ESR DATING OF PLEISTOCENE DEPOSITS
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by

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ABSTRACT

Near Medicine Hat, Alberta, Pleistocene deposits are exposed on numerous bluffs along the South Saskatchewan River. The Quaternary beds are very fossiliferous, yielding a large number of mammal bones and teeth. The enamel (calcium hydroxyapatite) portion of teeth within the sediments, is used to date the deposits with the electron spin resonance (ESR) dating method. The ESR age is strongly dependent on the dose rate which in turn depends on the uranium accumulation in the tooth fragments. Two U uptake models are used based on an early and a continuous, linear accumulation of uranium.

At young, well dated sites the ESR ages are in relatively good agreement with independent estimates. For slightly older samples (approx. 100 ka), the linear U uptake model comes closer to the estimated age at one site, but at another site, the early U uptake model agrees more favourably with the estimated age. Based on the ESR ages, several older sites can be assigned to interglacial stages 7, 9 and 13, however, these ages are much younger than those determined by faunal and stratigraphic correlation (>0.5 Ma). Samples with extremely high U contents in dentine and enamel gave unreliable ESR results. These samples may have experienced a late stage of U accumulation.
ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION
1.1 SCOPE AND OBJECTIVE

Dating by electron spin resonance (ESR) is based upon the ability of minerals to accumulate trapped electrons during geologic time. The trapped electrons result from ionization caused by natural radiation from the decay of radioactive elements within and/or surrounding the minerals and from cosmic rays. Detection of the unpaired, trapped electrons is made possible with ESR spectroscopy. With time, the natural radiation causes a steady increase of the trapped electron population. The ESR signal, which is proportional to the population of free electrons, will therefore also increase.

The ESR age of the sample can be deduced from the following simplified formula,

\[ \text{Age} = \frac{\text{Accumulated Dose}}{\text{Annual Dose}}. \] (1.1)

The accumulated dose (AD) which the sample attained since the time of formation is evaluated by ESR spectroscopy. The annual dose that the sample received is determined from the analysis of U, Th and K of the sample and its surroundings.

The objective of this thesis is to apply ESR dating to Quaternary deposits. The feasibility of the method depends on the following conditions:
1) The sample to be dated must have formed during the depositional period.
2) The sample must not have undergone subsequent recrystallization or other alteration.
3) The sample must yield an ESR signal that accurately reflects the accumulated dose.
4) The various traps in the crystal lattice to be used for dating, must not be saturated with electrons.
5) The traps must have remained stable with time.
6) Electrons, once trapped, must not have spontaneously leached out of the traps.
7) All the parameters that contribute to the annual dose must be known.

The Quaternary deposits near Medicine Hat, Alberta, were chosen because they contain units which are very fossiliferous. The bone and teeth fragments in these units were laid down with the sediment and are therefore possible candidates for ESR dating. The enamel portion of teeth was chosen for dating because it consists almost completely of crystalline calcium phosphate (96-97%; Driessens, 1980) with a crystallographic organization resembling calcium hydroxyapatite, $\text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2$ (Weatherall and Robinson, 1973). ESR dating of apatite has been applied by Zeller et al. (1967), and their conclusions indicate that it is a suitable mineral for ESR dating. Bones, ivory tusks and the dentine/cementum
portion of teeth were not used. They contain organic components up to 25% (Driessens, 1980), are less dense and more porous than enamel, and are therefore more susceptible to alteration after deposition.

1.2 QUATERNARY GEOLOGY OF SOUTHERN ALBERTA

Quaternary sediments in the Prairies of southern Alberta and Saskatchewan (Fig. 1.1) have been extensively described by A. M. Stalker (eg. Stalker 1963, 1969, 1972, and 1976). C. S. Churcher has studied and identified bones in the same areas (eg. Stalker and Churcher, 1972 and 1982). Quaternary deposits in the Foothills of southwestern Alberta, where both Laurentide and Cordilleran tills overlie each other, are described by Alley and Harris (1974) and Stalker and Harrison (1977). The sediments around Cypress Hills, southern Alberta, one of the few areas in Canada that escaped glaciation during the Quaternary, are described by Westgate (1972). The most recent Quaternary composite stratigraphic section for the southwestern Canadian Prairies is given by Stalker and Churcher (1982).

1.2.1 PROBLEMS ENCOUNTERED IN QUATERNARY STRATIGRAPHY

The Quaternary composite section of southern Alberta (Table 1.2; Stalker and Churcher, 1982) relates specific
FIG. 1.1. Map of Alberta and Saskatchewan showing location of sample sites. More precise locations of the Medicine Hat sites are shown in Fig. 3.1. The approximate coordinates for the other sites are:

B - 49°55'N 111°30'W
E - 50°57'40"N 110°1'W
R - 52°15'5"N 106°35'25"W
W - 50°40'25"N 107°51'50"W
B = Bow Island Site; E = Empress Site
M = Medicine Hat Sites; R = Riddell Site
W = Wellsch Valley Site
interglacial periods with vertebrate faunal assemblages. The section is based on the assumption that there were only four major continental glaciations during Pleistocene time: the Wisconsin, Illinoian, Kansan and Nebraskan. This has led to a number of problems in interpretation. First, in the Medicine Hat area, names given to glacial and stadial units beyond the range of carbon-14 dating have been obtained from the identification of vertebrate fossils. These names do not necessarily correlate directly with the nomenclature used by glacial geologists, and are generally older (Stalker, 1969).

The second problem is that the four continental glacial stage names have been used too loosely in the past. Too often, at any given locality the youngest Pleistocene glacial cycle has been labelled the Wisconsin, the first interglacial cycle the Sangamon, the second glacial cycle Illinoian and so on. This sort of "counting from the top" naming process has lead to a considerable overlap of the glacial and interglacial time spans (Fig. 1.2).

Lastly, Shackleton and Opdyke's (1973 and 1976) oxygen isotope records of deep sea cores, indicate that rather than 4, there have been over 20 glaciations during the Pleistocene (Gibbons et al., 1984). Figure 1.3 shows that interval "A" representing the time period from 0 to 0.9 Ma, had 10 major glacial cycles. Intervals "B" and "C" spanning the time
FIG. 1.2. Usage of pre-Wisconsin stage terms. The chronology for the Iowa and Nebraska sequences are based on fission track dating of volcanic glass shards. The chronology for the Gulf of Mexico and South Atlantic sequences are based on paleomagnetic dating. (After Boellstorff, 1978).
FIG. 1.3. Oxygen isotope record for entire Pleistocene core V28-239 (Shackleton and Opdyke, 1976). Based on the duration and amplitude of the glacial/interglacial cycles, the Pleistocene record can be subdivided into 3 intervals, "A", "B", and "C". X denotes a glacial stage. (From Gibbons et al., 1984)
The diagram illustrates the relationship between age, depth, and oxygen-isotope stage. It shows three intervals labeled "A," "B," and "C," with corresponding cycles and noted durations.

**Interval A**
- 10 cycles
- Duration and perhaps lesser amplitude than after 0.9 m.y.

**Interval B**
- 10 cycles
- Shorter duration and perhaps lesser amplitude than after 0.9 m.y.

**Interval C**
- 4? cycles
- Similar duration but lesser (?) amplitude than after 0.9 m.y.

The diagram also includes references to "Pre-Pleistocene."
period 0.9 to 1.87 Ma, had 14 glacial cycles but of shorter
duration and lesser amplitude. Furthermore, reef terraces in
Barbados, dated by Bender et al. (1979), suggest that there
were at least 7 interglacial cycles during the past 640,000
years. Their results agree favourably with the oxygen
isotope stages as defined by Shackleton and Opdyke (1973).
Each interglacial isotope stage back to 640,000 years is
represented by at least one Barbados reef tract.

The record of glaciation as defined by the presence of a
till unit is a selective one because glacial advances will
generally obliterate tills deposited by less extensive
previous glacial advances. This process of obliteration of a
till unit when overlapped by a later, more extensive glacial
advance is termed "obliterative overlap". Gibbons et al.
(1984) applied a probability analysis model to study the
impact of obliterative overlap on the completeness of a
glacial record. Their probability model considers the
following 3 assumptions:

1) The distribution of relative distances of glacial
   advances is random over time.
2) Tills of a given succession are restricted to the
   same glacial pathway.
3) The only till units to survive obliterative overlap
   are those deposited at greater distances than any
   subsequent till deposit.
A close examination of Fig. 1.3 suggests that only the 10 glaciations during the past 0.9 Ma need to be considered because older glacial cycles were of lesser amplitude and therefore would have been susceptible to obliteration by the first major glaciation of interval "A". On the basis of the probability model, if 10 glacial episodes took place, the number of surviving tills and the probability of their survival is given in Table 1.1.

<table>
<thead>
<tr>
<th>No. of surviving tills</th>
<th>Probability of survival</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10%</td>
</tr>
<tr>
<td>2</td>
<td>28%</td>
</tr>
<tr>
<td>3</td>
<td>32%</td>
</tr>
<tr>
<td>4</td>
<td>20%</td>
</tr>
<tr>
<td>&gt;5</td>
<td>10%</td>
</tr>
</tbody>
</table>

**TABLE 1.1.** The probability of the survival of till deposits after 10 glacial episodes. (Gibbons et al., 1984)

There is a 90% chance that after 10 glacial episodes only 1 to 4 tills will survive. The predicted probabilities are close to the observed 1 to 4 and more commonly 2 to 3 till units represented in the deposits of a given glacial
valley or ice-sheet lobe. The numerical mismatch between the
typical 2 to 3 till units of the global Pleistocene and the
number of major Pleistocene glacial-interglacial oscilla-
tions (probably 10 but perhaps as many as 24), matches the
expected outcome of the process of obliteratorive overlap,
functioning in a random manner over time (Gibbons et al.,
1984).

1.2.2 THE MEDICINE HAT AREA

Medicine Hat is situated on the South Saskatchewan River
in southern Alberta (Fig. 1.1). A complex system of buried
valleys, ranging in age from possibly pre-Quaternary to pre
"Classical Wisconsin", criss-crosses the area near Medicine
Hat. The buried valleys are filled with material deposited
by successive glaciers, lakes, aggrading rivers and wind
(Stalker, 1969). The deposits are now exposed on numerous
bluffs along the modern South Saskatchewan River. Stalker
(1969) noted that the stratigraphy is highly variable, not
only from bluff to bluff, but even within any single, long
exposure. A strong glaciation will generally have had a
drastic effect on the features left by earlier glaciers. This
has led to an intermittent and very incomplete sedimentary
record. The interpretation is therefore difficult, for it
involves dealing with scattered remnants of sediment, com-
monly of unknown age or correlating between different types
of features (Stalker and Harrison, 1977).

Near Medicine Hat, the Quaternary beds are very fossiliferous, yielding a large number of mammal bones. In certain areas, up to eight till sheets are present, alternating with several bone bearing beds (Stalker, 1972). However, even with such well exposed sequences, there has still been difficulty in relating the glacial (till) deposits here to sequences found elsewhere in North America. Stalker (1972) has even found it difficult to correlate these deposits with others found upstream along the Oldman River.

All the tills in the area were deposited by Laurentide glaciers and are identifiable as such by the presence of Shield Stone (stones derived from the Canadian Shield to the east and northeast). Cordilleran tills are confined to the area west of Lethbridge, Alberta (Stalker and Harrison, 1977). Since no single exposure exhibits a complete record, the composite stratigraphic section of the southwestern Prairies (Table 1.2; Stalker and Churcher, 1982) is based on information obtained from 12 separate sections near Medicine Hat and one from the Wellsch Valley site, 40 km north of Swift Current, Saskatchewan (Fig. 1.1). For want of a better alternative, Stalker and Churcher (1982) used the midcontinental chronology, which is based on the assumption that there were only 4 major glaciations during Pleistocene time.
TABLE 1.2. Pleistocene composite stratigraphic section of the southwestern Canadian Prairies (modified from Stalker and Churcher, 1982). \( C = ^{14}C, \ F = \text{fauna}, \ FT = \text{fission-track}, \ M = \text{paleomagnetism}, \) and US = uranium-series.

<table>
<thead>
<tr>
<th>UNIT NUMBER</th>
<th>TYPE OF DEPOSIT</th>
<th>ORIGIN OF DEPOSIT</th>
<th># OF SPECIES IN FOSSILIF. UNIT</th>
<th>TIME SUBDIVISION</th>
<th>ESTIMATED AGES (years)</th>
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</thead>
<tbody>
<tr>
<td>XXX</td>
<td>silt &amp; sand</td>
<td>river slip-off slopes and floodplains</td>
<td>2</td>
<td>Postglacial</td>
<td>1,100 (C) 6,600 (C) 8,100 (C)</td>
</tr>
<tr>
<td>XXIX</td>
<td>sand &amp; gravel</td>
<td>river terraces</td>
<td>5</td>
<td></td>
<td>9,500 (US) 11,200 (C)</td>
</tr>
<tr>
<td>XXXIII</td>
<td>sand &amp; gravel</td>
<td>deltas &amp; river channels</td>
<td>2</td>
<td></td>
<td>14,000 (F)</td>
</tr>
<tr>
<td>XVII</td>
<td>till</td>
<td>directly from glacier</td>
<td></td>
<td></td>
<td>Young Wisconsin</td>
</tr>
<tr>
<td>XXVI</td>
<td>sand &amp; gravel</td>
<td>stream floodplains and shallow ponds</td>
<td>6</td>
<td></td>
<td>20,000 (F) 73,000 (US)</td>
</tr>
<tr>
<td>XXV</td>
<td>till</td>
<td>directly from glacier</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XXIV</td>
<td>silt</td>
<td>stream floodplains</td>
<td></td>
<td></td>
<td>Mid Wisconsin</td>
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<td>XXXIII</td>
<td>organic silt</td>
<td>river floodplains</td>
<td></td>
<td></td>
<td>24,000 (C) 28,600 (C) 430,000 (FT)</td>
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<td>lakes, river floodplains</td>
<td>14</td>
<td></td>
<td>38,000 (C) 45,000 (F)</td>
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<tr>
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<td>sand</td>
<td>river deposition</td>
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<td>Older Wisconsin</td>
</tr>
<tr>
<td>IX</td>
<td>till</td>
<td>directly from glacier</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VIII</td>
<td>till</td>
<td>directly from glacier</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td>clay &amp; silt</td>
<td>stream &amp; lake deposition</td>
<td>3</td>
<td></td>
<td>&gt;38,000 (C) 65,000 (F)</td>
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<tr>
<td>VI</td>
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<tr>
<td>V</td>
<td>till</td>
<td>directly from glacier</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XIV</td>
<td>sand &amp; gravel</td>
<td>stream floodplains and braided stream channels</td>
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(continued)
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<tr>
<th>UNIT NUMBER</th>
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<th>ORIGIN OF DEPOSIT</th>
<th># OF SPECIES</th>
<th>TIME SUBDIVISION</th>
<th>ESTIMATED AGES (years)</th>
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<td>sand &amp; gravel</td>
<td>stream floodplains and braided stream channels</td>
<td>31</td>
<td>Sangamon</td>
<td>72,000 (US) 100,000 (F)</td>
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<tr>
<td>XI</td>
<td>gravel</td>
<td>stream lag from till</td>
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</tr>
<tr>
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<td>till</td>
<td>directly from glacier</td>
<td></td>
<td>Illinoian</td>
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</tr>
<tr>
<td>VIII</td>
<td>till</td>
<td>directly from glacier</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VIIb</td>
<td>silt &amp; sand</td>
<td>preglacial lake deposition</td>
<td>3</td>
<td>Yarmouthian</td>
<td>195,000 (US) 420,000 (F)</td>
</tr>
<tr>
<td>VIIa</td>
<td>clay &amp; silt</td>
<td>preglacial lake deposition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>clay, sand &amp; gravel beds</td>
<td>river floodplains</td>
<td></td>
<td>Late Kansan</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>gravel, minor clay</td>
<td>river floodplains and channels</td>
<td>11</td>
<td></td>
<td>&gt;200,000 (US) 600,000 (F)</td>
</tr>
<tr>
<td>IV</td>
<td>sand &amp; gravel</td>
<td>flash floods, slope wash &amp; streams</td>
<td></td>
<td>Nebraskan</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>silt &amp; sand with pebble bands</td>
<td>flash floods, slope wash &amp; streams</td>
<td>17</td>
<td></td>
<td>2 reversals (P) 690,000 (FT) 1,750,000 (F)</td>
</tr>
<tr>
<td>II</td>
<td>gravel</td>
<td>flash floods, slope wash &amp; streams</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>bedrock</td>
<td></td>
<td></td>
<td></td>
<td>Cretaceous</td>
</tr>
</tbody>
</table>
The section at Wellsch Valley consists of one bone bearing unit, resting unconformably on bedrock or gravel deposits and is overlain by at least 4 till units. The bones here are more mineralized than bones from any of the horizons at Medicine Hat. The fauna of this unit, probably greater than 1.5 Ma, also indicates an age older than any at Medicine Hat (Stalker and Churcher, 1972). The base of this section (ie. units II - IV in Table 1.2) is therefore placed at the bottom of the composite stratigraphic record. The age of the four or so tills above the bone bearing unit cannot be estimated, nor can they be correlated with tills found elsewhere in the Prairies.

The numerous bluffs near Medicine Hat each contain from 1 to 4 bone bearing horizons. Based on the faunal assemblage, 8 different bone bearing units can be distinguished (Stalker and Churcher, 1982). The oldest unit (V) contains a fauna of mid to late "Kansan" age and is placed above the Wellsch Valley units in the composite stratigraphic record. The remaining fossiliferous units are interbedded with tills and other sediments and comprise the rest of the stratigraphic record up to the present (Table 1.2).

Although the composite record extends intermittently back to approximately 2 Ma, it only records a small part of Quaternary time. The gap of more than one million years
between deposition of units IV and V alone encompasses more time than is recorded by all the other Quaternary deposits shown (Stalker and Churcher, 1982).

1.2.3 INDEPENDENT CHRONOLOGICAL CONTROL

Radiocarbon dating has been carried out on bones, wood, and buried soils within the various units. The oldest unit datable by carbon-14 is unit XXII, and yields an age of 38,000 years near its base (Stalker, 1976). The age estimates of the units beyond the range of radiocarbon dating are almost entirely based on the chronology obtained from the vertebrate fauna. In certain sections, there is some difficulty in determining the age of the fauna because of intermingling of taxa that are usually found separated in time (Stalker and Churcher, 1972). Although the faunal assemblage can in most cases be satisfactorily correlated with faunas found elsewhere on the continent, assignment of absolute ages to the various faunas is more difficult, due to uncertainties in the boundary dates of land mammal faunal stages (eg. compare: Flint, 1971, Fig.21-2 and Table 29D; Harington, 1984, Fig. 1).

Ages of till deposits are estimated, and are based on their position with respect to beds containing a well-defined faunal assemblage. For example, the lowest till deposit
(unit VIII) is assigned an "Illinoian" age, and is based on its position above beds containing "Yarmouthian" vertebrate fossils and below beds containing a well-developed "Sangamon" vertebrate fauna (Stalker, 1976).

Paleomagnetic work was carried out on a number of interglacial sediments (Foster and Stalker, 1976; Barendregt and Stalker, 1978). Unit III at Wellsch Valley was the only site where magnetically reversed sediments were observed.

Fission track dating on a vitric tuff bed 4 m above the fossiliferous horizon of unit III at Wellsch Valley was attempted by Westgate et al. (1978). Ages of 0.63±0.06 and 0.69±0.11 Ma were obtained. The dates should be regarded as minimum estimates, given the susceptibility of tracks in glass to annealing. Westgate et al. (1978) also obtained a fission track date of 0.43 Ma on a vitric ash, 7 m above a bone-bearing horizon in unit XII near Medicine Hat. Radiocarbon dates of 37,900±1,000 and 38,700±1,100 a from 1 m above the same horizon were reported by Stalker (1976). However, the magnitude of the ages suggests that they are probably infinite radiocarbon dates.

$^{230}$Th and $^{231}$Pa dating of bones from a number of sites near Medicine Hat was attempted by Szabo et al. (1973). In general, there is a large discrepancy between the uranium
series dates and the age estimates derived by other means (ie. faunal correlation; see Table 1.2). The discrepancies could arise from:

1) incorrect identification of the faunas;
2) incorrect correlation of the faunas with faunas elsewhere;
3) incorrect age estimates or age restrictions for the reference faunas;
4) incorrect stratigraphic correlation of units between various bluffs;
5) incorrect results from isotope dating, and
6) inclusion of bones reworked from earlier deposits which would result in older dates.

Since there was no alternative means of checking the ages of the various units, causes for the discrepancies were indeterminable.
CHAPTER 2

PRINCIPLES OF ESR DATING
2.1 **ELECTRON TRAPPING**

Radioactive elements within minerals and in the surrounding environment emit alpha-, beta-, and gamma-particles as a result of their decay. This radiation as well as cosmic rays, can ionize atoms or molecules within the mineral. The ionization process leading to trapping of electrons is shown in Fig. 2.1. The ionized electrons will diffuse within the crystal (in its conduction band) until they are trapped at charge defect centers (electron or hole traps) in the crystal lattice structure or until they recombine with electron holes. Trapped electrons in tooth enamel are associated with CO$_3^{3-}$ radicals within the inorganic hydroxyapatite matrix (Cevc et al., 1972; Sato, 1979). The paramagnetic CO$_3^{3-}$ center forms due to capture of an electron by the CO$_2^{2-}$ radical which replaces PO$_4^{3-}$ in the apatite structure (Gilinskaya et al., 1971).

2.2 **PHYSICAL BASIS OF ESR**

An unpaired trapped electron is characterized by its intrinsic angular momentum and associated magnetic moment. The magnetic moment ($\vec{\mu}_S$) is related to the angular momentum (spin $\frac{3}{2}$) by the following equation:

$$\vec{\mu}_S = -g\mu_B \frac{\hbar}{\hbar}$$  \hspace{1cm} (2.1)
FIG. 2.1. Illustration of the trapping process.

$E_a =$ activation energy, i.e. trap depth.
where \( g \) is the Landé-factor or the "electron free-spin g value" \( (g = 2.0023 \text{ for a free electron}) \), \( \mu_B \) is the Bohr magneton, and \( \hbar = h/2\pi \) \( (h \) is Planck's constant).

When unpaired electrons are placed in an external static magnetic field, the direction of the electron spin vector may be either the same or opposite to the magnetic field vector. Only these two states with spin quantum number \( (M_s) +1/2 \) and \(-1/2 \) are allowed according to the laws of quantum mechanics (Fig. 2.2). The two states are energetically different (Fig. 2.3). The splitting of the initial energy level \( (E_0) \) into two discrete energy levels \( E_+ \) and \( E_- \) by an external magnetic field is known as the Zeeman effect. The energy difference \( (\Delta E) \) between these two levels is,

\[
\Delta E = g\mu_B H
\]

where \( H \) is the external magnetic field strength (Gauss).

If an external electromagnetic wave (microwave) of frequency \( \nu \) is applied to the electrons, flipping of spins from one direction to another will occur if the condition \( h\nu = \Delta E \) is met. The microwave is absorbed due to the transition from one state to another. This absorption of microwave energy is called electron spin resonance (ESR).
FIG. 2.2. Electron spin orientation in an external magnetic field ($\omega =$ resonance frequency $= 2\pi \nu$ ).
FIG. 2.3. Zeeman splitting into two energy levels for free electrons ($s = 1/2$) by an external magnetic field.
2.3 ESR SPECTROMETER

A Bruker ER100D ESR spectrometer with a TE4101 cavity, of the Chemistry Department at McMaster University was used for all the samples analysed. An ESR spectrometer is principally built of three components (Fig. 2.4):

1) An electromagnet and its associated power supply.
2) A klystron that generates microwaves and is attached by a waveguide to the resonant cavity suspended between the magnetic polepieces.
3) Electronic circuitry for signal detection, processing and recording.

A powdered sample is placed in a glass tube which is inserted into the resonant cavity. The klystron generates microwave radiation which is conducted to the resonant cavity by means of a waveguide. The normal microwave frequency ($\nu$) used is near 9.5 GHz (X-band) at a magnetic field $H = 3,500$ G. Since the frequency used is dependent on the geometry of the waveguide and resonant cavity, $\nu$ is kept constant while $H$ is varied. Resonance occurs when $H = h\nu/g\mu_B$ (ie. $h\nu = \Delta E = g\mu_B H$). Microwave energy is absorbed and an absorption signal (Fig. 2.5, top) is picked up by a detector. The signal is processed by additional electronic circuitry and is transmitted to an X-Y recorder which plots the first derivative of the ESR signal ($I$) against magnetic field strength ($H$). (Fig.
FIG. 2.4. A block diagram of an ESR spectrometer.
FIG. 2.5. ESR absorption line and its first derivative (ESR signal) obtained by a magnetic field modulation ($H_m$).
Absorption Intensity $I$

Magnetic Field $H$

ESR signal $dI/dH$

$H_m$
2.5, bottom). The intensity of the ESR signal is proportional to the total number of trapped electrons of a particular g-value.

2.4 ESR DATING - GENERAL METHOD

ESR dating of geological materials was first suggested by Zeller et al. (1967). This was followed by McMorris (1969) and then more vigorously by Ikeya (1975, 1978, etc). Presently there are over 30 laboratories engaged in ESR dating. The most recent papers covering the major aspects of ESR dating in Quaternary geology are by Hennig and Grdn (1983) and Ikeya (1985).

The ESR signal intensity of a natural mineral (Fig. 2.6) is proportional to the total number of unpaired electrons that have accumulated in electron traps since time of formation of the sample. The trapped electron population in turn is proportional to the radiation dose (or accumulated dose - AD) that the sample has received over this time period. If the effective annual dose emitted from radioactive elements within (internal dose rate - IDR) and surrounding (external dose rate - EDR) the sample can be determined, then the age of the sample is deduced by the following simplified equation,

\[ \text{Age (a)} = \frac{\text{AD (rad)}}{\text{EDR + IDR (rad/a)}}. \]  

\[ (2.3) \]
FIG. 2.6. ESR signal of tooth enamel. The signal intensity at \( g = 2.0015 \) is used for ESR dating.
Tooth enamel
20mg
9.765 GHz
0.5 Gpp
2 mW

MAGNETIC FIELD (G)
The accumulated dose (AD) that a sample received during geologic time is determined by the additive dose method (Fig. 2.7). Several equal, homogeneous aliquots of a sample are exposed to successive increasing doses of gamma irradiation and their corresponding increasing ESR signal is recorded. The AD is determined by extrapolating a linear fit through the data points to zero ESR intensity.

AD determination of extremely old samples or samples exposed to a high annual dose may be difficult, since such samples can display saturation effects. The effect is one where a major fraction of the electron traps are filled with electrons and additional gamma irradiation results in a non-linear increase of the ESR signal. This non-linearity will continue until all the traps are filled and maximum ESR intensity (\(I_{\text{max}}\)) is attained (Fig. 2.8a). Apers et al. (1981) proposed a model that could lead to reliable values of AD if saturation effects are observed. The model is based on plotting the ESR intensity in terms of \(-\ln(1 - I/I_{\text{max}})\) instead of \(I\). Such an approach can lead to reasonable linear graphs with good correlation coefficients (Fig. 2.8b).

As noted above, the annual dose in most cases, consists of two parts, the external or environmental dose rate (EDR) and the internal dose rate (IDR). The EDR can be determined by three methods:
FIG. 2.7. Determination of the accumulated dose (AD) by the additive dose method.
Sample 84M19e
Camel tooth enamel

ESR SIGNAL INTENSITY (a.u.)

GAMMA DOSE (krad)
FIG. 2.8. An alternative method of AD evaluation if saturation effects are observed upon additional exposure to gamma doses. $I_{\text{max}}$ = maximum ESR signal intensity attained under extremely high gamma dose exposures. In Fig. 2.8a, $a$ = linear extrapolation from points up to 50 krads, $b$ = exponential fit (from Hennig and Grön, 1983).
1) Chemical analysis of the surrounding sediment for U, Th and K.

2) Gamma ray spectroscopy at the sampling site.

3) TL dosimetry, - burying a TL dosimeter at the same location as the sample for a period of one year.

The IDR can be determined by analysing the sample for U and its daughter isotopes. Th and K are generally found in negligible concentrations within tooth enamel.
CHAPTER 3

ANALYTICAL PROCEDURE
3.1 SAMPLE PREPARATION

Fossil teeth were collected from five sites in southern Alberta and Saskatchewan. (Fig. 1.1). The Medicine Hat Site (Fig. 3.1), consists of 7 separate exposures along the South Saskatchewan River and one (Frisch Site) occurs in an outlier of Quaternary sediments, several kilometers distant from the river. Additional samples came from the collection of Dr. C. S. Churcher, University of Toronto.

All the samples are fragments of tooth from large land mammals, predominantly horse, elephant, camel and bison. The tooth fragments are composed mainly of enamel; most have varying amounts of dentine/cementum attached. The sediment surrounding the sample was collected for U, Th and K analysis so that an environmental dose rate (EDR) could be determined.

The samples were cleaned with water to remove any remaining sediment. The thickness of the enamel was measured and the geometry of the samples noted for future beta dose rate calculations. The dentine/cementum was chiseled away from the enamel and any remaining dentine/cementum as well as the outer 100 micrometers of enamel was removed with a high speed, dental drill. The cleaned enamel was ground with a mortar and pestle until it passed through a 0.5 mm sieve. The dentine/cementum and some of the enamel were saved for U
FIG. 3.1. Map of Medicine Hat district showing location of sites along the South Saskatchewan River where fossil samples were collected.
analysis so that the dentine and enamel dose rate contribution could be determined.

3.2 SPECTROMETRY PROCEDURE

All enamel samples analysed on the ESR spectrometer were transferred into a 4 mm pyrex tube sealed at one end. The tube was marked at a determined height to ensure that all the samples would be positioned at the same location in the cavity. Each sample was run 3 times and the signal intensity at $g = 2.0015$ (Fig. 2.6) was recorded and averaged. After numerous runs, the data revealed that one run per aliquot of sample was sufficient to yield an AD with a good correlation coefficient. For tooth enamel the best instrumental settings were found to be:

- Microwave power: 2 mW
- Modulation amplitude: 0.5 Gpp
- Sweep width: 100 G
- Sweep time: 200 s
- Time constant: 10 to 50 ms.

3.3 ARTIFICIAL IRRADIATION

Six aliquots, each 20 mg in weight were taken from the cleaned, crushed enamel. Five aliquots were exposed to successively increasing doses of artificial gamma rays from a
$^{60}$Co source. All irradiations were performed at the Gamma Irradiation Facility, McMaster Nuclear Reactor. The samples were irradiated in 4 mm diameter glass tubing with 1 mm thick walls. The tubes were aligned so that all samples were the same distance from the irradiation source (i.e. there was no shielding by other samples). One enamel sample was also irradiated in glass tubing with 2 mm wall thickness to determine if any irradiating rays with lower energies would be attenuated by the additional thickness of glass and to test whether the "buildup" of secondary beta rays was sufficient in the 4 mm tubes. The difference in the AD of the sample irradiated in tubes with 1 mm and 2 mm thick walls was negligible.

A test of the possible effect of dose rate on the determination of AD is shown in Fig. 3.2. The agreement between AD's becomes progressively poorer as lower dose rates are approached. A possibility for this phenomena is that sample irradiation at lower dose rates took place further away from the $^{60}$Co source, closer to the backwall of the irradiation chamber. In this area, scattered gamma rays of lower energies may become more prominent, resulting in inconsistent irradiation of the sample. Since higher dose rates gave consistent AD's, all samples were irradiated at a dose rate of 10 or 20 krad/hr. Other experiments with lithium fluoride (Tochilin and Goldstein, 1966) demonstrated that a dose rate as high as $10^{10}$ rads per second can be used.
Fig. 3.2. Dependence of AD on the gamma dose rate of the artificial irradiation from a $^{60}$Co source. The 3 different symbols represent 3 separate tests.
CHAPTER 4

DETERMINATION OF AD
4.1 SATURATION

Five aliquots of each sample were irradiated at doses of 20, 40, 60, 80 and 100 krad respectively. In all cases the ESR signal intensity increased linearly over the 100 krad dose range. Two samples with AD's of 2.2 and 120 krad were intentionally irradiated to a dose of 500 krad to test for saturation (Figs. 4.1 and 4.2). Signs of saturation appeared at a dose (artificial + AD) of 150 and 370 krad respectively.

Fig. 4.3a demonstrates that as saturation is approached, ESR signal intensity is no longer linearly proportional to the dose the sample received. Onset of saturation is characterized by a decrease in the slope of the ESR intensity (ie. a decrease in the sensitivity of the sample to irradiation). The lower sensitivity will result in an overestimate of the AD (Fig. 4.3a & b).

A comparison of normalized ESR sensitivity with the AD of 35 enamel samples is shown in Fig. 4.4. At higher AD's there is a decrease of the ESR sensitivity. The decrease in sensitivity is attributed to saturation; the trend being similar to the saturation conditions encountered in samples 84LN3 and 84RG3 (Fig. 4.1 and 4.2). However, the sensitivity of all visibly altered samples is low regardless of their AD (Fig. 4.4). Therefore in some cases (ie. when alteration has
FIG. 4.1. Bison tooth irradiated at high gamma dose levels to test for saturation.
FIG. 4.2. Horse tooth irradiated at high gamma dose levels to test for saturation.
FIG. 4.3. The effects of saturation on ESR signal growth and the AD.
a) 

![Graph showing relationship between ESR intensity and AD (krad) or Time (a) or Dose (krad).]

b) 

![Graph showing normalized ESR intensity vs. AD (krad).]
FIG. 4.4. Variation of ESR sensitivity with increasing AD.
occurred but is not visible) the decrease in sensitivity could be attributed to "aging" of the samples (ie. paramagnetic CO$_3^{2-}$ centers and/or CO$_2^{3-}$ ions are either removed or CO$_3^{2-}$ are bound with other radicals). It is advisable to perform saturation tests on samples with AD's greater than 50 krad. If saturation conditions are revealed, then the AD must be determined by the method described by Apers et al. (1981).

4.2 SAMPLE WEIGHT AND GRAIN SIZE

From the powdered enamel, at least 0.4 g is removed for U analysis. Since most of the samples are small, only a small portion will be left for ESR analysis. A test was therefore performed to find the minimum weight required for a reliable AD determination. The results displayed in Fig. 4.5 show that a sample weight as low as 10 mg can be used. The deviation of the 5 mg sample is attributed to an increase in the weighing error. This is supported by a decrease in the 5 mg AD correlation coefficient.

To determine if the grain size of powdered enamel has any effect on the AD, a sample was subdivided into 4 grain size fractions (Fig. 4.6). The AD does not appear to be dependent on enamel grain size. Also, the similar AD's of the fine and coarse fraction indicates that grinding has no influence on the ESR signal. The 0.150 - 0.250 mm fraction
FIG. 4.5. The AD of an elephant tooth determined at different weights.
OCR: ELEPHANT TOOTH

MEAN 19.5
S.D. 0.7

SAMPLE WEIGHT (mg)
FIG. 4.6. Dependence of AD on enamel grain size.
OCR: ELEPHANT TOOTH

ENAMEL GRAIN SIZE (mm)

AD (krad)

Mean 20.2
S.D. 1.2
is the easiest to work with and was therefore used for all the analysis. The <0.150 mm fraction leaves a fine powder in the sample tube after the enamel is removed. To prevent contamination the sample tube should be cleaned between each analysis if this size fraction is used. The >0.250 mm fraction was not used because the coarse grains tend to "bridge" when the sample is transferred into the analyzing tube.

4.3 MODULATION AMPLITUDE AND MICROWAVE POWER

Due to the low signal-to-noise ratio of the ESR signal, it is transformed into an amplitude modulation signal, rather than being directly amplified. This is achieved by modulating the magnetic field \( H \) by a small additional magnetic field \( H_m \) generated by a 100 kHz oscillator (Fig. 2.4). To prevent masking of any part of the signal and to get the highest resolution, a low modulation should be used (ie. the amplitude of the additional magnetic field \( H_m \) should not exceed the linewidth of the ESR absorption signal (Fig. 2.5).

In order to determine the appropriate modulation setting for tooth enamel, the modulation amplitude was varied from 0.2 to 5 Gpp (Gauss peak to peak). Over this amplitude range, the modulation had no influence on the AD (Fig. 4.7). However, certain enamel samples display an additional signal
FIG. 4.7. Dependence of AD on modulation amplitude.
OCR: ELEPHANT TOOTH

![Graph](image)

- ESR INTENSITY (a.u.)
- GAMMA DOSE (krad)

Points and lines indicate different gamma doses.
that interferes with the trapped electron signal at \( g = 2.0015 \). This additional peak (Fig. 4.8) is attributed to alanine radicals (Ikeya, 1981) and can be detected in tooth enamel at lower modulation amplitudes (eg. 0.5 Gpp).

Hennig and Grön (1983) found that the AD of certain speleothem samples can be dependent on the microwave power generated by the klystron. The AD of an enamel sample determined at variable microwave powers, reveals that AD is not influenced by microwave power (Fig. 4.9). Other experiments (Grön, 1985) showed saturation effects of enamel at a microwave power of about 6 mW and hence, it is advisable to use a lower microwave power of 2 mW or less.

4.4 SIGNAL FADEING AND BLEACHING

Anomalous fading (ie. other than thermal) has been observed in TL investigations of certain minerals (Wintle, 1977). To test for abnormal fading, Grön and Invernati (1985) irradiated a recent elephant tooth with a gamma dose of 10 krad. One year after irradiation the enamel sample was prepared for AD determination. The derived AD of 10.5 krad indicates that anomalous fading can be neglected.

At Empress, Alberta, a majority of samples were found lying on the surface, exposed to sunlight. The AD of two
FIG. 4.8. ESR signal of a natural and 20 krad irradiated enamel sample. A modulation of 0.5 Gpp is used to differentiate the alanine signal from the free electron signal ($g_1$).
Sample 84EM10
Elephant tooth
9.769 GHz  +20 krad
0.5 Gpp
2mW
20mg
AD= 84 krad

Natural

Signal intensity

(a)

---

3460 3470 3480 3490 3500 3510

Magnetic field (G)

(b)

Alanine Radicals

g⊥
g∥
FIG. 4.9. Dependence of AD on microwave power.
OCR: ELEPHANT TOOTH
exposed samples (84EM5: $AD = 4.51$ krad; 84EM8: $AD = 6.68$ krad) do not show any marked difference from a buried sample (84EM4a: $AD = 5.22$ krad). This indicates that for enamel, the ESR signal at $g = 2.0015$ is not affected by bleaching and therefore sample preparation and analysis may be carried out under normal light conditions.

4.5 **EFFECT OF FLUORINE AND CARBONATE CONTENT**

With time, fluorine ions are taken up by hydroxyapatite, displacing the OH$^-$ radical in the molecule. The process is dependent upon the removal of part of the organic component so that the apatite molecule is accessible to groundwater (Molleson, 1981). Ikeya (1985) believes that an increase of fluorine content in bone will result in a lower AD determination. Gilinskaya et al. (1971), Cevc et al. (1972) and Sato (1979) concluded that the ESR signal ($g = 2.0015$ in this study) of tooth enamel is due to paramagnetic CO$_3^{2-}$ centers at PO$_4^{3-}$ sites in the apatite structure. Since fluorine uptake involves exchange with OH$^-$ radicals, it is not clear how this would effect the AD.

The relationship between ESR sensitivity and CO$_3$/PO$_4$ ratio in tooth enamel is shown in Fig. 4.10. If the ESR signal is associated with CO$_3^{2-}$ centers, then samples with lower CO$_3$/PO$_4$ ratios are expected to saturate at lower doses.
FIG. 4.10. Dependence of ESR sensitivity on the CO$_3$/PO$_4$ ratio of tooth enamel.
However, a decrease in ESR sensitivity with a corresponding decrease in CO$_3$/PO$_4$ in enamel is not observed (Fig. 4.10). Since CO$_3$ in hydroxyapatite can replace both PO$_4^{2-}$ and OH$^-$, it is not certain whether the CO$_3$ groups at OH$^-$ sites are paramagnetic. The comparison between CO$_3$(total)/PO$_4$ ratio and ESR sensitivity is therefore not a good test for determining the paramagnetic nature of CO$_3^-$ centers.

4.6 STABILITY OF ELECTRON TRAPS

The mean-life ($\tau$) of trapped electrons exposed to a temperature T (°K) is give by,

$$\tau = s^{-1} \exp(E_a/kT) \quad (4.1)$$

where $k$ is the Boltzman's constant (8.617 x $10^{-5}$ eV/°K), $E_a$ (eV) is the activation energy required to release the electrons from their traps (ie. trap depth, see Fig. 2.1), and $s$ (sec$^{-1}$) is the frequency factor which expresses the attempts of the trapped charges to escape.

The mean-life can be determined by isothermal annealing experiments, where several aliquots of enamel are heated at different temperatures. For each annealing temperature, the ESR intensity ($I$) is recorded with increasing time ($t$) (Fig. 4.11a). At $I_{1/2}$ the half-life ($t_{1/2}$) is determined. The mean-life ($\tau$) of trapped electrons at a temperature T is given by the expression,
FIG. 4.11.  a) Determination of mean-life ($T$) by isothermal annealing experiments.

b) Arrhenius plot of mean-life obtained by isothermal annealing experiments. Linear extrapolation of the experimental mean-lives gives the estimated mean-life at environmental temperatures.
\[ \tau(T) = \frac{t_{1/2}}{\ln 2}. \] (4.2)

An Arrhenius plot of \( \log(\tau) \) vs \( 1/T \) should then yield a linear relation (Fig. 4.11b). The mean-life of the sample at normal environmental temperatures can then be calculated by extrapolation.

For enamel, the mean-life is difficult to determine because the signal is very stable at low temperatures (Hennig and Grönl, 1983), e.g. holding a sample for two weeks at 140 °C has very little effect on signal intensity. An accurate determination of the mean-life would therefore involve very long laboratory time intervals. A second problem is that at elevated temperatures, the ESR signal begins to change its form (split), which can lead to inaccurate measurements of the signal intensity.

Isothermal annealing experiments on apatite (bone) by Ikeya (1985) resulted in a mean-life estimate of 10 Ma. Well within this estimate, is a 3 Ma ESR age estimate on a fossil tooth which agrees favourably with the expected geological age (Grönl, unpublished). It appears that for Pleistocene age fossil teeth exposed to normal environmental temperatures, the trapped electrons can be considered stable.
CHAPTER 5

DETERMINATION OF THE ANNUAL DOSE
5.1 DOSE RATE

The dose rate is defined as dose per unit time. In ESR dating, the term annual dose is used and is measured in rads (or millirads, mrad) per year. The radiation dose a sample receives over geologic time originates from alpha, beta and gamma particles emitted by the radionuclides of U and Th decay chains and by $^{40}$K present in the surrounding environment and in the sample. If the samples were lying on or near the surface for extensive time periods, then gamma ray contribution by cosmic radiation must also be considered.

The uranium content of enamel and dentine/cementum was determined by delayed neutron activation analysis (DNAA). The surrounding matrix was also analysed for U and Th by DNAA and for K by XRF. Table 5.1 (Hennig and Grönn, 1983) is used to convert the concentration levels of the radioactive elements to alpha, beta and gamma dose rate values. Similar radiation dose rate data was determined by Bell (1976, 1977 and 1979). New dose rate values calculated by Nambi and Aitken (pers. comm., 1985) do not show great deviations (<5%) from Table 5.1.

Determination of the annual dose for tooth enamel usually consists of 3 separate dose rate calculations; the environmental (EDR), the dentine (DDR) and the internal (enamel,
TABLE 5.1. Dose rates (in mrad/a) for 1 ppm of uranium series, 1 ppm of thorium series, 1% of potassium and 100 ppm of rubidium. (From Hennig and Grøn, 1983).

<table>
<thead>
<tr>
<th>Radioisotope or Decay Chain from-to (abund.)</th>
<th>$\alpha$-energies (MeV)</th>
<th>$\alpha$-dose rates (mrad/a)</th>
<th>$\beta$-energies (MeV)</th>
<th>$\beta$-dose rate (mrad/a)</th>
<th>$\gamma$-energies (MeV)</th>
<th>$\gamma$-dose rate (mrad/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{U} \rightarrow ^{206}\text{Pb}$ (0.9928)</td>
<td>42.866</td>
<td>257.60</td>
<td>2.2939</td>
<td>14.39</td>
<td>1.8634</td>
<td>11.64</td>
</tr>
<tr>
<td>$^{234}\text{U} \rightarrow ^{206}\text{Pb}$ (0.9928)</td>
<td>38.681</td>
<td>241.48</td>
<td>1.4108</td>
<td>8.81</td>
<td>1.8041</td>
<td>11.26</td>
</tr>
<tr>
<td>$^{230}\text{Th} \rightarrow ^{206}\text{Pb}$ (0.9928)</td>
<td>33.922</td>
<td>211.77</td>
<td>1.4108</td>
<td>8.81</td>
<td>1.7891</td>
<td>11.17</td>
</tr>
<tr>
<td>$^{226}\text{Ra} \rightarrow ^{206}\text{Pb}$ (0.9928)</td>
<td>29.264</td>
<td>182.69</td>
<td>1.3938</td>
<td>8.73</td>
<td>1.7885</td>
<td>11.16</td>
</tr>
<tr>
<td>$^{222}\text{Rn} \rightarrow ^{206}\text{Pb}$ (0.9928)</td>
<td>24.489</td>
<td>152.88</td>
<td>1.3956</td>
<td>8.70</td>
<td>1.7795</td>
<td>11.11</td>
</tr>
<tr>
<td>$^{235}\text{U} \rightarrow ^{207}\text{Pb}$ (0.0072)</td>
<td>41.776</td>
<td>12.16</td>
<td>1.2011</td>
<td>0.35</td>
<td>0.5740</td>
<td>0.17</td>
</tr>
<tr>
<td>$^{231}\text{Pa} \rightarrow ^{207}\text{Pb}$ (0.0072)</td>
<td>37.386</td>
<td>10.89</td>
<td>1.075</td>
<td>0.31</td>
<td>0.4104</td>
<td>0.12</td>
</tr>
<tr>
<td>Both $U$-Decay Series (1.0)</td>
<td></td>
<td>279.76</td>
<td></td>
<td>14.67</td>
<td></td>
<td>11.81</td>
</tr>
<tr>
<td>$^{230}\text{Th} \rightarrow ^{208}\text{Pb}$</td>
<td>35.398</td>
<td>73.74</td>
<td>1.4061</td>
<td>2.89</td>
<td>2.427</td>
<td>4.98</td>
</tr>
<tr>
<td>Potassium ($^{40}\text{K} = 0.01157$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% $\text{K}_2\text{O}$</td>
<td></td>
<td>0.503 (0.89)</td>
<td>68.93</td>
<td>1.461 (0.11)</td>
<td>20.69</td>
<td></td>
</tr>
<tr>
<td>1% K</td>
<td></td>
<td>83.03</td>
<td></td>
<td></td>
<td>24.92</td>
<td></td>
</tr>
<tr>
<td>100 ppm Rubidium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.64</td>
<td></td>
</tr>
</tbody>
</table>
 IDR) contribution. The effective penetration range of alpha, beta and gamma particles, approximately 25 micrometers, 2 mm and 30 cm respectively (for sample density of 2.7 g/cm³) (Aitken, 1974), must also be considered in the dose rate calculations.

5.2 ENVIRONMENTAL DOSE RATE (EDR)

The environmental dose rate (EDR) is determined from the U, Th and K content of the surrounding matrix. Since the effective range of gamma rays is considerably greater than the thickness of the samples, gamma ray attenuation by the sample can be neglected. Beta particle contribution to EDR is dependent on sample geometry and is discussed in detail in chapter 5.5. Since the outer 100 micrometers of enamel is shaved away, alpha particle contribution from the surrounding matrix can be neglected.

The $^{234}$U/$^{238}$U and $^{230}$Th/$^{234}$U activity ratios of sediments from 3 different sites (of different ages) are all near 1.0, indicating the U-decay chain is in equilibrium. Beta and gamma dose rates for the entire U chain (Table 5.1) are therefore used.

At ground level, cosmic rays contribute 30 mrad/a to the dose rate and at a depth of 2 m it decreases to a level of 15
mrad/a. The cosmic ray dose rate (CDR) at a depth \( x \) (cm) can be calculated by the equation of Yokoyama et al. (1982),

\[
CDR = 5.2 \exp(-x/20) + 12.1 \exp(-x/160) + 12.5 \exp(-x/2500) \tag{5.1}
\]

where \( \rho \) is the density \((g/cm^3)\) of the matrix. Since all samples were buried at depths of several meters, cosmic ray contribution was considered negligible. Contribution from rubidium, radiocarbon and other radioactive elements is also negligible when compared to the dose rate originating from U, Th, K and their daughter products.

5.3 **DENTINE DOSE RATE (DDR)**

Most of the tooth fragments were buried with dentine/cementum still attached to the enamel. Dentine in living animals contains virtually no uranium. The fossilized dentine however, contains 4.2 to 1820 ppm U. Charalambous and Papastefanou (1977) found that the radioactivity in fossil bones is only due to the radionuclides of the uranium series. Radionuclides of the thorium series and \(^{40}K\) are absent and can therefore be neglected.

The number of gamma rays emanating from U within the dentine, compared to that from the surrounding environment (i.e. 30 cm effective radius) is very small. Its effect on enamel can therefore be considered negligible. Since the outermost 100 micrometers of enamel is shaved away, alpha
particles from dentine/cementum do not contribute to the dose rate. Only beta particles, which have an average effective range of approximately 2 mm, must be considered when determining the dentine's contribution (DDR) to the dose rate. The overall beta contribution is dependent on sample geometry and is discussed in chapter 5.5.

5.4 INTERNAL DOSE RATE (IDR)

Uranium concentration levels in the enamel range from 0.3 to 28.8 ppm. The internal dose rate (IDR) is dependent entirely on alpha and beta particles emitted by radionuclides of the U-decay chains. As for dentine, the gamma ray contribution can be neglected. The alpha efficiency or k-factor (ie. the effectiveness of alpha dose to beta or gamma dose) is known to vary for different minerals. Grön and Invernati (1985) experimentally determined the k-factor for enamel to be 0.15. DeCanniere et al. (1986) also obtained an alpha efficiency factor of 0.15±0.02 for mammoth tooth enamel. This value was used for all dose rate calculations.

For internal beta rays, a beta correction factor (G₁) is required, since some of the particles will penetrate through into the dentine and sediment. The correction factor is obtained from the following relationship,
\[ G_I = 1 - G_E \]  \hspace{1cm} (5.2)

where \( G_E \) is the beta ray attenuation correction factor for external radiation (sediment and dentine). The derivation of \( G_E \) is discussed in chapter 5.5.

5.5 BETA DOSE ATTENUATION

Contribution to the dose rate by beta rays is strongly dependent on the sample geometry (ie. the spatial distribution of dentine with respect to the enamel) and the thickness of the enamel. Buried tooth fragments are usually found in one of the following three situations (Fig. 5.1):

1) A separate fragment of enamel, detached from dentine.

2) A tooth fragment with dentine/cementum attached to one side of the enamel.

3) A tooth fragment with dentine/cementum attached on both sides of the enamel.

Consideration of the sample geometry is essential for precise dose rate calculations. Usually the geometry of a sample is such that the U concentration is different on either side of an enamel layer. It is therefore advisable to consider each side of the enamel separately and then sum the beta contributions to the total dose rate.
FIG. 5.1. Tooth fragments within a sediment can be found in three different configurations.
Yokoyama et al. (1982) and Grdn (1986) proposed a simplified model for determining the beta ray attenuation factor for external radiation. Such a model has to be applied because the range of the beta particles from the sediment and/or dentine is comparable to the thickness of the shell or enamel analysed. The effective beta range $P$ (cm) of a beta particle with maximum energy $E_{\text{max}}$ (MeV) penetrating into a sample of density $\rho$ (g/cm$^3$) is,

$$P = 0.0825((1 + 22.4E_{\text{max}}^2)^{-0.5} - 1)/\rho.$$  \hspace{1cm} (5.3)

For external beta rays, the attenuation correction factor $G_E$, is the fraction of the total beta dose that is received by an enamel sample of thickness $d$ (cm). It can be calculated using the following equation (for $2\pi$ geometry),

$$G_E = 0.5 \left(1 - \exp(\mu d)\right)/(\mu d)$$ \hspace{1cm} (5.4)

where $\mu$ is the attenuation coefficient per cm ($\mu = 3.3\rho$).

The beta correction factor for an enamel sample where a thickness $x$ (cm) has been removed from the total thickness $d$ is (Aitken et al., 1985; Grdn, 1986),

$$G_E(d-x) = [0.5/(\mu(d-x))][\exp(-\mu x) - \exp(-\mu d)].$$ \hspace{1cm} (5.5)

The integral beta dose $D$ received by an enamel layer subjected to a beta source of infinite matrix dose $D_o$ is,

$$D = G_E \times D_o.$$ \hspace{1cm} (5.6)

Within a given decay chain there are several beta emitters (ie. beta decays). Each beta emitter can have several
transitions with a definite frequency f of occurrence. When observing a large number of transitions, the beta particles have an energy distribution ranging from zero up to some maximum value \( E_{\text{max}} \) (Martin and Blichert-Toft, 1970). A beta transition to a particular energy level is characterized by \( E_{\text{max}} \) and the average energy \( E_{\text{av}} \) of the emitted beta particles.

For each beta emitter within a decay chain, the beta correction factor \( G_{\text{EB}} \) is,

\[
G_{\text{EB}} = \frac{\sum_{T=1}^{n} G_{\text{E}}(T) \cdot f_{T} \cdot E_{\text{av}}(T)}{\sum_{T=1}^{n} E_{\text{av}}(T)}
\]  

(5.7)

where \( n \) represents the total number of transitions. For the entire decay chain, the beta correction factor \( G_{\text{EC}} \) is,

\[
G_{\text{EC}} = \frac{\sum_{b=1}^{N} G_{\text{EB}}(b) \cdot f_{b} \cdot E_{\text{av}}(b)}{\sum_{b=1}^{N} E_{\text{av}}(b)}
\]  

(5.8)

where \( N \) represents the total number of beta emitters. The integral beta doses obtained by the above method are shown in Fig. 5.2. For U and Th decay chains, the results agree favourably with the experimental attenuation curves of Aitken et al. (1985). For K, there are at present no experimental attenuation curves to compare with.

The beta ray contribution from sediment can be derived directly from Fig. 5.2, assuming the decay chains are in equilibrium. Dentine/cementum however, accumulates uranium after deposition. Hence the \( ^{238}\text{U} \) decay chain in dentine will display \( ^{230}\text{Th}/^{234}\text{U} \) disequilibrium. Fig. 5.3 shows that the
FIG. 5.2. Integral beta doses in samples (2π geometry) for $^{40}$K, $^{238}$U, $^{235}$U and $^{232}$Th decay chains. (Grün, 1986).
K-40 decay
U-238 decay chain
U-235 decay chain
Th-232 decay chain
\( \varphi = 2.7 \text{ [g/cm}^3\text{]} \)

integral beta dose

thickness of sample
FIG. 5.3. Integral beta doses in samples (2π geometry) for beta decays between $^{238}\text{U} - ^{230}\text{Th}$ & $^{230}\text{Th} - ^{206}\text{Pb}$. (Grön, 1986).
integral beta doses produced by beta emitters from $^{238}\text{U}$ to $^{230}\text{Th}$ are significantly greater than those from $^{230}\text{Th}$ to $^{206}\text{Pb}$ (Grön, 1986). The $^{230}\text{Th}/^{234}\text{U}$ disequilibrium and corresponding different beta correction factors have to be considered for more precise beta dose rate calculations.

The integral beta doses received by a sample from the $^{232}\text{Th}$, $^{238}\text{U}$ & $^{235}\text{U}$ decay chains and $^{40}\text{K}$ decay is summarized in Table 5.2. For the $^{238}\text{U}$ decay chain, values above and below $^{230}\text{Th}$ are given. It should be noted that this beta ray attenuation model represents a somewhat simplified approach because the shapes of beta spectra of single transitions may vary. Also, most of the thin enamel samples have rough surfaces of varying thickness, which makes it difficult to accurately determine the beta ray contribution.

5.6 **WATER ATTENUATION FACTOR**

Part of the alpha, beta and gamma energies can be absorbed by water, causing a reduction of the effective annual dose. A water attenuation factor must therefore be included in the dose rate calculation. The correction factor $W_C$ is obtained from the following formula (Bowman, 1976),

$$W_C = (1 + H_C K/(1 - K))^{-1}$$

(5.9)

where $K$ is the water content (wt.%/100) of the enamel, dentine or sediment and $H_C$ is a correction factor for the
TABLE 5.2. Integral beta doses (as percentage of the infinite matrix dose) for samples with densities of
(a) 2.70 g/cm³ - calcite, and (b) 2.95 g/cm³ - hydroxyapatite/aragonite, irradiated from one
side (2π geometry).

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>(232_{\text{Th}})</th>
<th>(238_{\text{U}} - 230_{\text{Th}})</th>
<th>(230_{\text{Th}} - 206_{\text{pb}})</th>
<th>(235_{\text{U}})</th>
<th>(40_{\text{K}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>42.8 42.6</td>
<td>48.7 48.6</td>
<td>44.8 44.7</td>
<td>43.2 43.0</td>
<td>49.0 48.9</td>
</tr>
<tr>
<td>0.05</td>
<td>40.3 40.6</td>
<td>47.4 47.2</td>
<td>43.1 42.9</td>
<td>40.6 40.3</td>
<td>47.5 47.3</td>
</tr>
<tr>
<td>0.1</td>
<td>38.6 38.2</td>
<td>45.6 45.3</td>
<td>40.8 40.4</td>
<td>37.9 37.5</td>
<td>45.2 44.8</td>
</tr>
<tr>
<td>0.2</td>
<td>35.1 34.5</td>
<td>42.9 42.5</td>
<td>37.0 36.3</td>
<td>34.0 33.3</td>
<td>41.1 40.3</td>
</tr>
<tr>
<td>0.3</td>
<td>32.3 31.6</td>
<td>40.6 40.0</td>
<td>33.7 32.9</td>
<td>30.9 30.1</td>
<td>37.4 36.5</td>
</tr>
<tr>
<td>0.4</td>
<td>29.9 29.1</td>
<td>38.5 37.8</td>
<td>31.0 30.0</td>
<td>28.2 27.4</td>
<td>34.2 33.0</td>
</tr>
<tr>
<td>0.5</td>
<td>27.9 27.0</td>
<td>27.3 27.7</td>
<td>28.6 27.6</td>
<td>26.0 25.0</td>
<td>31.4 30.2</td>
</tr>
<tr>
<td>0.6</td>
<td>26.4 25.1</td>
<td>34.8 33.9</td>
<td>26.5 25.4</td>
<td>23.9 22.9</td>
<td>28.8 27.6</td>
</tr>
<tr>
<td>0.8</td>
<td>23.0 22.0</td>
<td>31.6 30.5</td>
<td>23.0 22.0</td>
<td>20.6 19.5</td>
<td>24.7 23.3</td>
</tr>
<tr>
<td>1.0</td>
<td>20.5 19.5</td>
<td>28.8 27.6</td>
<td>20.3 19.3</td>
<td>17.9 16.9</td>
<td>21.3 20.0</td>
</tr>
<tr>
<td>1.2</td>
<td>18.4 17.4</td>
<td>26.4 25.1</td>
<td>18.1 17.1</td>
<td>15.7 14.7</td>
<td>18.7 17.4</td>
</tr>
<tr>
<td>1.4</td>
<td>16.6 15.7</td>
<td>24.2 23.0</td>
<td>16.4 15.4</td>
<td>14.0 13.0</td>
<td>16.5 15.3</td>
</tr>
<tr>
<td>1.6</td>
<td>15.2 14.2</td>
<td>22.3 21.1</td>
<td>14.9 13.9</td>
<td>12.5 11.6</td>
<td>14.7 13.6</td>
</tr>
<tr>
<td>2.0</td>
<td>12.8 11.9</td>
<td>19.2 18.0</td>
<td>12.5 11.7</td>
<td>10.3 9.5</td>
<td>12.1 11.1</td>
</tr>
<tr>
<td>2.5</td>
<td>10.6 9.8</td>
<td>16.2 15.0</td>
<td>10.5 9.7</td>
<td>8.3 7.7</td>
<td>9.8 8.9</td>
</tr>
<tr>
<td>3.0</td>
<td>9.0 8.3</td>
<td>13.9 12.8</td>
<td>8.9 8.3</td>
<td>7.0 6.4</td>
<td>8.2 7.5</td>
</tr>
</tbody>
</table>
energy absorption by water and has values of 1.49, 1.25 and 1.14 for alpha, beta and gamma rays respectively (Aitken, 1974). Some groups use $H_\gamma = 1.0$.

Teeth from living animals have a water content of 0.9 to 2.5% in enamel, 8 to 16% in dentine and up to 32% in cementum (Weatherell and Robinson, 1973). During fossilization, inorganic minerals present in solutions which enter the samples from the exterior will precipitate, filling in any internal voids (Badone and Farquhar, 1982). Fossilized samples can therefore be considered to have a negligible water content.

The water content of the surrounding sediment depends on the nature of the sediment (eg. clay, sand, gravel) and the degree of cementation and compaction. Since the sediment samples had dried to some extent between the time they were collected and analysed, the water content was not determined. A water content of 10 wt% (20% by volume) was therefore assumed for all sediment samples. Although this value may have a high degree of error, its effect on the ESR age is not great. For an arbitrary sample, Table 5.3 demonstrates that a sediment with a water content of 20±10 wt.% (40±20% by vol.) implies an uncertainty of only 3.8% in the ESR age. It should be noted that the water content may have fluctuated in the past. But as Table 5.3 demonstrates, the uncertainty of the water content will only lead to small errors in the ESR age.
TABLE 5.3. Dependence of the error in the ESR age on the uncertainty in the water content of the sediment.

For an arbitrary sample:

$AD = 10 \text{ krad}$

$U = 1 \text{ ppm in enamel}$

$U = 100 \text{ ppm in dentine}$

$\frac{234U}{238U} = 1.5$

$k = 0.15$

Sediment has: $U = 2 \text{ ppm}$

$Th = 6 \text{ ppm}$

$K_2O = 1.6\%$

<table>
<thead>
<tr>
<th>Water Content (wt. %)</th>
<th>Uncertainty of Water Content (%)</th>
<th>Error in ESR Age (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>±10</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>±20</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>±40</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>±50</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>±60</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>±80</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>±100</td>
<td>7.6</td>
</tr>
</tbody>
</table>
5.7 RADIUM AND RADON LOSS

$^{226}$Ra and $^{222}$Rn deficiencies in fossil bones have been reported by a number of authors (eg. Charalambous and Papastefanou, 1977; Ikeya, 1982; Yokoyama et al., 1982). Due to the high geochemical mobility of radium, it can be leached out from samples by percolating water. Chemically inert radon gas can escape by diffusion. In terms of dose rates, $^{226}$Ra leaching can be treated the same as $^{222}$Rn loss, since the difference between the nuclides is the emission of only one alpha particle. No separate correction for the loss of $^{226}$Ra has been made. The effect of 50% loss of $^{226}$Ra would be comparable to that of $^{222}$Rn loss; in fact it is unlikely that more than a few percent of $^{226}$Ra would be lost from the relatively compact dentine, or from enamel.

In most cases, the uranium concentration in the samples is considerably higher than in the surrounding sediment. $^{222}$Rn loss from dentine (and enamel, if it has a high U concentration) should therefore be incorporated in the dose rate calculation. Failure to do so can result in an overestimate of the annual dose. Charalambous and Papastefanou (1977) calculated radon loss in fossil bones to range from 30 to 65%. Since enamel and dentine have a lower porosity than bone, the dose rate calculations are based on no radon loss as well as a continuous radon loss of 50%. Radon
loss from the surrounding sediment can be neglected, since the thick sequences can be considered to behave as closed systems.

5.8 URANIUM DISEQUILIBRIUM

During fossilization, uranium is incorporated into dentine/cementum and enamel. The $^{230}$Th and $^{231}$Pa radio-nuclides are not fixed with uranium since they are insoluble in water which percolates through the sediment. Samples of Quaternary age will therefore exhibit some degree of disequilibrium, particularly with regard to $^{234}$U, $^{230}$Th and $^{231}$Pa. Dose rate corrections must be applied to the U-decay chains to take into account any excess $^{234}$U and deficient $^{230}$Th and $^{231}$Pa. The annual dose therefore becomes time dependent, increasing according to the growth of uranium daughter nuclides (Fig. 5.4).

For enamel and dentine, the dose rate $D(t)$ (i.e. IDR(t) and DDR(t)) can be calculated using a modified equation of Ikeya (1982 & 1985),

$$D(t) = D_{238} + D_{235} + D_{234}(r_0 - 1)\exp(-\lambda_{234}t) - D_{234}\exp(-\lambda_{234}t) - D_{230}(1 - (230\text{Th}/238\text{U})t)$$

where $t$ is the time since formation, $D_{238}$, $D_{235}$, $D_{234}$, $D_{231}$ & $D_{230}$ are the effective dose rates of the U-series decays from $^{238}$U to $^{206}$Pb, $^{235}$U to $^{207}$Pb, $^{234}$U to $^{230}$Th, $^{231}$Pa to $^{207}$Pb & $^{230}$Th to $^{206}$Pb respectively, and $r_0$ is the initial $^{234}$U/$^{238}$U.
FIG. 5.4. Increase with age of the average annual dose by the uranium series radionuclides for 1 ppm U. $^{238}\text{U} = 99.28\%, \quad ^{235}\text{U} = 0.72\%, \quad (^{230}\text{Th}/^{234}\text{U})_0 = 0$, $(^{231}\text{Pa}/^{235}\text{U})_0 = 0$, and $(^{234}\text{U}/^{238}\text{U})_0 = 1.0$. 
activity ratio. To avoid measurement of the $^{230}$Th/$^{238}$U activity ratio, equation 5.10 can be rewritten as,

$$D(t) = D_{238} + D_{235} + D_{234}(r_0 - 1)\exp(-\lambda_{234}t) - D_{231}\exp(-\lambda_{234}t)$$

$$-D_{230}(\exp(-\lambda_{230}t) - (r_0 - 1)\exp(-\lambda_{234}t) - \exp(-\lambda_{230}t)\lambda_{230}/\lambda_{230} - \lambda_{234})) \quad (5.11)$$

The first two terms of the equation are due to $^{238}$U & $^{235}$U alone, the third term to excess of $^{234}$U, and the fourth and fifth terms to insufficient buildup of $^{231}$Pa & $^{230}$Th.

Equation 5.11 contains two unknowns, the initial $^{234}$U/$^{238}$U activity ratio ($r_0$) and the time $t$. From the Medicine Hat area, the $^{234}$U/$^{238}$U ratio of 8 bone samples ranging in age from 11,000 to >200,000 a, have an average value of 1.41±.08 (Szabo et al., 1973). An initial $^{234}$U/$^{238}$U ratio of 1.41 is therefore assumed and used in all age calculations. The time $t$ is calculated iteratively and is discussed in chapter 5.10.

5.9 URANIUM ACCUMULATION

The fossil teeth in this study have uranium concentrations ranging from 4.2 to 1,820 ppm in dentine/cementum and 0.3 to 28.8 ppm in enamel. One of the main problems in the attempt to date these samples lies in determining the nature of uranium uptake during fossilization. The two most frequently used models are based on either rapid uranium uptake shortly after deposition of the tooth or continuous, linear
uranium accumulation during the total burial history. The annual dose is strongly dependent on the model used and can result in a deviation of the ESR age by a factor of 2.

A comparison of U-series and $^{14}$C ages of 8 bone samples from varied geological environments, indicates that the average time lag for U uptake is about 2,700 a (Szabo, 1980). Concordant $^{230}$Th and $^{231}$Pa dates obtained on several samples from the Medicine Hat area (Szabo et al., 1973) indicates that after U fixation, the bones behaved as closed systems. U-series dating of fossil teeth by McKinney (1978) also suggests early U uptake in enamel. Dentine and bone, however, gave anomalous U-series ages, suggesting open system behaviour.

A study of the radioactivity of fossil bones of various geological ages was carried out by Charalambous and Papa-stefanou (1977). Their results show that older Pliocene to Upper Miocene bones have throughout a higher U content than younger samples of Holocene to Pleistocene age. This suggests that U uptake may be a continuous process. It also indicates that Pleistocene samples have not reached saturation and are still able to accumulate uranium. Similar results were reported by Hennig and Grön (1983). Ikeya (1982) also noted that more comparable ESR ages for bones can be obtained if a linear uranium accumulation model is used.
In this thesis, dose rate calculations for models of both early and continuous linear uranium accumulation will be used.

5.10 EARLY URANIUM UPTAKE MODEL

For samples which accumulate uranium very early and subsequently remain as closed systems, the dose rate $D(t)$ can be calculated using equation 5.11. The U uptake is assumed to be instantaneous in both the enamel and dentine. The total dose $T_{DE}$ can be obtained by integrating $D(t)$ from $t = 0$ to $t = T$,

$$T_{DE} = \int_0^T D(t)dt. \quad (5.12)$$

$T_{DE}$ can now be expressed as,

$$T_{DE} = D_{238U} + D_{235U} + D_{234U} (r_0 - 1) \left( 1 - \exp(-\lambda_{234U}T) \right) / \lambda_{234}$$

$$- D_{231U} \left( 1 - \exp(-\lambda_{231U}T) \right) / \lambda_{231} - D_{230U} \left( 1 - \exp(-\lambda_{230U}T) \right) / \lambda_{230}$$

$$- (r_0 - 1) \left( 1 - (\lambda_{230U}\exp(-\lambda_{234U}T) - \lambda_{234U}\exp(-\lambda_{230U}T)) / (\lambda_{230U} - \lambda_{234U}) \right) / \lambda_{230} \quad (5.13)$$

where the symbols have the same meaning as in equation 5.10.

For enamel,

$$T_{DE} = \left( \sum_{i=1}^{3} T_{DE}(i) \right) + EDR \cdot T \quad (5.14)$$

where $T_{DE1}$, $T_{DE2}$, $T_{DE3}$ and $EDR \cdot T$ correspond to the total dose fraction received from dentine layer 1, dentine layer 2, enamel and the surrounding environment respectively.

The age $T$ (a) of the sample is derived by iterating equation 5.14 until $T_{DE}$ is equal to the experimentally derived AD. The calculation is easily carried out with a
computer program (Appendix II). The program takes into account all the dose rate parameters discussed in chapter 5.

5.11 CONTINUOUS LINEAR URANIUM UPTAKE MODEL

If uranium accumulation in both dentine and enamel progressed in a continuous, linear manner, then the total dose TD_L can be expressed as (Ikeya, 1982),

\[ TD_L = \left( \frac{C_u}{T} \right) \int_0^T TDE(t) dt \]  \hspace{1cm} (5.15)

where \( C_u \) is the present uranium concentration. Incorporating \( C_u \) into \( D_{238}, D_{235}, D_{234}, D_{231} & D_{230} \) and integrating the equation gives,

\[ TD_L = D_{238}T/2 + D_{235}T/2 + D_{234}(r_0 - 1)[1 - ((1 - \exp(\lambda_{231}T))/\lambda_{231})] + D_{230}(r_0 - 1)[1 - ((1 - \exp(\lambda_{230}T))/\lambda_{230})] \]  \hspace{1cm} (5.16)

Again, the age of the enamel sample is solved by iteration of equation 5.14.

5.12 OTHER URANIUM UPTAKE MODELS

The continuous U uptake model assumes that uranium accumulation in fossil samples progressed in a linear manner (Ikeya, 1982). However, this may not be the case. Uranium accumulation could have been rapid at first and then increased more slowly. Or perhaps an "episodic" uptake should be considered, where uranium accumulation was con-
trolled by groundwater fluctuation (Hansen and Begg, 1970). It has also been proposed that uranium absorbed in the sample during the decay of organic material, is leached out by groundwater after the decay ceases (Seitz and Taylor, 1974; Badone and Farquhar, 1982). However, the data of Charalambous and Papastefanou (1977) and Hennig and Grön (1983) suggests that the U leaching stage is not reached for Pleistocene samples.

Each model will lead to a different average annual dose, which in turn affects the estimated ESR age. At present, it is impossible to determine the mode of continuous U uptake (i.e. linear, exponential, episodic, etc.). However, the linear approach is easier to model and represents the "average estimate" of the other possibilities.

A few samples with extremely high U concentrations (>20 ppm in enamel and/or >800 ppm in dentine/cementum), yield very low ESR dates compared to the estimated ages. These samples could have accumulated additional uranium at a very late stage. The late U uptake would not have contributed to the average annual dose and its incorporation in the dose rate calculation can result in a gross underestimate of the ESR age. The relative merit of the various models may become more evident when comparing the ESR dates to independently estimated ages of the samples.
CHAPTER 6

ESR AGES OF TOOTH ENAMEL FROM ALBERTA AND SASKATCHEWAN
6.1 **ANALYTICAL DATA**

The analytical data for all samples is given in Appendix I. The ESR ages are based on this information and were calculated using both an early and a continuous, linear U uptake model. The ESR data for each site are given in Table 6.1 and are compared to what is known of the absolute age of each site with either \(^{14}C\) or U-series dates of bone, fission track dates of volcanic ash or paleomagnetic, stratigraphic and faunal data. Beyond the \(^{14}C\) dating range of approximately 30,000 a, these age estimates should be considered very approximate, as is evident from the large age discrepancies between these estimates at some sites. U-series ages are based on early uranium fixation and subsequent closed system behaviour in bone. They should therefore only be compared with the early uranium uptake ESR dates. All fission track dates should be considered as minima, given the susceptibility of tracks in volcanic glass to annealing.

The faunal assemblages at the various sites can in most cases be satisfactorily correlated with faunas found elsewhere in the continent. Assignment of absolute ages to these various faunas is more difficult, since the relation of land mammal ages to the subdivision of the Pleistocene, is at present uncertain. At some sites, difficulties can also arise in determining the age of the fauna because of inter-
TABLE 6.1. ESR data for teeth samples from Alberta and Saskatchewan. All ages are given in ka. ESR dates are based on the following models:
1) Early U uptake, no radon loss.
2) Early U uptake, 50% radon loss.
3) Continuous, linear U uptake, no radon loss.
4) Continuous, linear U uptake, 50% radon loss.

Independent age information is based on:
C = carbon-14 date,
F = fauna associated with teeth,
FT = fission track of ash beds,
M = paleomagnetism,
S = stratigraphic correlation,
US = uranium series age of bone.
* = ESR age based on estimation of one of the dose rate parameters.
** = ESR age based on external dose rate only.

<table>
<thead>
<tr>
<th>Sample Locality</th>
<th>AD and Number</th>
<th>ESR Age (ka)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lindoe Bluff</td>
<td>(C= 11.2±0.2; US= 9.5±1.5)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>84LN1</td>
<td>3.98</td>
<td>8.1</td>
<td>8.2</td>
<td>13.8</td>
<td>14.0</td>
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<td>3.61</td>
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<td>12.7</td>
<td>18.3</td>
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<td>12.8</td>
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<td>19.4</td>
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<td>12.2</td>
<td>20.5</td>
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<tr>
<td>Average</td>
<td>11.3±1.8</td>
<td>11.5±1.9</td>
<td>18.0±2.5</td>
<td>18.1±2.5</td>
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<td></td>
</tr>
<tr>
<td>Empress Site</td>
<td>(F,S= &lt;80)</td>
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<tr>
<td>84EM2*</td>
<td>5.27</td>
<td>34</td>
<td>35</td>
<td>41</td>
<td>42</td>
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<td>36</td>
<td>37</td>
<td>44</td>
<td>45</td>
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<td>84EM4e</td>
<td>4.95</td>
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<td>26</td>
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<td>84EM5</td>
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<td>40</td>
<td>42</td>
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<td>84EM8</td>
<td>6.68</td>
<td>34</td>
<td>35</td>
<td>44</td>
<td>46</td>
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<tr>
<td>Average</td>
<td>33.8±4.3</td>
<td>34.6±4.7</td>
<td>41.8±2.2</td>
<td>42.8±2.5</td>
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<td>Older Samples:</td>
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<td>84EM4d</td>
<td>32.4</td>
<td>128</td>
<td>139</td>
<td>201</td>
<td>215</td>
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<td>652</td>
<td>845</td>
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<td>84.1</td>
<td>363</td>
<td>363</td>
<td>525</td>
<td>525</td>
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<tr>
<td>Reservoir Gully</td>
<td>(S= 18-25; F= &lt;175; US= 73±6 &amp; &gt;64)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td>84RG3</td>
<td>138.0</td>
<td>205</td>
<td>234</td>
<td>353</td>
<td>398</td>
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(continued)
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<tr>
<th>Sample Locality</th>
<th>AD And Number</th>
<th>ESR Age (ka)</th>
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</thead>
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<tr>
<td></td>
<td>(krad) 1 2 3 4</td>
<td></td>
</tr>
<tr>
<td><strong>Galt Island</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C = &gt;39; FT = 430±70; F,S = 45 &quot;Mid Wisconsin&quot;)</td>
<td></td>
<td></td>
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<tr>
<td>84GI6**</td>
<td>62.2 &lt;349 &lt;349 &lt;349 &lt;349</td>
<td></td>
</tr>
<tr>
<td><strong>Mitchell Bluff</strong></td>
<td>a: (US = &gt;71 &amp; 72±6; F = 80-130 &quot;Sangamon&quot;)</td>
<td></td>
</tr>
<tr>
<td>84MI9e</td>
<td>19.5 38 40 61 64</td>
<td></td>
</tr>
<tr>
<td>84MI91</td>
<td>19.3 35 37 57 60</td>
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</tr>
<tr>
<td>84MI11</td>
<td>34.1 50 53 84 89</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>41±7 44±7 67±12 71±13</td>
<td></td>
</tr>
<tr>
<td>b: (US = &gt;162 &amp; &gt;200; F = 600-1000 &quot;Kansan&quot;)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>84MI10</td>
<td>693.1 130 150 246 285</td>
<td></td>
</tr>
<tr>
<td><strong>Riddell Site</strong></td>
<td>(M = &lt;730; FT,S = 600-700; F = 80-130 &quot;Sangamon&quot;)</td>
<td></td>
</tr>
<tr>
<td>84RS1</td>
<td>43.7 99 108 169 183</td>
<td></td>
</tr>
<tr>
<td><strong>Surprise Bluff</strong></td>
<td>(F,S = 400-600 &quot;Yarmouthian&quot;)</td>
<td></td>
</tr>
<tr>
<td>84SB4</td>
<td>95.0 139 148 238 251</td>
<td></td>
</tr>
<tr>
<td><strong>Island Bluff</strong></td>
<td>(F,S = 600-1000 &quot;Kansan&quot;)</td>
<td></td>
</tr>
<tr>
<td>84IB7</td>
<td>31.6 239 242 288 291</td>
<td></td>
</tr>
<tr>
<td>84IB9*</td>
<td>35.7 269 312 269 312</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>254±15 277±35 279±10 302±11</td>
<td></td>
</tr>
<tr>
<td><strong>Low Bluff</strong></td>
<td>(F,S = 600-1000 &quot;Kansan&quot;)</td>
<td></td>
</tr>
<tr>
<td>84LB1</td>
<td>183.0 87 99 164 187</td>
<td></td>
</tr>
<tr>
<td><strong>Bow Island</strong></td>
<td>(F,S = ? preglacial)</td>
<td></td>
</tr>
<tr>
<td>84BOW3**</td>
<td>18.0 &lt;118 &lt;118 &lt;118 &lt;118</td>
<td></td>
</tr>
<tr>
<td><strong>Frisch Site</strong></td>
<td>(F = &gt;1000)</td>
<td></td>
</tr>
<tr>
<td>84FR2</td>
<td>231.7 236 262 406 445</td>
<td></td>
</tr>
<tr>
<td>84FR4*</td>
<td>236.2 267 295 457 500</td>
<td></td>
</tr>
<tr>
<td>84FR6*</td>
<td>233.0 277 303 474 513</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>260±18 287±18 446±29 486±30</td>
<td></td>
</tr>
<tr>
<td><strong>Wellsch Valley</strong></td>
<td>(F = &gt;1500; combined FT &amp; M = 1000-1600)</td>
<td></td>
</tr>
<tr>
<td>84WV5</td>
<td>456.0 167 181 314 340</td>
<td></td>
</tr>
</tbody>
</table>
mingling of taxa that are usually found separate in time (Stalker and Churcher, 1982). Due to these problems, as well as other problems encountered in Quaternary stratigraphy (chapter 1.2.1), the age estimates based on faunal assemblages should be regarded as very approximate.

Lindoe Bluff

At Lindoe Bluff, $^{14}$C and U-series ages are available to compare with the ESR data. Given a time period of approximately 2 to 3 thousand years for uranium fixation in bone after burial, the U-series age of 9.5 ka (Szabo et al., 1973) is in good agreement with the radiocarbon date of 11.2 ka. The ESR ages (average 11.3±1.8 and 11.5±1.9 ka) agree very well with the other two estimates, particularly for the early U uptake model. The samples also show good agreement within the ESR results. Sample 84LN6al is altered. However, the resulting age is in good agreement with the non-altered samples, which suggests that the AD was not affected by alteration (which probably happened recently). Based on these dates, Lindoe Bluff can be assigned to interglacial stage 1 (Fig. 1.3).

Empress Site

The Empress Site has not been dated by any absolute dating method. However, based on the fauna and its stratigraphic position, it is believed to be a relatively young
deposit, either latest Wisconsin (stage 2) or Mid-Wisconsin (stage 3) (A.M. Stalker and C.S. Churcher, pers. comm. 1984). ESR dates obtained on five samples are consistent with stage 3, regardless of the uptake model used. Three other samples give older results. The presence of numerous dinosaur bones in the same deposit suggests that the older samples represent recycled tooth fragments from earlier interglacial deposits.

**Reservoir Gully**

The 18 - 20 ka age estimate for Reservoir Gully is partly based on stratigraphic position. The faunal assemblage, particularly the presence of *Mammuthus* sp. and *Equus conversidens* (Mexican ass) (Stalker and Churcher, 1982), is typical of the Late Rancholabrean (<175,000). U-series dates suggest an age of >64 ka (Szabo et al., 1973) and the ESR estimate indicates an older age (>205 ka). Perhaps the tooth fragment represents recycled material from an older deposit. Since only one sample was available, the results are inconclusive.

**Galt Island**

At Galt Island, again only one tooth sample was available for analysis. The sample had insufficient dentine and enamel for U analysis; hence the beta dose contribution could not be determined. However, if only the environmental dose rate is used, an upper age limit can be obtained. The <349 ka ESR date suggests that the fission track age of 430 ka
(Westgate et al., 1978) is too high. The overall faunal assemblage (14 different species; Stalker and Churcher, 1982) is characteristic of Rancholabrean age (consistent with an age of 475 ka). The estimated age of 45 ka for the site is based on the presence of a mammoth of unknown species and a radiocarbon date of 39 ka (Stalker and Churcher, 1982). However, the magnitude of the 14C date suggests that it is an infinite date. The high AD (62.2 krad) indicates a somewhat older age. U-series dating on two bones samples proved unsuccessful due to extensive migration of uranium and/or daughter elements (Szabo et al., 1973).

**Mitchell Bluff**

The main bone horizon at Mitchell Bluff contains a diverse faunal assemblage. Of 31 identified species, 11 represent a distinct "Sangamon" (stage 5) faunal assemblage (Stalker, 1976; Stalker and Churcher, 1982). U-series ages are also available. Both the U-series and ESR dates are somewhat younger than the estimated faunal age. However, sample 84MI11 is within the estimated 80 - 130 (stage 5) range if the linear U uptake model is used. Szabo et al. (1973) obtained some discordant 231Pa and 230Th dates on bone, indicating open system behaviour. Hence the continuous linear U uptake model is expected to come closer to the "true" age.
One sample (84MI10) from a lower bone horizon on the same outcrop, is believed on the basis of associated fauna, to have an age of 600 - 1,000 ka (Stalker and Churcher, 1982). The ESR date of 130 to 285 ka is inconsistent with this age assignment. The tooth sample contained extremely high amounts of uranium, both in the enamel (23 ppm) and dentine (1820 ppm). It might be likely that this sample has undergone late stage uranium accumulation. More samples are needed to verify the age assignment of this unit.

Riddell Site

The associated fauna at the Riddell Site, particularly *Ondatra zibathicus* (muskrat) and *Lagurus curtatus* (sagebrush vole), is representative of Late Rancholabrean time (Skwara-Woolf, 1981). The beginning of Late Rancholabrean time in North America seems to correlate best with the beginning of 18O stage 6, dated at ca. 175,000 a (Repenning, 1980). The paleoecological evidence and stratigraphic position indicates that the composite Riddell fauna is of "Sangamon" age (stage 5) (Skwara-Woolf, 1981). Another age of 600 - 700 ka is based on stratigraphic correlation with the Wascana Creek Ash near Regina, dated by fission track (Westgate et al., 1976). However, one of the above co-authors (Christiansen, pers. comm. 1984) believes that Skwara-Woolf's age estimate for the Riddell Site is more consistent with the local stratigraphy. The single tooth analysed gave an ESR age (99 to 108 ka) in
good agreement with the latter age (stage 5) estimate, using
the early U uptake model. The continuous U uptake model
implies a somewhat older age.

**Surprise, Island and Low Bluffs**

Surprise Bluff, Island Bluff and Low Bluff are three
outcrops along the bank of the South Saskatchewan River.
Faunal and stratigraphic dates suggests that these sites are
quite old (>0.5 Ma) (Stalker and Churcher, 1982). The ESR
data however, indicates much younger ages in all cases. The
dose rate values for samples 84IB7 and 84IB9 are shown in
Table 7.1. For the Island Bluff samples, the EDR, which has
the lowest uncertainty of all dose rate calculations, is the
main contributor to the dose. Hence, the ESR dates should
more accurately reflect the "true" age of the sample. Using
the linear U uptake model, Surprise Bluff and Island Bluff
can be assigned to interglacial stages 7 and 9 respectively.
The ESR age of Low Bluff is questionable since the dentine
has a high U concentration, possibly of late accumulation.

**Bow Island**

The sediments at Bow Island are believed to represent
preglacial valley deposits (Stalker and Churcher, pers. comm.
1984). There are no till beds present here. Sediments
higher up in the sequence are contorted and thrusted, sug-
gest that at one time a glacier overrode the region but
either did not deposit any till or the till deposits have subsequently been eroded. The sample contained insufficient dentine and enamel for U analysis. The ESR age is therefore based on the environmental dose rate and should be considered an overestimate. The ESR data shows that the age of these sediments has to be younger than 118 ka and cannot possibly represent preglacial sediments.

Frisch Site

The Frisch Site is located east of Medicine Hat, several kilometers distant from the South Saskatchewan River. The site occurs in an outlier of Quaternary sediment. There are no absolute dates for this site. Current identification of the fauna by C.S. Churcher (Dept. of Zoology, University of Toronto) and stratigraphic correlation by A.M. Stalker (GSC), suggests that the deposit is older than 1,000 ka. The ESR dates are considerably younger, and there is good agreement between the ESR ages of the three samples. The ESR dates (average 446±29 & 486±30 ka, linear U uptake) suggest that the age of this site can be assigned to stage 13, much younger than the 1,000 ka estimate.

Wellsch Valley

The Wellsch Valley Site probably represents one of the oldest known Pleistocene deposits in the Prairies. Based on an Early Irvingtonian land mammal faunal assemblage (Stalker
and Churcher, 1972), paleomagnetism and fission track data, the age of the bone horizon is estimated at >1,500 ka (Fig. 6.1). The ESR data represents a gross underestimate of this age. The sample has a very high U content in enamel (29 ppm) and dentine (825 ppm), which may have accumulated at a late stage. ESR analysis on additional samples should prove useful since this is one of the few Pleistocene sites in western North America with good geochronological control.
Land Mammal Stage

Ages (ka)

Rancholabrean

Jaramillo

Irvingtonian

Olduvai

730
690±110
900
970
1670

Magnetic Stratigraphy

N.A.
Normal polarity
Reverse polarity

... Volcanic ash

/// Main bone horizon
CHAPTER 7

CONCLUDING REMARKS
7.1 DISCUSSION

No errors were assigned to the ESR age estimates in Table 6.1. At present, there are still several assumed parameters in the dose rate calculation which can lead to unrealistically high and/or meaningless error estimates. In most cases, the various inputs to the calculation tend to cancel each other; some increase the dose rate, while others decrease it.

The high U content in dentine represents the major source of error in the age calculation, since it has a strong influence on the dose rate (Table 7.1). The main problem lies in the determination of the nature of U accumulation in dentine. Presently this problem cannot be solved. The fact that some fossil bones give concordant U-series ages while others discordant (Szabo et al., 1973), indicates that U uptake may have been early in some samples, while others remained open systems over their burial history. ESR studies on a mammoth tooth by Grön and Invernati (1985) produced similar conclusions. They applied a direct and linear U accumulation model on five different regions of a mammoth tooth. The ESR results demonstrated that samples from regions of the tooth not affected by U accumulation yielded good ages with both models, whereas samples of other regions give only reliable results when the "right" model is applied.
TABLE 7.1. IDR, DDR and EDR contribution of several samples, for early (E), and linear (L) U uptake models, with no radon loss.

<table>
<thead>
<tr>
<th>Sample</th>
<th>AD U Concentration (ppm)</th>
<th>Dose Rate (mrad/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Enamel Dentine Soil U Th/K2O</td>
<td>IDR DDR EDR</td>
</tr>
<tr>
<td></td>
<td>E L E L E L</td>
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<tr>
<td>84LN1</td>
<td>3.98 3.3 109x2 2.0/7.7/1.45</td>
<td>48.9 24.8 362.4 182.2 81.5 81.5</td>
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<tr>
<td>84LN3</td>
<td>3.51 1.7 102 2.0/7.7/1.45</td>
<td>27.7 13.7 157.8 78.3 105.5 105.5</td>
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<tr>
<td>84EM4a</td>
<td>5.22 0.37 26.5 1.6/4.3/1.87</td>
<td>8.0 3.7 43.9 21.2 94.0 94.0</td>
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<td>84M111</td>
<td>34.1 4.81 231 2.1/6.9/1.95</td>
<td>114.8 59.3 450.9 229.1 119.4 119.4</td>
</tr>
<tr>
<td>84SB4</td>
<td>95.0 9.2 89.9 1.9/5.5/1.69</td>
<td>326.4 166.1 250.3 125.5 106.6 106.6</td>
</tr>
<tr>
<td>84IB7</td>
<td>31.6 0.67 8.4 2.0/6.0/1.77</td>
<td>31.0 14.1 10.8 5.1 90.5 90.5</td>
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<tr>
<td>84IB9</td>
<td>35.7 0.7 2.0/6.0/1.77</td>
<td>33.6 15.2</td>
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<td>84FR2</td>
<td>231.7 7.53 171 3.4/10./2.01</td>
<td>322.6 161.9 503.7 252.6 156.2 156.2</td>
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<tr>
<td>84W5V5</td>
<td>456.0 28.8 825x2 2.5/7.5/2.04</td>
<td>1215.6 631.6 1417.8 723.9 96.9 96.9</td>
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</table>
It therefore seems to be necessary to find some indicators for determining the model of U uptake for each sample to be dated.

Another problem involves the distribution of U in dentine. Fission track analysis by Grön and Invernati (1985) indicates that there can be a large variation in uranium concentration between the outer and inner part of teeth. High U concentrations at the outer edge of a thick dentine layer may not contribute to the dose rate, resulting in an underestimate of the ESR age. It is advisable to perform fission track mapping of dentine for more precise beta dose attenuation calculations.

The error in the determination of the AD is rather low. AD results can usually be reproduced with a deviation of <5%. The good agreement between AD's from samples collected at the same site also suggests that the AD represents the true accumulated dose of the samples. To test this hypothesis, a modern tooth was irradiated with a gamma dose of 20 krad. The AD derived from the sample was 21 krad, an uncertainty of only 5%. Similar results are reported by Grön and Invernati (1985).

Additional sources of error could arise from:

1) analytical error in determination of (U, Th and K),
2) saturation of traps with electrons,
3) competition for traps by non-paramagnetic radicals (eg. fluorine; Ikeya, 1985),
4) over/under estimate of the initial $^{234}\text{U}/^{238}\text{U}$ ratio,
5) over/under estimate of Rn loss,
6) late stage U accumulation/leaching, and
7) inclusion of teeth reworked from earlier deposits.

7.2 CONCLUSIONS

ESR dates based on early and linear U uptake models were compared to the estimated ages of several sites in southern Alberta and Saskatchewan. The wide range and uncertainty of independent age estimates at some sites causes difficulties in determining which ESR model most accurately reflects the "true" age of the sample. The ESR ages are in relatively good agreement with independent estimates at the young, well dated sites. For slightly older samples (approx. 100 ka), the linear U uptake model comes closer to the estimated age at one site (Mitchell Bluff), but for the Riddell Site, the early U uptake model agrees more favourably with the estimated age. For even older samples (Mitchell Bluff(b), Low Bluff and Wellsch Valley), the ESR models yield highly underestimated ages. However, these samples have very high U concentrations and may have experienced a late stage of U accumulation.
ESR gives ages for some sites which are younger than those determined by faunal and stratigraphic correlation. Using the linear U uptake model, Surprise Bluff, Island Bluff and the Frisch Site can be assigned to interglacial stages 7, 9 and 13 respectively. These age assignments may represent more realistic values, since the faunal and stratigraphic correlation is sometimes unclear. For example, note the discrepancies between these independent dates within the following four sites,

- Reservoir Gully - F,S: 18-25 ka; US: >64 & 73±6 ka
- Galt Island - F,S: 45 ka; FT: 430±70 ka
- Mitchell Bluff(a) - F,S: 80-130 ka; US: >71 & 72±6 ka
- Riddell Site - F: 80-130 ka; FT: 600-700 ka

Another problem associated with the faunal and stratigraphic age estimates is that they are based on the assumption that there were only four glacial-interglacial cycles during Pleistocene time. However, as is evident from Fig. 1.2, it is not clear what ages the interglacials/glacials (eg. Yarmouthian, Kansan, etc.) really represent. Use of a more modern classification based on isotope stages (Fig. 1.3) is recommended.

At some sites, the analysed sample may represent an older, recycled tooth fragment. This is particularly evident at the Empress Site, where five samples yielded similar ESR
dates in good agreement with the estimated age of the deposit and three other samples give varying older ages. The recycled nature of the older samples is supported by the presence of dinosaur bones in the same deposit. It is therefore essential to analyse and compare the data of several samples (5 or more) from each site.

Finally, it appears that the U accumulation process can vary from sample to sample and it would therefore be futile to use one general model of U uptake. A partial solution to the problem may be to analyse several samples from each site. If some of the samples display uniform AD values (as for Empress and Frisch samples), then they may prove easier to model. Samples with anomalously high U concentrations should be avoided since they yield highly underestimated ESR dates. Whenever possible, the ESR dates should be compared to ¹⁴C, U-series, fission track and paleomagnetic data.

7.3 SUGGESTIONS FOR FUTURE WORK

At a number of sites, only one sample was available for analysis. For reliable and meaningful ESR age determinations it is required that several samples be analysed from each site.
Some outcrops along the bank of the South Saskatchewan River contain 3 to 4 fossiliferous horizons. Sampling along such vertical sequences will allow for a better comparison of ESR dates for samples with unquestionable sequences of ages.

More sites with established absolute ages are required to test the ESR models. Wellsch Valley probably represents the oldest known fossiliferous Pleistocene deposit in North America. The good absolute age control at this site should prove useful in testing the upper limit of ESR dating.

Determination of U concentration and distribution in dentine and enamel by fission track mapping is advised for more precise beta ray attenuation calculations. Fission track analysis may also prove useful in determining the appropriate U accumulation model.
REFERENCES


Stalker, A.Macs. and Harrison, J.E., 1977. Quaternary glacia


APPENDIX I

TABLE I-1. Analytical data for samples used in this study.

( ) = Estimated value based on comparison with other sample.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Av. Enamel Thickness (mm)</th>
<th>AD (krad)</th>
<th>U Concentration (ppm)</th>
<th>Th Conc. Sediment (ppm)</th>
<th>K₂O Conc. Sediment (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Uncleaned</td>
<td>Cleaned</td>
<td></td>
<td>Enamel</td>
<td>Dentin1</td>
</tr>
<tr>
<td>84LM1</td>
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<td>0.7</td>
<td>3.98</td>
<td>3.3</td>
<td>109</td>
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<tr>
<td>84LM2</td>
<td>1.1</td>
<td>0.9</td>
<td>3.61</td>
<td>1.7</td>
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<td>0.9</td>
<td>4.22</td>
<td>5.69</td>
<td>88.4</td>
</tr>
<tr>
<td>84LM6alt</td>
<td>1.1</td>
<td>0.9</td>
<td>7.74</td>
<td>24.8</td>
<td>88.4</td>
</tr>
<tr>
<td>84EH2</td>
<td>0.8</td>
<td>0.6</td>
<td>5.27</td>
<td>0.55</td>
<td>(20)</td>
</tr>
<tr>
<td>84EH4a</td>
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<td>1.0</td>
<td>5.22</td>
<td>0.37</td>
<td>26.5</td>
</tr>
<tr>
<td>84EH4d</td>
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<td>0.8</td>
<td>32.4</td>
<td>1.5</td>
<td>27.1</td>
</tr>
<tr>
<td>84EH4e</td>
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<td>0.8</td>
<td>4.95</td>
<td>0.9</td>
<td>30.6</td>
</tr>
<tr>
<td>84EH5</td>
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<td>4.51</td>
<td>0.3</td>
<td>4.2</td>
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<tr>
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<td>0.7</td>
<td>6.68</td>
<td>1.29</td>
<td>36.9</td>
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<td>145.8</td>
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<td>1.6</td>
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<td>84.1</td>
<td>2.7</td>
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<tr>
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<td>95.0</td>
<td>9.2</td>
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<td>31.6</td>
<td>0.67</td>
<td>8.4</td>
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<tr>
<td>84EM9</td>
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<td>2.0</td>
<td>35.7</td>
<td>(0.7)</td>
<td></td>
</tr>
<tr>
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<td>1.6</td>
<td>183.0</td>
<td>0.6</td>
<td>887</td>
</tr>
<tr>
<td>84EM23</td>
<td>0.9</td>
<td>0.7</td>
<td>18.0</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>84FR2</td>
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<td>231.7</td>
<td>7.53</td>
<td>171</td>
</tr>
<tr>
<td>84FR4</td>
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<td>1.0</td>
<td>236.2</td>
<td>6.73</td>
<td>(170)</td>
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<tr>
<td>84FR6</td>
<td>1.5</td>
<td>1.3</td>
<td>233.0</td>
<td>(7)</td>
<td>(170)</td>
</tr>
<tr>
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<td>2.0</td>
<td>456.0</td>
<td>28.8</td>
<td>825</td>
</tr>
</tbody>
</table>
APPENDIX II

COMPUTER PROGRAM (APPLE II BASIC)

FOR ESR ENAMEL DATING
10 REM *** ESR ENAMEL DATING ***
20 HOME : CLEAR : PRINT
30 PRINT "*********** ESR AGE DETERMINATION ***********": PRINT : PRINT
40 PRINT "GIVE ALL PERCENTAGE VALUES": PRINT : PRINT
50 REM *** INPUT DATA ***
60 INPUT "SAMPLE NAME? ":NM$: PRINT
70 INPUT 'NUMBER OF DENTINE LAYERS? (0, 1 or 2)? ":D2
80 INPUT "AD (KRAD)? ":A$: A$ = VAL (A$)
90 IF A$ < =0 THEN PRINT; PRINT "AD MUST BE GREATER THAN ZERO."; PRINT
100 IF A$ < =0 THEN 90
110 INPUT 'U (PPM) SAMPLE? ":B$: B$ = VAL (B$)
120 IF D2 =0 THEN 100
130 INPUT 'U (PPM) DENTINE-1? ":C$: C$ = VAL (C$)
140 IF D2 =1 THEN 160
150 INPUT 'U (PPM) DENTINE-2? ":D$: D$ = VAL (D$)
160 INPUT 'U (PPM) SEDIMENT? ":E$: E$ = VAL (E$)
170 IF E$ =0 THEN 210
180 INPUT 'Th (PPM) SEDIMENT? ":F$: F$ = VAL (F$)
190 INPUT 'K20 (%) SEDIMENT? ":G$: G$ = VAL (G$); G$ = G$ * 0.83015
200 IF E$ > 0 THEN 220
210 INPUT "EXTERNAL GAMMA RADIATION (MRAD/A)? ":S$: S$ = VAL (S$)
220 INPUT "INITIAL 234U/238U RATIO OF SAMPLE? ":U$: U$ = VAL (U$)
230 IF U$ < 1 THEN LET U$ = 1
240 INPUT "K-Y VALUE? ":Y$: Y$ = VAL (Y$)
250 IF Y$ < =0 THEN LET Y$ = 0.15
260 INPUT "WATER CONTENT (wt.%) OF SAMPLE? ":V$: V$ = VAL (V$)
270 IF C$ =0 THEN 290
280 INPUT "DENTINE? ":X$: X$ = VAL (X$)
290 IF E$ =0 THEN 310
300 INPUT "SEDIMENT? ":W$: W$ = VAL (W$)
310 INPUT "RADIUM LOSS (%)? ":Z$: Z$ = VAL (Z$)
320 LET C$1 = 2.841E - 6; C$2 = 9.217E - 6; C$3 = 2.133E - 6
330 IF C$ = 0 AND E$ = 0 THEN 940
340 REM *** CALCULATE BETA ATTENUATION ***
350 PRINT : PRINT
360 PRINT "SAMPLE SYMMETRY FOR THE CALCULATION OF BETA RAY ATTENUATION
OF THIN SAMPLES"
370 PRINT : PRINT
380 PRINT "A-SIDE / SAMPLE / B-SIDE"
390 PRINT "----------/----------/----------";
400 PRINT "DENTINE-1 / ENAMEL / DENTINE-2"
410 PRINT "DENTINE-1 / ENAMEL / SEDIMENT"
420 PRINT "SEDIMENT / ENAMEL / SEDIMENT"
430 PRINT : PRINT
440 INPUT "DENSITY OF SAMPLE? ":D$: D$ = VAL (D$)
450 IF D$ < =0 THEN LET D$ = 2.95
460 INPUT "INITIAL SAMPLE THICKNESS (MICRON)? ":T$: T$ = VAL (T$)
470 LET TT$ = T$ / 1000
480 INPUT "REMOVED THICKNESS A-SIDE (MICRON)? ":A$: A$ = VAL (A$)
490 LET AA$ = A$ / 1000
500 INPUT "REMOVED THICKNESS B-SIDE (MICRON)? ";BB = VAL (BB$)
510 LET BB = BB / 1000
520 IF AA + BB < TT THEN 570
530 PRINT : PRINT
540 PRINT : PRINT "THE THICKNESS REMOVED IS GREATER THAN"
550 PRINT "THE TOTAL THICKNESS OF THE SAMPLE."
560 PRINT "CHECK YOUR INPUTS AND REENTER."; PRINT : PRINT : GOTO 460
570 HOME 1 PRINT 1 PRINT:
580 IF G = 0 THEN 1270
590 AB = 1; MM = .1619; GOSUB 820: R3 = R1: R4 = R2: GOSUB 860
600 IF C = 0 THEN LET M1 = R3
610 IF D = 0 THEN LET M2 = R4
620 LET L = M1 + M2; R3 = 0; R4 = 0
630 FOR NN = 1 TO 8: READ AB, MM: GOSUB 820: NEXT NN: GOSUB 860
640 FOR NN = 1 TO 24: READ AB, MM: GOSUB 820: NEXT NN: GOSUB 860
650 FOR NN = 1 TO 16: READ AB, MM: GOSUB 820: NEXT NN: GOSUB 860
660 IF F = 0 OR D > 0 THEN 940
670 FOR NN = 1 TO 27: READ AB, MM: GOSUB 820: NEXT NN: GOSUB 860
680 IF C = 0 THEN LET M1 = R3
690 IF D = 0 THEN LET M2 = R4
700 LET K = M1 + M2
710 GOTO 940
720 DATA .0001, .0002, .0009, .0012, .0064, .0035, .0454, .0114, .0001
730 DATA , .0495, .9364, .3029, .006, .1928, .0048, .1528
740 DATA .0008, .0115, .0014, .0493, .0001, .056, .0697, .0738, .0716
750 DATA , .0821, .0054, .0919, .0014, .1158, .0172, .1229
760 DATA .0159, .1286, .0135, .1385, .0139, .1556, .0055, .1728, .0309
770 DATA , .1785, .0682, .1899, .0064, .0049, .0099, .0057
780 DATA .0148, .2229, .0049, .2402, .0426, .2459, .1768, .4448, .0023
790 DATA , .0013, .2728, .1401, .0492, .0016, .0178, .0002
800 DATA .0001, .0055, .0059, .0112, .0006, .0121, .031, .02, .0247, .0231
810 DATA , .0055, .0007, .0005, .0183, .0089, .0534
820 DATA .0044, .1127, .3612, .1703, .0004, .0584, .0003, .0525, .418
830 DATA , .1793, .0109, .0001, .0418, .0009, .0738, .0026
840 DATA .01, .001, .005, .0421, .0071, .0471, .0061, .0642, .0181, .1
850 DATA , .167, .0082, .1209, .0289, .135
860 DATA .1082, .1428, .0612, .2246, .0124, .2343, .0323, .2731, .10014
870 DATA , .0073, .0513, .0284, .023, .0572, .006, .04
880 DATA .0001, .0568, .003, .0649, .0021, .0798, .0188, .0191, .3234
890 DATA , .2957, .0024, .1221, .0266, .1581, .0311, .0014
900 DATA .0861, .2311, .0419, .0012, .0135, .0001, .0464, .0014
910 LET MM = .33 / (MM * (TT - AA - BB)) + (EXP (- MM * AA) - EXP (- MM * (TT - BB))) * AB
920 LET R2 = .5 / (MM * (TT - AA - BB)) + (EXP (- MM * BB) - EXP (- MM * (TT - AA))) * AB
930 LET R3 = R3 + R1: R4 = R4 + R2: RETURN
860 LET R3 = INT(R3 * 10000 + .5) / 10000
870 LET R4 = INT(R4 * 10000 + .5) / 10000
880 LET M1 = 0: M2 = 0: M3 = 0: M4 = 0: M5 = 0: RETURN
890 IF C > 0 THEN LET M1 = R3
900 IF D > 0 THEN LET M2 = R4
910 IF C = 0 THEN LET M3 = R3
920 IF D = 0 THEN LET M4 = R4
930 LET M5 = M3 + M4: R3 = 0: R4 = 0: RETURN
940 REM *** PRINTOUT OF INPUT VALUES ***
950 PRINT "AD (krad) = "; A
960 PRINT "U (ppm) SAMPLE = "; B
970 IF C = 0 THEN 1020
980 PRINT "U (ppm) DENTINE-1 = "; C
990 IF D = 0 THEN 1020
1000 PRINT "U (ppm) DENTINE-2 = "; D
1010 IF E = 0 THEN 1060
1020 PRINT "Th (ppm) SEDIMENT = "; E
1030 PRINT "Th (ppm) SEDIMENT = "; F
1040 PRINT "K2O (%) SEDIMENT = "; G
1050 IF C = 0 AND E = 0 THEN 1260
1060 PRINT "EFFECTIVE BETA CONTRIBUTION"
1070 PRINT "INITIAL SAMPLE THICKNESS (MICRON) = "; H
1080 PRINT "REMOVED THICKNESS A-SIDE (MICRON) = "; I
1090 PRINT "REMOVED THICKNESS B-SIDE (MICRON) = "; J
1100 PRINT "DENSIY OF THE SAMPLE (g/cm3) = "; K
1110 IF E = 0 OR D > 0 THEN 1180
1120 IF C = 0 THEN 1260
1130 PRINT "SEDIMENT (238U-230Th) = "; L
1140 PRINT "(230Th-206Pb) = "; M
1150 PRINT "(235U) = "; N
1160 PRINT "(232Th) = "; O
1170 PRINT "(40K) = "; P
1180 IF C = 0 THEN 1260
1190 PRINT "DENTINE-1 (238U-230Th) = "; Q
1200 PRINT "(230Th-206Pb) = "; R
1210 PRINT "(235U) = "; S
1220 IF D = 0 THEN 1260
1230 PRINT "DENTINE-2 (238U-230Th) = "; T
1240 PRINT "(230Th-206Pb) = "; U
1250 PRINT "(235U) = "; V
1260 IF S = 0 THEN 1280
1270 PRINT "EXTERNAL GAMMA RADIATION (MRAD/A) = "; W
1280 PRINT "INITIAL 234U/238U RATIO OF SAMPLE = "; X
1290 PRINT "K-VALUE = "; Y
1300 PRINT "WATER CONTENT (WT.%) OF SAMPLE = "; Z
1310 IF C = 0 THEN 1330
1320 PRINT "DENTINE = "; AA
1330 IF E = 0 THEN 1350
1340 PRINT "SEDIMENT = "; BB
1350 IF S = 0 THEN 1370
1360 PRINT "RADON LOSS (%) = "; CC
1370 PRINT ; PRINT
1380 REM *** CALCULATE WATER ATTENUATION ***
1390 LET W1 = 1 + 1.49 * V / (1 - V)
1400 LET W2 = 1 + 1.25 * V / (1 - V)
1410 LET W3 = 1 + 1.25 * X / (1 - X)
1420 LET W4 = 1 + 1.25 * W / (1 - W)
1430 LET W5 = 1 + 1.14 * W / (1 - W)
1440 REM *** CALCULATE ENVIRONMENTAL DOSE RATE ***
1450 LET A1 = E * (11.81 + F * 4.98 + G * 24.92 + H) / W5
1460 LET A2 = E * (H * 5.51 + I * B.81 + J * 0.35) + F * K * 2.89 + L * 83.03) / W4
1470 REM *** CALCULATE EFFECTIVE INTERNAL BETA DOSE ***
1480 LET B1 = 1 - l + M + PI
1490 LET B2 = 1 - I + N + Q
1500 LET B3 = 1 - J + 0 + R
1510 REM *** CALCULATE INTERNAL & DENTINE DOSE RATES ***
1520 LET S1 = B * (Y * 267.6 / W1 + (B1 * 5.51 + B2 * B.81) / W2)
1530 LET S2 = B * (U - 1) * (Y * 29.71) / W1
1540 LET S3 = B * (Y * 12.16 / W1 + B3 * 0.35 / W2)
1550 LET E1 = C * (M * 5.51 + N * (B.81 - RN * RB)) / W3
1560 LET E3 = C * 0 * 0.35 / W3
1570 LET F1 = D * (P * 5.51 + Q * (B.81 - RN * RB)) / W3
1580 LET F3 = C * R * 0.35 / W3
1590 LET DA = S1 + S3: DJ = E1 + E3 + F1 + F3: DB = S2: DD = A1 + A2
1600 LET DI = B * (Y * 211.77 / W1 + B2 * B.81) / W2
1610 LET DF = C * M * (B.81 - RN * RB) / W3
1620 LET DG = D * (P * 5.51 + Q * (B.81 - RN * RB)) / W3
1630 LET DC = DF + DG
1640 LET DE = B * (Y * 10.89 / W1 + B3 * 0.31 / W2)
1650 LET DK = C * Q * 0.31 / W3 + D * R * 0.31 / W3
1660 REM *** CALCULATE AGE - DIRECT U UPTAKE ***
1680 LET TB = (1 - EXP (- C1 * T)): C1
1690 LET TC = (1 - EXP (- C2 * T)): C2
1700 LET TD = (U - 1) * (1 - (C2 * EXP (- C1 * T) - C1 * EXP (- C2 * T))) / (C2 - C1)): C1
1710 LET TE = (1 - EXP (- C3 * T)): C3
1720 LET X1 = (DA * T + DB * TB - DI * (TC - TD) - DE * TE) / 1E6
1730 LET X2 = (DJ * T - DC * (TC - TD) - DK * TE) / 1E6
1740 LET X3 = DD * T / 1E6
1750 LET AD = X1 + X2 + X3
1760 IF AD > (A) THEN LET TH = T: T = (TH + TL) / 2
1770 IF AD < (A) THEN LET TL = T: T = (TH + TL) / 2
1780 IF (TH / TL - 1) > 0.001 THEN 1670
1790 IF T > 100000 THEN LET T = INT (T * .001 + .5): T = T / .001: 60 TO 1790
1800 IF T > 1000 THEN LET T = INT (T * .01 + .5): T = T / .01: 60 TO 1790
1810 IF T > 1000 THEN LET T = INT (T * .1 + .5): T = T / .1: 60 TO 1790
1780 LET T = INT (T)
1790 IF M7 = 0 THEN PRINT "AGE (a) FOR DIRECT U-UPAKE MODEL =" ; T
1800 IF M7 = 1 THEN PRINT "AGE (a) FOR DIRECT U-UPAKE MODEL (" ; RN $ 1
00; "; RN LOSS) = " ; T
1802 PRINT " EDR (mrad/a) = "; X3 / T $ 1E6
1804 PRINT " DDR (mrad/a) = "; X2 / T $ 1E6
1806 PRINT " IDR (mrad/a) = "; X1 / T $ 1E6
1810 REM *** CALCULATE AGE - LINEAR U-UPAKE ***
1820 LET TH = 2 * TH TL = T $ T = (TH + TL) / 2
1830 LET Tc = (1 - (1 - EXP (- C1 * T)) / (C1 * T)) / C1
1840 LET TD = (U - 1) * (1 - (C2 ^ 2 - (1 - EXP (- C1 * T)) - C1 * 2 * 
(1 - EXP (- C2 * T))) / (C1 * C2 * T * (C2 - C1))) / C1
1850 LET TE = (1 - (1 - EXP (- C3 * T)) / (C3 * T)) / C3
1860 LET KD = Y + 82 * N1 + 82 * N2: RB = 8.7
1870 IF Z > 0 THEN LET RN = Z: M7 = 1: GOTO 1520
1880 IF T > 100000 THEN LET T = INT (T $ .001 + .5): T = T / .001: GOTO 1950
1890 IF T > 10000 THEN LET T = INT (T $ .01 + .5): T = T / .01: GOTO 1
950
1900 IF T = 1000 THEN LET T = INT (T $ .1 + .5): T = T / .1: GOTO 1950
1910 IF T > 1520 THEN LET T = INT (T $ .001 + .5): T = T / .001: GOTO 1
950
1920 IF T > 1520 THEN LET T = INT (T $ .001 + .5): T = T / .001: GOTO 1
950
1930 LET T = INT (T)
1940 IF M7 = 0 THEN PRINT "AGE (a) FOR LINEAR U-UPAKE MODEL = " ; T
1950 IF M7 = 1 THEN PRINT "AGE (a) FOR LINEAR U-UPAKE MODEL (" ; RN $ 1
00; "; RN LOSS) = " ; T
1960 PRINT " EDR (mrad/a) = "; X3 / T $ 1E6
1962 PRINT " DDR (mrad/a) = "; X2 / T $ 1E6
1964 PRINT " IDR (mrad/a) = "; X1 / T $ 1E6
1966 LET RA = Y * 152.98 / W1 + B2 * 8.7 / W2: RB = 8.7
1970 IF T > 0 THEN LET RN = Z: M7 = 1: GOTO 1520
1980 PRINT " DO YOU WANT TO CONTINUE (Y OR N)?" 
1990 GET CO$: IF CO$ = "Y" THEN 10
2000 IF T > 0 THEN LET RN = Z: M7 = 1: GOTO 1520
2010 PRINT " DO YOU WANT TO CONTINUE (Y OR N)?" 
2020 GET CO$: IF CO$ = "Y" THEN 10
2030 END
Sample of Output:

84IB7

AD (krad) = 31.6
U (ppm) SAMPLE = .67
U (ppm) DENTINE-1 = 8.4
U (ppm) SEDIMENT = 2
Th (ppm) SEDIMENT = 6
K2O (%) SEDIMENT = 1.77

EFFECTIVE BETA CONTRIBUTION

INITIAL SAMPLE THICKNESS (MICRON) = 2400
REMOVED THICKNESS A-SIDE (MICRON) = 300
REMOVED THICKNESS B-SIDE (MICRON) = 300
DENSITY OF THE SAMPLE (g/cm3) = 2.95

SEDIMENT (238U-230Th) = .1353
(230Th-206Pb) = .0763
(235U) = .0555
(232Th) = .08
(40K) = .0628

DENTINE-1 (238U-230Th) = .1353
(230Th-206Pb) = .0763
(235U) = .0555

INITIAL 234U/238U RATIO OF SAMPLE = 1.41
K-VALUE = .15
WATER CONTENT (WT.%) OF SAMPLE = 0
DENTINE = 0
SEDIMENT = .1
RADON LOSS (%) = .5

AGE (a) FOR DIRECT U-UPTAKE MODEL = 239000
EDR (mrad/a) = 90.3504745
DDR (mrad/a) = 10.8269153
IDR (mrad/a) = 31.0163979

AGE (a) FOR LINEAR U-UPTAKE MODEL = 288000
EDR (mrad/a) = 90.5119361
DDR (mrad/a) = 5.11562415
IDR (mrad/a) = 14.1108543

AGE (a) FOR DIRECT U-UPTAKE MODEL (50% RN LOSS) = 242000
EDR (mrad/a) = 90.6440924
DDR (mrad/a) = 8.67972403
IDR (mrad/a) = 31.2560443

AGE (a) FOR LINEAR U-UPTAKE MODEL (50% RN LOSS) = 291000
EDR (mrad/a) = 90.3456476
DDR (mrad/a) = 4.16386954
IDR (mrad/a) = 14.1225761