method - *PACT*, 9: 381-389
- Yokoyama, Y.; Falgueres, C.; Bibron, R. 1988 Direct dating of Neanderthalian remains and animal bones by the non-destructive gamma-ray spectrometry: comparison with other methods - in : M. Otte (ed), L'homme de Néandertal, 1: 135-141
- Zeuner, F. E. 1953 The chronology of the Mousterian at Gorham's cave, Gibraltar -Proceedings of the Prehistoric Society, 8:180-188
- Zeuner, F. E.; Sutcliffe, A 1964 Preliminary report on the Mammalia of Gorham's cave, Gibraltar - in: J. d'A. Waechter (Ed.), The excavation of Gorham's cave, Gibraltar, Bulletin of the Institute of Archaeology, 4: 213-216
- Zhou, L. P.; McDermott, F.; Rhodes, E. J.; Marseglia, E. A.; Mellars, P. A. 1997 ESR and massspectrometric uranium-series dating studies of a mammoth tooth from Stanton Harcourt, Oxfordshire, England - Quaternary Geochronology, 16: 445-454
- Zollikofer, C; Ponce de Leon , M. S.; Martin, R. D.; Stucki, P. 1995 Neanderthal computer skulls - Nature, 375: 283-285
- Zubrow, E. 1989 The demographic modelling of Neanderthal extinction in: P. Mellars; C. B. Stringer (Eds.), *The human revolution: behavioural and biological perspective on the origins of modern humans* - Princeton University Press, Princeton, N. J.: 212-231

250