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GEOCHEMISTRY OF TUNGSTEN IN BASALTS AND ANDESITES

GEOCHEMISTRY OF TUNGSTEN IN BASALTS AND ANDESITES

By

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ABSTRACT

Few methods exist to analyse tungsten at the ppm level in rocks. Consequently, the amount of data is very scarce and often conclusions are drawn from a very small number of samples. In this study, a NAA radiochemical separation method was used to obtain information on tungsten contents in some 125 volcanic rocks. Besides the major oxide data, which were in most cases obtained from the donors of the samples, additional information was gathered with XRF methods on the following trace elements: Rb, Sr, Ni, Y, Zr, Nb, Zn, Pb, U and Th. Factor analysis was applied in order to process this vast array of newly obtained data. Knowledge of the local geology is necessary if not essential for the interpretation of these data.

The wide variety of rocks involved in this study comprises predominantly basalts (alkaline and subalkaline) and andesites, but also includes some felsic differentiates as well as some ultramafic rocks. An attempt, although not always successful, was made to obtain as fresh samples as possible. These rocks are derived from differing tectonic areas - (1) ocean floors and islands, (2) island arcs and continental margins and (3) continental areas.

Tungsten is an incompatible element accumulating in residual liquids together with elements such as K, Rb, Zr, etc. Existing tungsten estimates for both basalts and andesites are too high. Tungsten contents for basalts and andesites vary according to their petrotectonic environment. Among these rocks, ocean floor basalts have the lowest values followed by island arc basalts and andesites and ocean island basalts. Tungsten contents generally are higher in alkaline basalts and their range is wider than for subalkaline basalts. No differences seem to exist between subalkaline ocean island and continental basalts.

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Sincere thanks go to the many donors of samples and data without which the realization of this work would not have been possible.

Mr. J.R. Muysson provided space in his laboratory, chemical analyses and a chance for a talk. To him the best of luck.

Mr. J. Whorwood is thanked for reproducing, reducing, printing, glueing, framing, etc. many obscure drawings and photos, and for chatting, of course.

Special thanks go to Helen (Elliott), who despite her trout-fishing addiction and other activities, managed to unravel, rearrange and type this tungsten manuscript in time.

"Mens sana in corpore sano" (Juvenalis, 47 A.D. - 127 A.D.). Thanks to some arm-twisters in- and outside the department, a healthy mind was pursued and hopefully kept (?) during the regular Friday afternoon seminars. Among this vast army of arm-twisters I wish to thank and remember particularly Ko Griep, who always could involve me in the application of his theoretical studies on fC_2H_5 OH (so far unpublished M.Sc. thesis);Dr. M. Schau; Mike Marchand, who taught me yet another language (Fortran); Dr. C. Dupuy; Bob Dalrymple; Dick Hyde; Hart Baitis, who still owes me three pitchers; Botswana, alias Nick Massey for his suggestions on greywackes; Drs. J. Schindler, W. Mercer, A. Fallick, CFFFSA and A. Riccardi, who keeps coming back to Mac; and many others too numerous to mention.

Sincere thanks go as well to Knud Wolfram. For all these years, he induced optimism when the tungsten story got the better part of me.

Last but not least, to my wife Montserrat, who kept up with this WWWWWW nonsense for so many years, my sincere thanks for her PATIENCE and encouragement.

I gratefully acknowledge and give thanks for financial assistance, through grants from the National Research Council of Canada and the Geology Department of McMaster University.

"Why the devil should I be interested in your tungsten? Why should anyone?"

(Denison, October 3rd, 2070)

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Excerpt from "Minerales", Canto General I, by Pablo Neruda.

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CHAPTER I

TUNGSTEN ... FACTS, MYTHS AND HERESY ...!

1.1 Introduction and purpose

In discussing recent improvements in the quality of abundance data for many elements, Jeffery (1959) points out that "One exception to this is the data for tungsten, which is still very sparse and contradictory in character". The situation has not changed very much ever since. Recent literature still starts off lamenting on the lack of available data. This situation becomes understandable when one takes into consideration all the difficulties involved with the analysis of tungsten as a trace element. Analytical methods are not abundant and attempts to make some of these work can become a very frustrating, if not at times an impossible, task. Personal experience (Helsen, 1970) in this respect became eventually a challenge (or an obsession?) to continue the pursuit of the unravelling of "The Secrets of Major Tungsten". Emphasis in this study has been put on tungsten and its relationship with other elements in volcanic rocks, in particular basalts and andesites.

1.2 Some new information from post-1968 literature

Wiendl (1968) reviewed in a very exhaustive way the existing literature on tungsten geochemistry and ore deposits up to 1968. Krauskopf (1970) used this dissertation as the basis for Chapter 74 in The Handbook of Geochemistry. It is not the purpose of this study to review the post-1968 literature, although some of the highlights of this period will be commented on below.

Ivanova et al. (1968) studied the transport of tungsten in hydrothermal solutions. They suggested that the most probable tungsten compound is orthotungstic acid or HWO_4^-. Complex oxyfluorotungstates may form if a hydrothermal solution is rich in fluorine, e.g. in the process of greisenization. On the other hand, Kozlov et al. (1974) report that the longstanding observation of extensive pneumatolytic and hydrothermal tungsten mineralization, associated with extensively greisenized muscovite granites, have relatively low (0.10%) mean fluorine contents, whereas greisen with low muscovite but high fluorine content (0.3%) have also low tungsten content. The former suggestion is based on a thermodynamical study and the latter on the geochemistry of Mesozoic plumasite leucocratic granites.

Lyakhovich et al. (1969) mention that sphene and ilmenite act as concentrator minerals for tungsten, with respectively 20 ppm W and 60 ppm W for granitoid rocks.

Simon (1972) studied distribution coefficients of tungsten in rocks and minerals (biotite, hornblende, magnetite and sphene) of the southern California batholith, which show more scatter (although not completely random) than would be expected from an equilibrium situation in which tungsten is in the mineral structure. The tungsten contents are lowest in hornblende and always high in sphene (mean content is 9.4 ppm W, ranging from 4.6 to 14 ppm W). Simon also believes in the existence of tungsten in the structure (solid solution) as well as a discrete phase. Yaroslavskiy et al. (1974) comment on tungsten in granulites and claim plagioclase to be the chief host mineral. Ukhanov et al. (1973), evaluating the tungsten contents of ultramafic rocks, regard kimberlite as a concentrator rock for dispersed elements since it has about five times as much tungsten as peridotites (mean value of 0.2 ppm W for peridotites).

Experimental research (Foster, 1972) concerning the behaviour of known amounts of scheelite mixed with a granite fraction and about 10 wt.% water (up to 2 kbars) shows the low solubility of tungsten (<3%) in granitic melts.

Cathro (<u>in</u> Garrett, 1971 and Rowe, 1973) refers to Potato Hills in the Yukon as a porphyry tungsten pluton. Garrett (1971) suggests the existence of other porphyry tungsten deposits in the Mayo area (S.E. Yukon) and draws at the same time attention to the eventual use of uranium as a potential pathfinder for tungsten.

1.3 Tungsten deposits: some facts, myth ... and heresy?

Geochemical and geological studies of the classical tungsten ore deposits occur with a certain regularity in literature, particularly Russian literature. This section, however, will deal mainly with a so far less common type of tungsten mineralization. For a long time, taking into consideration the very few exceptions (e.g. Fisher, 1951), most tungsten ore deposits have been related in one way or another to granitoid plutons. Krauskopf (1971), reconsidering the Sierra Nevada batholith (California) and its associated tungsten deposits, takes a closer look at this relationship. In a "speculative discussion" on the source of ore metals, he questions seriously the validity of the granitoid rocks as possible concentrators for metals. On the basis of negative evidence or unsolved problems related to these deposits, Krauskopf (1967) in his own words "hazards a guess" that sedimentary agents are more effective to accomplish the early enrichment of metals in large volumes of material. This slight enrichment could then be followed by strong local concentration during igneous activity. As an example of negative evidence he mentions the conspicuous scarcity of feeder channels for tungsten-bearing fluids.

Petersen (1970) wonders why in Peru, obviously a tungsten-rich geochemical province, no commercial scheelite deposits have been discovered so far, inspite of the numerous contact-metasomatic deposits (Cu, Zn, Fe) and the great number of granitic (apparently barren) intrusive-limestone contacts with skarn. As possible causes he mentions a possible unknown physico-chemical effect or inadequate exploration.

The question which arises is the following: To what extent has the often observed spatial relationship between granitoid bodies and tungsten mineralization and, of course, the way of thinking of a certain epoch, contributed to the creation of a myth, if it really is one, of a close genetic relationship between W ore deposits and granitoid rocks? The present author throughout this work often felt himself to be a heretic. After all, who is looking for tungsten in basalts ...? And yet, could it be that the wrong questions were asked?

Some of the enigmas related to tungsten mineralization might be solved by the work of Maucher and his research team at the Institut für allgemeine und angewandte Geologie und Mineralogie (Munich University). Indeed, the discovery, during exploration for new stibnite ore deposits in southeast Sardinia, of strata-bound scheelite mineralization (Angermeier, in Maucher, 1972) in graphite-sericite schists, established the potential for far-reaching scientific and economic consequences.[1] The realization of the significance of the strata-bound character of stibnite, its paragenesis with scheelite

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[1] The newly founded WOLFRAM G.m.b.H. is bringing into operation tungsten deposits in Styria (Austria). (The Northern Miner, 1975).

and the close connection of these syn-genetic Sardinian ores with alternating layers of submarine volcanics and sediments, and not with the granites of the area, has lead further research into new directions. During a period of about ten years ample evidence has accumulated for the existence throughout the world of many other strata-bound stibnite deposits, very often accompanied by scheelite and/or cinnabar, and always in very similar volcanic-sedimentary series of stratified rocks (Maucher, 1972) as, for example, in Austria (Höll, 1969; Lahusen, 1972; Höll et al., 1972), Norway (Skaarup, 1974), and many other places such as Spain, France, Turkey, Korea etc. (<u>in</u> Maucher, 1972). Maucher also realized that most of these ore-bearing units are time-bound to the Lower Paleozoic. In a particular region (Maucher et al., 1968) some of these rock units containing considerably higher Sb, Hg and W contents, could be used as a geochemical-stratigraphical marker horizon. Thus in the Alps over a distance of more than 500 km, they (Maucher et al., 1968) were able to narrow down the debatable ages of certain metamorphic rocks. They also found more than fifty previously unknown scheelite occurrences (Höll, 1969; Höll, <u>in</u> Maucher, 1972). Although in some cases the scheelite content is very low and finely dispersed in the basic metavolcanics or metasediments, in other cases the scheelite becomes of economic value. It should further be mentioned that scheelite is a primary mineral in the volcanics and sediments (Maucher, 1972) and the tungsten mineralogy is dependent on or correlates with the metamorphic grade.

This digression on strata-bound tungsten ore deposits may have been lengthy. It nevertheless is the opinion of the author that it was needed for the reasons previously stated.

1.4 Approach of investigation

The collection of approximately 125 samples studied in this work was made available by many investigators throughout the world. A detailed list of sample localities, donors, etc. is given in Appendix I.

In the following chapters, the methods of investigation (i.e. determination of tungsten, processing of data with factor analysis) are dealt with, the geology of the various regions of interest is described briefly, and the geochemistry of tungsten is discussed.

Complete data information (major oxides, trace elements and norms) is given in Appendix II.

Appendix III describes XRF methods that have been used.

CHAPTER II

GEOLOGY OF THE VARIOUS AREAS UNDER INVESTIGATION

2.1 Introduction

Only a limited number of samples has been analyzed for tungsten. Figure 2.1 shows the approximate distribution of the samples of this study. The samples first investigated were basalts from Hawaii and the Deep Sea Drilling Project (DSDP), because these samples were readily available at the time. Later samples were selected more carefully as the investigation proceeded to end up finally with suites of rocks representing two eruption cycles from a single volcano in the Galápagos Archipelago.

A general idea of the local geology of the various sampling areas will be given in the following sections of this Chapter, while further details on the samples can be obtained from the Appendices. In many cases very few samples were analyzed from a single area, mainly because of the slowness of the analytical method.

2.2 Oceanic Islands and Floor

2.2.1 Indian Ocean

The samples from the Indian Ocean area originate from

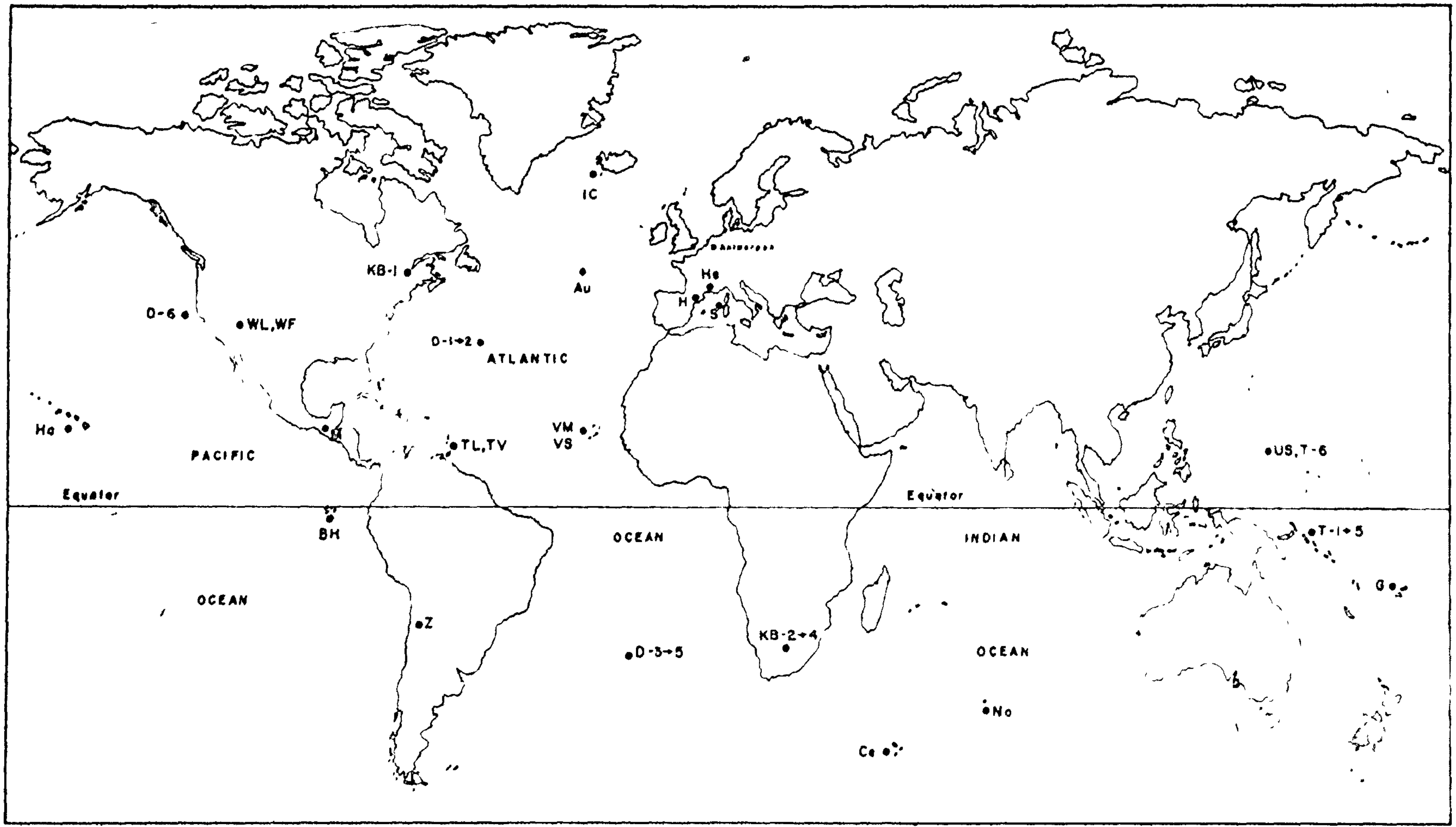

FIG 2 1 APPROXIMATE DISTRBUTION OF THE SAMPLES ON A WORLD MAP A SET OF ROCKS OF A PARTICULAR AREA IS INDICATED BY ● AND ITS CODE NUMBER(cf APPENDIX I) SYMBOL ● INDICATES IMPORTANT CITIES (Redrawn after Fullard, 1956) the Crozet Archipelago (S.W. Indian Ocean) and Amsterdam Island (S.E. Indian Ocean). The Crozet Archipelago is related to the S.W. Indian Ridge system, which is believed not to be actively spreading (Le Pichon, 1968). The samples (Ce-1 to Ce-5) themselves come from section B on East Island. Very little is known about the geology of East Island and what is known is mentioned by Gunn et al. (1970). The Island is a deeply dissected shield volcano (Pliocene or younger) with alkali basalt affinities. The basement of this complex, composed of many irregular dykes (90% of the outcrop in some areas), is overlain unconformably by a thick series of flat lying lavas. These lavas have high olivine and pyroxene contents which gradually diminish towards the end of the group (= cycle).

Only cursory work has been done on the geology of Amsterdam Island and nearby St. Paul Island by early investigators such as Hochstetter, Vélain, Phillips and Rheinisch (all in Gunn et al., 1971), although the importance of both islands seems obvious being the only outcrops in an area of several million km^2 of oceanic crust. The general geology of Amsterdam Island, an extinct shield volcano, has been taken mostly from Gunn et al. (1971). The island lies on the Amsterdam fracture zone, supposedly a transform fault of the S.E. Indian Ridge, with a 3 cm/year spreading rate (Schlich and Patriat, in Gunn et al., 1971). The rocks, all of tholeiitic affinities, are part of a series of lava flows being the youngest flows of the Mont de la Dives, a volcano on the rim of a central caldera and overlying partially an older cone. The geomagnetic polarities of these rocks belong to the Brunhes epoch, i.e. from 0-0.69 million years ago (Gunn et al., 1971).

Dredged rocks from the Indian Ocean ridge system are reported to be oceanic tholeiites (Engel and Engel, 1969; others in Gunn, 1971), whereas DSDP samples from the ocean floor of the Southern Indian Ocean (Leg 26, sites 251 and 254) are very low in K_2O and quartz normative and are called the most typical ocean floor tholeiites by Kempe (1973).

2.2.2 Atlantic Ocean

Although in the last ten years more information has become available, the general geology of the Cape Verde Islands can still be considered as of a reconnaissance character, while the work of Bebiano as yet remains unsurpassed (Mittchell-Thomé, 1972). This group of 15 islands situated on the continental slope some 500 km off the African coast, can be resolved into two trends: a N.W. trend, which may be related to a transverse fracture zone (Le Pichon and Fox, 1971), and a N.E. trend related to a deep structure in the Atlantic since Mesozoic times (Klerkx et al., in Klerkx et al., 1974). Those trends are repudiated by Mitchell-Thomé (1972) until better evidence is gathered. The whole Archipelago with only one active volcano (Fogo) has been built up by highly alkaline, very undersaturated mafic rocks, e.g. basanites, nephelinites, carbonatites, with only minor phonolitic rocks. Assuncao et al. (1968) and others (in Assuncao et al., 1968) compare the Archipelago with the East African Rift Valley.

The island Maio, interesting in many respects, is the only island with sediments older than Miocene and defined by Trauth (in Mitchell-Thomé, 1972) as Neocomian. These sediments are underlain by non-fossiliferous limestones, possibly upper Jurassic or lower Cretaceous (Serralheiro, in Mitchell-Thomé, 1972). Serralheiro also mentions the importance of tectonism on Maio as compared to the other Islands, although structural disturbance in the whole of the Archipelago is only minor (Mittchell-Thomé, 1972). Contrary to previous beliefs, there is no evidence for a Paleozoic basement (Bebiano, in Mitchell-Thomé, 1972), and the general consensus is that, Maio excluded, the islands did not exist before Neogene times. Nor is there any evidence for any connection with the African continent (Klerkx et al., 1974).

One of the conclusions drawn at the American Geophysical Union Conference on the Deep Sea Drilling Project (DSDP) (Christensen et al., 1973) was the existence of a still greater chemical diversity in igneous rocks than might have been expected from the information obtained from dredged samples. The overwhelming majority of DSDP samples point towards a large ion lithophile (LIL)-element depleted olivine tholeiite.

In some cases it was suggested that these olivine tholeiites (especially Leg 26) are less olivine normative than dredged DSDP and Mid-Ocean Ridge basalts (MORB) (Christensen et al., 1973).

Because most DSDP igneous cores were taken from the very upper part of oceanic layer 2, showing undoubtedly evidence of sills, it is obvious that the real basement is not represented in the DSDP cores up to Leg 34 (Nazca plate). Although drill cores of Leg 34 showed extremely fresh basalts at a depth of less than 60 m, penetration into layer 2 at a single hole (Leg 37, Famous area, Atlantic MOR at latitude 37°N) going as deep as 582 m through basaltic flows, intrusions and breccias, found sediment intercalations to a depth of at least 450 m. Some analogies seem to exist between basement complexes of oceanic islands and certain deep sea series, e.g. Mayo Island sediments and cherts from DSDP cores (Watson, in Christensen et al., 1973; Mittchell-Thomé, 1972), as well as between the web-like basement complexes, e.g. East Island, Crozet Archipelago (Gunn et al., 1970), and the igneous basement on positive large abyssal areas. The DSDP samples from Legs 2 and 3 represent oceanic crust away from the Atlantic MOR, as opposed to most dredged basalts. The samples cored at both sides of the MOR, range in age from 18 to about 70x10^6 years (Frey et al., 1974).

Dredged samples come from 2 different areas in the North Atlantic Ocean. The first one is the extensively studied area between latitudes 45°N and 46°N (Aumento et al., 1971; Aumento, 1969) with samples showing a continuous variation from quartz normative tholeiites to nepheline normative alkali-basalts. The olivine tholeiite of the 45°N area, dredged from the Median Valley, is like sample D-1 not depleted in LIL-elements (Frey et al., 1974), and has an age of less than 100,000 years and possibly younger than the last Ice Age. Aumento et al. (1971) suggest that the ocean floor in this area, a test case for sea floor spreading, at least approximates the complexities found in continental areas.

The second area, comprising the post-glacial Reykjanes Ridge axis and its extension over the middle neo-volcanic zones on Iceland, was studied by Schilling (1973a,b). Contrary to most MOR tholeiites, clinopyroxene is a common mineral, becoming more abundant towards Iceland. Other changes take place when approaching Iceland from latitude 60°N, like for example increases in LIL-elements. Schilling (1973a,b) relates these changes to hot mantle plume activities. Samples of the area include both quartz and olivine normative tholeiites with the former more abundant than the latter. This study includes a hawaiite from Heymay, situated on the eastern flank of the actively spreading rift, being the most differentiated rock from that suite so far (Thorarinsson et al., 1973).

2.2.3 Pacific Ocean

Hawaii Archipelago: A submarine ridge, the so-called

Hawaiin ridge, extending N.W. over a distance of about 3000 km, from Hawaii to beyond Midway, forms the backbone for the Hawaiian Islands (Figure 2.2). These islands emerge above sea level in the S.E. part of this ridge system. Within 100 km the flanks of this mid-oceanic basaltic province drop sharply to ocean floor depths of about 4500 m, called the Hawaiian Deep. Hawaii, the most southern and largest of all Hawaiian islands is built up by five shield volcanoes of which only two, Mauna Loa and Kilauea, are still active. The islands grow older (McDougall, 1964) and more eroded following the N.W. trend, with Hawaii being built by its five volcanoes within the last 700,000 years (McDougall et al., 1972). On Oahu subaerial activity of the Waianae volcano covers a period of 1.2 m.y., starting some 3.6 m.y. ago and preceding the Koolau eruptions (Doell et al., 1973).

The bulk of the Hawaiian Island, made up by these shield building primitive basalts, is considered to be of a rather uniform tholeiitic silica saturated character (Powers, 1955; McDonald et al., 1964). More recent and detailed investigations, however, show that significant chemical and mineralogical variation takes place, which can be correlated with the eruption site and chronology (Murata and Richter, 1966; Richter and Murata, 1966). Carmichael et al. (1974) conclude that this "uniform", apparently tholeiitic bulk, making up the great volcano shields, ranges from quartz normative tholeiitic basalts (Mauna Loa and Kilauea) through olivine tholeiites

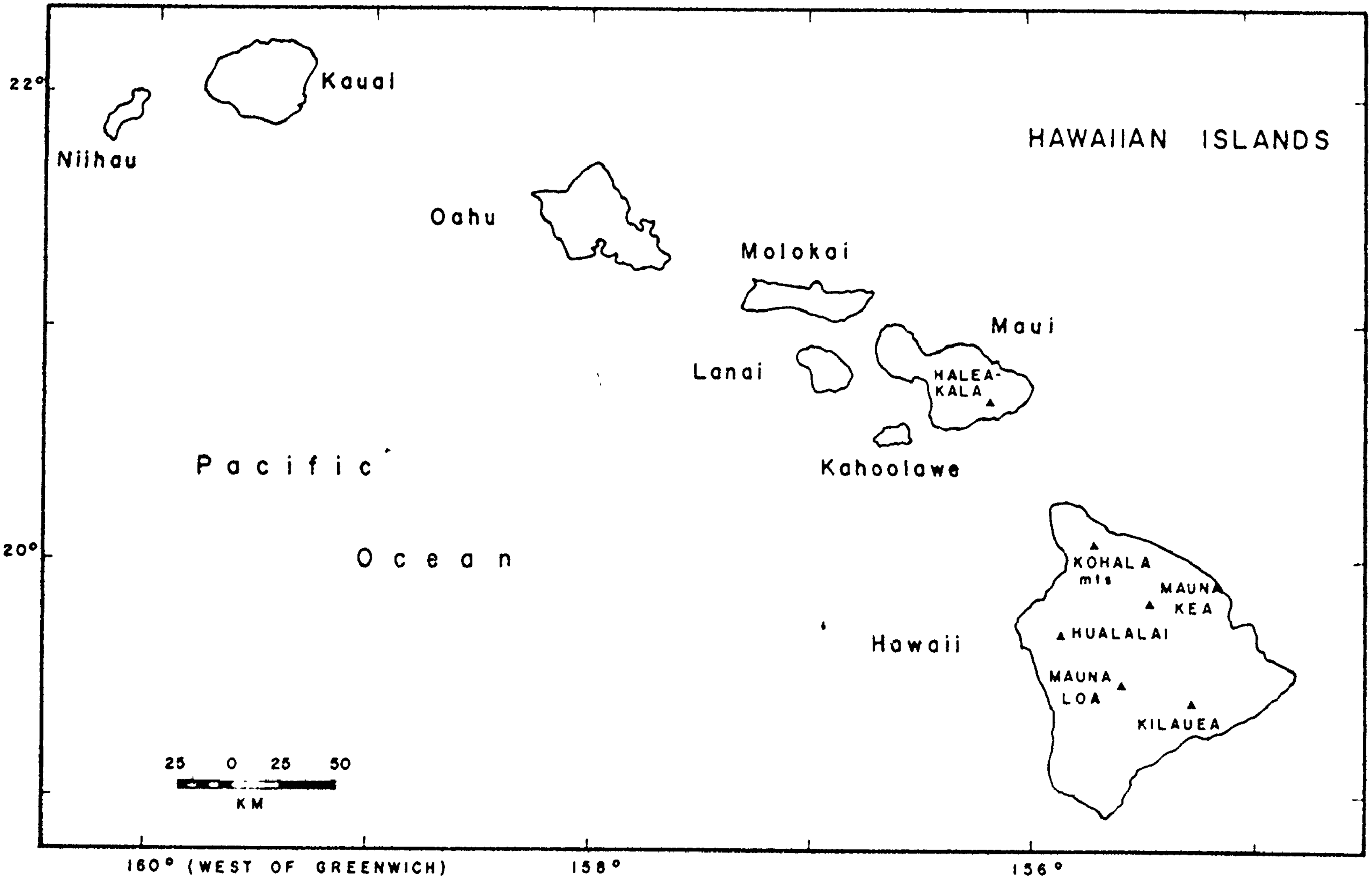

FIG. 2.2 THE HAWAIIAN ISLANDS. (After The World Atlas, Moscow, 1967)

(Mauna Kea, Hualalai, Haleakala on Maui) to even nepheline normative alkali basalts (Hualalai). They compare this range with the combination of predominating basalt magmas of the Western Galápagos, Ascencion and the Azores and suggest that the uniform tholeiitic composition should be taken in the broadest possible sense.

After building up these primitive shields, the volcano is now in a mature stage and a change in eruptive pattern usually takes place, accompanied at the same time by a compositional change towards more alkaline rocks (predominantly hawaiites and mugearites) (MacDonald, 1960; MacDonald et al., 1964). These rocks may alternate with tholeiitic basalts. After a long period of quiescence, which may take more than one m.y. and during which strong erosion takes place, renewed volcanism may occur as, for example, in the case of the Honolulu series, Oahu (Funkhauser et al., and Dymond and Hubbard, unpub. data, in MacDonald et al., 1970). This flare-up of volcanic activity leads towards a final unconformable capping of the remnants of the volcano with even more alkaline and undersaturated volcanics, like that on Maui, Oahu and two other N.W. islands (MacDonald et al., 1964; Carmichael et al., 1974). Carmichael et al. (1974) take the progressive volcanic activity down the Hawaiian Ridge as probably the most convincing volcanic tectonic chronological synthesis in the field of plate tectonics, i.e. motion of the Pacific lithospheric plate.

Galápagos Archipelago: Most of the information for this section is taken from Williams (1966,), McBirney (1967) and McBirney et al. (1969). Williams in the Proceedings of the Galápagos Symposia (1966) states his surprise about the little amount of work done on the Galápagos Archipelago (Figure 2.3) since the significant contributions by Darwin in 1846. Darwin at that time recognized the particular (rectilinear) pattern of the Galápagos volcanoes along a N.N.W. and an E.N.E. trend. At the intersection of these trends occur the biggest shield volcanoes of the Archipelago, as is shown by J-shaped Isabela (Albemarle) island. Raff (1968) on the basis of magnetic anomalies refers to an approximate configuration of three radial rifting lines in the Galápagos area which would create a pattern of large polygonal plates. At the center of this configuration, due to upwelling of mantle material, radial spreading would occur (triple junction?). Most later authors (in Swanson et al., 1974) agree that the Galápagos Islands lie to the south of the Galápagos rift and near the intersection of two aseismic ridges (Cocos and Carnegie ridges). This group of 14 islands, halfway between the coast of Ecuador and the East Pacific Rise, constituting one of the most active groups of oceanic volcanoes, grew from a broad shallow (1500 m) submarine platform (Galápagos Platform) near the East Pacific Rise. Uplifted submarine lavas with fossiliferous interbeds (an uplift mentioned as "scanty and imperfect" by Darwin) from a N30W trending belt in the centre of the Archipelago, represent the oldest volcanics of the area (tholeiites,

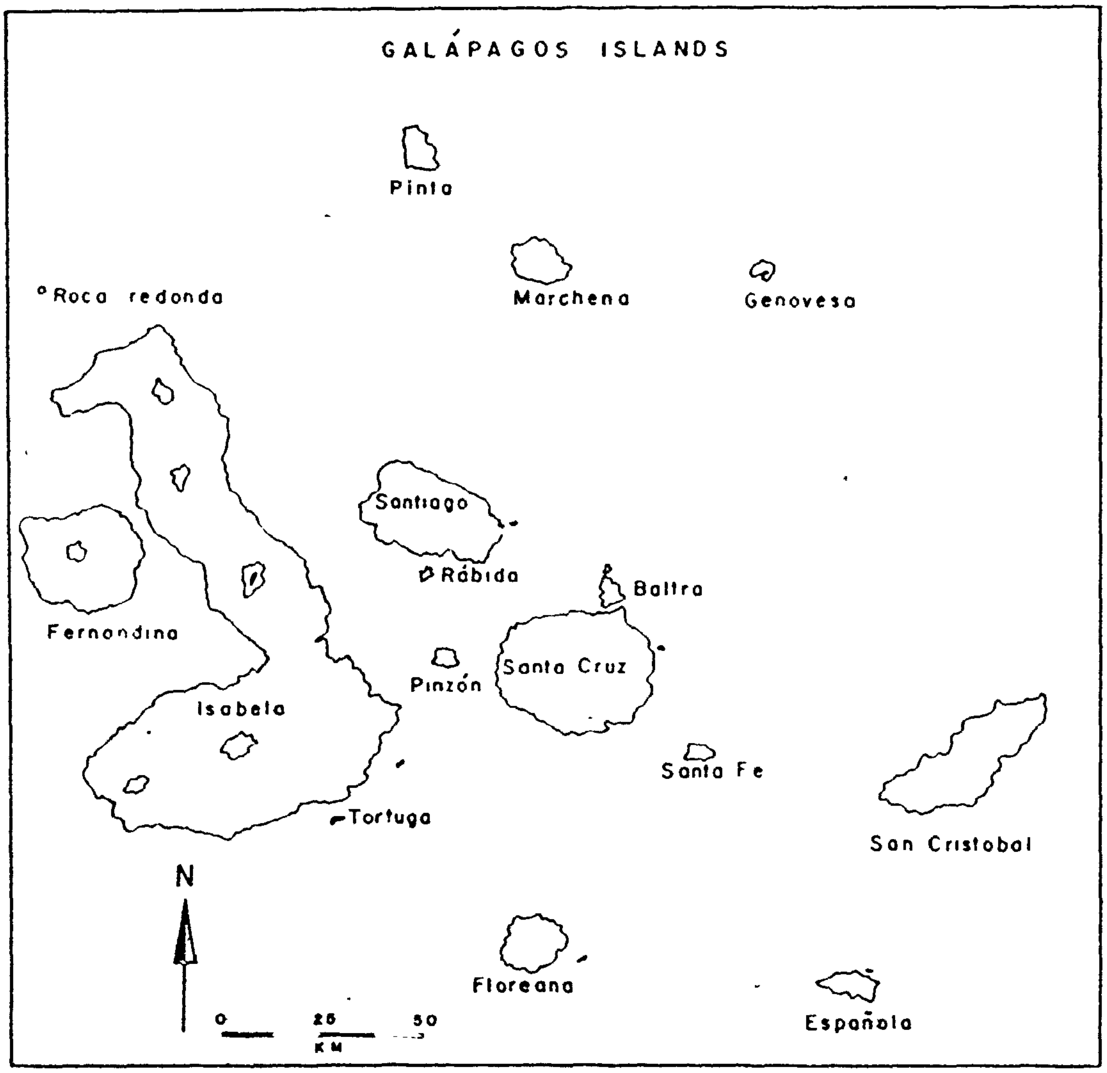

FIG 2.3 THE GALÁPAGOS ARCHIPELAGO.(After The World Atlas,Moscow,1967)

probably high-alumina basalts and alkali basalts). A maximum age of 1.45±0.40 m.y. was determined for submarine lavas on Santa Cruz (Indefatigable) Island and an age of less than 1 m.y. for the oldest visible subaerial lavas (Cox et al., 1966). McBirney et al. (1969) divide the younger basalts into three groups:

(i) Western Islands: Fernandina (Narborough), Isabela (Albemarle) and some smaller islands are made up by tholeiites (all hypersthene- and most quartz-normative) and from shield volcanoes with calderas;

(ii) Northeastern Islands: these smaller islands on the N.E. side of the Archipelago are more complex in their volcanic history (and periods of activity) and they include tholeiitic (more olivine- than quartz-normative) and magnesium-poor alkali-basalts with commonly abundant plagioclase phenocrysts;

(iii) Central Islands: southern part consists of magnesium-rich alkali-basalts which built up large mature volcanoes, without calderas so far; northern part including the islands Santiago (James), Pinzón (Duncan) and Rábida (Jervis). These islands also have a complex history of volcanic activity but they are particularly interesting because they contain lavas showing the greatest variety in composition and also the most strongly differentiated end-products (less than 1% of the total mass). Two successive series of very differentiated lavas from Pinzon Island, the geology of which has been studied in detail by Baitis (Ph.D. thesis in progress), form the object of this study.

According to McBirney et al. (1966) the tholeiites are nearly identical in chemical composition to sea floor samples dredged on the East Pacific Rise. These authors also draw attention to noticeable differences that exist between tholeiites from Hawaii and Galapagos.

Whether or not these islands have always been isolated from each other and from the continent is a matter of controversy and subject to more intensive study. Darwin (1846) believed they always were, but Wilson (1963) and others after him suggested a drifting of newly-formed islands away from their origin, i.e. the Mid-Ocean ridges. These islands, therefore, grow older away from the ridges. Swanson et al. (1974), however, state that the correlation between age and distance from the ridge, i.e. the Galapagos ridge, is weak.

More investigation is also needed on the character of the underlying crust (Williams, 1966), although McBirney et al. (1969) state there is no evidence for an underlying sialic continental crust (Shumway et al., 1961). Such investigation, now underway for the Nazca plate (Supko et al., 1975) has been suggested for the Panama basin as well (Christensen et al., 1973).

The only DSDP sample available from the Pacific is D-6 (Leg 5-36) just north of the Mendocino fracture zone. The sample is probably Middle Eocene in age (McManus et al., 1970).

2.3 Island Arcs and Continental Margins

Samples originating from island arc systems in the western Pacific Ocean, from the Lesser Antilles in the Atlantic Ocean and from continental margins from Central America (Guatemala), South America (Chile) and Sardinia, were analyzed in order to study the calc-alkaline volcanic rocks. The samples will be treated according to their area, in the following paragraphs.

2.3.1 Island arcs of the western Pacific Ocean

Notwithstanding the existing chemical and physical differences between the various islands and/or volcanoes under investigation, one major factor they all have in common is the complete lack of continental crust in the area.

The geology of the Mariana island arc is described by Cloud et al. (1956) and Schmidt (1957). The arc lies to the west of the Mariana trench, which dips away from the western Pacific basin. Saipan, the second largest island, consists of a volcanic core, which has been enveloped by younger limestones. The oldest rocks are andesitic xenoliths in subaerial dacites

(Sanka Kuyama formation), probably of Eocene age or older. These dacites are subsequently overlain by andesites (Hagman formation) and derived sediments and limestones of Eocene age. Oligocene (?) andesitic flows and submarine tuffs (Fina Sisu formation) form with the Eocene rocks the core of Saipan, which is succeeded by sediments ranging from Miocene, probably Pliocene (?) to Recent.

The dacites are generally glassy, whereas the andesites are comparatively crystalline. The Saipan volcanics in general show high SiO_2, Al_2O_3, low K_2O, Ti_2O_5 and P_2O_5 (Schmidt, 1957). The andesites are extremely calcic. The islands more to the north of Saipan (Agrihan, Pagan, Alamagan) as well as northern Saipan are more basaltic in character.

Further to the south, where the Pacific and Australian plates meet, the island arc and trench systems become more intricate, exemplified by the two-component down-wharp of the Solomon Sea plate to the north under New Britain, and to the east under Bougainville, i.e. dipping 85° toward the Pacific basin (annual spreading rate of 10 cm; Le Pichon, 1968; Johnson et al., 1972). The backbone of Bougainville, the largest and northern most island of the Solomons, is made up by 17 volcanoes of post-Miocene age, of which Bagana is the only active one (Blake, 1968). The oldest rocks are basaltic and andesitic volcanics and derived sediments (Upper Oligocene?), overlain by Lower Miocene sediments and by Pliocene to Recent andesites (minor dacites). The Bagana basaltic andesites , and andesites with many pyroxene and plagioclase phenocrysts in glassy or fine crystalline matrix, are more alkaline than equivalents in similar regions (Blake, 1968; Carmichael et al., 1974). There is little or no evidence of strong folding or major faulting (Blake, 1968).

The Fiji islands lie halfway between the New Hebrides and the Tonga islands. The Australian plate is underthrusting steeply the New Hebrides island arc in a northeastern direction, and the Pacific plate dips toward the west under the Tonga island arc (Johnson et al., 1972). Chase (1971) calls the tectonic setting of the Fiji islands, which are flanked by three active sea floor spreading centres "probably unique" and "wonderfully complex". The Fiji islands, whose geology is mostly based on Rodda (1967) and Chase (1971), consists of two major islands and several smaller ones, and rise from the shallow, flat and hot Fiji plateau. Gravity data and the presence of plutons (particularly tonalites) on Viti Levu suggest a continental crust under the Fiji platform within the ocean basin, although Gill (1970) believes in the evolution of Viti Levu as part of an island arc system. The oldest rocks of Viti Levu are andesites with limestone lenses, ranging from Eocene to Early Oligocene, succeeded by thick series of basaltic to andesitic material on the top (probably Early to Middle Miocene), with increasing amounts of marine sediments. These two sequences, tectonically affected in the south, are unconformably overlain by Upper Miocene to Lower Pliocene calc-alkaline andesitic volcanics and limestones, and are succeeded by basaltic shield accumulations. The complexity of the area between the Tonga and New Hebrides trenches, where crust is consumed from opposite directions (Karig, 1971; Chase, 1971) is obvious.

2.3.2 Lesser Antilles island arc

Samples of the Lesser Antilles (Figure 2.4) for this study originate from the islands of St. Lucia and St. Vincent. These samples were donated by Dr. Tomblin, who did extensive field work on these islands. The general geology as described here is taken from summaries of Tomblin's work by Pushkar (1968, 1973).

The Lesser Antilles island arc, which forms the boundary between the Atlantic and the Caribbean plate, extends from Grenada island to Guadeloupe island, where it branches out into eastern and western arms. The eastern arm is composed of islands made up of sediments overlying a Tertiary volcanic basement. These islands do not show signs of any recent volcanism. The western arm and the island south of Guadeloupe are built up by volcanic rocks, ranging in age from Eocene to Recent with several active volcanoes.

The Puerto Rico trench parallels the arc system to the north and curves slightly to the southeast to be replaced by the Barbados ridge. Fisher and Hess (in Pushkar, 1968) suggest that the Barbados ridge system was formed by the

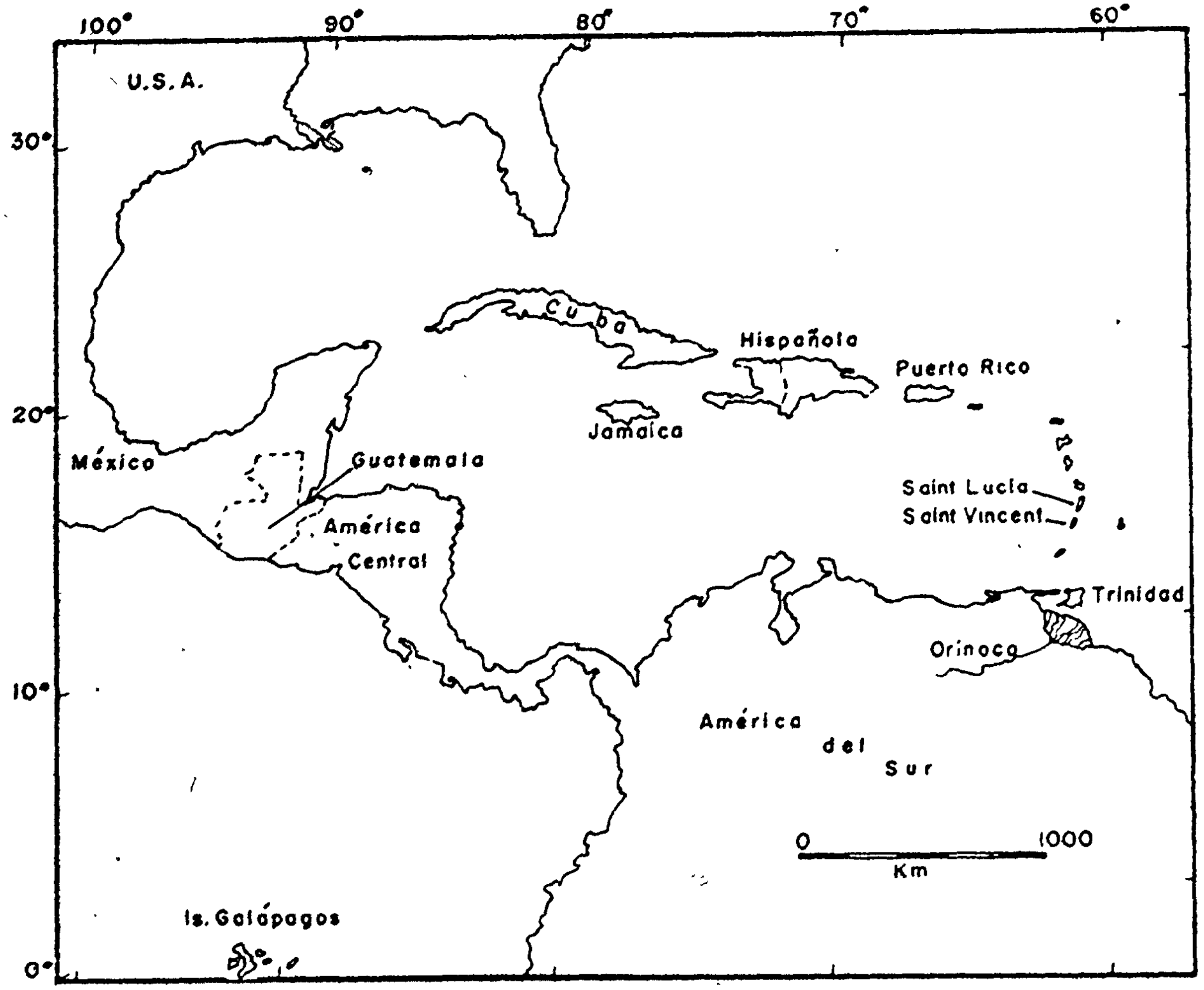

FIG. 2.4 THE CARIBBEAN AND COCOS PLATE AREAS. (After The World Atlas, Moscow, 1967)

filling of the previous southern part of the Puerto Rico trench by debris carried by the vast Orinoco River system. These sediments were then buckled up to form the Barbados ridge. Baker (1968) and Pushkar (1973) both mention Tomblin as stating the overwhelming predominance of andesitic material, invariably porphyritic, in the Lesser Antilles. For this reason the composition of St. Vincent, built up exclusively of basalts and basaltic andesites, is all the more interesting. Plagioclase-rich ultramafic cumulate nodules occur frequently as tephra on the slopes of the Soufrière volcano.

Although basalts predominate in the northern part, St. Lucia on the other hand may be considered as being more felsic in general. The island is built up by andesites and daçites. Tomblin observed several phases of volcanic activity, which are of importance, in the S.W. part, including Qualibou volcano. These phases are:

(i) Aphyric and porphyritic basalt lavas erupt during Early Pliocene, followed by a long period of subaerial erosion.

(ii) Andesite strato-volcanoes build up during Early Pleistocene. There is no compositional gradation between phases (i) and (ii).

(iii) Felsic andesite pyroclasts erupt, followed by caldera collaps (more than 0.5 m.y. ago).

(iv) Andesite and dacite dome lavas and pumice eruptions take place within the caldera (younger

eruption ±40,000 years ago). Present day
activity is solfataze.

A vast source of information on the geology of the Antilles in general is available in Weyl (1966).

2.3.3 Central America

The geology of Central America (Figure 2.4) in general, as described here, is based on compilations by Dengo (1973) and Weyl (1961). Central America can be divided into two distinctive areas, i.e. a northern and a southern province, because of differences in character of the basement underlying the volcanic series. Both provinces, however, have much in common as well, especially in their later geological evolution as shown by Tertiary and Quaternary volcanism and tectonism. Common to both provinces is the underthrusting Cocos plate which seems to change its dip angle (Stoiber and Carr, 1974). The Middle American trench is separated from the chain of Quaternary volcanoes by a flat coastal area (at its widest in Guatemala), and thought to be underlain by a granitic complex (de Cserna, _in_ Dengo, 1973). Dengo (1973) considers this trench system, the shallowest in existence, to be more similar to the Chile-Peru trench than to a real island arc system.

The boundary between the two provinces seems slightly south of the Nicaragua-Honduras border. The basement of the southern province (Meridional) is made up by mafic igneous rocks and Upper Cretaceous marine sediments and is believed to be part of the Pacific Ocean (Dengo, 1973). The northern province (Septentrional) is underlain by a continental crust of igneous granites and metamorphic rocks of Paleozoic and possibly Precambrian age (Gomberg et al., 1968). There has been volcanic activity during Paleozoic and Mesozoic times, but extensive volcanism did not happen until the Upper Tertiary. In Central Guatemala rhyolite and dacite pumice were laid down in vast amounts by "Nuées ardentes" from fractures, whereas basaltic to rhyolitic lavas and tuffs erupted in S.E. Guatemala (Williams et al., 1964a) as well as ignimbrites. Quaternary volcanism in Central America was extensively studied for more than twenty years by Williams and associates. In N.W. Guatemala most volcanoes emit pyroxene andesites and few have parasitic cones on their flanks which erupt basaltic cinders (Williams et al., 1964b). In later stages many of these volcanoes discharge large volumes of dacite pumice. In S.E. Guatemala most volcanoes are mainly or wholly basaltic (Williams et al., 1964a). The calc-alkaline lavas of the Quaternary volcanic chain are more siliceous hypersthene-andesites in Guatemala to become more mafic pigeonite-bearing basaltic andesites in Nicaragua, which seems to reflect the difference in underlying basement complexes (McBirney, 1969). This chain of Quaternary volcanoes, in fact, is segmented by offset-faults along which many so-called double-volcanoes occur (Stoiber and Carr, 1974).

2.3.4 Chile

The geology of the Quebrada Paipote, described by Segersholm (*in* Zeil, 1964) is part of an area in the Atacama desert, which can be divided roughly into three units (Zeil, 1964). To the west lies the Cordillera de la Costa, a Precambrian to Paleozoic, strongly folded and metamorphosed basement, with many Cretaceous batholiths and with a thick cover of sediments and volcanics of Jurassic and Cretaceous age ("Porphyry formation"). The inner part is a depression (Pliocene graben system) which is not always continuous over the whole of Chile. To the east lies the Cordillera de los Andes which in northern Chile is predominantly volcanic (Miocene and Pliocene) with ignimbrites (Rhyolite formation) and, in about equal proportions, rocks of the "Andesite formation". Volcanic activity is meagre compared to the highly explosive situation more to the south (Pichler and Zeil, 1969, 1972) and subduction occurs at about 6 cm/year (Le Pichon, 1968), with deep trenches in the north without sediments (Hayes, 1966).

The few samples collected by Dr. Zentilli along a geotraverse at latitude 27°S through Chile well into Argentina, will not be emphasized too strongly in this study. An attempt was made throughout this study to obtain fresh and young (Tertiary and Quaternary) samples. These "Chilean" samples, the youngest of which is Eocene in age (±50 m.y.) although they might very well be much older due to incorrect dating because of argon loss, underwent extensive metasomatism (Zentilli, 1974, pers. comm.). Zentilli also mentioned that only the Neogene rocks (<20 m.y.) are free (?) of alteration-contamination by intrusives. Tungsten is associated with all Tertiary intrusive episodes and lavas were taken from the vicinity of coeval plutons, but the samples used for this research were chosen and analyzed before all this information became available. The data, therefore, should be considered keeping all this in mind.

2.3.5 Sardinia

Both Sardinia and Corsica (Figure 2.5) formed a single complex already in existence in Cambrian times (Gignoux, 1955). In tracing the position of western Mediterranean microplates, Alvarez (1972), Alvarez et al. (1974) and others (Westphal et al., 1973; De Jong et al., 1973) came to the conclusion that evidence exists for the rotation away from France of the Corsica-Sardinia-Calabria microplate in Oligocene times, that is after the Cretaceous-Eocene Alpine orogeny and before the Apennine-Maghrebian deformations of Miocene times. The rotation of this one single plate creates a type of localized subduction zone, similar to the Recent Calabrian arc (Barberi et al., 1973), which cannot be compared with the western Pacific general subduction of the Pacific plate (Alvarez et al., 1974). At the same time, the Ligurian Sea began to form and andesitic volcanism started, to last from Late Oligocene to Middle

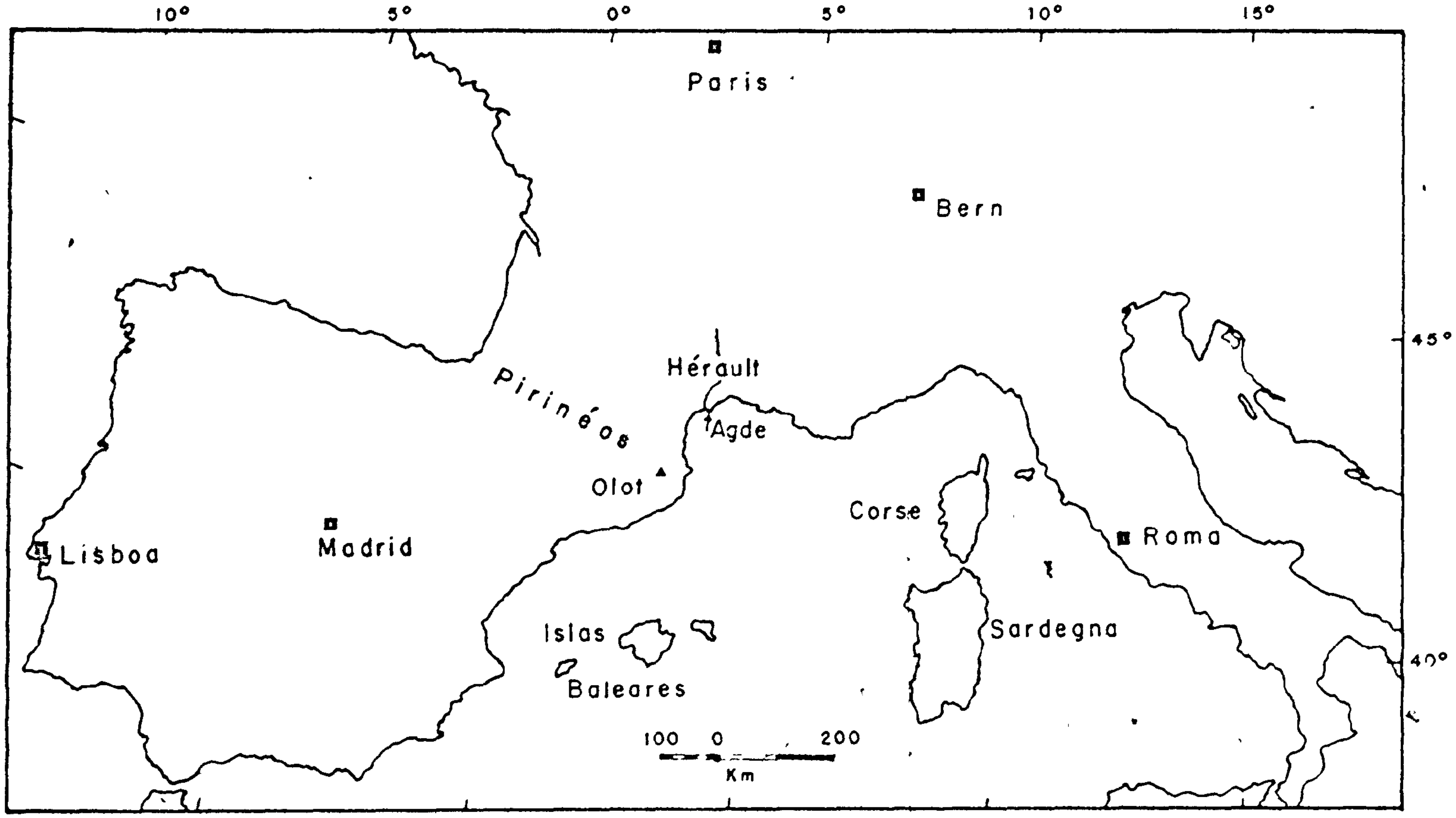

FIG. 2.5 THE WESTERN MEDITERRANEAN SEA AREA. (After The World Atlas, 1967)

Miocene accompanied by Graben formation in Oligocene (Le Pichon et al., 1971). In subsequent episodes, of less interest here, this microplate rotated further anticlockwise and moved down in a southeastern direction, while breaking up into several parts (Alvarez et al.,1974; Auzende et al., 1974). The Oligocene graben in Sardinia runs roughly north-south and is flanked by an eastern and less well developed western horst. The graben is filled with Cenozoic and Quaternary volcanics and sediments. These volcanics can be divided into Pliocene and Quaternary predominantly alkali-basalts and associated rocks. Of interest for this study are the more abundant "Andesite series" of Oligocene and Miocene age from the Logudoro and Bosano areas in N.W. Sardinia. Coulon et al. (1973), from whom most of the geological data on Sardinia were taken, divide the calc-alkaline volcanics, which they relate to a continental margin, into a:

high-aluminum Lower Andesite series, of Oligocene to Lower Miocene age;

Upper Andesite series, composed of mainly andesites and later associated dacites;

Final Andesite series of Middle Miocene age. This series, although less voluminous, shows much greater diversification.

The bulk of the Andesite series, each series having distinctive evolutive chemical properties, is represented by about 30% basalts, 65% andesites and only 5% dacites and rhyolites. These rocks are relatively enriched in K_2O content towards the north, suggesting a deepening of the aforementioned Benioff zone (Coulon et al., 1975). The rocks of Logudoro and Bosano have a mineralogy which is typically calc-alkaline (Coulon et al., 1973) and made up mainly by zoned plagioclase phenocryst. Other phenocrysts are olivine (basalts and basaltic andesites), clinopyroxene and orthopyroxene (andesites and dacites). Amphibole and biotite occur occasionally except in the "Final Series" where hornblende is omnipresent. Amphibole also occurs in the andesites of southern Sardinia. Coulon et al. (1973, 1975) emphasize the fact that the mineralogy of the andesitic lavas of the whole island is rather constant, which contrasts strongly with their varying chemistry.

2.4 Continental Regions

Samples from southern France, northeastern Spain, as well as the southwestern United States of America, which are believed to be continental in their origin, will be considered in the next few paragraphs. Some kimberlites from Africa and Quebec are shortly dealt with as well.

2.4.1 France and Spain

Several authors (Rutten, 1969; Gèze, 1962) see the Pliocene and Quaternary volcanic activity in southern France (Figure 2.5) as outer-Alpine and therefore only controlled by blockfaulting. Gèze (1962) mentions some 200 small lava outflows in the Causses and Bas-Languedoc along a north-south trend of some 150 km. The Hérault valley forms one of the several north-south alignments of volcanic activity (Gèze, 1955), along which the size of the lava out-pourings increases from small mafic to ultramafic eruption spots through Mesozoic sediments (Causses) to impressive volcanoes (e.g. Agde), built up by true basalts rich in olivine, upon the Cenozoic sedimentary plain of Bas-Languedoc (Gèze, 1955). These basalts are considered to be alkali-basalts, although some of them are hypersthene normative (Lefèvre et al., 1972). Peridotite nodules seem to be abundant.

Rutten (1969) extended this north-south line of volcanic activity from the Massif Central via the Agde volcano down to southeastern Spain, mentioning on the way down the small, but volcanically intensive, area of Olot (Gerona, N.E. Spain). Despite the very early work of Washington (Johannsen, in Tournon, 1969) not very much research has been done until recently. The composition of the Olot volcanics can be divided according to their mineralogy into alkali-basalts, analcite-basanites (abundant among Tertiary lavas) and even leucite-basanites (abundant among Quaternary effusives) (Tournon, 1969). These rocks show close similarities with the lavas from the Causses (Gèze, 1962).

De Roever et al. (1975) speculate that these leucite-bearing rocks are related to Cenozoic subduction zones in

France and Spain.

The volcanic area of Olot is situated in the Tertiary Ampurdán basin, framed to the north by the Paleozoic and Mesozoic eastern Pyrenees, to the southeast by the Paleozoic Catalán coastal range and to the southwest by the Tertiary Ebro-basin. The Middle and Upper Pleistocene basalt cones of Olot, which in several cases are remarkably well-preserved, protrude the Eocene sediments of the aforementioned basin (Wagner et al., 1971). The area is now proclaimed a volcanological museum and directed by Solé-Sabarís of the University of Barcelona.

2.4.2 New Mexico and Arizona

On a continental scale Cenozoic volcanism in the western U.S.A. has been correlated with tectonic setting, i.e. plate tectonics (e.g. Lipman et al., 1972; Christiansen et al., 1972). In a first stage voluminous andesites and related rocks erupted during Eocene times in the N.W. U.S.A. This volcanism, shifting southward during the Oligocene, has been linked to the evolution of a subduction zone (Farallón plate) under the continental margin. With a change in tectonic pattern occurring at the end of the Oligocene, there coincides a major change in volcanic associations. The late Cenozoic volcano-tectonic transition, which takes place in a region characterized by tectonic extension, starts in southern New Mexico and Arizona and moves northwestward through Miocene, Pliocene and Quaternary times. The predominantly andesitic volcanism is now replaced by "fundamentally basaltic volcanism" (Christiansen et al., 1972) caused this time by the collision of the East Pacific Rise with a mid-Tertiary continental margin trench, which in turn causes direct contact between the American and Pacific plates.

On a more local scale the Bandera lava field (western New Mexico) and the Arizona volcanics, should consequently be related to this "fundamentally basaltic volcanism". The Arizona volcanics (samples WL-6,7) are probably from the same flow, although collected several miles apart (Laughlin, pers. comm.). The Bandera lava field is situated on the Colorado plateau (about 40 km thick) and consists of both tholeiitic and alkalic basalts, which erupted within a short time span. The Laguna flow, considered to be one of the oldest flows of the Bandera lava field, probably erupted during the last normal magnetic epoch ($\pm 10 \times 10^6$ years B.P.). The lava field apparently lies on the intersection of two major structural lineaments, i.e. one trending SE-NW and a less conspicuous NE-SW one trending into Arizona (Laughlin et al., 1972a,b).

2.4.3 Kimberlites

Only 4 kimberlites were analyzed. The Ile Bizard kimberlite (KB-1) originates from the Monteregian province (Québec) and is situated close to the Oka carbonatite complex and lies in an alnoïtic region (Clark, in Marchand, 1970).

The other kimberlites are all from South Africa, though not from the same area. The following information was given to M. Marchand by D. Gold in a written communication (1973). KB-2 (1750 m.y.) is a mica-poor agglomeratic kimberlite from near Pretoria. KB-3 is a late basaltic kimberlite, intruded into an early agglomeratic kimberlite, from the Kimberley area, and KB-4 is a 'kimberlite', consisting of fine-grained phlogopite, carbonate and olivine phenocrysts, from the Bellsbank Main Fissure some 100 km northwest of Kimberley.

These kimberlites are 'exotic' ultramafic rocks and do not fit in very well with the basalts and intermediate rocks under investigation in this study. Despite the very few analyses which preclude any significant conclusion, they nevertheless are of interest because of the scarcity of such data.

2.5 Summary

A world-wide sampling of volcanic rocks was made, but relatively few samples could be analyzed from each region, because of the laborious analytical procedure. The provenance of the samples is summarized in Table 2.1 and Figure 2.1. For further details reference is made to Appendix I.

Table 2.1 Summary of the provenance of the samples analyzed in this study

Region	Locality	Code No.*	No. of samples
ROCKS FROM OCEAN ISLANDS AND FLOORS			
Indian Ocean	Crozet Archipelago	Ce	5
	Amsterdam Island	Na	4
Atlantic Ocean	Cape Verde Archipelago	VM,VS	5
	Heymay, Iceland	IC-1	1
	DSDP, Legs 2 & 3	D-1 to 5	5
	MORB, 45°N	AU	1
	Reykjanes ridge	IC-2 & 3	2
Pacific Ocean	Mendocino fracture	D-6	1
	Hawaii Island	Ha	6
	Galápagos Archipelago	BH	12
ROCKS FROM SUBDUCTION ZONES			
Pacific Plate Margin	Fiji Islands	G	3
	Bougainville	T-1 to 5	5
	Marianas	T-6, US	6
Cocos Plate Margin	Guatemala	M	4
Lesser Antilles	St. Lucia	TL	5
	St. Vincent	TV	6
Mediterranean Sea	Sardinia	S	6
ROCKS FROM CONTINENTAL AREAS			
France	Hérault	He	14
Spain	Olot	H	2
S.W. U.S.A.	New Mexico & Arizona	WL,WF	12
Canada	Québec	KB-1	1
S. Africa	Kimberley, Pretoria	KB-2 to 4	3

*These code numbers are used throughout the text to indicate the various groups of samples

CHAPTER III

DETERMINATION OF TUNGSTEN

3.1 Introduction

In Chapter I the scarcity of available data on tungsten in rocks was explained as being a consequence of the lack of good analytical methods. As a matter of fact previous experience (Helsen, 1970) shows that several methods, such as spectrographic and colorimetric analysis, were found to be neither accurate nor sensitive enough for the study of small amounts of tungsten in volcanic rocks. Consequently attention was focussed upon a more suitable approach by applying the neutron activation analysis (NAA) radiochemical method developed by Atkins and Smales (1960). This method has been changed only slightly in a few steps.

When this study was well under way, the existence of a newly developed NAA was mentioned by Simon (written comm.). In spite of some potential improvements, this new method, however, was never tested, not to mention used, because of the advanced stage of this study.

3.2 Sample and standard preparation

Prior to irradiation the samples, if not already available as a powder from the donor, were wrapped in a cotton mailbag, broken into small chips with a hammer and then crushed with a pulverizer with aluminum oxide discs and the resulting powder split. One sample split was further ground in an agate mortar until the whole passed through a 200 mesh sieve. Amounts of this rock powder, ranging from 50-150 mg were weighed into a silica ampoule (3 mm O.D. and 4.5 cm long) and heat sealed.

For the preparation of the standard solutions a "specpure" (Johnson, Matthey and Mallory Co.) tungsten trioxide powder was used: An adequate amount of this powder was dissolved in about 1 N ammonia (warm) and kept on a hot plate until completely dissolved. This solution was then diluted to 500 ml. A 100 ml aliquot, taken from this solution was then further diluted to 500 ml. This final solution represents the flux monitor standard solution with a tungsten concentration of 0.03203±0.00011 mg W/ml.[1] The density of this standard solution was determined subsequently.

A certain amount (about 0.040 ml) of this standard solution was transferred by a capillary glass pipet into a thoroughly cleaned and weighed silica ampoule containing quartz powder (100<mesh powder<50 mesh). The weight of the

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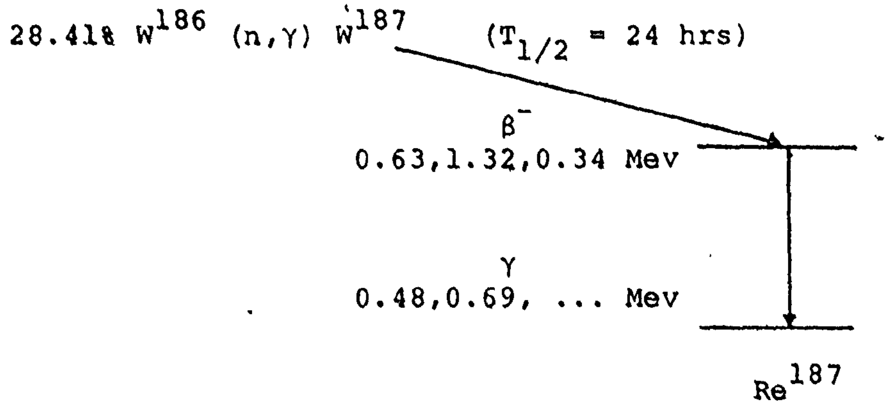
[1] It is realized that the ±0.00011 value is the sum of all possible errors and therefore is probably too high.

standard solution was determined by difference. The quartz powder, prepared from crushed high purity quartz tubing, was used to absorb the tungsten standard solution and to fill up the ampoules to the same height as the rock samples. The ampoules and contents were dried overnight at 65-70°C and sealed with polyethylene plugs. It was customary to prepare a large number of ampoules containing the standard solution ready for irradiation well in advance, to avoid any possible contamination of samples, as well as to obtain uniformity among the standards used in different irradiations. Whenever a new standard solution was made up it was compared with the previous one.[1]

3.3 Irradiation

The determination of tungsten by NAA is based on the following reaction:



The thermal neutron capture cross-section (σ) is 40 barns

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[1] No significant differences were observed to exist among the different standard solutions.

Details concerning irradiation theory, i.e. activity, etc., are treated by Chyi (1972) and many others (e.g. De Soete et al., 1972). Characteristics of the McMaster University Nuclear Reactor are given by Tong (in Chyi, 1972), and nuclear data for tungsten are compiled by Heath (1968).

Due to the long chemical separation period required to obtain a radiochemical pure tungsten compound, only four samples were irradiated at a time. Four standards usually accompanied the samples. Sample and standard ampoules were arranged alternatively and put into an aluminum can and irradiated for 12 hours at an approximate neutron flux of 1.5×10^{13} neutrons/cm^2/sec or 3.5 hours at 5×10^{13} neutrons/cm^2/sec, followed by a cooling period of about 20 hours.[1]

The flux variation within a group of adjacent samples was reported to be no greater than 5% (Dostal, 1973; Chyi, 1972).

3.4 Chemical separation procedure

3.4.1 Samples

1.* Cover the bottom of a 35 ml zirconium crucible with a layer of sodium peroxide. Transfer the irradiated sample into the zirconium crucible.

2.* Sinter the samples for 20 minutes in a furnace maintained at 570±20°C.

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[1] Necessary because of Na^{24} activity.

Steps marked * indicate slight changes have been made, as compared with the procedure of Atkins et al. (1960)

3. Remove the crucibles and cool quickly in water.

4.* Transfer the cake to a 400 ml beaker and carefully add a previously prepared mixture containing exactly 5 ml sodium tungstate (7 mg W/ml), 10 ml of 20% tartaric acid (wt/v) and 70 ml of distilled water containing 5 g ammonium chloride. Rinse thoroughly both crucible and carrier beaker with distilled water.

5. Acidify with 10% (v/v) sulphuric acid until all solids dissolve and then boil this solution.

6. Add ammonia dropwise until the solution is just alkaline, followed by 50% (v/v) hydrochloric acid until the solution is acidic and then add two drops in excess.

7. Add slowly and with constant stirring 70 ml hot 2% (wt/v) tannin solution. Boil gently to coagulate the precipitate. Remove from the hot plate and add, again slowly and with constant stirring, 10 ml of 5% (wt/v) cinchonine in 25% (v/v) hydrochloric acid to the hot solution. Digest for at least 30 minutes.

8. Filter through an 11 cm Whatman No.541 filter paper and wash the precipitate with hot 2% (wt/v) ammonium chloride solution. Discard the washings.

9. Transfer the washed tannin-cinchonine precipitate to a 250 ml beaker and add 20 ml concentrated (conc.) nitric acid and 5 ml conc. sulphuric acid. Heat on a hot plate until all the organic material is destroyed. Add more

nitric acid if necessary. Fume off any excess nitric acid.

10. Cool and add 50 ml demineralized water to precipitate the hydrated tungsten oxide.

11. Add 5 ml. conc. hydrochloric acid and boil. Transfer both liquid and precipitate to a polyethylene tube and centrifuge. Discard the supernate.

12.* Slurry the precipitate with 20 ml of a 0.4 M hydrofluoric acid-6 M sulphuric acid mixture into a teflon crucible containing another 30 ml of this mixture, previously heated on a sandbath. Cover and heat the whole for about 15 minutes or until the mixture just starts to boil.

13. Cool the mixture and transfer to a 100 ml separatory funnel containing 15 ml methyl iso-butyl ketone (hexone), previously treated with the 0.4 M hydrofluoric acid-6 M sulphuric acid mixture. Shake for 2 minutes. Bring the tungsten-containing phase over into another 100 ml separatory funnel. Repeat the same process and let stand for about 20 minutes.

14. Transfer the aqueous phase to a 250 ml beaker. Add 15 ml conc. nitric acid and digest on a hot plate. Cool, transfer the liquid to glass tubes and centrifuge. Discard the supernatant liquid.

15. Wash the tungsten oxide precipitate, with hot conc. nitric acid, centrifuge and discard the washings.
16. Dissolve the tungsten oxide in 15 ml 0.88 M ammonia solution. Centrifuge and discard the residue, if any.
17. Add 5 ml conc. nitric acid and digest on a waterbath to precipitate the tungsten oxide and centrifuge.
18. The cycle consisting of steps 15, 16 and 17 should be repeated at least once.
19. Dissolve the tungsten oxide in a minimum volume of 0.88 M ammonia solution. Heat the solution to boiling (on a waterbath) and then add very slowly 1 ml 5% (wt/v) 8-hydroxy-quinoline solution in 2 N acetic acid to precipitate tungsten oxinate. Acidify with acetic acid. Centrifuge and discard the supernatant liquid.
20. Wash the precipitate first with water, then with alcohol and slurry the precipitate with a little alcohol onto a weighed counting tray. Dry carefully with an infra-red heating lamp, weigh for chemical yield determination and count.

3.4.2 Standards

1. Clean the ampoules with acetone and then with distilled water, dry and open.
2. Empty the quartz powder into a 150 ml beaker and leave the silica ampoules as well.

3. Add exactly 5 ml sodium tungstate carrier solution, 5 ml 25% (v/v) ammonia solution and 20 ml distilled water. Heat the beaker and its contents gently on a hotplate. Stir frequently and rinse (with a capillary pipet) the empty ampoule thoroughly. Pass the solution through a Whatman filter No. 541 into a 400 ml beaker.

4. With the exception of carrier addition, repeat step 3 twice with 5 ml 25% ammonia and 20 ml distilled water, and twice more with 25 ml distilled water only to ensure complete removal of the absorbed activity.

5. Add 20 ml conc. nitric acid and digest on a hotplate. Cool, discard the greater part of the supernatant liquid and centrifuge the rest.

6. Go to step 15 (sample procedure) and treat the standards from now on in the same way as the samples and count.

3.5 Counting and calculation

3.5.1 Instrumentation

The counting equipment used in this research includes a Nuclear-Chicago gamma counting system consisting of a well-type 3"x3" NaI (Tl) scintillation detector (or a 25 cm^3 Ge(Li) diode), an analog to digital converter, a 1600 channel memory and a teletype paper printout.

Interference from isotopes other than W^{187} was expected when this study started. For this reason the samples of earlier irradiations were counted on the Ge(Li) detector because of its higher resolution. When it was realized, however, that the tungsten oxinates were radiochemically pure, the use of the Ge(Li) detector was discontinued in favour of the NaI(Tl) detector because of its higher sensitivity (Yule, 1970).

3.5.2 Peak evaluation and calculation

The radiochemical purity of the final tungsten compound was examined by following closely the decay curve, by comparing the obtained gamma spectra with published W^{187} spectra (Heath, 1964) and by evaluating the energies of the different photo peaks. No interference from other radionuclides was detected. Only in one case (an apatite mineral) the tungsten oxinate was contaminated by a foreign radionuclide (0.32 Mev) without interfering, however, with any of the tungsten peaks.

The 0.480 Mev peak was selected for calculation of the W^{187} activity according to the classical total peak area, as described by Yule (1969). The 0.686 Mev peak, however, was also used as a basis of calculation to check the results obtained with the 0.480 Mev peak. The peak ratio variation between samples and/or standards was small and was usually less than 1.5%. Only in the case of very long counting periods was a change in this ratio observed.

Before determining the concentration of tungsten in rocks, a possible source for error due to the production of W^{187} by other than (n,γ) reactions should be mentioned. The samples in this study were irradiated in a neutron flux which represents the total reactor neutron spectrum. The greater part of this spectrum is composed of lower energy or thermal neutrons which activate tungsten according to the reaction $W^{186}(n,\gamma)W^{187}$. This neutron spectrum, however, also contains neutrons with higher energies, for example, epithermal, slow and fast neutrons (Lapp et al., 1963; Steinnes, 1970). Some of these high energy neutrons can produce W^{187} according to reactions given in Table 3.1.

Table 3.1 Fast neutron irradiation (14 Mev) reactions producing W^{187} from Re^{187} and Os^{190}, cross-sections σ (in millibarn) and natural abundances (%) of Re^{187} and Os^{190} and Re and Os contents in BCR-1

Reaction	σ*	Natural* abundance	Abundance in BCR-1**
$Re^{187}(n,p)W^{187}$	3.9	62.9	0.00085 ppm
$Os^{190}(n,\alpha)W^{187}$	0.6	26.4	<0.000095 ppm

* De Soete et al. (1972)

**Schindler (pers. comm.); the Re content of BCR-1 is the mean value of 25 analyses

As pointed out earlier by Atkins et al. (1960), the very low abundances of Re and Os, as well as the very small cross-sections for both elements in a fast neutron flux make it indeed very unlikely that W^{187} will be produced at significant levels by any reaction other than $W^{186}(n,\gamma)W^{187}$. (For further information on the neutron spectrum of the McMaster Nuclear Reactor see Tong, 1971).

Using the raw data obtained during counting, after correcting for background, counter deadtime and decay during counting (Wright, 1971), the concentration of tungsten present in the sample was calculated (in ppm) using the following equation:

$$C_s = \frac{A_s \times Y_S \times M_{wS} \times 10^6}{A_S \times Y_s \times M_s} \text{ ppm}$$

where

C = concentration
A = activity
Y = chemical yield
M = weight
s = sample
S = standard
w = metal (tungsten)

3.5.3 Accuracy and precision

Some idea of the precision of the method may be acquired from the results obtained during multiple analysis of some standard rocks (Table 3.2).

With reference to the tungsten content of BCR-1, Steinnes (pers. comm., 1973) noted that the BCR-1 values of 1971 are an improvement over the 1970 values, whereas an estimated value only of about 0.48 ppm W could be obtained from Wänke (1975, Figure 4, p.269).

Table 3.2 Mean tungsten content and standard deviation (ppm) in four U.S.G.S. standard rocks obtained in this work and from the literature

Rock	This work	1	2	3
AGV-1	0.89±0.21 (7)	1.1	0.57±0.07 (5)	0.45±0.06(3)
BCR-1	0.51±0.05 (18)	0.7	0.35±0.06 (5)	0.24±0.06(3) 0.38±0.02(4)
PCC-1	0.009,<0.009(2)	0.2	0.007±0.002(5)	-
DTS-1	0.018±0.002 (3)	0.2	0.016±0.002(5)	-

Values in parentheses indicate number of analyses done

1. Chan and Riley (1967) colorimetry
2. Simon (1972, 1975) NAA
3. Johansen & Steinnes (1970) NAA
4. Brunfelt & Steinnes (1971) NAA

W-1 was also analyzed for tungsten. The first value obtained was 0.51 ppm. Because of the known inhomogeneity of W-1 (Flanagan, 1969) an attempt was made to homogenize the sample. This attempt, however, resulted in an even greater inhomogeneity because too small a sample was used in too large a container, with the subsequent loss of the finer fraction of this sample on the container wall due to static electricity. This fact may be reflected in the erroneous results up to about three times the first value. Consequently W-1 was discarded and BCR-1 was used throughout this research to estimate precision and accuracy. BCR-1 was analyzed twenty times in total, but two results, exceeding the mean value by more than three standard deviations, were rejected. Figure 3.1 shows the distribution of the eighteen accepted values on a frequency histogram. The 95% confidence limits of the true mean are given by 0.51±0.026 ppm.

In one of the last irradiations performed in this study three different splits of BCR-1 were analyzed. The purpose of this irradiation was to obtain an idea of the homogeneity of the rock as well as to see how the results of this work compare with the values obtained by other investigators for the same split of BCR-1. Simon (written comm.) used one split (out of five available) for analysis of the U.S.G.S. standard rocks, but did not notice at that time the split number. Therefore, split 72/8 was chosen arbitrarily among the five different BCR-1 splits received from Simon. The results of this irradiation are given in Table 3.3.

Table 3.3 Tungsten content (ppm) of four BCR-1 samples representing three different splits

Split	Donor	Tungsten content
6/32*	Crocket	0.488
6/32	Crocket	0.489
18/13	Steinnes	0.496
72/8	Simon	0.485

*This split was used throughout this research

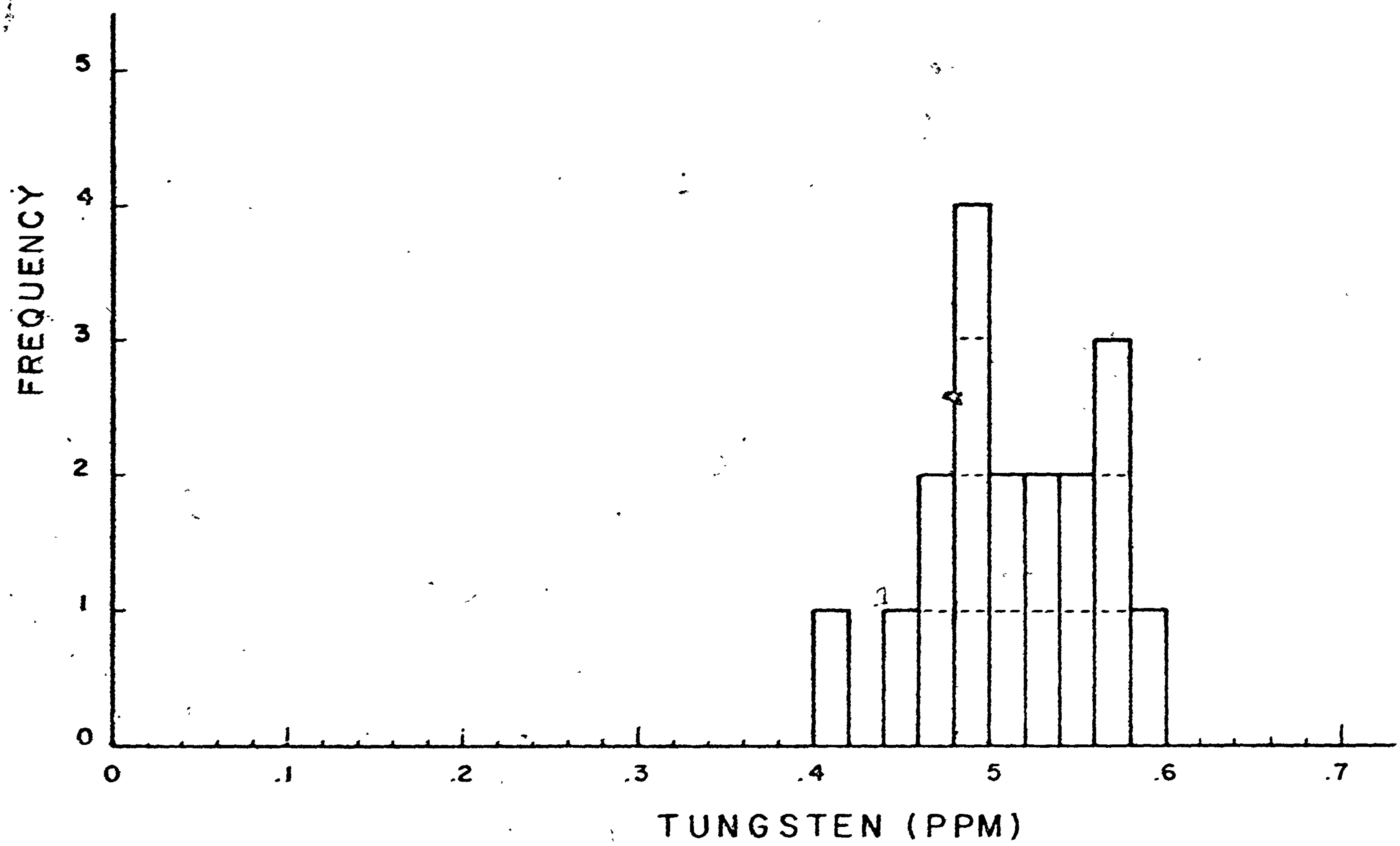


Fig. 3.1 Distribution of tungsten in BCR-1

3.5.4 Detection limit

With reference to the sensitivity of the method, Atkins et al. (1970) reported tungsten determinations at levels down to 2.10^{-9} g but concluded that the tungsten sensitivity can be improved (i.e. possibly down to 10^{-11} g) under the correct conditions, for example, longer irradiation time, etc. The most sensitive values of this study were obtained for the two ultramafic rocks PCC-1 and DTS-1 in two different irradiations, I and II (Table 3.4).

Table 3.4 Sensitivity for gamma detection and some factors influencing this sensitivity for two ultramafic rocks, subjected to a neutron flux of $5\times10^{13}/cm^2/sec$ in two different irradiations.

Rock name	PCC-1				DTS-1			
Irradiation	I		II		I		II	
Time (hrs.)	3.5		5		3.5		5	
Chemical yield (%)	36.16		45.53		52.21		35.39	
Sample amount (mg)	131		128		115		116	
Peak (Mev)	0.480-0.686		0.480-0.686		0.480-0.686		0.480-0.686	
Background (cpm)	90	46	90	46	93	47	93	47
Peak/background	1.54	1.82	1.80	2.48	2.55	3.55	2.38	3.70
Amount W counted ($\mu gW\times10^{-4}$)	4.12	4.19	5.29	5.38	9.49	9.78	6.86	6.91
Amount W in sample (ppm)	.0087	.0089	.00895	.0091	.0159	.0163	.0169	.0170

By irradiating, for example, for a slightly longer period or by using more sample, the peak to background ratio could be improved and reach a ratio of 2.0 as suggested as the minimum detection limit, according to Crocket (1970). According to these suggested limits, some of the results for PCC-1 are apparently below the detection limit. The results within a single irradiation (i.e. for both peaks) agree with each other, as well as the results of the two irradiations. It should be kept in mind that the results for PCC-1 were the most sensitive of this investigation.

3.6 Summary

Tungsten was determined by a NAA radiochemical method following the reaction $W^{186}(n,\gamma)W^{187}$.

Precision of the method averages 10% (standard deviation) of the amount present for mafic igneous rocks. The detection limit is about 0.9×10^{-9} g W on a 100 mg sample, or 0.009 ppm W.

Accuracy was investigated by analyzing international standard reference rock powders. The values obtained include 0.51 ppm (BCR-1), 0.89 ppm (AGV-1), 0.009 ppm (PCC-1), 0.018 ppm (DTS-1) and 2.12 ppm (BR). The accuracy appears satisfactory, but few other reliably established results exist for comparison.

The method is tedious because of the very long chemical separation period (about thirteen hours).

CHAPTER IV

FACTOR ANALYSIS AND ITS APPLICATION

4.1 Introduction

A large number of data has been accumulated since the start of this research project. In order to process these data factor analysis (hereafter F.A.) was used as a tool, to help find the relationship that exists within a set of a certain number of variables (m) and which is regarded to reflect the correlations of each of the variables with a certain number (p) of mutually uncorrelated underlying factors, assuming $p<m$ (Davis, 1973).

Much has been written on F.A. since its development in 1904, ascribed to Charles Spearman (in Harman, 1970). For a more in-depth study of F.A., reference should be made to Harman (1970) and many others, but for the purpose of interpreting the results of this study the work of Davis (1973) was found to be both very helpful and elucidating.

4.2 Conditions under which factor analysis was applied

R-mode F.A. was performed by using the program BMDO8M (Former BMDX72) of Sampson and Jennrich (1972). Several options are available in this program, for example oblimin or orthogonal rotation, i.e. quartimax or varimax, etc. The options as used in this study are stipulated below:

- A correlation matrix was used without altering the diagonal elements and because of the standardization of the variables the estimated communalities will be equal to 1.000.

- Eigenvectors are computed prior to rotation in a normalized form, which means that they define a vector of unit length. Every element of the normalized eigenvector is then multiplied with the square root of its corresponding eigenvalue which produces the factor, i.e. a vector weighted proportionally to the amount of the total variance it represents. The number of factors that will be rotated is determined by the smaller of the two following numbers: m/2, where m is the number of the variables and the number of eigenvalues greater than a (chosen) constant C. C=0.500 in most cases in this research.

- Kaiser's varimax (orthogonal) rotation simplifies the columns, or factors, of the factor matrix in an attempt to meet the requirements for simple structure (Kaiser, in Harman, 1970). No other rotation than Kaiser's varimax was applied, although it is the belief of Spencer (1966) that the orthogonal rotation (varimax) is not ideally suited for geochemical data. This is in contradistinction with the need to keep the underlying factors mutually uncorrelated. In choosing to relax the restriction on orthogonality the introduced intercorrelations between factors is going to make the relationship between factors and original variables much more complex (Davis, 1973). According to Davis (1973) non-orthogonal rotation schemes allow the factors to be expressed in terms of the original variables. Thus if no pattern emerges in the factor loadings, reality should be faced instead of coming full circle from variables to factors (to reduce the size of the problem) back to variables needed to interpret the factors, since in such a case the same information could have been obtained altogether from the original correlation matrix.

After performing the mentioned rotation the obtained factor loadings are then plotted in a circular coordinate system, where each axis represents a factor lying between extreme limits of +1 and -1.

An attempt is made to use factors 1 and 2 as often as possible because these factors carry always the largest proportion of the total variance, and consequently have more significance. In cases where the original variables seem to be well correlated, few factors are needed to represent a large proportion of the total variance of the data set. In cases, however, where the original data show little or no correlation, many more factors will be needed to represent the same amount of the total variance, i.e. the fewer factors the better correlation one can expect generally. In such a case of good correlation high communalities might be expected as well. As mentioned earlier, the use of a correlation matrix implies estimated communalities equal to 1.000 for each variable.

Subsequently the final (obtained) communality should be near this value of 1.000 as much as possible. The difference between the estimated and final communality for each variable is called the uniqueness, and the amount of uniqueness indicates the extent to which the common factors fail to account for the total unit variance of the variable, which may include errors due to unreliability in measurement (Harman, 1970). According to Davis (1973) the communality can provide an index to the efficiency of the reduced set of factors, i.e. the appropriateness of the factor model.

In conclusion, when interpreting F.A. the degree of importance of each factor should be kept in mind. Also, if strange correlations do occur it might be advisable to take into consideration the communality of the variables involved. Choosing a set of data that is going to be subjected to F.A. might turn out to be the most important asset. Throughout this research the same experience was obtained concerning the selection of sets of rocks as mentioned by Spencer (1966, p.13): "For instance, it has been the author's experience that if factor analysis is applied indiscriminately to data from sediments of diverse origin, the results can be chaotic and uninterpretable. However, by separating heterogeneous data into logical groups before the factor analysis, order can be restored. Factor analysis is not a screen at which one can throw garbage and expect to sieve out significant results".

Before proceeding with a case history, it should be pointed out that R-mode F.A. was performed on a set of variables which included major oxides, trace elements and to some degree ratios. For the sake of consistency, the major oxides were normalized on a H_2O and CO_2-free basis and total iron was expressed as Fe_2O_3. The major oxides, however, that appear in the various tables in this Chapter (see Tables 4.2 and 4.3) and in Chapter V are taken from Appendix II, without any normalization involved as yet.

Where no data were available for P_2O_5 a content of 0.1% was assigned, which is more in agreement with reality than a previous assumption of 0.01% (Shaw et al., 1974). The trace elements involved are Li, Rb, Sr, Ba, Cr, Co, Ni, Cu, Y, Zr, Nb, Zn, Pb, U, Th and W. This does not mean that values for all those elements are always available. Where some of the rocks within a particular set of samples have values below the detection limit for a certain trace element, this element was generally omitted rather than assuming an unreal low value.

Element ratios were included with the raw data to form the correlation matrix to be used in F.A. The results obtained by including ratios added little to the interpretation and use of these ratios was gradually reduced, with the exception of K_2O/Na_2O.

Chayes (1971) refers to such ratios as "degenerate" ratios and exemplifies the complexity of their use with a K/Rb and K correlation in two sets of submarine basalts. In one set this correlation is strongly positive, whereas in the other set it is strongly negative, a shift ascribed mainly to the vulnerability of correlation estimates to sample size.

Major oxides will be indicated by the cation only, thus SiO_2 becomes Si in both text and F.A. plots.

For reasons of space the ratios (Appendix II) will be designated by the first letter of the element (or oxide) symbol (formula) involved: thus K/N represents K_2O/Na_2O, whereas K/R stands for K/Rb, S/S for Sr^{87}/Sr^{86}, etc.

4.3 Case history of Pinzón Island

4.3.1 Introduction

In order to illustrate the aforementioned, a case study of a single volcano will be considered. Pinzón Island (Duncan) in the Galápagos Archipelago has been studied by Swanson et al. (1974). On one of the sea cliffs (Plate 4.1) within a stratigraphic section of more than 300 m thickness, a succession of at least 7 eruption cycles can be observed. These cycles show in general an upsection that starts at the base with siliceous trachyte or icelandite tuffs, overlain by aphanitic and often glassy icelandites. These are generally phenocryst-free. Then follow the predominant phenocryst-rich tholeiites and olivine tholeiites which contain up to 50% or more plagioclase megacrysts in some flows. According to Swanson et al. (1974) each sequence of flows sampled represents a magma chamber that was compositionally zones. Fairly

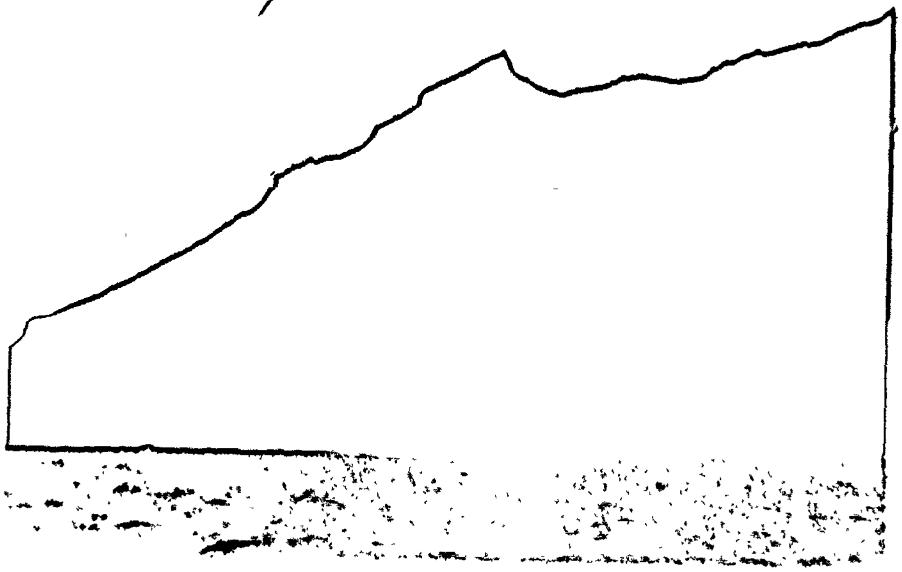


Plate 4.1 Southwestern side of Pinzón Island, Galápagos
(Courtesy Hart Baitis)

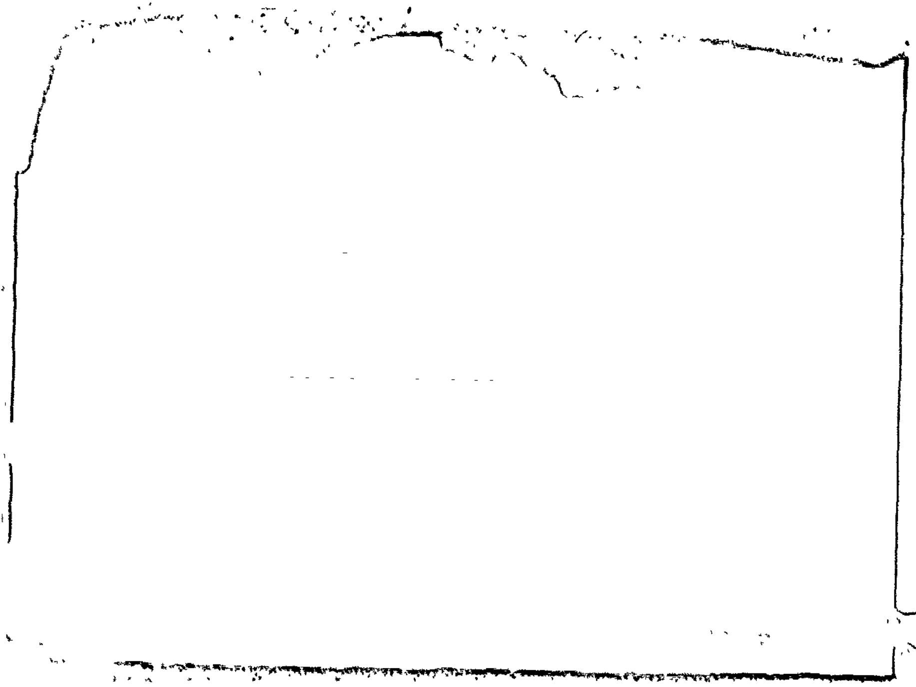


Plate 4.2 Sea cliff on the southwestern side of Pinzón Island, Galápagos, from which the rocks of suites A and B were sampled
(Courtesy Hart Baitis)

extensive crystal fractionation occurred in the magma chamber. During each eruptive cycle subsequent (deeper) levels of the magma chamber were topped, so that the more felsic layer at the bottom of each cycle represents actually the uppermost zone of the magma chamber below.

A detailed stratigraphic study of the succession of the layer within the various cycles was done by Baitis (unpub. data), who also provided the samples for the two cycles under investigation here (Plate 4.2). Suite A represents a lower cycle (8 samples BH-BO), whereas suite B represents the overlying cycle (4 samples BP-BT).

F.A. was applied to the two suites A and B combined and then to each suite separately. Table 4.1 shows the rotated factor (loading) matrix for these suites.

4.3.2 Combined suites A and B

Some information on the chemistry and petrography of the previously mentioned suites A and B is necessary for the interpretation of section 4.3 and is therefore given in Tables 4.2, 4.3 and 4.4 (additional data are available in Appendix II).

Only four factors were needed to account for more than 95% of the total variance. Of this total variance 67% is represented by Factor 1 (F-1), whereas F-2 represents 18% of the total variance. Consequently only 11% of the total variance will be divided among F-3 and F-4, making them

Table 4.1 Rotated factor loadings, final communalities, eigenvalues, cumulative proportion of the total variance for each factor for the Galápagos samples.

Factor / Variable	Sequences A & B (samples BE to BT)					Sequence A (samples BE to BO)						Sequence B (samples BP to BT)			
	1	2	3	4	Final comm.	1	2	3	4	5	Final comm.	1	2	3*	Final comm.
SiO_2	.93	-.23	-.27	-.02	.998	-.99	.05	-.01	.05	-.04	.999	.95	-.31		.998
TiO_2	-.76	.53	.24	-.21	.967	.15	-.93	.13	.08	-.28	.991	-.96	.21		.969
Al_2O_3	-.08	-.42	.20	.86	.962	.39	.88	.06	-.17	-.09	.978	.30	.37	-.99	.224
Fe_2O_3**	-.82	.47	.24	-.22	.991	.49	-.91	-.05	.08	.09	.998	-.97	.23		.984
MnO	-.52	.82	.14	-.17	.986	-.73	-.45	.01	.45	-.05	.943	-.97	.17		.979
MgO	-.96	.02	.23	-.10	.986	.96	-.15	-.07	.06	.21	.991	-.95	.30		.999
CaO	-.94	.10	.28	.12	.990	.98	.19	.02	-.03	.01	.999	-.94	.34		.999
Na_2O	.86	-.29	-.35	-.02	.947	-.92	-.07	.02	-.35	-.06	.982	.97	-.16		.972
K_2O	.95	-.08	-.29	-.05	.999	-.98	-.04	.04	.17	-.13	.999	.94	-.35		.959
P_2O_5	.27	.94	-.02	.02	.966	-.98	-.04	.02	.13	-.13	.999	-.96	-.27		.999
Rb	.98	-.05	-.15	-.06	.999	-.98	-.01	.07	.10	-.15	.999	.86	-.50		.997
Sr	-.84	.08	-.14	.47	.961	.69	.71	.07	-.03	.01	.986	-.52	.83		.964
Ni	-.92	-.27	.18	-.10	.965	.92	-.11	-.18	-.13	.30	.992	-.91	.48		.989
Y	.86	.06	-.48	-.04	.982	-.97	-.13	-.01	.15	-.11	.998	.98	-.05		.934
Zr	.86	-.18	-.46	-.01	.980	-.98	-.07	.02	.13	-.10	.999	.98	-.08		.972
Nb	.88	-.03	-.47	-.01	.993	-.97	-.02	-.06	.19	-.09	.995	.98	-.11		.974
Zn	-.97	.92	.19	-.25	.947	-.88	-.40	-.08	.18	-.10	.976	-.97	-.18		.976
Pb	-.21	.40	.78	-.08	.819	-.08	-.00	.99	-.07	-.10	.999	-.93	-.36		.989
Th	.28	-.34	-.10	-.91	.899	-.44	-.10	.13	-.13	-.87	.991	.90	-.41		.981
U	.85	.26	.33	-.23	.951	-.98	-.04	.06	.14	.03	.994	.13	-.98		.977
K_2O/Na_2O	.93	.22	-.22	-.10	.972	-.93	-.07	.05	.32	-.14	.994	.65	-.52		.995
K/Rb	.30	.91	-.87	-.24	.904	-.33	-.42	-.14	.81	.17	.997	.14+	-.97+		.371
Rb/Sr	[illegible]	-.14	.03	-.12	.985	-.98	-.04	.06	.09	-.14	.999	-	-		-
Th/K	[illegible]	-.34	.24	.32	.926	-	-	-	-	-	-	-	-		-
Eigenvalues	16.16	4.21	1.77	0.91		16.29	3.65	1.46	0.81	0.59		17.47	3.39	1.14	-
Cum. proport. tot. variance	0.67	0.85	0.92	0.96		0.71	0.87	0.93	0.97	0.99		0.79	0.95	1.00	-

* Factor III is solely taken up by Al

**Total iron as Fe_2O_3

\+ Values for U in place of K/Rb

Table 4.2 Some major oxides (%), trace elements (ppm) and K_2O/Na_2O ratio for Suite A samples from Pinsón island

Samples / Variables	BH	BI	BJ	BK	BL	BM	BN	BO
SiO_2	54.09	53.64	49.12	48.30	47.62	48.80	48.13	47.65
TiO_2	2.21	2.64	2.78	2.46	2.66	2.57	2.63	2.03
Na_2O	3.85	3.83	3.13	2.93	2.54	3.36	3.07	2.81
K_2O	1.38	1.29	.67	.40	.47	.37	.44	.34
P_2O_5	.66	.64	.38	.26	.20	.27	.20	.24
Rb	24	22	12	7	8	8	8	7
Sr	282	283	297	311	306	304	306	356
Ni	16	14	53	89	81	85	74	68
Y	36	36	35	29	30	28	29	25
Zr	421	404	230	172	175	172	173	140
Nb	38	33	18	14	17	13	15	12
W	.71	.57	.32	.24	.20	.19	.18	.14
K_2O/Na_2O	.36	.34	.21	.14	.19	.11	.14	.12

Table 4.3 Some major oxides (%), trace elements (ppm) and K_2O/Na_2O ratio for Suite B samples from Pinsón island

Samples / Variables	BP	BR*	BS	BT
SiO_2	62.20	64.66	48.06	48.52
TiO_2	.89	.64	3.04	2.50
Na_2O	5.15	6.35	3.30	2.95
K_2O	2.09	2.20	.57	.42
P_2O_5	.27	.20	.35	.31
Rb	39	33	12	8
Sr	198	282	303	330
Ni	11	10	52	64
Y	58	78	35	31
Zr	619	686	226	189
Nb	42	57	18	15
W	1.05	.29	.54	.20
K_2O/Na_2O	.41	.35	.17	.14

* BR major oxides are calculated on a water free basis

Table 4.4 Petrography of the samples of suites A and B (H. Baitis, pers. comm.)

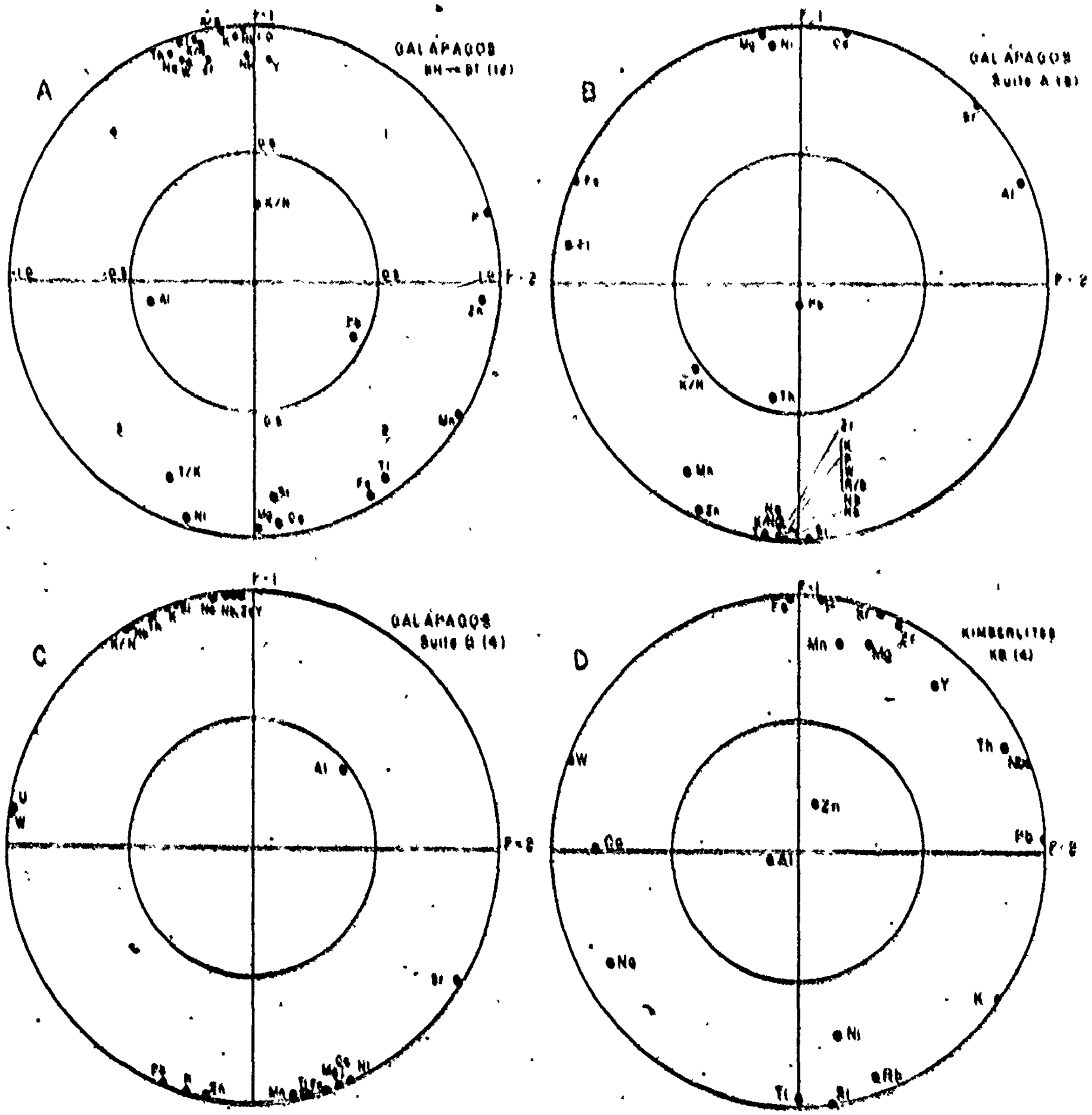
	Phenocrysts (%)			Matrix						
Sample	pgcl	cpx	ol	pgcl	cpx	cpx	ol	ilm	mgt	glass
SUITE A										
BH	6	2	min	x	x	–	–	x	x	x
BI	6	2	min	x	x	–	–	x	x	x
BJ	20	3	2	x	x	x	–	x	x	x
BK	25	–	10	x	x	–	x	x	–	x
BL	30	–	10	x	x	–	x	x	–	–
BM	25	–	few	x	x	–	x	x	–	x
BN	30	–	5	x	x	–	x	x	–	–
BO	30	–	4	x	x	–	x	–	x	–
SUITE B										
BP	3	min	min	x	x	–	–	–	–	x
BR				not available						
BS	29	–	4	x	x	–	x	opaques		x
BT	40	x	7	x	x	–	x	abundant	–	min

x = present; – = not present or not mentioned; min = minor amounts considerably less significant. In Figure 4.1A almost all the variables have significantly high loadings and only Al, Pb and K/Rb are insignificant.

What does all this mean in geological or petrographical terms? Because the samples can be described as members of two differentiation suites (Swanson et al., 1974; Baitis, pers. comm.), the clustering of certain elements at both the +1 and -1 ends of F-1 can very well be recognized as early and late stage elements. The relationship between Ni and Mg, i.e. olivine, and Sr and Ca, i.e. plagioclase, seems to show the influence of the settling of these minerals (early stage) on certain trace elements.

By the same token the clustering of incompatible elements like Rb, Y, Zr, Nb and Th at the opposite end of F-1, with late stage mineral-forming elements Si, K and Na, seems to reflect their accumulation in the late stage of the differentiation process. W obviously can be accepted as an incompatible element as well. Consequently F-1 could be called the factor governing the elements which take part in an obvious way in the differentiation process. The fact that Fe and Ti correlate well, seems normal, but one would also expect to see Mn together with Fe. In any case, both Fe and Ti and even more so Mn, show an increasing dependence on F-2. The chemical analyses for both TiO_2 and Fe_2O_3 (Table 4.2 and Appendix II) show little variation throughout the suite A samples, and the same can be said for the magnetite and ilmenite norms, as well

Figure 4.1 Factor analysis for various sets of rocks. The loadings on factors 1 and 2 lie between the extreme limits 1.0 and -1.0 as shown in A. The suite of samples and number involved in a particular F.A. plot is as indicated. These remarks are valid for all subsequent F.A. plots.


A
GALÁPAGOS
NH → ST (12)
B
GALÁPAGOS
Suite A (8)
C
GALÁPAGOS
Suite B (4)
D
KIMBERLITES
KB (4)
F-1
F-2
K/N
Al
Pb
Zn
Mn
Ti
Fe
Si
Ni
Mg
Ca
T/K
Sr
Th
Zr
U
W
Na
Y
Nb
K
Rb

as for the petrography (Table 4.4). These implications, however, are much less true for the samples of suite B (Table 4.3 and Appendix II), which show a gradual decrease in amounts of TiO_2 and total Fe_2O_3, as well as in magnetite and ilmenite norms. The most mafic member of suite B shows abundant ilmenite, according to Baitis.

4.3.3 Suite A

A slight increase in total variance of F-1 to the detriment of the other factors is observed (Table 4.1), but the overall pattern emerging now is not very different from the previous pattern (Figure 4.1A,B). The slight difference could be called a slight improvement, since the late stage elements Si, Na, K, P, Rb, Y, Zr, Nb and also W show an even tighter clustering at one end of F-1, while the early stage elements are located at the opposite end. This confirms F-1 as the differentiation factor. The predictions concerning the stability of Fe and Ti, as made from chemical and petrographical observations, are confirmed as well, and shown by their strong dependence upon F-2.

4.3.4 Suite B

This suite consists of only four samples. The overall pattern remains one in which the early stage (compatible) elements are very well separated from the late stage (incompatible) ones (Figure 4.1C). Fe and Ti this time cluster together with the early stage elements which actually confirms the chemical and petrographical observations. Indeed samples BS and BT are ferrobasalts, and BT contains abundant ilmenite (Baitis, pers. comm.), i.e. Fe and Ti do not show the stability as observed in suite A. W this time does not associate so obviously as before with the late stage (incompatible) elements and takes up a more independent position. It is known, however, that sample BR has a very low W-content for such a felsic rock, which is difficult to explain unless some depletion mechanism, but more probably an error in chemical analysis, is invoked.

Admittedly, it can be argued that four samples is a very small number to make up a population. Nevertheless from the geology, petrography and chemistry of this suite certain associations of elements, and maybe the abnormal behaviour of some of them, can be expected, expectations which were confirmed by the application of F.A. In order to illustrate this further a comparison is drawn from the application of F.A. on four kimberlites from widely different areas (Appendices I and II). The chemistry does not suggest the existence of any significant element association, to the contrary. This was confirmed by the lack of any significant pattern in Figure 4.1D.

4.3.5 Summary

Only two factors were needed to explain the correlation of almost every variable. Whenever a variable had very low factor loadings for F-1 and F-2 it almost invariably formed a factor on its own, which may be explained either by an irregular distribution throughout the sequence or by a less reliable chemical analysis. F-1 represented a factor governing differentiation throughout the suites, whereas F-2, uncorrelated to F-1, represented elements which did not vary very much. W established itself as an incompatible element among the other ones.

4.4 Conclusions on the application of factor analysis

Information on the geology and petrography of a set of rocks must be available in order to understand and interpret the F.A. circular plots. Such was the case of the stratigraphic section of lavas representing two differentiation suites within a single volcano on Pinzón Island. Meaningful trends could have been detected by other means, for example, bivariate graphs, as shown in Figure 4.2, which represents the relationships between W and eight other elements in the twelve samples from Pinzón Island. This is, however, a rather tedious and time consuming process, particularly when many data are available. F.A. proved to be a quick tool in order to process this vast array of data. Certain patterns emerged which confirmed trends already noticed or suspected.

If a certain number of samples constitute a coherent, logical set, such as suite A, then the first factor will be very strong, i.e. it will take up a large portion of the total variance, and consequently very few factors will be

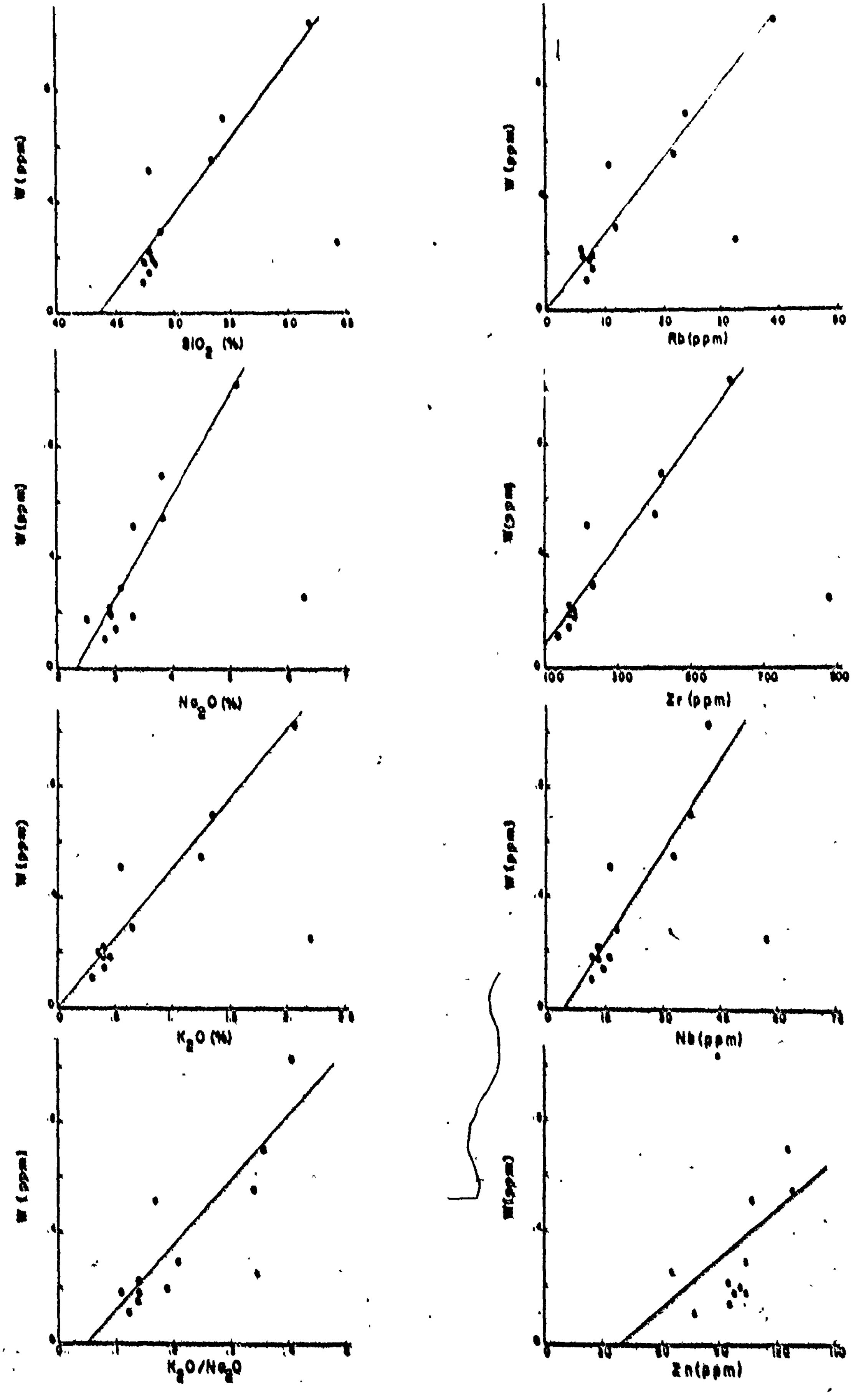


Fig. 4.2 Scatter diagrams of tungsten vs. other elements

needed to cover most of the total variance. In such cases most of the time a plot of factor loadings like Figure 4.1A can give as much information as Figure 4.2, although the information of course is not the same. In other words, the anomalous behaviour of W shows up in the bivariate graphs of Figure 4.2, which it does not in the F.A. plot involving all 12 samples. However Figure 4.2 was drawn after finding with which elements W associates, as is shown in Figure 4.1A. One drawback of very strong factors, such as F-1 in suite A and/or suite B, is their strength, i.e. strong factors can bear such an influence on an enlarged set of samples, so that they bring forward correlations or associations which actually do not exist, and consequently mask existing associations or correlations. Such a case for example occurs (Figure 5.6.B) when submitting all subalkalic rocks of oceanic islands to F.A.

If the set of samples does not constitute such a coherent entity, then the factors become less strong, that is each carry smaller portions of the total variance and consequently more factors will be needed to explain the same amount of the total variance. The first two factors, however, remain the most important ones and experience has shown that F-3 and F-4 generally represent the variables which had very low factor loadings in F-1 and F-2.

In the following Chapter, F.A. application will be used first as a tool in order to reveal correlations or associations of elements, and second as a graphical way to illustrate these associations. A notation like F-1,2 (75,13) will be used to indicate that factors one and two represent respectively 75% and 13% of the total variance.

CHAPTER V

GEOCHEMISTRY OF TUNGSTEN IN RELATION TO MAJOR OXIDES AND TRACE ELEMENTS

5.1 General considerations

The scarcity of available data on tungsten contents in rocks in general has led to certain suggestions, as well as estimates, which obviously need more investigation. Vinogradov et al. (1958), for example, propose that there is a tendency toward higher tungsten contents in basalts and diabases than in gabbros. It should be mentioned, however, that their study is based on a set of samples which is rather small and, at the same time, very diverse in space, chemistry and time. This generalization for mafic rocks is based on three basalts (Kamshatka), four diabases (Caucasus and Baikal), of which one is a metamorphosed Archean diabase and another is considered young (Archean age given), and four gabbros. Those authors also suggest a parallel increase of tungsten with silica. Wiendl (1968), besides reiterating the aforementioned tendency towards higher tungsten contents in mafic extrusives, expanded this general idea by implicating more felsic rocks. In fact, Wiendl claims that this discrepancy between extrusives and intrusives becomes even bigger in more felsic rocks.

It is obvious that the few available data on tungsten contents also will leave an imprint on suggested average values for basalts (and andesites) on a world-wide scale. Indeed, Wiendl (1968) suggested an average world value for basalts of 1.17 ppm W, whereas Vinogradov (1962) proposed a value of 1.1 ppm W for andesites.

Some 125 rocks are under investigation in this study. The distribution of these samples on both an alkali versus silica and an AFM diagram is shown in Figure 5.1, with the exclusion of sample VS-3 from Figure 5.1A because of its very high (16.58%) alkali content. In order to detect possible correlations between tungsten and any of the major oxides, F.A. was performed on all these rocks. In this F.A. tungsten did not show any association but forms a factor on its own, i.e. F-4(8). The correlation coefficient (r) of W with Si, for example, has a value r = -0.04, thus being insignificant. This complete lack of correlation is probably due to the great diversity of the samples involved. Consequently, in order to study tungsten abundances and possible associations with other elements, the vast array of samples will be broken down into smaller groups according to their tectonic environment, and will be studied separately in various sections below. These tectonic environments are:

(i) oceanic environment, which includes samples from both the ocean floors and islands;

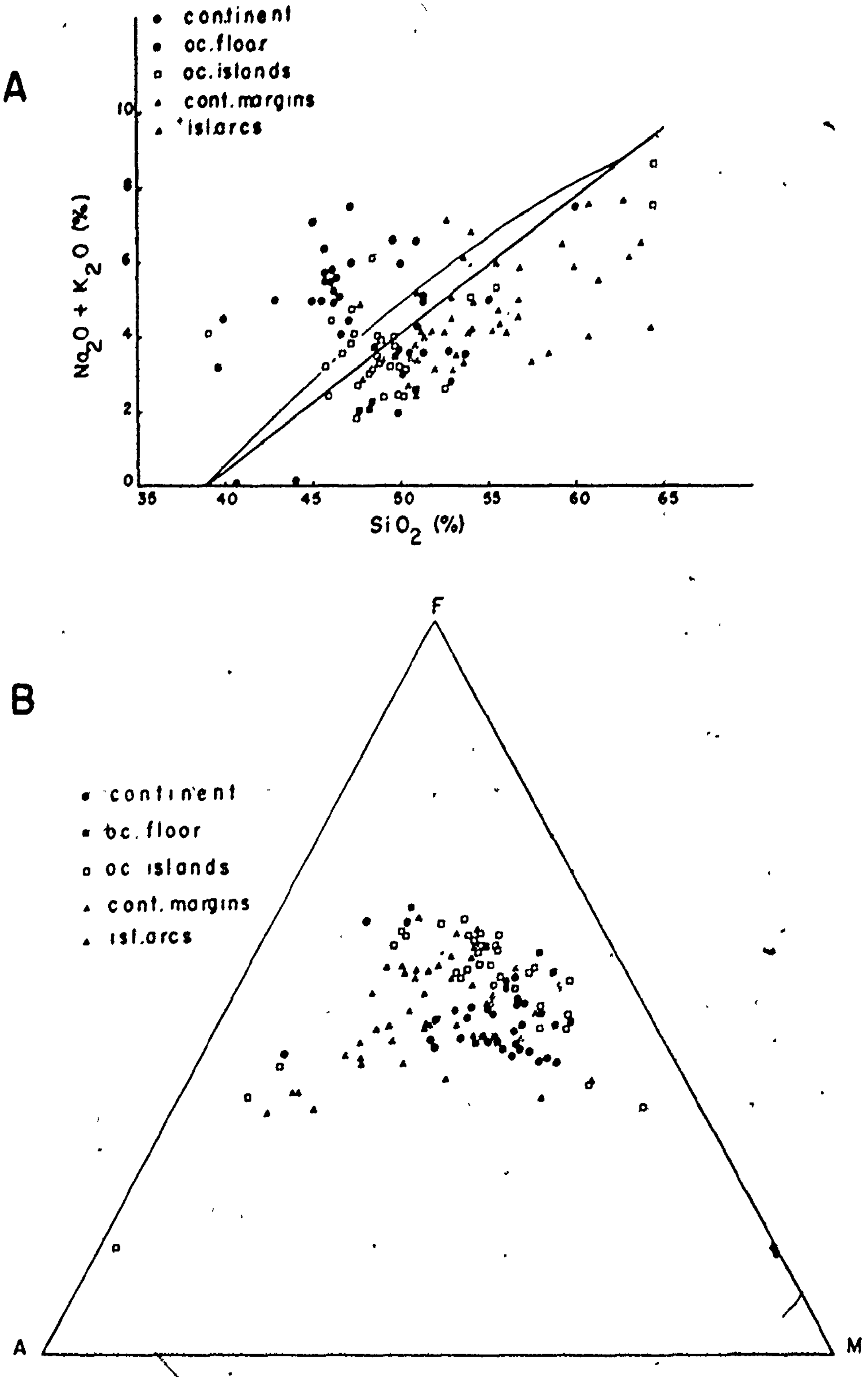


Fig. 5.1 Alkali - silica diagram (a) and AFM diagram (b) for all samples The straight line in (a) is MacDonald & Katsura's (1964) dividing line and the curve is the Irvine & Baragar (1971) dividing line In plot (b) $A = Na_2O + K_2O$; $F = FeO + 0.9 Fe_2O_3$ $M = MgO$, all in weight percent.

(ii) subduction zone environment, which includes samples from both island arcs and continental margins (either active or fossil);

(iii) continental environments.

5.2 Oceanic environment

Before looking into the various groups which constitute the oceanic environment, an appraisal will first be given on the distribution of tungsten in all such rocks, 42 in total, which represent both the ocean floor (9) and islands (33). Figure 5.2A,B shows the distribution of these rocks on an alkali *versus* silica diagram, excluding VS-3 because of its very high alkali content, and on an AFM diagram (D-1 not recalculated, see below). Only a small fraction of these samples represent late stage differentiation products, which may reflect the actual bulk composition of oceanic environments. A histogram (Figure 5.3) for W in all oceanic rocks shows that out of 42 analyses only 3 rocks have tungsten contents greater than 1 ppm, and of these 3 rocks 2 are late stage differentiation products, i.e. VS-3 (phonolite) and BP (trachyte), whereas VM-2 has a high nepheline norm. Numerical data from this histogram are given in Table 5.1. The first line contains data on the whole set of samples, whereas late stage differentiation products VS-3, BH, BI, BP and BR are excluded in the second line of values in order to get a value more representative for basalts (s.l.) in an oceanic environment.

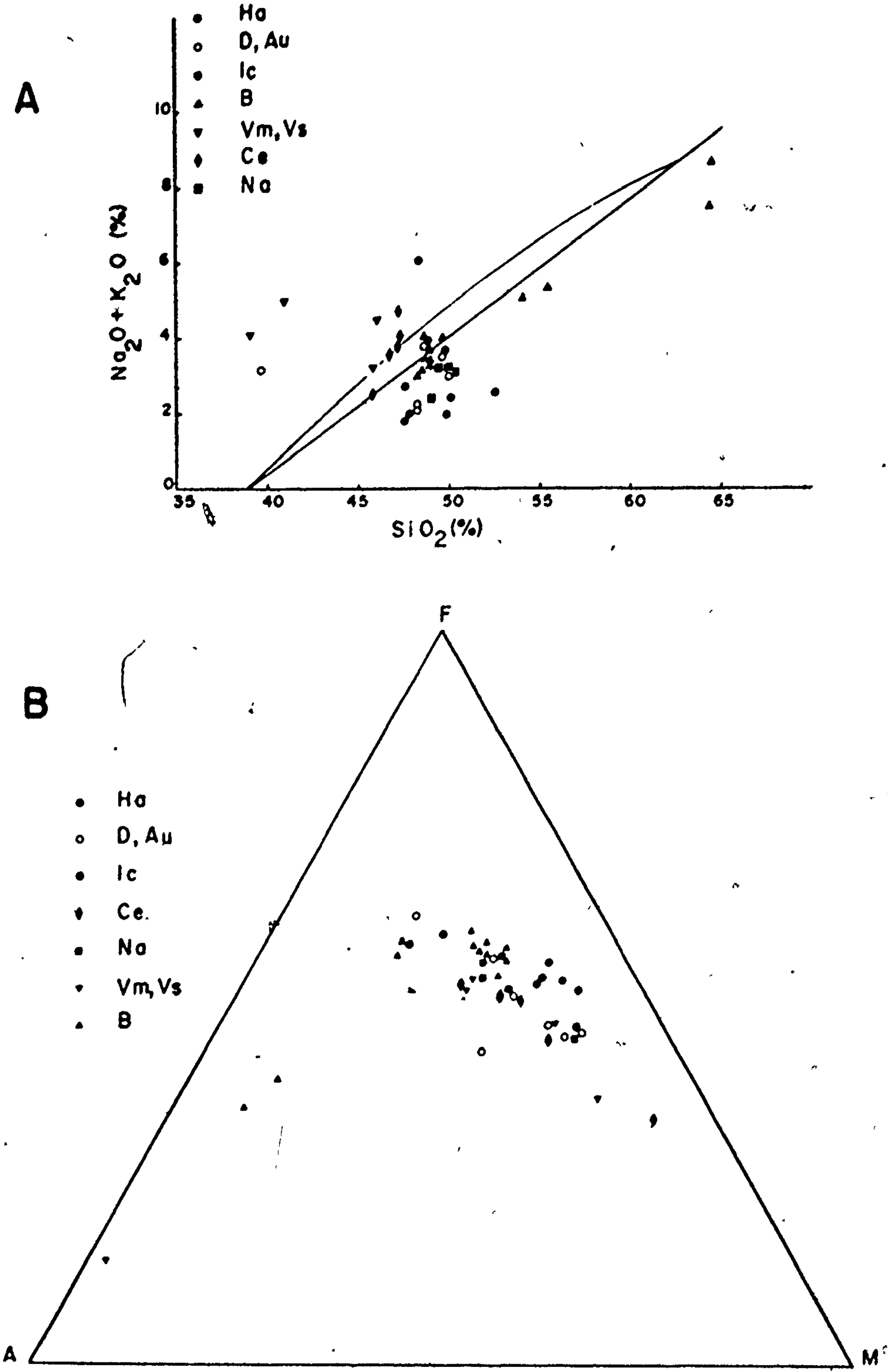


Fig. 5.2 . Alkali - silica diagram (a) and AFM diagram (b) for oceanic (floor and islands) samples. For more details see Fig. 5.1 and Table 2.1

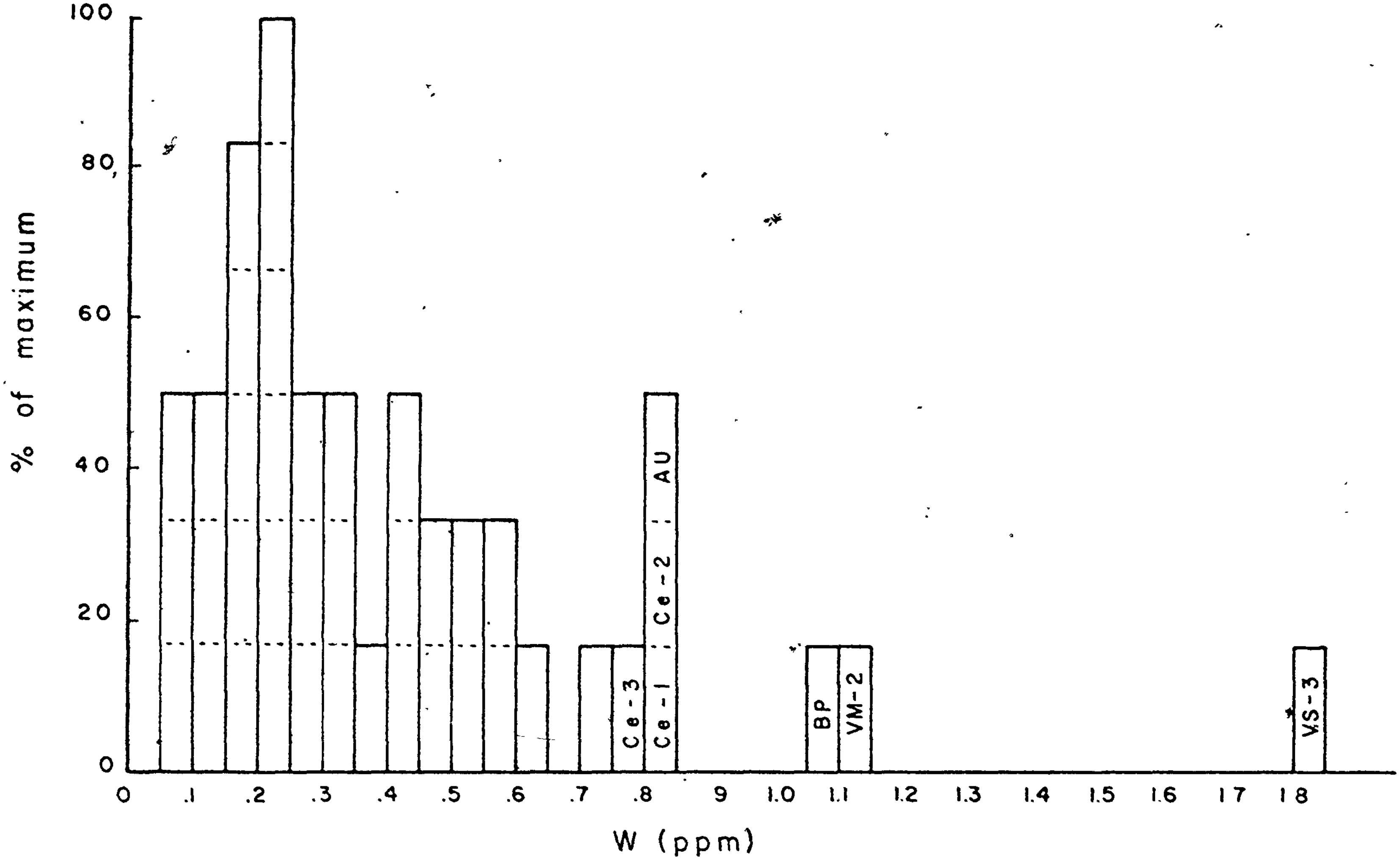


Fig. 5.3 Distribution of tungsten in oceanic rocks (42 samples)

Table 5.1 Mean, median, mode and range of tungsten distribution in oceanic rocks (ppm)

	Mean	Median	Mode	Range
42 samples	0.43	0.32	0.20(6x)	0.05 - 1.81
37 samples*	0.36	0.25	0.20(6x)	0.05 - 1.13

*5 samples omitted (see text)

From these data it becomes obvious that the mean and median are not strongly affected by leaving out late stage differentiation products. It also becomes obvious, if a value of 0.36 ppm W may be considered representative for oceanic basalts (s.l.), that this value lies well below other suggested values (see above). This will be discussed in more detail later on.

5.2.1 The ocean floor

The ocean floor is represented by 9 samples in total. Six of these come from the Deep Sea Drilling Project (DSDP) involving cores from Legs 2, 3 and 5. Similar samples from Legs 2 and 3 have been exhaustively studied by Frey et al. (1974). The two IC samples belong to a suite of fresh pillow basalts and crusts dredged along the Reykjanes Ridge axis (Schilling, 1973), and AU comes from the Median Valley in the anomalous 45°N latitude area (Muir et al., 1964; Aumento et al., 1971; Aumento, 1973). Some data of particular use for this section

Table 5.2 Some major oxides (%), trace elements (ppm) and ratios for nine ocean floor samples

Samples Variables	$D-1^{+}{}^{o}$ 2-10	D-2 2-11A	D-3 3-15	D-4 3-18	D-5 3-19	D-6 5-36	IC-2	IC-3	AU
SiO_2	49.50	49.39	48.71	46.98	46.65	47.72	49.50	47.60	50.69
TiO_2	1.76	1.40	1.86	.67	1.20	.81	1.00	1.80	1.20
Na_2O	2.72	2.59	2.76	1.91	2.61	1.92	1.80	1.80	2.46
K_2O	1.31	.39	.65	.19	1.02	.17	.06	.23	.13
P_2O_5	.28	.13	.18	.04	.29	.05	.12	.22	.11
H_2O^{++}	1.25	1.33	1.78	2.74	3.29	1.26	.54	.32	.54
Li	12	6	8	14	12	11	-	-	6
Ba	216	45	36	27	72	45	-	-	66
Cr	331	301	212	397	390	376	224	282	-
W	.29	.09	.11	.05	.25	.11	.15	.22	.84
K_2O/Na_2O	.48	.15	.24	.10	.39	.09	.03	.13	.05
Fe_2O_3/Fe	.90	.88	1.38	1.12	4.26	.41	.05	.14	.17

+ The values of D-1 are the recalculated values after subtracting an equivalent amount of calcite for 9.13 % CO_2

o D.S.D.P. identification system: e.g. 2 = Leg and 10 = Hole

++ H_2O is total water excepting the IC samples where water is H_2O^+

are illustrated in Table 5.2. For further information see Appendices I and II.

A first feature to be considered is the distribution of W in these rocks (Table 5.3).

Table 5.3 Mean, median and range of W distribution (ppm) in ocean floor basalts with and without sample AU*

	Mean	Median	Range
With AU	0.23	0.15	0.05 - 0.84
Without AU	0.16	0.13	0.05 - 0.29

*The recalculated value of D-1 was used (see text below)

All rocks show low values except AU, which has a very high W content. This high value coincides with the fact that the area is known as anomalous, since Muir et al. (1964) and Aumento (1973) reported that 6 <u>in situ</u> basalt drill cores from the Median Valley have a chemistry typical of the incompatible element enriched compositions characteristic of 45°N area.

In order to find possible correlations existing between W and any other variable, i.e. major oxide or trace element, F.A. was performed on three groups of samples. Data for these F.A.'s are given in Table 5.4, and the F.A. plots are shown in Figure 5.4.

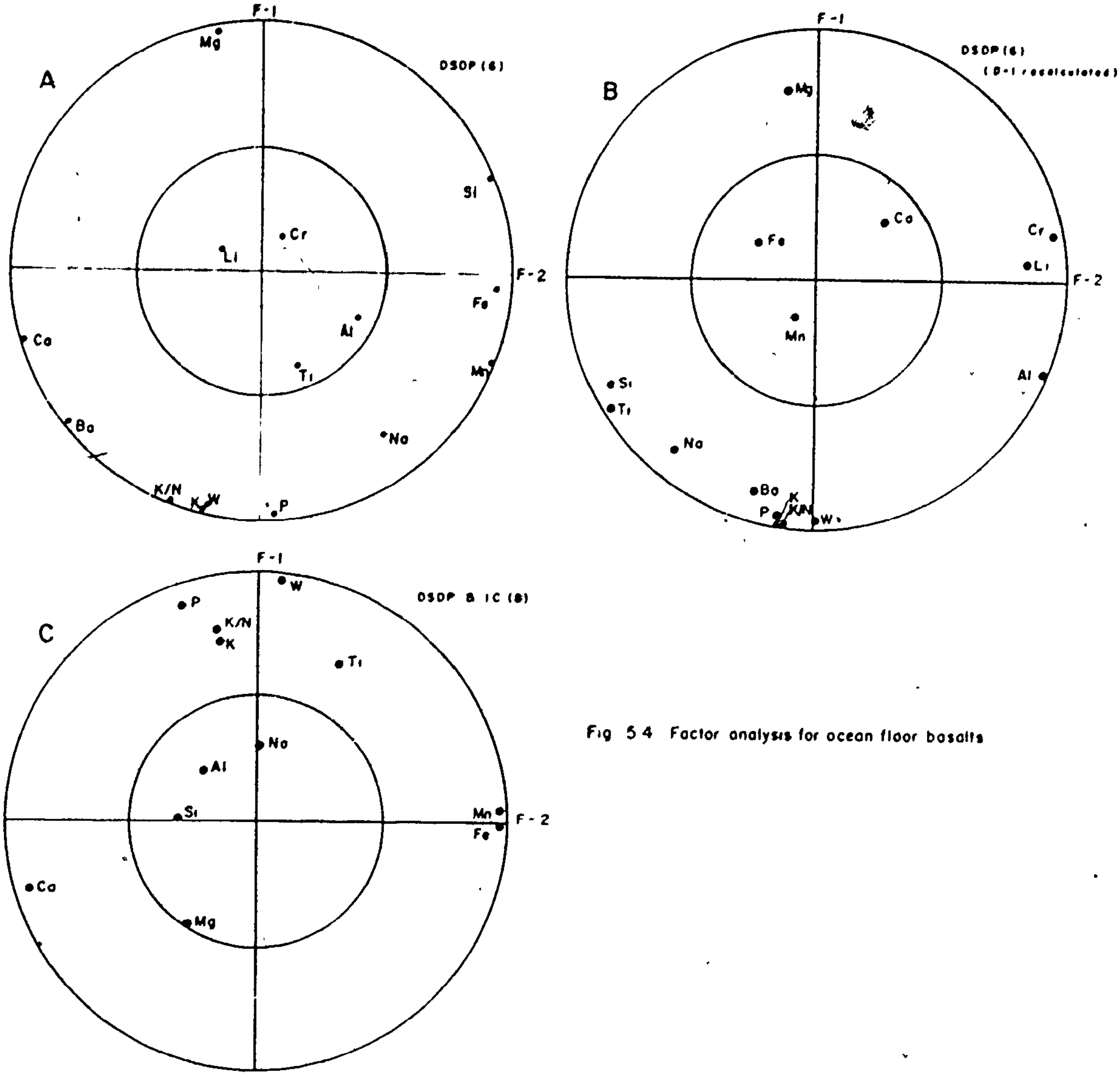


Fig 5 4 Factor analysis for ocean floor basalts

Table 5.4 Various correlation coefficients (r) for W with some other variables (x) and the proportion of the total variance for factors 1 and 2

Group of samples	r⩾.90	r⩾.80	r⩾.70	F-1	F-2
D(6)	K,P,K/N	-	Ba	46	30
D(6) with D-1 recalculated	K,P,K/N	Ba	-	50	25
D and IC (8)*	-	P	K,K/N	45	28

*AU omitted because of its high W content

From both Table 5.4 and Figure 5.4A,B it is obvious that a strong association is noticeable between W, P and K and K/Na. It is also obvious that after recalculating D-1 by subtracting calcite equivalent to ±9.13% CO_2 some elements rearrange themselves into a more logical pattern, i.e. Si is now among the late stage elements and Ca among early stage elements. Nevertheless the correlation between Li and Cr is puzzling. The recalculation of D-1 can be justified by the fact that this sample is known to contain carbonate veins and disseminated fine-grained crystals (Frey et al., 1974; Peterson et al., 1970), as well as by personal experience of the present author.

For this recalculation of D-1 it was assumed that the carbonate was rather pure, i.e. very little or no contamination caused by other elements. This assumption will certainly be more valid for certain elements than for others. In the case of W, which is of major concern here, this assumption may be accepted because of low reported W-values for oceanic carbonates (Horn et al., 1966; Krauskopf, 1970).

Before proceeding with the interpretation of the strong correlations existing between W and K or P, a few facts will be pointed out or a few comments made, regarding the samples involved, either as a population or an individual:

- When referring to analyses of Frey et al. (1974) the DSDP identification will be used, e.g. sample 2-10, otherwise samples will be indicated by D-1, etc. (see also Table 5.2).

- Admittedly a population of 6 samples, even when enlarged with the 2 IC samples and AU, is a small one.

- Major and trace element analyses for the D samples reflect the composition of the whole rock, i.e. including crystalline and glass fractions, which explains the high K_2O, H_2O and Fe_2O_3/FeO values for some of the samples. It would be difficult to compare these data with the data as obtained by Frey et al. (1974), because these authors obtained their major oxide data by analyzing exclusively fresh glasses (Table 3, p.5513). The picture is slightly more favourable for the trace element data, because Frey et al. (1974) analyzed both glasses and altered crystalline rocks containing glass (Table 6, pp.5516-5517), although it should not be forgotten that in most cases the analyses are not performed on the same part of the drillcore section. For example, Frey et al. (1974) analyzed part 60-61 cm of section 1 for sample 3-19, whereas the part analyzed for this study was 80-82 cm (D-1) of the same section. Nevertheless it can be said that the trace elements are comparable within a range much less than an order of magnitude. Table 5.5. illustrates this comparison.

Table 5.5 Comparison of trace elements in one DSDP core by two different authors (ppm)

Sample	Element Cr	 Ni	 Sr	 Ba	 Y	 Zr
D-2 (this work)	301	97	115	45	30	82
Site 2-11A* (Frey et al., 1974)	310	100	105	11	35	85

*Table 6, pp.5516-5517

- The K_2O contents of fresh glasses of the DSDP samples are low when compared to the crystalline basalt of site 2-10 (Table 3, Frey et al., 1974) and this sample has about the same amount of K_2O (1.13%) as the recalculated value for D-1 (1.31%). Site 2-10 (D-1) represents an oceanic tholeiite (Engel et al., 1966) but it is not depleted in large ion lithophile elements (LIL-elements) and is therefore more similar to island tholeiites and Mid-Atlantic Ridge basalts (MAR basalts) dredged near oceanic islands, which suggests a different mantle source than the LIL-elements depleted tholeiites (Frey et al., 1974). With respect to the similarity of D-1 with MAR basalts such as those dredged in the 45°N area, sample AU is in a peculiar position with its very high W-content (about three times higher than in D-1).

- When considering the samples IC-2 and IC-3, which according to Schilling (1973) show a regular and progressive increase in LIL-elements as well as Ti and P and Na relative to Ca along the MAR axis up to Iceland, it is obvious that these samples resemble the low K_2O, LIL-element depleted oceanic tholeiites (Engel et al., 1966; Kay et al., 1970). This seems to be true for W as well, in a way.

The strong correlation between W and K (or P), as mentioned earlier is clearly illustrated in Figure 5.5. The question now arising is whether this correlation is real or apparent, primary or secondary. In order to evaluate this question several possible causes or mechanisms should be considered, as follows:

(i) regional heterogeneity;
(ii) differentiation;
(iii) alteration and/or weathering.

These possibilities will now be discussed, in turn:

(i) Heterogeneity due to regional variation should not be dismissed lightly. Ample evidence for this heterogeneity is given by sample AU, and may be to a lesser extent by sample D-1. To which extent the strong correlation between W and K is caused by regional heterogeneity, and as such this correlation would be purely coincidental, is difficult

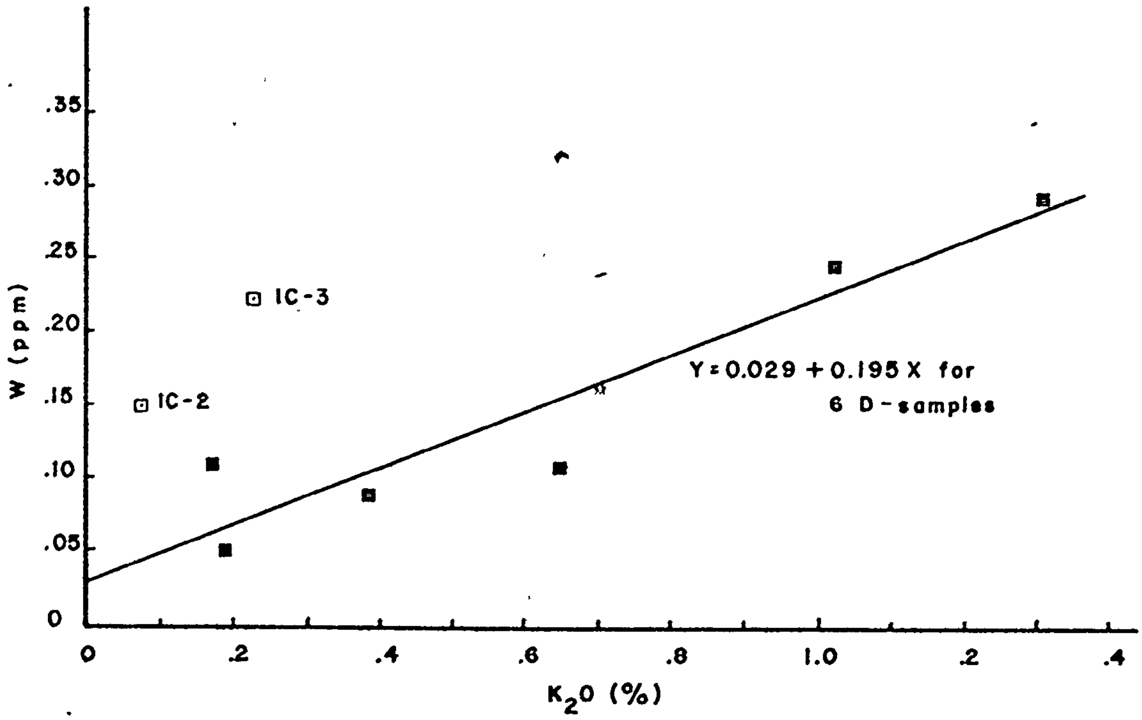


Fig. 5.5 Scatter diagram of tungsten vs potash for eight ocean-floor basalts

to assess unless many more rocks are analyzed. Interesting in this respect is the fact that when adding the two IC samples to the D sample population, the correlation coefficients drop (Table 5.4).

(ii) Differentiation: Frey et al. (1974) attempted to establish a fractional crystallization model (i.e. a least squares petrologic mixing programme of Bryan et al., in Frey et al., 1974) in order to account for elemental abundance trends, using glasses of Leg 3 basalts. The basalts of concern here were 3-14 (least differentiated), 3-15 (most differentiated) and 3-19. 3-18 (D-4) is very similar to 3-14, which was not available to the present author. These authors report that qualitatively the model works for all elemental abundance trends, a statement which, however, is not applicable to W (Table 5.2). Quantitatively the model accounts for most major and trace element abundances, but there are a few significant exceptions precluding the possibility that the Leg 3 basalts are related to each other by simple fractional crystallization. These exceptions are reflected in the factors by which La, Ce, Y, Zr and Hf are enriched (2-3 times) in 3-19 basalts in comparison with 3-14 basalts (Table 9, p.5522), whereas removal of solids (olivine, plagioclase and chromite), required by the major elements, leads to a much lower enrichment factor, i.e. 1.5: hence a big discrepancy between observed and calculated enrichment factors. The conclusions of Frey et al. (1974) were that, despite the fact that the Leg 3 basalts are not related to each other by simple fractional crystallization, fractionation of olivine and plagioclase is important and that 3-14 and 3-18 (D-4) may be examples of primary magma. This last conclusion is of interest with respect to W which, in sample D-4, reaches the lowest content of all basalts analyzed in this work. Another interesting fact is that W is enriched in D-5 (3-19) 5 times, in comparison to D-4, which is significantly higher than the reported 2-3 factor of Frey et al. (1974). This high enrichment factor may be partly due to fractionation, as pointed out in this section, but another mechanism, i.e. alteration, might have played a role as well (see below).

(iii) Alteration: very recently it was pointed out that no element seems to escape unaffected from sea water interaction (Aumento et al., 1975; Dostal, pers. comm.), this in contradiction to suggestions (Frey et al., 1974; Hart, 1973) that certain elements, for example Ti, Al, Y, Zr, Hf, Ta, etc., do not change markedly. When comparing the major element chemistry of the whole rock analyses of the D samples (Table 5.2) with their fresh glass counterparts (Frey et al., 1974, Table 3, p.5513) it is obvious that the D samples, as previously hinted at, have been altered. Evidence for their alteration, for example, is their SiO_2, K_2O, total H_2O content, Fe_2O_3/FeO ratio, etc. (Hart, 1973; Aumento, in Keen, 1975). This alteration may be due to either a geothermal sub-seafloor process (high temperature) as suggested by Spooner et al. (1973), or to low temperature sea water-layer II interaction (weathering) or both. The circulation of the sea water that comes in contact with the hot rocks of the seafloor spreading ridges, would strip these rocks of certain elements, which can precipitate elsewhere, thus creating a possible enrichment in overlying sediments. Spooner et al. (in press), for example, propose a variable depletion, based on a study of E. Ligurian metabasic rocks, in Au, Ag, W, Ni and Co, relative to the contents of unaltered deep sea basalts. This W depletion, however, would be in contradiction with the observed positive correlation between W and K, which is known to be taken up by the ocean floor basalts from the sea water (Hart, 1973). Sea water, however, would not be a good source for W, since sea water is strongly undersaturated in W (Krauskopf, 1956) with W abundances of less than 0.1 ppb (Ishibashi, in Krauskopf, 1956, 1970). However, plenty of evidence exists now (Maucher, 1972; Höll et al., 1972) on time and stratabound deposits of stibnite (± cinnabar) and scheelite related genetically to submarine volcanism. It is not implied that the enrichment here is due to such volcanism; it is only hinted at that a possible source for W enrichment can exist within the ocean basins.

5.2.2 Summary

Eight ocean floor basalts contain about 0.16 ppm W, but one anomalously high value of 0.84 ppm was found. Tungsten correlates positively with K, P, Ba, and this behaviour may indicate processes of either fractional crystallisation leading to accumulation of these and other elements in residual liquids or sea water alteration.

5.2.3 The ocean islands

Before studying the ocean island samples in detail, an overall picture should be given first. Some 33 samples including both subalkaline and alkaline rocks represent these ocean islands. Twenty two of these samples are subalkaline rocks from Hawaii (Ha), Amsterdam Island (Na) and Pinzon Island (B), whereas the rest are alkaline rocks from the Crozet (Ce) and Cape Verde (VM, VS) Archipelagos, and one sample from Heymay (IC-1). The distribution of these samples on an alkali *versus* silica and an AFM diagram was shown earlier (Figure 5.2A,B). As with ocean floor basalts, no data outside this study seem to be available for W abundances. Consequently the distribution pattern of W in oceanic rocks obtained in this study will be given in Table 5.6. Various groups are mentioned and in two cases some very obvious differentiation products will be left out in order to obtain a better estimate for W contents in ocean islands basalts (s.l.).

Table 5.6 Distribution of W (ppm) in various groups of ocean island rocks, with and without differentiation products

Group of samples	No. samples	Samples omitted	Mean	Median	Range
All samples	33	-	0.48	0.42	0.08 - 1.81
Alkaline	11	-	0.71	0.64	0.18 - 1.81
	10	VS-3	0.60	0.60	0.18 - 1.13
Subalkaline	22	-	0.36	0.32	0.08 - 1.05
	18	BH,BI BP,BR	0.30	0.28	0.08 - 0.54

The value for subalkaline ocean island basalts is twice as low as the average value for alkaline equivalents, which in turn are about half the value suggested by Wiendl (1968), i.e. 1.17 ppm W.

In a first exploratory appraisal for possible correlations between W and any other element, F.A. was performed, without any discrimination, on the three groups of samples mentioned in Table 5.7 (Figure 5.6 and Appendix II). W, when it associates with any element, invariably does so with late stage elements (e.g. Na, K, Rb, Nb, etc.) to some degree. Similarly, W invariably forms negative correlations with compatible elements (e.g. Ni, Cr, Mg, etc.).

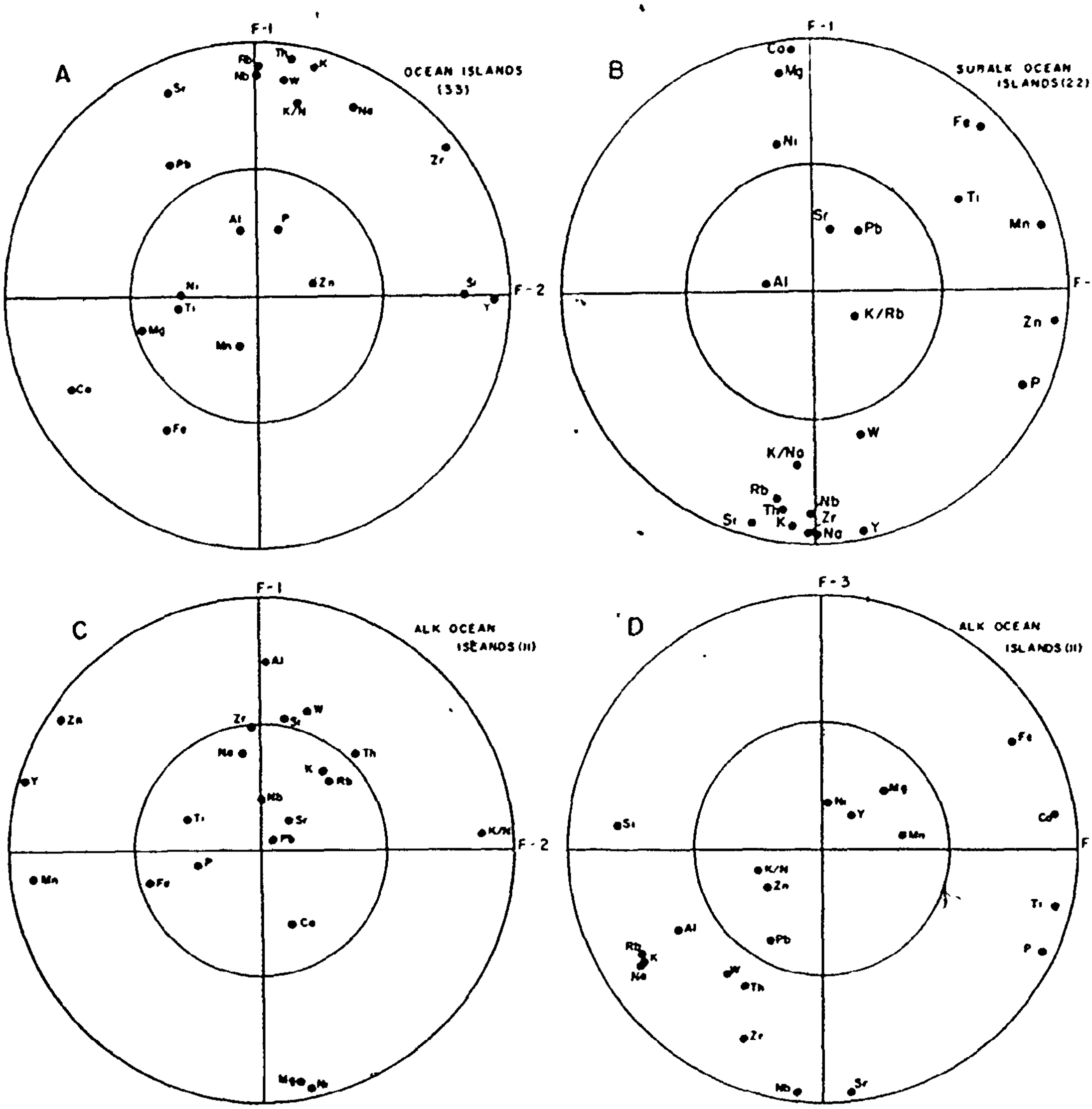


Fig 5.6 Factor analysis for ocean islands

Table 5.7 Some correlation coefficients (r) for W with other variables (x) and proportion of the total variance of several factors in ocean island samples

Group of samples	Correlation coefficient r*				Factor % of tot. var.			
	r≥.90	r≥.80	r≥.70	r≥.60	1	2	3	4
All samples	-	K,Rb,Th	Na,Nb	K/N	41	21	13	8
Alkaline	Th	Al,Na,K,Rb,Zr	Pb	Nb	51	22	16	6
Subalkaline	-	-	Rb,K/N	K,Nb	51	17	8	7

*r of W with Si is respectively 0.18, 0.56, 0.54

Si behaves independently from most late stage elements (Figure 5.6A). This behaviour is probably due to the mixing of both alkaline and subalkaline samples. When subdividing the ocean island samples into these two subgroups the correlation of W with Si improves (Footnote Table 5.7).

5.2.3.1 The subalkalic ocean island samples

Galápagos: In order to expose the possibilities and limitations of F.A., extensive use was made of the Galápagos samples as a case history (Chapter IV). To summarize, Figure 4.1A,B.C shows the importance of F-1,2. These factors, with the help of the known geology, chemistry and petrography of the samples involved, were considered to reflect fractional crystallization (F-1) with the incompatible elements accumulating in the residual liquid, and stability (F-2) with elements remaining rather stable throughout the whole differentiation sequence. As such, the described pattern confirms very well the suggested crystal fractionation (Swanson et al., 1974). In Figure 4.1A,B both Si and W accumulate, along with many other incompatible elements, in the residual liquid. The strong correlation between Si and W (r = 0.98) in sequence A is in accordance with the suggestion made by Vinogradov et al. (1958). This strong correlation is, after all, not surprising within a single differentiation sequence just because of the mere interrelation of the samples involved. It will be investigated below if the strong correlation between Si and W will be upheld in less ideal sets of samples.

Reference was made to the very low W content of a very felsic rock (BR with 0.29 ppm W). Both BP and BR are very similar rocks within suite B, especially with regard to the major oxides. The trace elements may differ but not substantially. It is therefore surprising to find such a low W content (about 3 times less W in BR than in BP) in a similar felsic rock. Possible explanations for this depletion are:

(i) an unknown differentiation mechanism. Such a mechanism would then suggest the enrichment of W in both an endmember (felsic) and an intermediate stage at the same time within the same suite, which is not very likely.

(ii) analytical error, although no information was recorded in the logbook on anything that went wrong during the radiochemical separation procedure for this particular batch of samples.

Taking into consideration these reflections, the distribution of W in basalts in the Galápagos samples may be seen in Table 5.8.

Table 5.8 Distribution of tungsten (ppm) in basalts* from Pinzón Island

Sample group	No. samples	Mean	Median	Range
Suite A+B	8	0.25	0.20	0.14 - 0.54
Suite A	6	0.21	0.195	0.14 - 0.32
Suite B	2	0.37	-	0.20 - 0.54

*differentiation products BH, BI, BP, BR left out

<u>Hawaii</u>: Some data for the Hawaiian samples are given in Table 5.9. For more data see Appendices I and II.

The Hawaiian samples, due to their diversity in sample location (Figure 2.2), can not really be combined into a coherent set. Nevertheless strong correlations exist between W and various late stage elements (Table 5.9) expressed graphically by F.A. (Figure 5.7). The correlation with Si, however, is negative. The W abundances span a range from 0.08-0.52 ppm with a mean of 0.28 ppm. Sample Ha-6 seems to be enriched in W when compared with the other samples, but it

Table 5.9 Some major oxides (%), trace elements (ppm) and correlation coefficients (r) of tungsten with each of these variables in six rocks from Hawaii

Samples Variables	Ha-1	Ha-2	Ha-3	Ha-4	Ha-5	Ha-6	r
SiO_2	50.08	52.65	47.32	49.65	46.74	48.00	-.46
TiO_2	3.08	3.52	2.52	2.41	2.27	3.31	.19
Na_2O	3.05	2.25	2.10	2.00	1.61	3.29	.78
K_2O	.62	.35	.54	.38	.20	.59	.81
P_2O_5	.33	.25	.26	.25	.20	.56	.86
Li	6	4	4	3	4	7	.79
Rb	13	6	12	6	2	6	.39
Sr	392	288	464	349	296	568	.94
Ba	367	179	305	305	206	564	.96
Y	29	20	20	26	20	34	.82
Zr	203	105	157	130	133	300	.95
Nb	21	3	16	9	5	32	.98
Ni	159	109	289	119	258	47	-.26
Cr	240	376	582	404	575	89	-.63
W	.36	.08	.32	.22	.18	.52	1.00

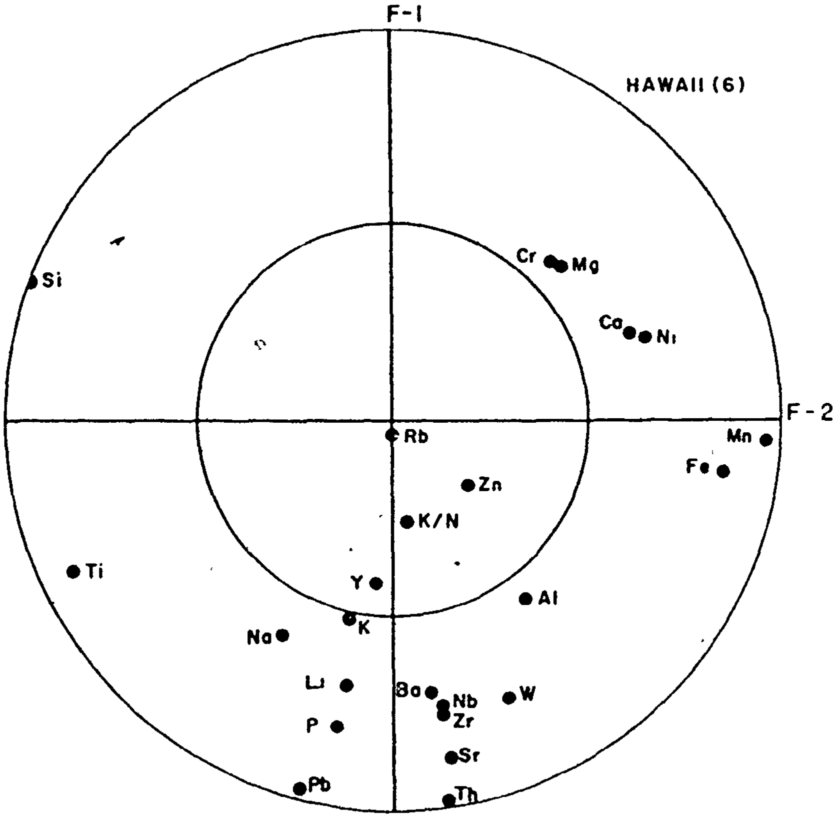


Fig 5.7 Factor analysis for samples from Hawaii

also has higher contents of Na, Li, Sr, Ba, Y, Zr, Nb. This rock is a border case. On the alkali vs. silica diagram (Figure 5.2A) it falls above the McDonald and Katsura (1964) dividing line, but below the Irvine and Baragar (1971) dividing line. The sample was treated as a subalkaline one. Sample Ha-2 has the lowest W content of all Hawaiian rocks, but it also shows lower values for Sr, Ba, Y, Zr, Nb. It cannot be called pure coincidence that the rocks with the lowest and highest W contents also show lower and higher contents for elements which normally accumulate in residual liquids. The ranges of distribution of W in the basalts of the Galápagos and Hawaii samples are similar as are their mean values (0.25 and 0.28 ppm, respectively), despite noticeable differences between the two petrogenetic provinces. Indeed, the Hawaiian rocks in general are richer in Cr, Ni and Sr (McBirney et al., 1969). The Hawaiian samples are also known for a preponderance of lavas containing various amounts of phenocrystic olivine (e.g. McDonald, 1944, 1949, in MacDonald et al., 1964; Powers, 1955), whereas plagioclase fractionation is more common in the Galápagos samples, an observation already made by Darwin (in Williams, 1966).

Amsterdam Island: Some data on the Amsterdam Islands are given in Table 5.10. Further details are in Appendices I and II.

Both Amsterdam and St. Paul Islands, which form part of

Table 5.10 Some major oxides (%) and trace elements (ppm) for four samples from Amsterdam island

Samples Variables	Na-1+	Na-2++	Na-3	Na-4
SiO_2	48.75	49.12	49.73	49.97
TiO_2	1.21	1.60	2.07	1.67
Na_2O	1.89	2.57	2.45	2.44
K_2O	.45	.67	.71	.65
P_2O_5	.12	.19	.22	.17
Rb	12	18	17	17
Ba	152	210	218	194
Cr	143	40	51	69
Ni	88	46	38	47
Y	17	20	26	22
Zr	81	110	143	121
Nb	18	23	29	24
W	.32	.42	.46	.45

+ Na-1 and Na-3 are aphyric olivine basalts

++ Na-2 and Na-4 are feldsparphyric basalts a unique volcanic province (Gunn et al., 1971, 1975) in the Indian Ocean, are made up by lavas of mainly tholeiitic affinities. The four samples from Amsterdam Island all belong to the youngest lava flows of the Mont de la Dives volcano, and can be divided into the two groups mentioned by Gunn et al. (1971), i.e. plagioclase basalts with bytownite phenocrysts of up to 1 cm and aphyric olivine basalts. It is obvious that plagioclase control is important (Gunn et al., 1971). No correlation coefficients were computed nor F.A. performed on this small set of samples, particularly because very little variation occurs among them. It can be mentioned, however, that the lowest W content occurs in the more mafic sample Na-1, which coincides with higher values for compatible elements (Mg, Ni, Cr) and lower values for incompatible elements (Na, K, Rb, Ba, Y, Zr, Nb, W) than for the other rocks. W contents range from 0.32-0.46 ppm, with a mean value of 0.41 ppm. Although these values fall within the ranges of W distribution for Galápagos and Hawaiian samples the mean value is slightly higher. A comparison of these values is given for the three provinces in Table 5.11.

Table 5.11 Mean and range of W distribution in the subalkaline ocean island basalts (ppm)

Province	No. samples	Mean	Median	Range
Galápagos	8	0.25	0.20	0.14 - 0.54
Hawaii	6	0.28	0.27	0.08 - 0.52
Amsterdam	4	0.41	0.44	0.32 - 0.46
All 18 rocks	18	0.30	0.28	0.08 - 0.54

5.2.3.2 Summary

It can be concluded that the W contents for subalkaline basalts from oceanic islands may vary, but only slightly and lie well below 1 ppm. Furthermore, whenever lower values were obtained for W within a particular area, these lower values coincided with a decrease in the abundances of several incompatible elements such as K, Rb, Zr, etc.

5.2.3.4 The alkaline ocean island samples

Reporting on the application of Q-mode F.A., Shaw et al. (1973) state that the alkalic basalts form a much more homogeneous group than the subalkalic ones. With respect to W as for many other elements, the alkaline basalts are very different, and will now be considered according to petrogenetic province.

Crozet Archipelago: The samples (Ce) under investigation here all come from section B (east of Shipwreck Bay on East Island). Some data concerning these rocks are given in Table 5.12, but more information can also be obtained from Appendices I and II.

Gunn et al. (1970) interpreted some 30 lavas of section B. This section is, like the Pinzón Island sea cliff (Plates 4.1 and 4.2), made up by several cycles of lavas, but the sampling was less systematic. In other words, the five Crozet samples do not belong to one and the same cycle of eruption. The first lavas of each cycle contain high amounts of olivine and pyroxene, but these amounts decrease gradually upward. The lavas are slightly nepheline normative and their composition varies from pyroxene- and olivine-rich oceanites and ankaramites to aphyric and feldspathic basalts.

F.A. was performed on this admittedly small sample because it was believed that the correlation coefficients were significant enough, at the 0.05 level (Table 5.12). The pattern (Figure 5.8) shows the 'ferromagnesian' elements (Mg, Ni, Cr) clustering together and opposite to this cluster the elements that normally accumulate in residual liquids. Gunnet al. (1970) believe in the existence of a remarkably uniform parental alkaline magma. They favour crystal fractionation over partial melting as a mechanism for generating these magmas, particularly because of the parallel increase of Al and Ti (r = 0.98) with other late stage elements.

Table 5.12 Some major oxides (%), trace elements (ppm) and correlation coefficients (r) for tungsten with each of these variables for five samples from the Crozet archipelago

Samples Variables	Ce-1	Ce-2	Ce-3	Ce-4	Ce-5	r^+
SiO_2	47.35	47.09	47.31	45.81	46.80	.97
TiO_2	3.34	3.03	2.54	1.88	2.85	.79
Na_2O	3.24	2.74	2.58	1.66	2.37	.91
K_2O	1.50	1.32	1.24	.70	1.19	.90
P_2O_5	.55	.45	.48	.26	.41	.91
Rb	36	34	34	18	31	.93
Sr	630	542	509	317	472	.91
Ba	326	255	249	186	272	.69
Cr	52	200	374	1028	159	-.76
Ni	65	106	238	551	109	-.76
Y	26	24	24	17	22	.92
Zr	278	247	273	145	216	.95
Nb	62	50	59	28	46	.90
W	.82	.83	.77	.18	.42	1.00

[+] Values for $r \geq .878$ are significant to very significant on a .05 level (acc. Brooks, 1972)

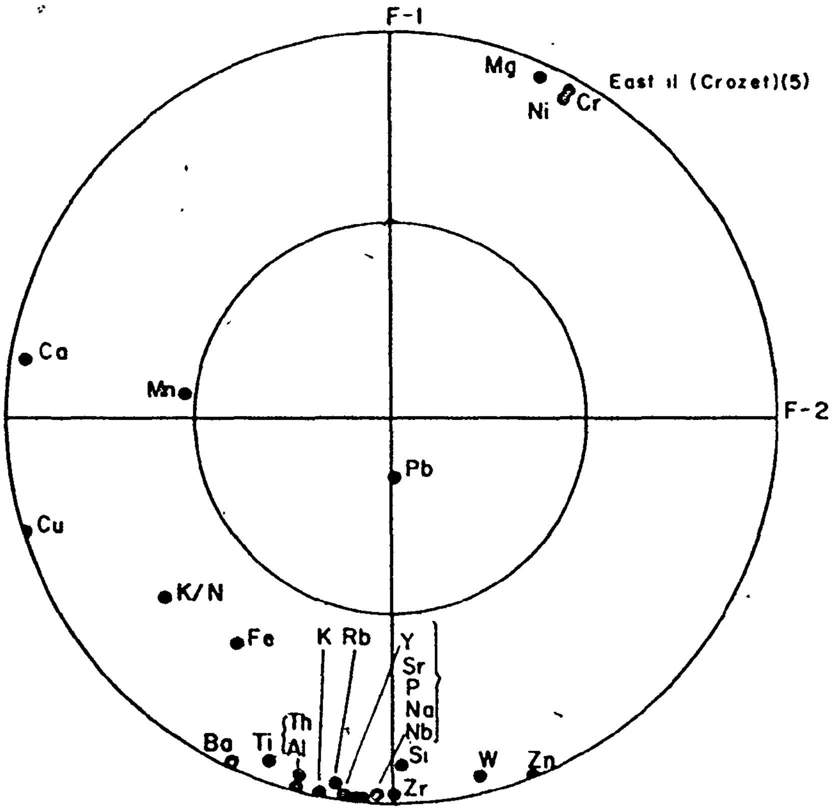


Fig. 5.8 Factor analysis for the Crozet archipelago

In partial melting Ti would have been enriched in the more mafic magma (MacGregor, 1969) and the Al-Ti correlation would have been negative. The behaviour of W in this set of rocks does not contradict its accumulation in residual liquids.

W ranges in this set of rocks from 0.18-0.83 ppm, with a mean of 0.60 ppm, which is considerably higher than in subalkaline rocks.

Cape Verde Archipelago: Little information is available even today on these islands. Five samples represent this soda alkaline province. These islands are known to have a petrologic succession similar to other Atlantic islands, but also to the East African Rift system (Mitchell-Thomé, 1972). This succession (Assuncao, 1968) consists of (i) basaltic lavas, (ii) strongly alkaline mafic and phonolitic lavas, and (iii) later basaltic lavas which are still operative at present. Bebiani (in Mitchell-Thomé, 1972) estimated the islands to be made up by some 83% of basic volcanics and tephra (the highest SiO_2 content recorded on any of the islands was 59.16%). Unfortunately no estimates exist on the amounts of each rock type. In Table 5.13 some data concerning the Cape Verde Islands Maio and Sal (VM and VS) can be found, but for further details reference is made to Appendices I and II.

Klerkx et al. (1974), on the basis of a constant Sr isotopic ratio with increasing K content, consider that all

Table 5.13 Some major oxides (%), trace elements (ppm), correlation coefficients (r) of tungsten with each of these variables, differentiation index (D.I.) and normative nepheline (Ne) for five samples from the Cape Verde Archipelago

Variables	VM-1	VM-2	VS-1	VS-2	VS-3	r*
SiO_2	45.85	41.05	39.00	45.36	54.53	0.68
TiO_2	4.42	4.90	3.43	2.45	0.56	-.45
Al_2O_3	15.12	13.13	9.60	13.47	22.20	0.82
Na_2O	3.26	3.65	2.87	2.31	10.52	0.92
K_2O	1.17	1.39	1.23	0.91	6.06	0.89
P_2O_5	0.84	0.80	0.78	0.30	0.06	-.46
Rb	18	42	34	20	197	0.89
Sr	1141	1011	992	508	1091	0.56
Ba	837	660	476	253	624	0.46
Cr	28	47	554	327	6	-.69
Ni	38	63	425	189	nd	-.64
Y	28	26	25	21	19	-.45
Zr	434	411	244	172	593	0.92
Nb	130	114	95	43	117	0.58
W	0.64	1.13	0.43	0.25	1.81	1.00
D.I.	35.5	29.8	20.8	23.9	86.9	-
Ne	2.0	17.4	15.2	3.0	40.3	-

nd = not detected; 6 ppm Ni were assumed for F.A.

\- = not determined

* r values > 0.878 are significant at the 0.05 level (Brooks, 1972)

rocks are derived from the same parental magma by differentiation. They suggest that this primary magma is nephelinitic and that it has been produced by partial melting of a phlogopite-peridotite, since it has such low K/Rb ratios. These low K/Rb ratios, in the opinion of this author however, are based on incorrect computations (i.e. the wrong conversion factor for K_2O to K).

Whereas Klerkx et al. (1974) imply that the rocks with higher K content are differentiation products derived at shallow levels from nephelinitic magmas, Wright (1971) points out the possibility of producing, under the right conditions, the full range of alkaline magmas from the upper mantle. In this respect, it is interesting to observe the behaviour of various elements in the VS group from the more mafic sample towards the more felsic one, i.e. from VS-1 to VS-3. Here a consistent decrease in Ti, Fe, Mn, Mg, Ca, P, Cr, Ni, Cu and Y occurs towards VS-3. This decrease of mostly compatible elements is accompanied first by a decrease of the incompatible elements, i.e. Na, K, Rb, Sr, Ba, Zr, Nb, Pb, U, Th, W towards VS-2, followed by a sharp increase towards VS-3. Such a pattern is difficult to reconcile with a normal differentiation process from nephelinitic magmas. The VM samples show a similar trend as the one from VS-1 to VS-2 (or _vice-versa_?), though less clear. That partial melting plays an important role in order to produce such alkaline magmas leaves no doubt, although much more information is needed before firm conclusions can be drawn on the origin and evolution of the volcanics of the Cape Verde Islands and the behaviour of W in these rocks.

F.A. was performed but was discarded because only 5 samples from two different islands were involved, but also because of the few significant correlation coefficients (0.05 level). Significant correlations, however, exist between W and Na, K, Rb, Zr (Table 5.13). These elements either accumulate in residual liquids or appear very early in partial melts (Gast, 1968). Considering the enrichment of these elements in the Cape Verde samples, W invariably lies between K and Rb (Table 5.14).

Table 5.14 Enrichment factors for various elements in the samples of the Cape Verde Islands

Sequence	Na	K	Rb	Zr	W
VS-2 to VS-1	1.2	1.4	1.8	1.4	1.7
VS-2 to VS-3	4.6	6.7	10.0	3.5	7.2
VM-1 to VM-2	1.1	1.2	2.4	0.9	1.7

The distribution of W in alkaline ocean island basalts (excluding phonolite VS-3 from the computations) is given in Table 5.15.

Table 5.15 Distribution of tungsten in alkaline ocean islands basalts (ppm)

Samples (No.)	Mean	Median	Range
All basalts* (10)	0.60	0.60	0.18 - 1.13
Crozet Islands (5)	0.60	0.77	0.18 - 0.83
Cape Verde** (4)	0.61	0.54	0.25 - 1.13

* VS-3 excluded but IC-1 included
**VS-3 excluded

5.2.4 Summary

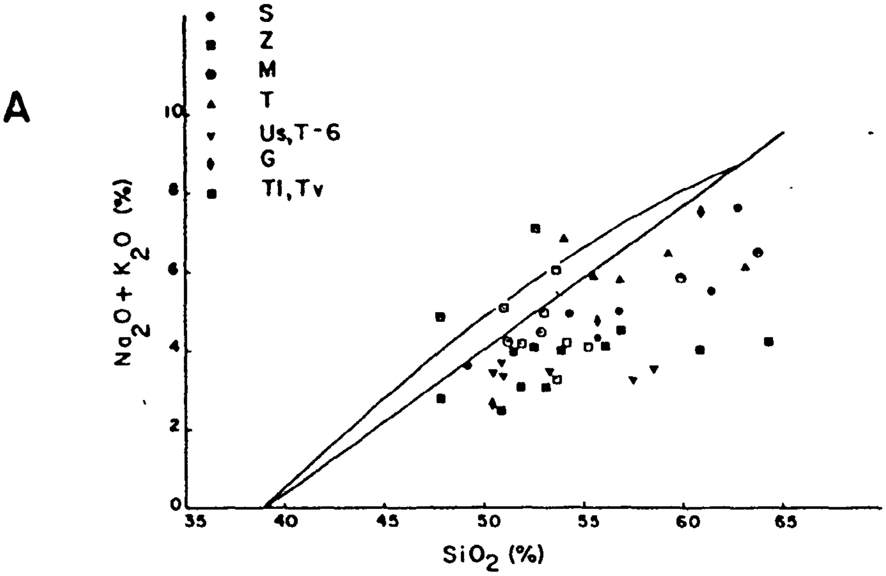
To summarize the findings on W in ocean island basalts the following can be said:

1. 18 subalkaline basalts contain about 0.30 ppm W, whereas 10 alkaline basalts contain about 0.60 ppm W, i.e. twice as much. These values are about two and four times the W content in ocean floor basalts;
2. the range of W distribution is wider in alkaline than in subalkaline basalts;
3. in both alkaline and subalkaline basalts, W correlates positively with several of the late stage elements (K,

Na, Rb, Sr, Y, Zr, Nb, etc.) depending on the set of samples involved. It correlates negatively with early stage elements such as Mg, Cr, Ni. The positive correlations can be ascribed to either fractional crystallization, during which these elements accumulate in residual liquids, or to partial melting in which W resembles the behaviour of K and Rb.

5.3 Subduction zone environment

For the same reason as for the oceanic rocks (section 5.2) a first general appraisal will be given on the distribution of tungsten in all rocks from subduction zone areas. The term 'subduction zone' is used here in its widest sense (section 5.1), without attempting to differentiate between islands arcs or continental margins, either fossil or active. Some 44 samples in total are representative for such subduction zone areas. Figure 5.9A,B shows the distribution of aforementioned rocks on an alkali versus silica diagram and an AFM diagram, whereas Figure 5.10 illustrates the frequency distribution of tungsten in all but one of the subduction zone samples. Sample S-2 was left out of this histogram because of its anomalously high W content (24 ppm). Some 9 rocks have W contents greater or equal to 1 ppm. Some of these 9 rocks are intermediate rocks in composition (e.g. TL-1, TL-2, M-1, M-2), others are very altered (e.g. Z-7, Z-5), and others have rather high alkali contents (e.g. S-1,



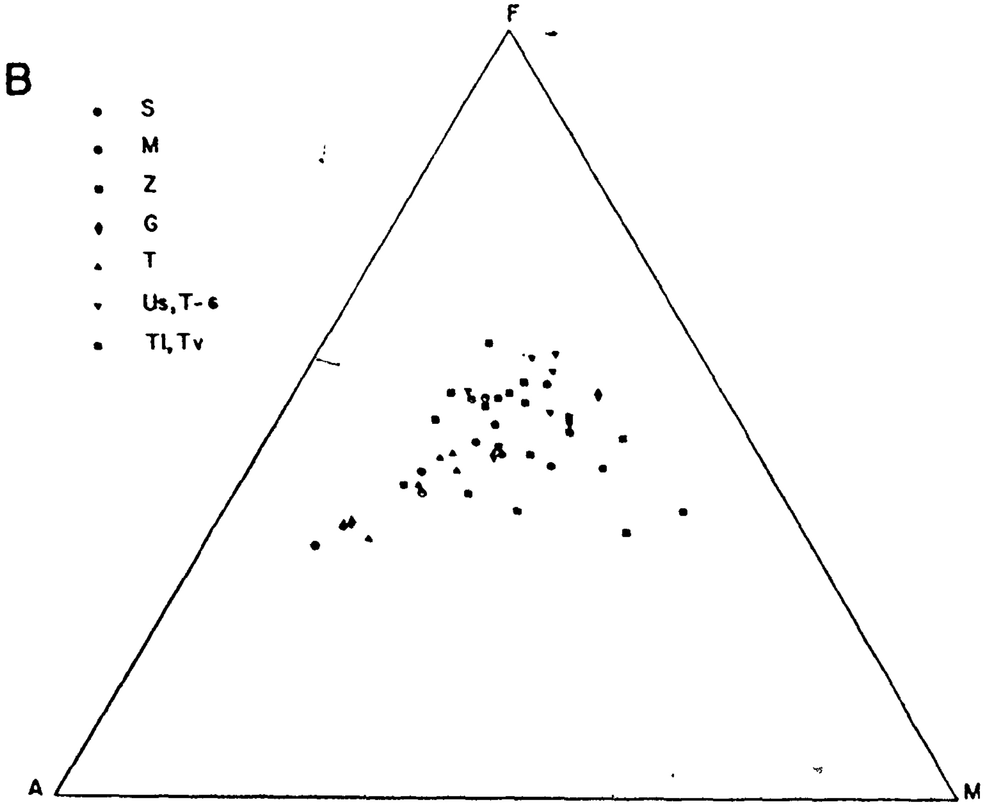


Fig 5.9 Alkali - silica diagram (a) and AFM diagram (b) for samples from subduction zone areas (island arcs and continental margins). For more details see Fig 5.1 and Table 2.1

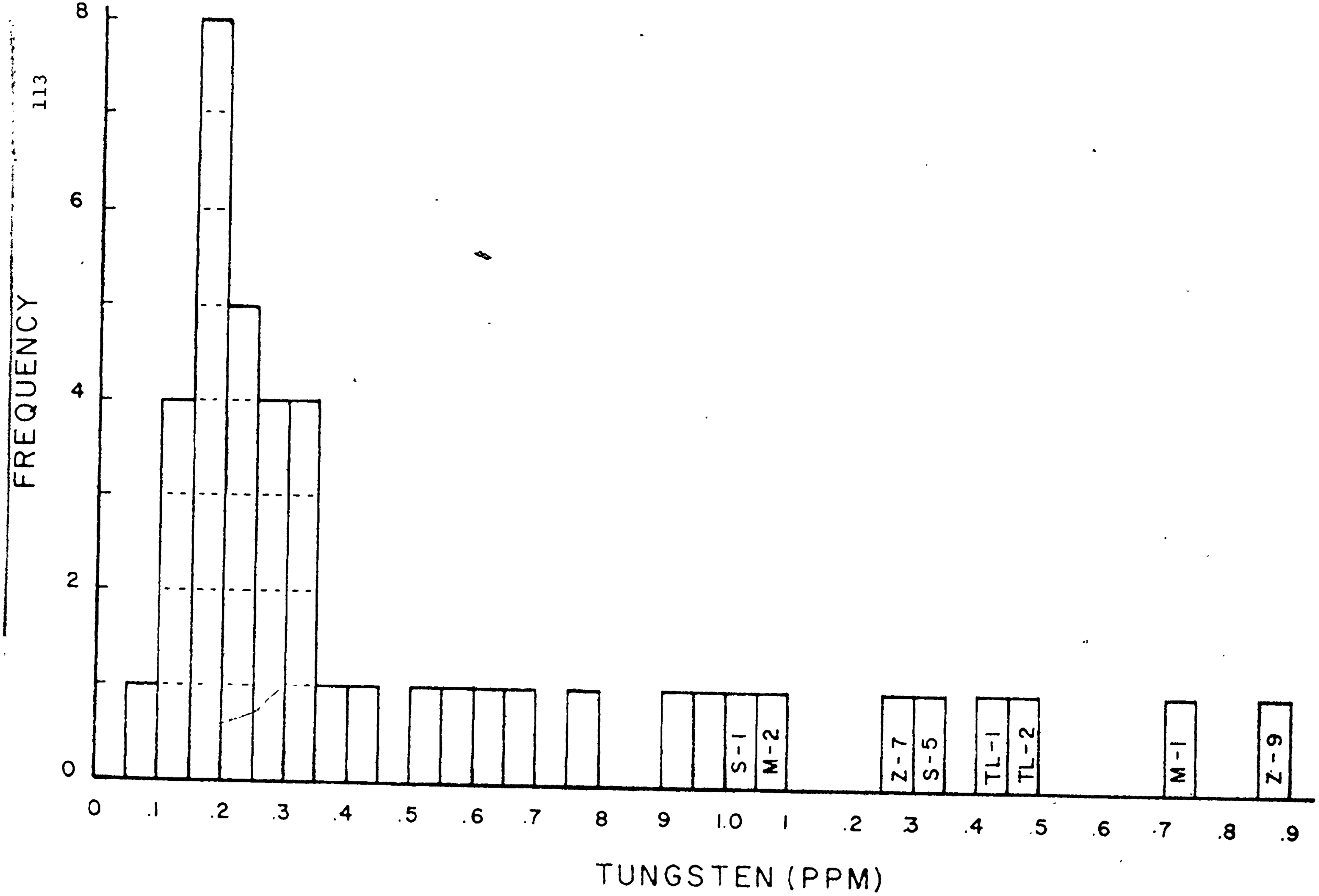


Fig 5.10 Distribution of tungsten in rocks from subduction zones (43 samples)

S-5). These rocks will be dealt with in more detail when discussing the samples according to their area. Table 5.16 gives numerical data from the W distribution histogram.

Table 5.16 Mean, median and range of tungsten distribution in rocks* from subduction zone areas (ppm)

Mean	Median	Range
0.52	0.27	0.09 - 1.85

*43 samples in total, excluding sample S-2

In an earlier section (5.2) dealing with the distribution of W in oceanic rocks, certain high values were left out under the pretext that these high values occurred in rocks, representing only a very small fraction of the total bulk of oceanic rocks, i.e. more felsic differentiation products. Although some samples here could also be excluded (e.g. S-2, 23 ppm W, and Z-9, 1.85 ppm W), it certainly would not be justifiable to exclude several other rocks with high W contents on the same grounds as the oceanic rocks. Indeed, several of these samples with higher W contents often, in fact, comprise the bulk of the rocks occurring in subduction zone areas.

5.3.1 Island arc systems

Before proceeding with a more detailed discussion on the various island arc samples, some general characteristics concerning these rocks should be pointed out. Some 25 samples in total represent either the western Pacific Ocean (samples G, T and US), or the Lesser Antilles island arc systems (samples TL and TV). More information about the localities of these rocks and their chemistry can be found in Appendices I and II.

Characteristic for all island arc samples is their very low Nb content. Only two samples, i.e. TL-1 and TL-2 have detectable amounts of Nb (2.9 and 4.0 ppm Nb, respectively), whereas the other samples show Nb contents below the detection limit (2 ppm Nb). These data will be dealt with below.

An exploratory F.A. (F-1,2 [44, 17], Figure 5.11) on all but 2 samples - US-2 and T-4 were excluded because no trace element data were available - shows W associating with some late stage elements (e.g. Th, Pb, Rb, Zr,), but at the same time its complete independence from others (e.g. K, Na). The correlation coefficients of W with these elements are, respectively, 0.93, 0.88, 0.74, 0.57, 0.14, -0.17. The most that can be said about W in this F.A. is that, as pointed out in previous sections, it does not associate with early stage elements (e.g. Mg, Ni, Ca, etc.)

The distribution of W in the island arc samples is

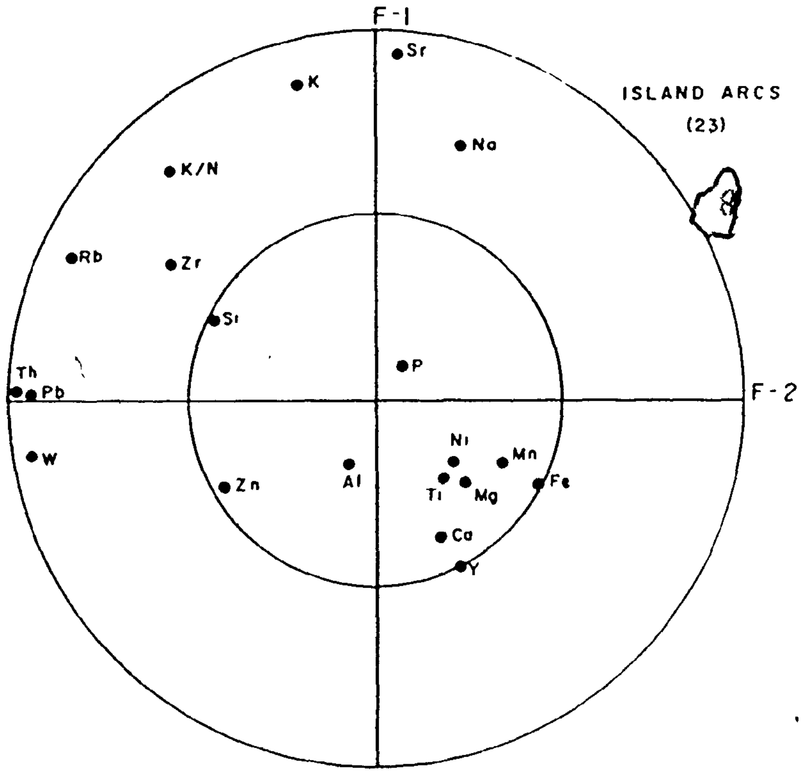


Fig 5.11 Factor analysis for all rocks from island arcs

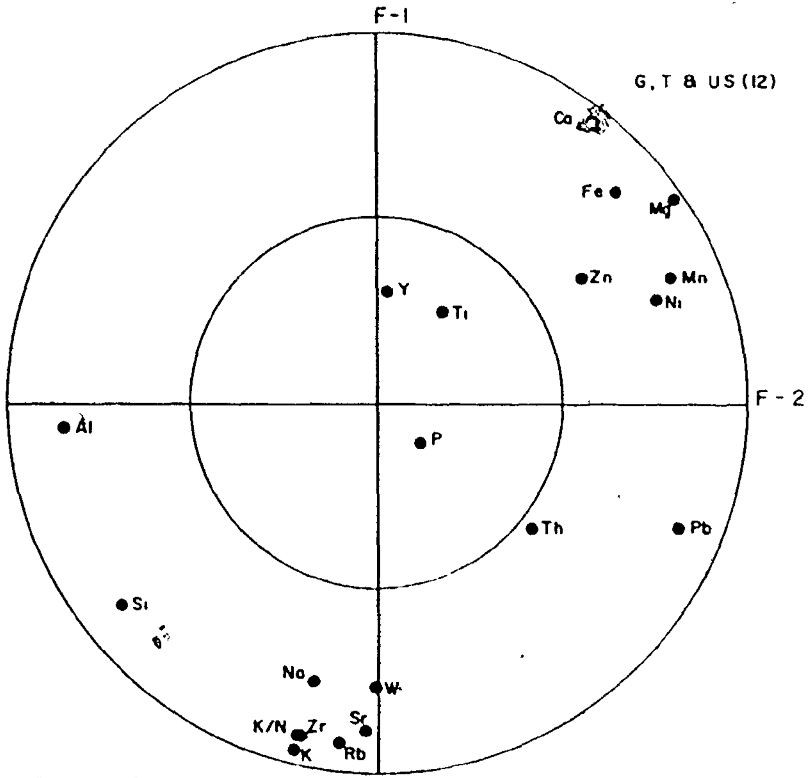


Fig 5.12 Factor analysis for island arc samples from the western Pacific Plate margin

given in Table 5.17. In this table all island arc samples are treated as a whole and subsequently are divided up into basalts and andesites.

Table 5.17 Distribution of tungsten in samples of island arcs (ppm)

Group of samples	No. of samples	Mean	Median	Range
All samples	25	0.35	0.20	0.09 - 1.49
Andesites	13	0.43	0.23	0.10 - 1.49
Basalts	12	0.27	0.19	0.09 - 0.67

The first area to be investigated includes some 14 samples from the border of the western Pacific Plate (Chapter II). Some data concerning these samples are shown in Table 5.18, but more complete information is available in Appendices I and II.

Figure 5.12 shows a F.A. (F-1,2 [52, 18]) for these island arc samples, excluding T-4 and US-2, because no trace element data were available. From this F.A. it becomes obvious once more that W associates closely with other late stage elements such as Na, K, Rb, Sr, Zr, and to a lesser degree with Si. With reference to some of these rocks (andesites T and US-1), Taylor et al. (1966, 1969) reported

Table 5.18 Some major oxides (%), trace elements (ppm), correlation coefficients (r) for tungsten with each of these variables and differentiation index (D.I.) for fourteen samples from island arcs from the western Pacific plate

Samples Variables+	G-1	G-2	G-3	T-1	T-2	T-3	T-4	T-5	T-6	US-1	US-2	US-3	US-4	US-5	r
SiO_2	50.04	55.43	60.64	54.00	55.20	56.50	58.80	62.70	57.40	57.20	50.99	53.09	50.52	50.87	.42
TiO_2	.74	.82	.62	.27	.90	.40	.81	.63	.62	.54	.97	.80	1.04	.95	-.40
MgO	6.73	4.26	2.18	4.55	3.80	3.30	3.25	2.20	2.40	4.65	4.74	6.00	5.37	5.55	-.43
CaO	12.25	8.36	5.74	8.40	7.70	7.85	6.35	6.30	8.48	8.85	10.03	10.20	10.75	10.64	-.56
Na_2O	2.12	3.42	4.47	5.20	4.30	4.10	3.60	4.10	2.76	2.50	2.90	2.57	2.68	2.63	.64
K_2O	.59	1.28	2.89	1.61	1.63	1.67	2.75	1.95	.74	.68	.78	.88	.76	.71	.65
Rb	18	19	54	28	26	27	-	38	13	13	-	18	14	13	.62
Sr	396	447	1314	838	822	799	-	748	168	262	-	281	344	333	.54
Ba	271	426	850	260	225	280	180	380	95	-	-	-	-	-	-
Ni	49	10	10	17	16	12	-	12	11	24	-	57	13	38	-.16
Y	15	13	16	16	18	16	-	14	20	22	-	21	17	20	-.19
Zr	41	74	158	79	83	90	-	100	47	82	-	75	46	53	.59
W	.09	.17	.25	.25	.13	.15	.75	.20	.17	.10	.16	.21	.11	.17	1.00
La	3	9	28	10	10	10	19	8	3	4	-	-	-	-	.55
D.I.	22.8	43.7	65.2	52.2	49.7	50.4	57.3	63.7	44.6	39.5	31.9	32.6	29.0	28.7	-

+ Nb was determined but not detected

low concentrations of large cations (Cs, Rb, Ba, Tl, Pb), rare earths and the highly charged cations (e.g. Zr, Hf, Th, U, Nb, Sn). These authors also mention that the concentration levels of these elements are reminiscent of concentrations in tholeiitic basalts, i.e. they are not 'intermediate' values between basalts and acidic rocks. These observations are confirmed by the low concentrations of W in these rocks (Table 5.19).

Table 5.19 Distribution of tungsten in samples of island arcs along the western Pacific Plate (ppm)

Samples	No. of samples	Mean	Median	Mode	Range
All samples	14	0.21	0.17	0.15	0.09 - 0.75
Andesites	9	0.24	0.17	0.15	0.10 - 0.75
Basalts	5	0.15	0.16	0.15	0.09 - 0.21

The values obtained for W in the island arc samples are very similar to oceanic subalkaline basalts (section 5.2). These low W contents for both andesites and basalts of island arcs too contrast strongly with the high suggested values mentioned earlier (section 5.1).

Since the high K andesites are known to show parallel increases in large and large highly charged cations (Taylor et al., 1969) as well as the rare earths, it is not surprising to see the high value for W in sample T-4 (0.75 ppm). By the same token, however, one would expect a similar amount in Sample G-3, also a high K andesite, unless regional differences can be invoked, as well as higher contents of other trace elements of T-4, when comparing both rocks. Despite the fact that no Sr^{87}/Sr^{86} values were available for the island arc andesites (samples T), the general absence of any crustal rocks in the area, as well as the low initial Sr^{87}/Sr^{86} values (0.704 or less) as reported by Pushkar (1968) for Saipan and the northern Marianas or Gill (written comm.) for Fiji, do not support any involvement of crustal contamination.

Wänke (1975), aware of the different conditions of formation, points out the very good correlation that exists between La^{3+} and W in lunar samples. W was plotted versus the few available La^{3+} data (Figure 5.13). It certainly would be desirable, in order to evaluate better the correlation between La and W, to obtain more data on both elements and this in a more varying set of rocks.

The Lesser Antilles island arc forms a much smaller system than the previously discussed island arcs of the western Pacific Plate. Some 11 rocks originating from only two islands, i.e. St. Lucia and St. Vincent, will be discussed below. Data needed for this discussion are given in Table 5.20, although more information is available in

Table 5.20 Some major oxides (%), trace elements (ppm), correlation coefficient (r) of tungsten with each of these variables and initial strontium isotopic ratio for eleven Lesser Antilles samples

Samples Variables	TL-1	TL-2	TL-3	TL-4	TL-5	TV-1	TV-2	TV-3	TV-4	TV-5	TV-6	r
SiO_2	63.06	59.13	50.49	51.74	52.99	55.78	50.51	47.74	52.72	56.24	51.29	.82
TiO_2	.55	.50	.69	1.03	1.14	.84	.83	1.06	.86	.77	1.08	-.72
MgO	1.80	2.86	5.37	3.28	3.73	3.33	7.28	11.99	6.85	4.29	4.12	-.55
CaO	6.96	7.36	11.51	7.77	9.24	8.70	11.27	11.38	9.41	7.11	9.08	-.45
Na_2O	2.81	2.34	2.47	3.59	3.26	3.47	2.09	2.21	2.55	3.73	3.47	-.21
K_2O	1.31	1.45	.56	.47	.76	.64	.43	.62	.60	.75	.60	.93
Rb	78	65	15	13	17	14	12	6	11	12	10	.95
Sr	327	299	238	201	201	224	237	241	369	238	235	.46
Ni	nd	nd	45	11	21	15	78	199	24	71	5	-
Y	16	18	16	28	27	25	21	18	19	23	32	-.51
Zr	160	117	56	80	113	97	74	61	61	90	86	.73
W	1.40	1.49	.67	.31	.63	.23	.17	.12	.34	.27	.20	1.00
Sr^{87}/Sr^{86}	.7080	.7092	.7054	.7046	.7043	.7041	.7038	.7040	.7039	.7037	.7043	.96

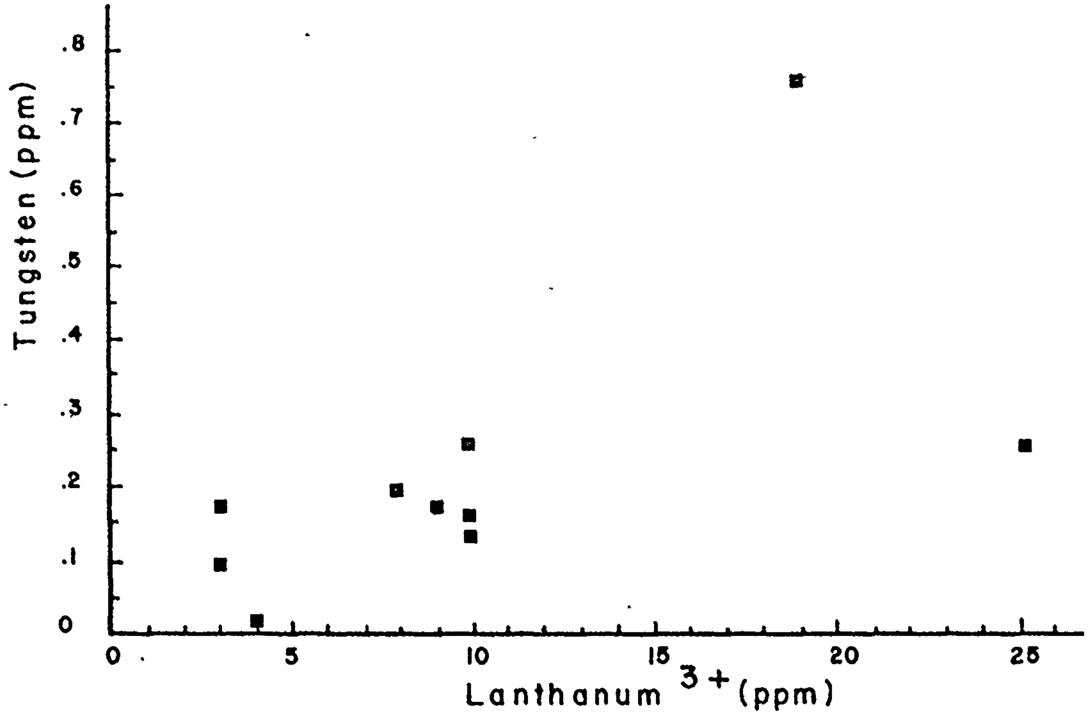


Fig. 5.13 Scatter diagram of tungsten vs lanthanum

Appendices I and II. Nb data are not given since only two samples, i.e. TL-1 and TL-2 (3 and 4 ppm, respectively) had detectable contents.

F.A. (F-1,2 [57, 21]) performed on these rocks (Fig. 5.14) illustrates a close association between K, Rb, Pb, Th, W and Sr^{87}/Sr^{86}, and to a lesser degree with Si and Zr. Puzzling, however, is the position of Na, which is probably due to the apparent increase of Na towards the more mafic members of the TL samples. Nevertheless, W forms an association with late stage elements.

The distribution of W in the Lesser Antilles' samples is given in Table 5.21.

Table 5.21 Distribution of tungsten in samples of the Lesser Antilles island arc (ppm)

Samples	No. of samples	Mean	Median	Range
TL + TV	11	0.53	0.31	0.12 - 1.49
TL	5	0.90	0.67	0.31 - 1.49
TL basalts	3	0.54	0.63	0.31 - 0.67
TV	6	0.22	0.22	0.12 - 0.34
TV basalts	4	0.21	0.19	0.12 - 0.34

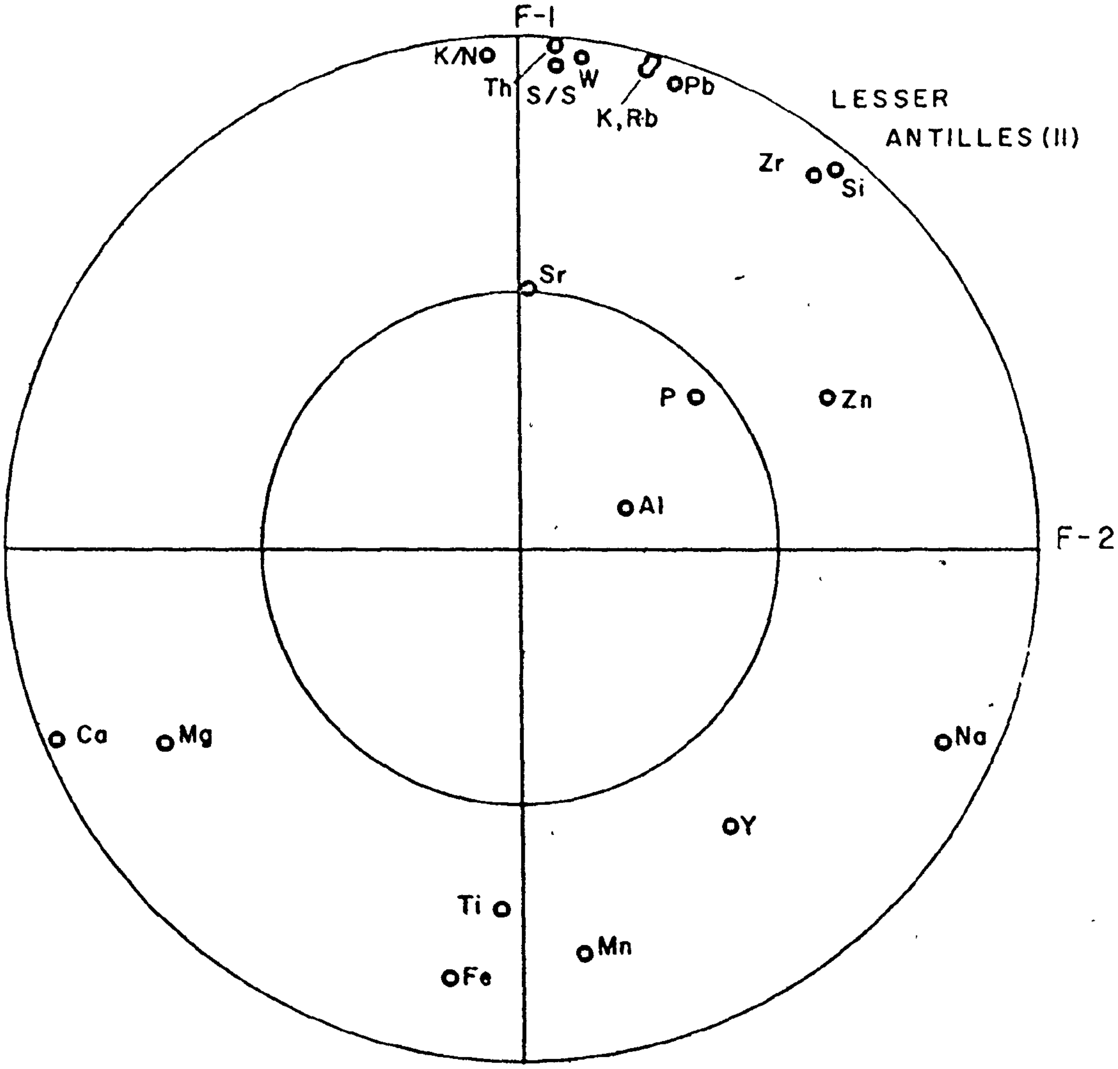


Fig. 5.14 Factor analysis for Lesser Antilles samples

The distribution of W in the St. Vincent samples (TV) is very similar to values obtained for west Pacific Plate boundary islands. The high values obtained for both andesites and basalts of St. Lucia require further explanation. As mentioned earlier (Chapter II), the two islands are very different ~~in~~ composition. St. Vincent, consisting exclusively of basalt and basaltic andesite, takes up a unique position among the larger islands of the Lesser Antilles, whereas St. Lucia is much more representative for the Lesser Antilles in general with its more felsic composition of andesites and dacites (Tomblin, in Pushkar et al., 1973).

Pushkar (1968) studied the initial Sr^{87}/Sr^{86} ratios in several non-ignimbrite calc-alkaline volcanic rocks from these island arcs, i.e. the western Pacific Ocean, Central America and the Lesser Antilles. With only two exceptions, values for initial Sr^{87}/Sr^{86} ratios lie in the range 0.703-0.705, with an average very close to 0.704. Similar ratios were found for tholeiitic lavas from the northern Marianas. Pushkar (1968) suggests a source area for formation of these rocks in the upper mantle or possibly in basaltic rocks of the oceanic crust, although the high initial Sr^{87}/Sr^{86} ratios cannot be explained in this way. In order to explain these high values (Table 5.20) Pushkar et al. (1973) focussed their attention on both St. Vincent and St. Lucia. With reference to St. Vincent these authors mention the tight clustering of the new initial Sr^{87}/Sr^{86} ratio values around 0.7040, which make them very similar to values of other island arcs (Pushkar, 1968). The same observation can be made for the W contents, i.e. little variation occurs and, as mentioned earlier, the W contents do not differ very much from other island arc samples (Tables 5.18 and 5.20). If the suggestion that no continental material is involved in the production of the andesites (Hedge et al., in Pushkar et al., 1973), a suggestion supported by isotopic evidence, is correct, then the andesites may be derived from the basalts which, in turn, probably originated in the mantle. This would explain the low W contents of St. Vincent rocks. The lowest W content occurs in sample TV-3 (0.12 ppm), the most mafic rock analyzed here. This coincides with the lowest Rb content and the highest Ni content. Although a gradual increase of Si, Na and K in a set of samples from a single volcano (Soufrière) suggests a differentiation sequence, this suggestion, however, is not substantiated by the trace elements.

With reference to St. Lucia, it is obvious that the W contents (Table 5.20) are considerably higher than those of many samples from oceanic and island arc environments. This increase in W goes hand in hand with an increase in initial Sr^{87}/Sr^{86} ratios (Pushkar, 1968; Pushkar et al., 1973). In order to explain these high initial Sr^{87}/Sr^{86} ratios (particularly TL-1,2,3) Pushkar et al. (1973) examined four possibilities, which are:

(a) the mantle locally contains high Sr^{87}/Sr^{86} ratios;

(b) the felsic volcanics with high Sr isotopic ratios are, largely or entirely, produced from crustal material;

(c) exchange of Sr isotopes between sea water and the magmas;

(d) melting of crustal material dragged down along the Benioff zone (e.g. Tomblin, 1974).

Pushkar et al. (1973) favour the fourth possibility, pointing out that the crustal material can be either marine sediments or debris from the Guyana shield, carried by the Orinoco River into the Puerto Rico trench to form later the Barbados ridge (Fisher et al., in Pushkar, 1968). Initial Sr isotopic ratios, however, of pelagic sediments cored to the east of the Lesser Antilles - 0.7083 and 0.7086 (Pushkar, 1968) - as well as additional geological and petrological evidence from the Qualibouvolcano (Tomblin, in Pushkar et al., 1973) support the possibility of magma formation by melting of crustal material, i.e. pelagic sediments. Assuming the hypothesis concerning the involvement of sediments is correct, the next step to be considered is the availability of W from sediments. Again, data on W contents are rather scarce, and believed to be similar to those in igneous rocks (1-2 ppm). Nevertheless, as mentioned earlier, there is plenty of evidence (e.g. Maucher, 1972 and many others, see Chapter I) of the existence of time- and strata-bound deposits of stibnite and scheelite on a world-wide scale, related to Ordovician and Silurian metavolcanics, and it is difficult to accept that this process would not go on nowadays. In fact, abnormal amounts of W (up to 70 ppm) have been reported for various types of pelagic sediments (e.g. Amiruddin et al., 1962; Isayeva, Petelin et al., in Krauskopf, 1970). These anomalous contents are believed to be rather localized and related to nearby volcanic activity. In other words, the involvement of sediments is supported by isotopic evidence and to say the least, the W data do not contradict this view. Moreover, sediments that would be able to concentrate to some degree W (e.g. shales) have been recognized in the Barbados zone (Tomblin, 1974).

5.3.2 Summary

It can be said that andesites of island arcs contain about 0.43 ppm W and basalts about 0.27 ppm. These values are obtained for island arcs without any further discrimination. The possibility of contamination by pelagic sediments, however, is real for the St. Lucia samples. Consequently the W contents for both island arc andesites and basalts will be reduced when the St. Lucia samples are omitted (Table 5.22). Thus, andesites will contain about 0.24 ppm W and basalts about 0.17 ppm W. These values are below the mean value of subalkaline ocean island basalts. In fact, the

Table 5.22 Distribution of tungsten (ppm) in rocks from island arcs, excluding St. Lucia

Samples (No.)	Mean	Median	Range
All rocks (20)	0.21	0.17	0.09 - 0.75
Andesites (11)	0.24	0.20	0.10 - 0.75
Basalts (9)	0.17	0.17	0.09 - 0.34

W contents of island arc basalts is almost identical to ocean floor basalts (0.16 ppm W). Further, the range within which W varies is very small, except for a few cases, i.e. St. Lucia and T-4 (high K andesite). Lastly, W again correlates with several late stage elements such as Na, K, Rb, Zr, Th, Pb, etc., though not all at the same time, and conversely never with any of the early stage elements.

5.3.3 Continental margins

Some 19 samples were available for continental margins, comprising rocks from Guatemala (M), Sardinia (S) and Chile (Z). F.A. (F-1,2 [40, 19]) was performed on 18 of these samples excluding S-2 because of its anomalous W content (24 ppm). No significant correlation between W and any other variable emerges from this F.A. (Figure 5.15). As a matter of fact, W forms a factor on its own (F-5 [9]). This general lack of any significant association is probably due to

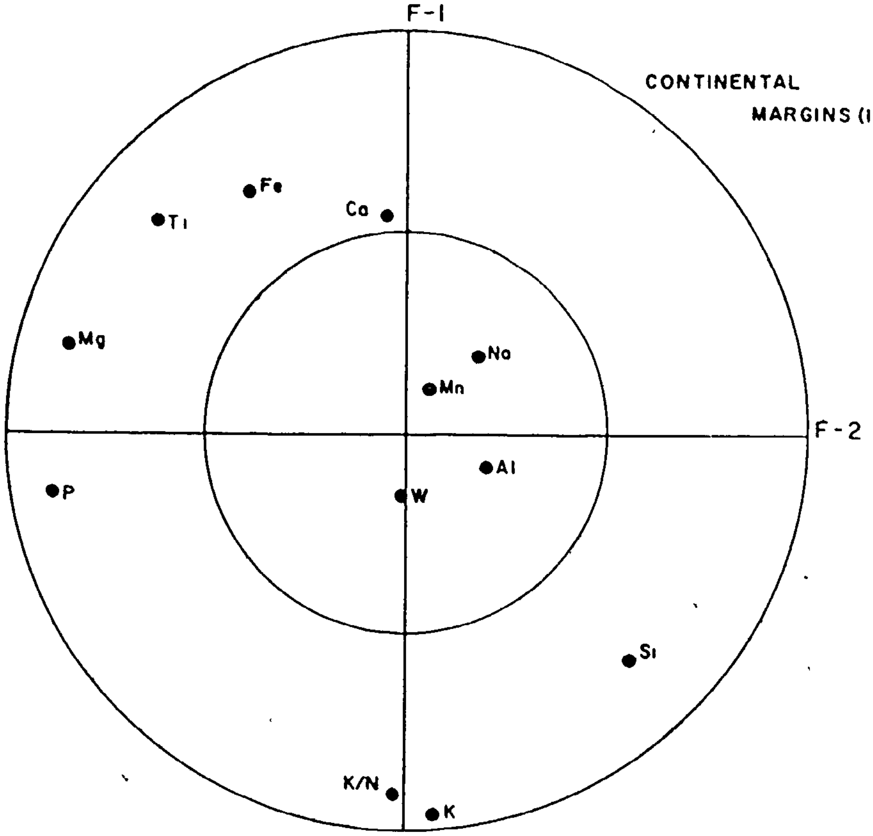


Fig 5.15 Factor analysis for continental margin samples

Table 5.24 Some major oxides (%), trace elements (ppm), correlation coefficients (r) of tungsten with each of these variables and initial strontium isotopic ratios for four samples from Guatemala

Samples Variables	M-1	M-2	M-3	M-4	r*
SiO_2	63.31	59.40	52.33	50.86	.99
TiO_2	.46	.73	1.39	1.20	-.97
MgO	1.75	2.99	6.08	3.45	-.79
CaO	4.66	6.18	9.09	9.69	-.99
Na_2O	4.74	3.75	3.07	3.43	.95
K_2O	1.59	1.98	1.25	.83	.70
Rb	32	53	-	-	-
Sr	477	461	-	-	-
Y	15	19	-	-	-
Zr	164	173	-	-	-
W	1.74	1.05	.22	.18	1.00
Sr^{87}/Sr^{86}	.7038	.7042	.7037	.7039	-

* values of $r > .95$ are significant at the .05 level (Brooks, 1972)

alteration in many of the samples involved, particularly the Chilean ones. The Nb contents, when available, are either low or below the detection limit, a feature already mentioned for the island arc samples. The distribution of W in all continental margin samples is given in Table 5.23.

Table 5.23 Distribution of tungsten (ppm) in samples from continental margins

Samples	Mean	Median	Range
Excluding S-2	0.75	0.54	0.18 - 1.85
Including S-2	1.87	0.55	0.18 - 23.7

<u>Central Guatemala</u> is represented by only four samples, of which only two were analyzed for all trace elements. These restrictions will make interpretation difficult and rather speculative. Some data on these rocks are given in Table 5.24. For more information see Appendices I and II.

The distribution of tungsten in the Guatemala rocks is given in Table 5.25. W increases strongly in the more felsic rocks, particularly M-1, whereas the two basaltic samples show W contents similar to the low contents found in island arc and oceanic basalts. Despite the underlying Paleozoic crystalline basement, Pushkar (1968), using the low initial

Sr^{87}/Sr^{86} ratios for both felsic and mafic rocks as evidence (Table 5.24), rejects the involvement of significant amounts of crustal rocks. As such the increase of W in more felsic rocks must be ascribed to fractional differentiation.

Table 5.25 Distribution of tungsten (ppm) in four rocks from Guatemala

Samples	Mean	Median	Range
All	0.80	0.64	0.18 - 1.74
Basalts	0.20	-	0.18 - 0.22

Sardinia: Full data on Sardinia are available in Appendices I and II, whereas the data of particular use for this section are given in Table 5.26.

A gradual increase of K, Li, Rb and Sr towards the north accompanying the change in major elements, is noticeable on a more regional scale. Ba remains constant, however, throughout all zones on Sardinia. This regional increase is taken as evidence for a magmatic zonation within the Cenozoic andesitic volcanism of Sardinia, which evolved from the south to the north (Coulon et al., 1975). Dupuy et al. (1975) report additional RE data which bring forth the similarity that exists between these element abundances of Sardinia and island arc rocks, particularly andesites from Bougainville and New Guinea. None of these features can be attributed to W, which does not show any significant correlation with any other element. The distribution of W is given in Table 5.27.

The W values of sardinia have not the same low average value as for many island arc samples. Even when excluding S-2 the mean W content is more than twice as high (0.74 ppm) as the mean value for all island arc samples (0.35 ppm) although the range is similar. The very high W content of

Table 5.26 Some major oxides (%), trace elements (ppm) and initial strontium isotopic ratios for six rocks from Sardinia

Variables	S-1 (III)*	S-2 (I)	S-3 (II)	S-4 (II)	S-5 (I)	S-6 (I)
SiO_2	52.82	48.70	55.17	61.35	59.81	54.46
TiO_2	0.71	1.00	0.80	0.60	0.72	0.85
MgO	4.47	5.38	3.68	1.65	2.70	3.85
Na_2O	2.71	2.63	2.47	3.81	2.96	2.84
K_2O	2.04	1.00	2.27	3.61	2.45	1.43
Rb	59	36	71	119	96	40
Sr	744	469	326	377	246	342
Zr	-	-	142	-	153	-
W	1.00	23.70	0.90	0.19	1.30	0.31
Sr^{87}/Sr^{86}	0.7080	0.7047	0.7064	0.7082	0.7066	0.7063

*Roman numbers refer to the series according to Dupuy et al. (1974)

Table 5.27 Distribution of tungsten (ppm) in six samples from Sardinia

Samples	Mean	Median	Range
With S-2	4.62	0.95	0.19 - 24.0
Without S-2	0.74	0.90	0.19 - 1.30

S-2, a basalt, is difficult to explain, especially when considering the low Sr^{87}/Sr^{86} ratio and K content. Contamination during crushing of the rocks is excluded (Dupuy, pers. comm.) and the same can be said for the processing of the samples in the laboratory. For these reasons it is suggested to look for geological reasons, for example local W enrichment. Some scheelite occurrences seem to exist in northwestern Sardinia (Höll, written comm.). Equally enigmatic is the very low W content of S-4, because this sample is the most felsic of all samples from Sardinia with rather high K and Rb contents as well as Sr^{87}/Sr^{86} ratio.

So far no explanation can be given for the often contradictory behaviour of W within this set of samples. It should be kept in mind, however, that the geologic history of the western Mediterranean is highly complex and controversial. In this context one only has to refer to the suggested direction of the subduction zone, i.e. Coulon et al. (1975) propose a south-north dip direction on geochemical grounds, whereas Bocaletti et al. (in Coulon et al., 1975) on geological grounds suggest a dip towards the west.

Chile: Table 5.28 gives some data needed for the interpretation of the 9 rocks of Chile and Argentina (2). More details are available in Appendices I and II.

Figure 5.16 shows the graphic result of F.A. on these 9 rocks. Some correlation exists between W and P, both of which are governed by both F-1,2 (30,20). Factor one regulates the uncommon association of Ti, Zr, Y and, to a lesser degree, Mg. Other uncommon associations are Na, Al and Mn. The extensive metasomatism that took place in these Chilean rocks (Z-1 through Z-7)* may very well be the main reason for the uncommon element association pattern of Figure 5.16. This metasomatism is reflected by the mineralogy of these rocks as obtained from Zentilli (written comm.). McNutt et al. (1975) studied a set of rocks originating from the same geotraverse. This set of samples was much larger and generally much fresher as well, and included both volcanic and plutonic rocks. Only the Neogene samples (i.e. younger than 20 m.y.) Z-9 and possibly Z-8 (because of the same sampling area) seem to be free of alteration-contamination from intrusives (Zentilli, written comm.).

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*Estimated modal analyses vary from 40-70% very altered plagioclase, 10-50% chlorite, 10-25% iron oxides and only minor pyroxene.

Table 5.28 Some major oxides (%), trace elements (ppm) and initial strontium isotopic ratios for nine samples from Chile and Argentina

Samples Variables	Z-1	Z-2	Z-3	Z-4	Z-5	Z-6	Z-7	Z-8	Z-9⁺
SiO_2	52.08	53.92	52.63	53.41	52.94	47.67	53.49	54.62	50.67
TiO_2	1.22	.95	1.10	1.12	1.01	1.10	1.44	1.38	1.25
Na_2O	3.27	2.92	4.94	4.52	3.90	4.61	2.29	3.54	2.66
K_2O	.90	1.22	2.25	1.52	1.15	.22	1.02	.61	2.38
P_2O_5	.38	.12	.19	.21	.16	.13	.23	.20	.42
Rb	16	18	61	27	13	5	14	11	71
Sr	691	958	820	506	458	467	328	327	569
Y	23	13	18	15	13	14	30	28	24
Zr	172	49	102	87	72	44	209	112	126
W	.33	.25	.54	.56	.39	.96	1.26	.41	1.85
Sr^{87}/Sr^{86}	-	-	.7036	-	.7037	-	.7035	-	.7060

⁺ Z-9 is the only sample with detectable Nb content (7ppm)

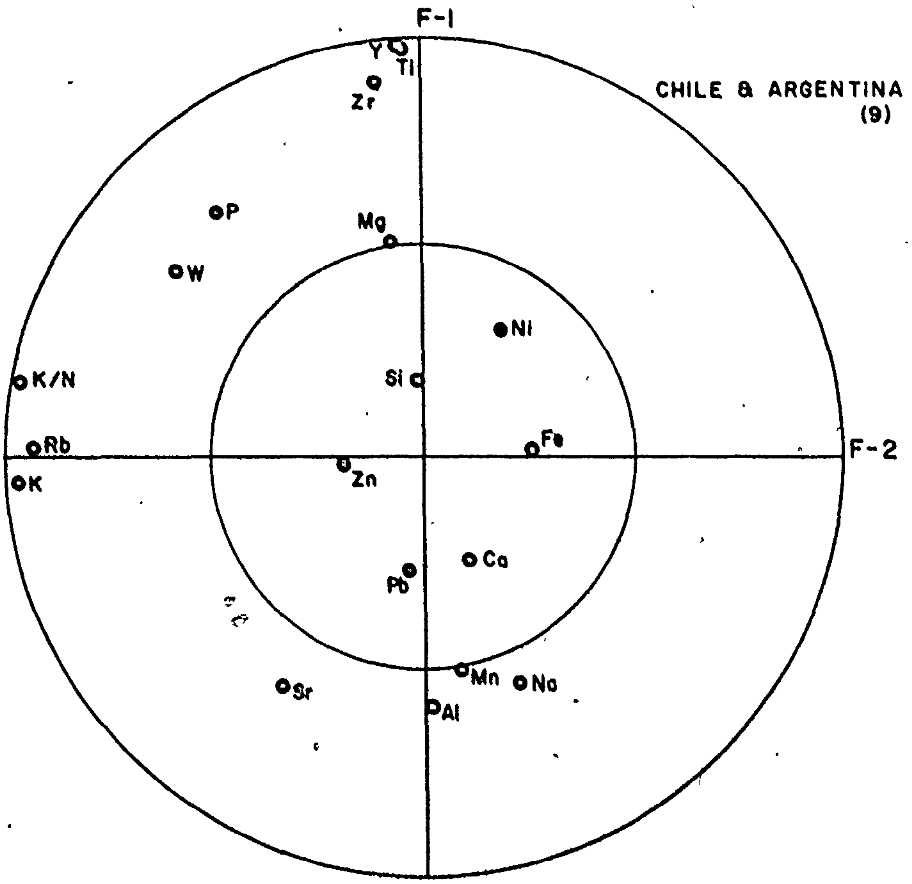

Fig. 5.16 Factor analysis for South American samples

High K and Rb contents of sample Z-9 coincide with a high W content, whereas sample Z-8 has low K, Rb and W contents, although Z-8 on the other hand is more felsic than Z-9. This generalization does not apply to the other (metasomatized) rocks. It is difficult to evaluate the behaviour of W with regard to any other element or even initial Sr^{87}/Sr^{86} ratios. It is also difficult, if not impossible, to say in which way the aforementioned metasomatism has affected these rocks with regard to their W content. This question arises here since it is known that W is always associated in this area with Tertiary intrusive episodes. The most that can be said is that the mean value of W in these rocks is considerably higher than any other value for similar areas (Table 5.29).

Table 5.29 Distribution of tungsten (ppm) in nine samples from Chile and Argentina

Samples	Mean	Median	Range
All 9	0.73	0.54	0.25 - 1.85

When combining all continental margin rocks and discriminating between andesites and basalts, keeping in mind that several of those rocks underwent alteration to some degree, the following values should be considered (Table 5.30).

Table 5.30 Distribution of tungsten (ppm) in nineteen rocks from continental margins

Samples	Mean	Median	Range
All rocks (19)	0.72	0.54	0.18 - 1.85
Basalts (12)	0.58	0.40	0.18 - 1.85
Andesites (7)	0.96	1.05	0.19 - 1.74

5.3.4 Summary

To summarize, the W contents of both basalts and andesites are considerably higher, i.e. respectively 0.58 ppm and 0.96 ppm, than for their island arc equivalents, even when including the St. Lucia samples. In fact, the continental margin rocks seem to be more comparable, in both W content and range of distribution of W, to the St. Lucia rocks. Alteration probably may account for these higher values. Alteration may also explain, to some degree, the less conspicuous or even lack of significant correlation existing between W and other late stage elements.

5.4 Continental environment

Before dealing with rocks from continental areas in detail, some general information will first be given. Beside the six standard rocks, i.e. five U.S.G.S. and one C.R.P.G. sample (see Appendix I), some 32 other rocks were analyzed. These include alkaline basalts from France and Spain (He and H), alkaline and subalkaline basalts from the southwestern U.S.A. (WL and WF), as well as four kimberlites (KB). Figure 5.17 shows the distribution of these rocks on an alkali versus silica diagram (KB-3 not included) and on an AFM diagram (samples KB not included). Table 5.31 illustrates the distribution of tungsten in these basalts (s.l.) and kimberlites. A histogram of the distribution of W (Figure 5.18) in these continental rocks does not show the skewness as expressed by histograms of samples from the ocean and subduction zone environments.

Table 5.31 Distribution of tungsten (ppm) in rocks from continental areas

Samples	Mean	Median	Range
All 38 rocks*	0.97	0.85	0.01 - 2.65
24 alk. basalts	1.29	1.35	0.17 - 2.65
6 subalk. basalts	0.36	0.30	0.23 - 0.53
Alk.+subalk.(30)basalts	1.11	1.09	0.17 - 2.65

*includes standard rocks and kimberlites

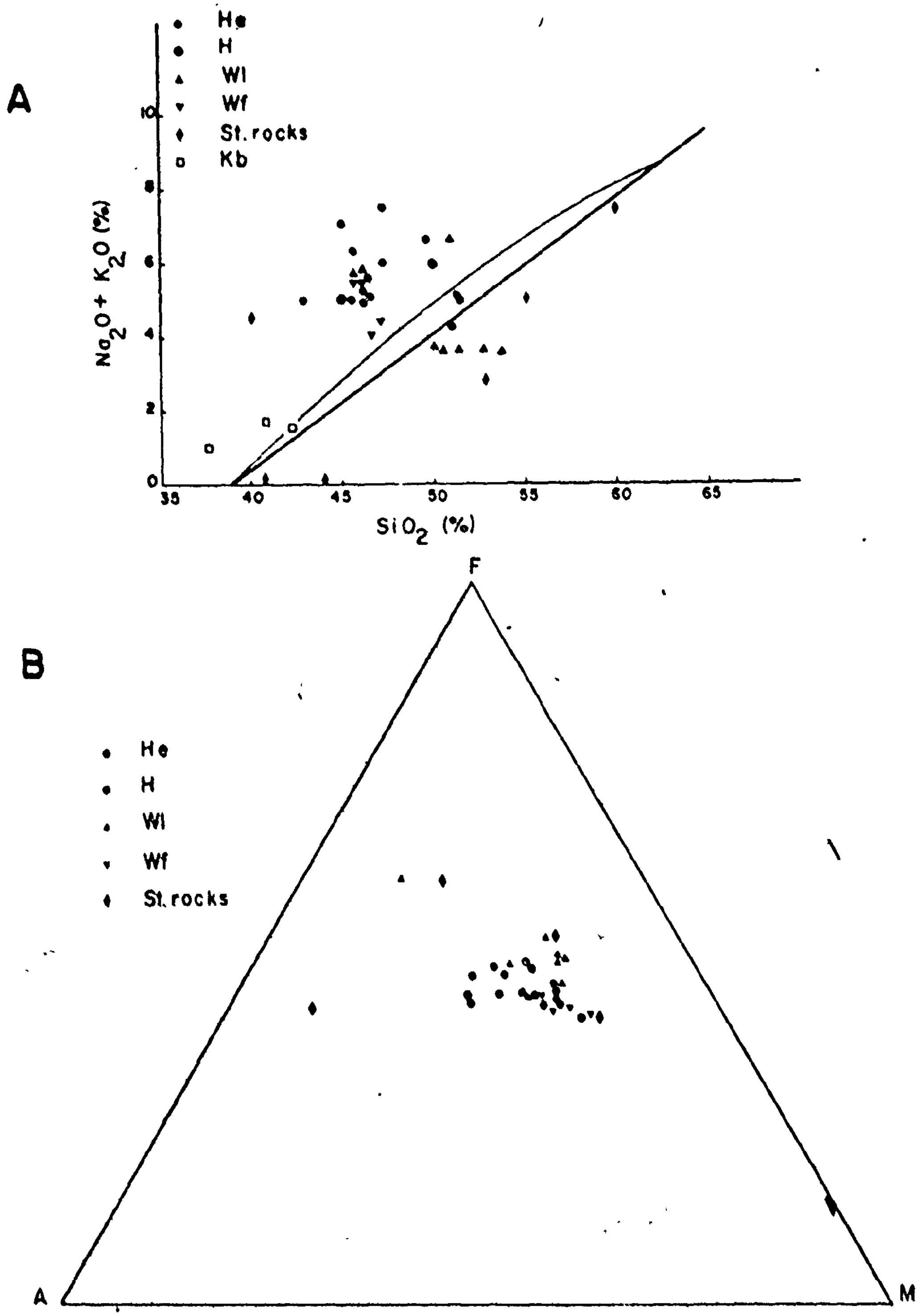

Fig. 5.17. Alkali - silica diagram (a) and AFM diagram (b) for samples from continental areas. For more details see Fig. 5.1 and Table 2.1

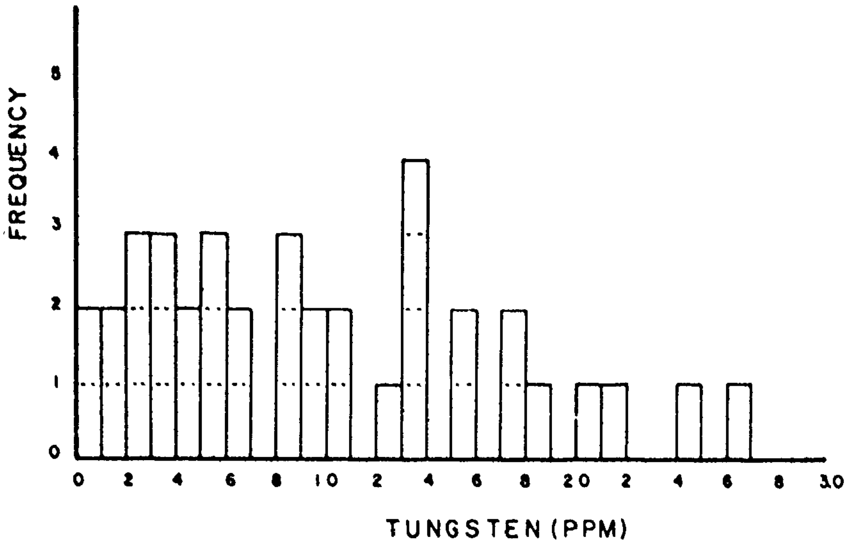

Fig 5.18 Distribution of tungsten in continental rocks (38 samples)

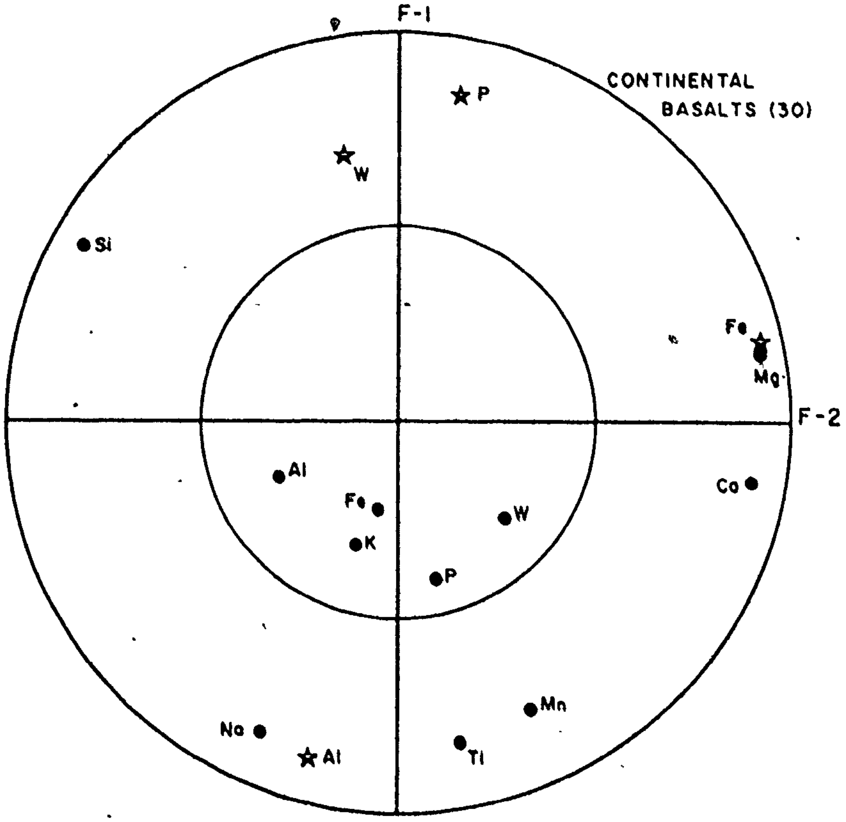

Fig. 5.19 Factor analysis for continental basalts. The symbol ★ represents loadings on factors 3 and 4

Figure 5.19 shows the result of a F.A. (F-1,2 [42,23]) performed on the alkaline and subalkaline basalts of Table 5.31. The negative correlation or total lack of any correlation between Si and all the other elements is the main pattern of this F.A. which will be discussed below. W shows some correlation with P (r = 0.79), but only in F-3 (12). The absence of any significant correlation may probably be ascribed to the mixing of both alkaline and subalkaline samples.

These rocks will be dealt with in detail below according to their area of origin or type.

5.4.1 Alkaline basalts from France and Spain

Some 17 samples (He, H and BR-1), all of which are alkaline basalts, represent the continental areas from France and Spain. Some data of interest for this section are given in Table 5.32. For more information see Appendices I and II. Sample BR-1 from the northeastern part of France has no geographical connection with the other French basalts, and as such is of interest only with respect to the general distribution pattern of W in these alkaline continental rocks.

With respect to the basalts of Hérault (He), Dupuy et al. (1972) claim, on the basis of geochemical evidence (see below), that these rocks can be divided into three groups, of which only groups I and III were investigated here. This subdivision coincides with their geographical position, i.e. group III in the northern part and group I in the southern

Table 5.32 Some major oxides (%), trace elements (ppm) and correlation coefficients (r) of tungsten with each of these variables for sixteen samples from France and Spain

Samples Variables	He-1	He-2	He-3	He-4	He-5	He-6	He-7	He-8	He-9	He-10	He-11	He-12	He-13	He-14	N-1	N-2	r*
				Group I (South)							Group III (North)						
SiO_2	46.02	46.09	46.29	44.73	50.93	46.89	51.35	50.54	44.23	45.28	48.50	44.84	41.97	46.78	49.93	44.84	-.44
TiO_2	2.15	2.07	2.07	2.92	1.29	2.36	1.88	1.93	2.99	2.84	2.31	2.97	3.14	2.75	2.15	2.66	.39
MgO	10.16	10.84	10.74	7.43	8.46	8.80	8.90	8.88	6.85	7.37	6.23	8.24	12.12	7.14	7.32	8.27	-.12
CaO	10.02	9.94	9.74	9.53	8.48	9.15	8.56	9.03	9.57	9.89	7.93	10.36	10.86	8.94	8.13	9.86	.21
Na_2O	3.45	3.60	3.55	3.89	3.47	3.95	3.54	3.28	4.13	4.39	5.03	3.81	3.98	4.29	4.07	3.10	.28
K_2O	1.44	1.57	1.52	2.27	1.52	1.85	1.35	1.00	2.79	1.09	1.45	1.01	.85	3.02	1.83	1.93	.67
P_2O_5	.77	.69	.74	.94	.46	.78	.40	.42	.77	.65	.65	.64	.78	.73	.45	.51	.64
Li	8	7	7	11	7	10	6	6	11	9	9	8	7	9	7	9	.55
Rb*	-	-	42	69	38	46	32	22	76	121	149	93	98	84	46	49	.27
Sr	-	-	780	1021	683	836	610	486	1167	1216	1226	1050	992	1081	691	904	.55
Ba	615	650	658	880	508	660	440	305	1843	950	998	860	845	933	591	708	.71
Ni	-	-	232	151	206	146	200	226	85	122	97	138	249	90	126	120	-.42
Y	-	-	25	28	19	25	16	21	29	25	29	28	26	26	24	27	.51
Zr	-	-	222	324	210	240	191	156	424	379	453	352	329	415	235	289	.60
Nb	-	-	93	133	76	96	63	46	166	161	168	129	140	155	68	90	.63
W	1.78	1.83	2.09	1.78	1.08	1.39	1.35	.96	2.65	1.38	1.57	1.57	1.34	2.40	1.09	1.20	1.00

* Correlation coefficients of W with Rb, Sr, Ni, Y, Zr and Nb are calculated without samples He-1 and He-2 since these trace element data were not available

part. This subdivision into more coherent sets of samples considerably improves the correlation between certain elements (Table 5.33).

Table 5.33 Correlation coefficients (r) of K_2O and W with several other elements in Hérault samples

Samples	SiO_2	TiO_2	MgO	CaO	Na_2O	K_2O*	Li	Ba	W
All	-.14	.22	-.51	-.25	.24	1.00	.73	.57	.78
Group I	-.63	.70	-.41	.28	.92	1.00	.93	.92	.44
Group III	.21	-.17	-.53	-.49	-.04	1.00	.78	.60	.96
All	-.49	.41	-.22	.14	.25	.78	.56	.71	1.00
Group I	-.85	.50	.54	.81	.32	.44	.31	.73	1.00
Group III	.06	-.003	-.48	-.34	-.13	.96	.78	.74	1.00

*K_2O and Rb have values of r = .98 and -.51 for group I and group III, respectively.

Dupuy et al. (1972) use Sr and Ni as indicators of fractional crystallization (i.e. plagioclase and olivine) and the concept that Sr contents change in function of the degree of partial fusion (inversely), whereas Ni remains constant (Gast, 1968). Consequently they suggest the following processes to have taken place:

(1) Partial fusion at variable degrees in the upper mantle should explain the fractionation of Sr. Confirmation of this hypothesis will be obtained by studying elements such as Rb, Ba, etc., which behave in the same way as Sr during partial fusion. This partial fusion seems to have been more important in the south (group I) than in the north (group III).

(2) Crystallization and separation of olivine, accounting for the variation of Ni, seems to have been more important in the north.

When applying F.A. to both groups, it becomes obvious that the two patterns are basically different (Figure 5.20 A,B). In the F.A. of group I samples (F-1,2·[66,21]) the elements that normally accumulate in residual liquids associate here with K, including Na, Li, Rb, Sr, Nb, and to a lesser extent Th and W, etc. The fact that several of these elements strongly oppose Si may well confirm the suggested importance of partial fusion.

As opposed to group I, F.A. (F-1,2 [50,32]) of the samples of group III show a seemingly more familiar 'differentiation' pattern in which Si does not dissociate itself from the late stage elements, and where these elements are more clearly opposite to early stage elements (e.g. Mg, Ni). Interesting in this 'differentiation' pattern is the strong correlation between W and K, which is almost independent from Si. Difficult to explain is the negative correlation between K and Rb.

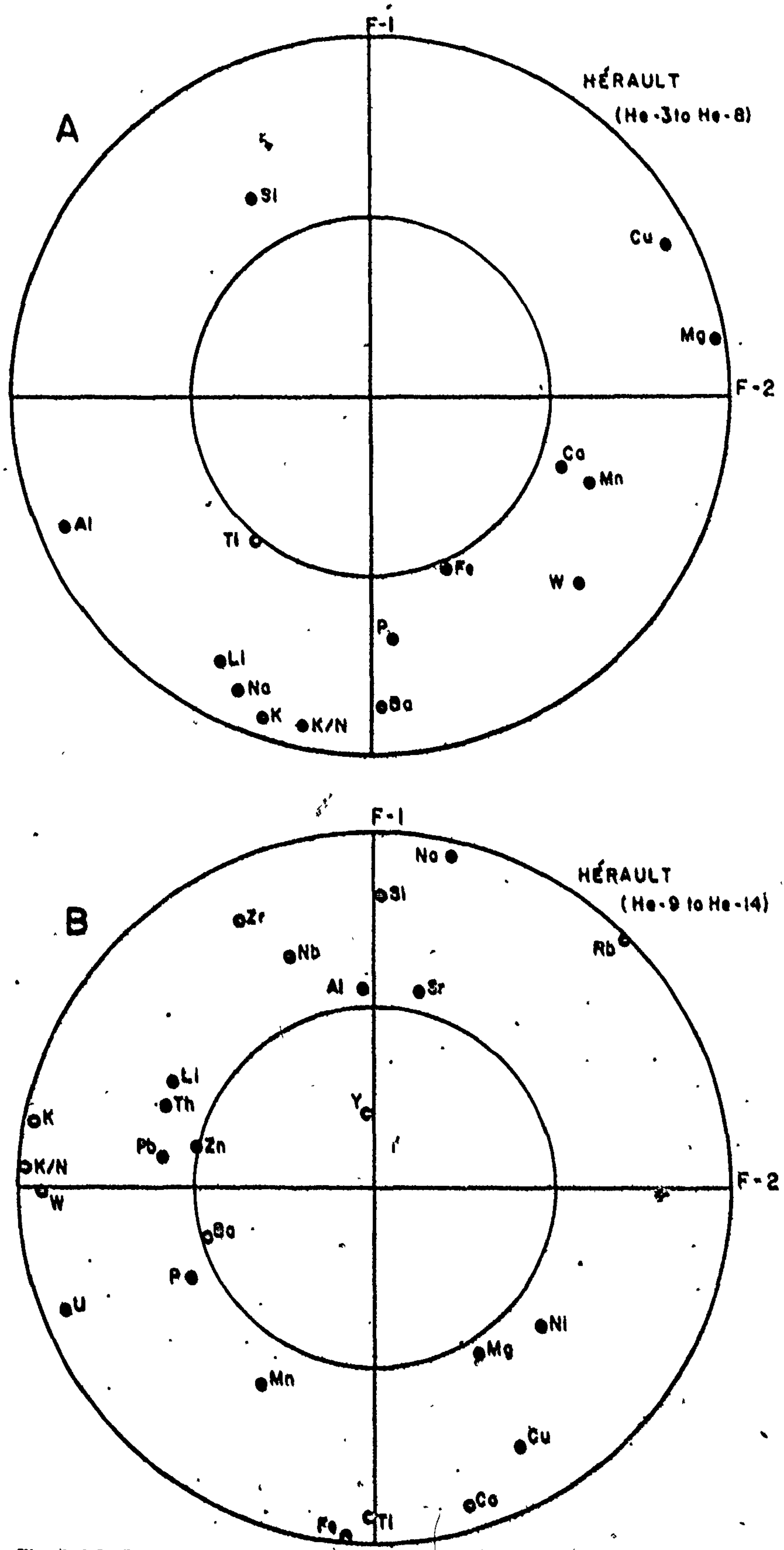

Fig. 5.20 Factor analysis for southern group I (A) and northern group III (B)

The Spanish samples are from an area known for its alkalinity (alkali basalts, analcime-basanites and even leucite-basanites). These rocks also are from a geographically different area and therefore difficult to integrate with the samples from Hérault. Nevertheless, they are of interest for the distribution pattern of W in continental alkaline basalts. This distribution pattern is given in Table 5.34.

Table 5.34 Distribution of tungsten (ppm) in continental alkaline basalts from France and Spain

Samples	Mean	Median	Range
All (17)*	1.62	1.57	0.96 - 2.65
Group I (8)	1.53	1.59	0.96 - 2.09
Group III (6)	1.81	1.57	1.34 - 2.65

*includes BR-1

These rocks contain the highest W contents so far encountered. These high contents occur in rocks with high nepheline norms, e.g. He-9 and He-14 with about 17% and 15%, respectively, normative nepheline and 2.65 and 2.40 ppm W. The lower values for W occur in samples He-5,7,8, which have no nepheline in their norm and with 1.08, 1.35 and 0.96 ppm W, respectively.

5.4.2 S.W. and western United States of America

The western U.S.A. are represented by some 13 alkaline and subalkaline basalts (WL, WF and BCR). Most of these rocks are from the Bandera lava field in New Mexico, but two are from Arizona (WL-6,7). Some data of interest for this section are given in Table 5.35. For more information see Appendices I and II.

The distribution of W in these continental basalts is given in Table 5.36.

Table 5.36 Distribution of tungsten (ppm) in basalts from the southwestern U.S.A.

Samples	Mean	Median	Range
All basalts* (13)	0.43	0.34	0.17 - 0.99
Subalk. basalts* (6)	0.36	0.30	0.23 - 0.53
Alk. basalts (7)	0.50	0.47	0.17 - 0.99

*including BCR-1

A comparison with subalkaline ocean island basalts shows that there is hardly any difference to be noticed (Table 5.11).

Table 5.35 Some major oxides (%), trace elements (ppm) and correlation coefficients (r) of tungsten with each of these variables for twelve basalts from the Southwestern U.S.A.

Samples Variables	WL-1*	WL-2*	WL-3	WL-4*	WL-5*	WL-6	WL-7*	WL-8	WP-1	WP-2	WP-3	WP-4	r_{sub}	r_{alk}
SiO_2	50.40	50.82	45.90	54.07	49.86	50.65	52.01	45.40	45.50	46.20	46.10	44.90	.71	-.66
TiO_2	1.50	1.57	2.55	1.32	1.38	3.32	1.49	2.66	2.69	2.28	2.25	2.12	-.83	-.30
CaO	9.19	8.75	8.63	9.35	8.81	7.18	7.90	9.22	9.72	9.48	9.78	9.42	.63	.18
Na_2O	2.78	2.80	3.77	3.04	3.02	4.69	2.81	3.88	3.62	2.88	2.71	3.54	.67	-.02
K_2O	.72	.80	2.00	.47	.56	1.96	.87	1.71	1.69	1.39	1.32	1.67	-.85	.43
Rb	16	15	24	9	13	24	22	20	-	-	-	-	-.83	-
Sr	297	340	833	253	250	374	298	656	-	-	-	-	-.59	-
Ni	131	160	120	149	209	23	169	222	-	-	-	-	-.24	-
Y	20	21	21	18	20	55	24	23	-	-	-	-	-.83	-
Zr	103	123	268	87	87	366	133	207	-	-	-	-	-.68	-
Nb	5	13	52	4	9	74	10	43	-	-	-	-	-.71	-
W	.29	.27	.99	.53	.30	.17	.23	.47	.62	.34	.32	.58	1.00	1.00

* Subalkaline basalts

The alkaline continental basalts of the western U.S.A. show W contents slightly below the W contents of the alkaline ocean island basalts (Table 5.15), although the ranges of distribution are similar.

The samples were divided into a subalkaline and an alkaline group and subjected to F.A. In the subalkaline group several late stage elements cluster together (e.g. K, Rb, Zr, etc.), but the positive correlation between Mg and these elements is difficult to explain. W does not form part of this late stage element association, nor do Si or Na. The pattern of the alkaline rocks seems less enigmatic in general. W, however, behaves independently of any of the other elements (Figure 5.21). The strange behaviour of W, and for that matter Si and Na also, is difficult to explain unless the following facts are taken into consideration. The sample populations are small and, although the samples with the exception of two are from the same lava field, there is quite a variety in the sample locations (i.e. different lava flows). This same criticism is valid for the non-continental areas as well, despite the conspicuity of the petrochemical and initial strontium ratio variations within a single basalt flow, i.e. the McCartys flow (Brookins et al., 1975; Carden et al., 1974; Laughlin et al., 1972b). A detailed study revealed the gradual change from a quartz-normative tholeiite with plagioclase phenocrysts into an olivine-normative tholeiite with olivine phenocrysts. Laughlin et al. (1972b)on the basis

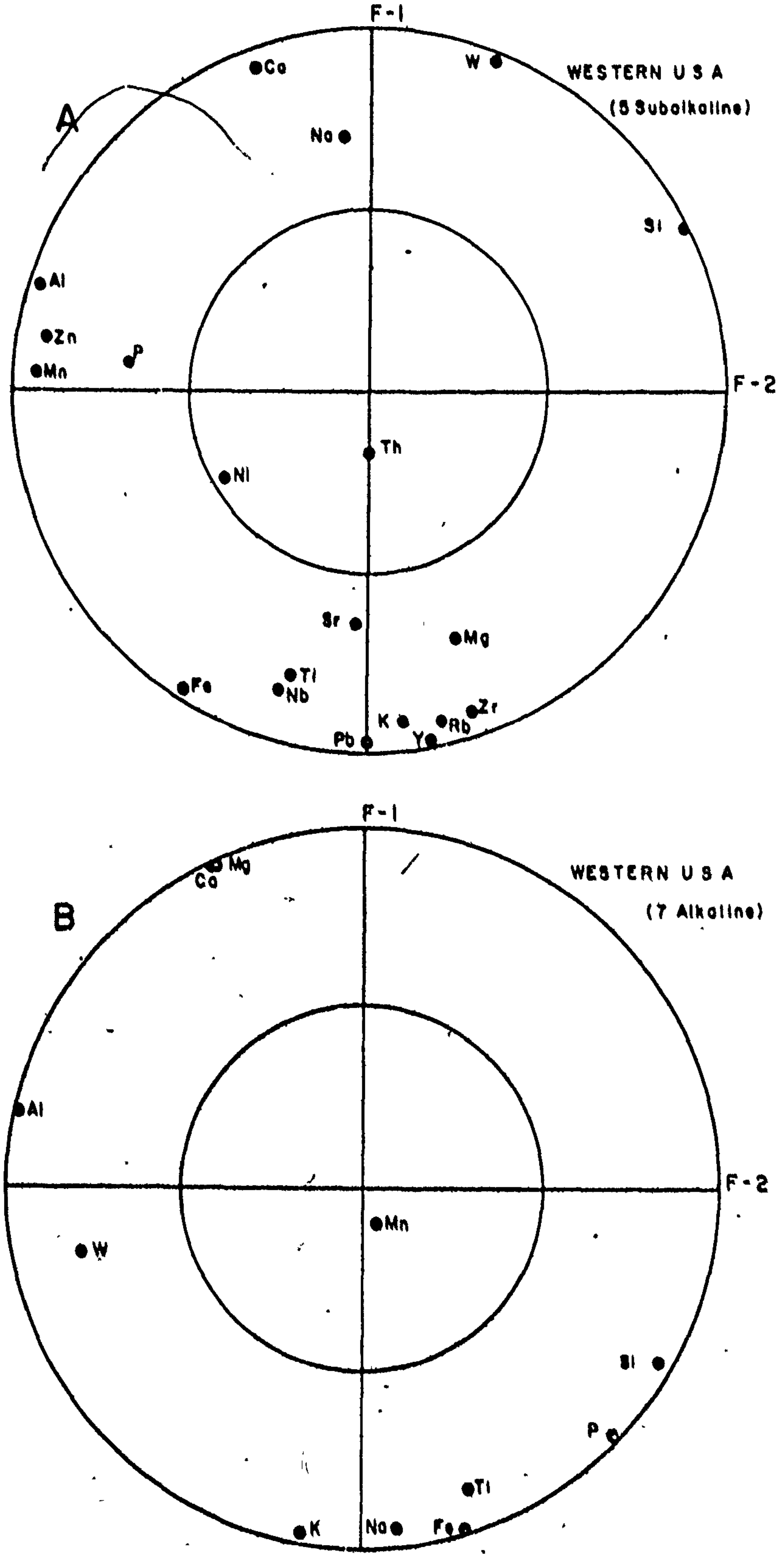

Fig. 5.21 Factor analysis for rocks from the southwestern U.S A

of the extremely large variations in the initial strontium ratios (0.7040 to 0.7084) and the presence of xenoliths of sedimentary rocks in this basalt flow, suggest a heterogeneous near-surface crustal contamination. It is difficult, if not impossible, to say whether this contamination has affected the W contents of the rocks, particularly because they are similar to ocean island basalts. Affecting other elements may have had an indirect influence upon W explaining its strange behaviour.

5.4.3 Kimberlites

Four kimberlites (KB) were analyzed as well and some data are presented in Table 5.37.

It was already pointed out in Chapter IV (Figure 4.4) that no significant correlations exist between W and any other late stage element. Moreover several element associations are very uncommon. No attempt was made to explain the overall pattern, because only four samples from very different areas were available. The W values for that reason are of interest solely to obtain an idea of its distribution in kimberlites (mean W content is 0.54 ppm; median value is 0.61 ppm). Some of these values are below the kimberlite values of Ukhanov et al. (1973). In the case of KB-4 the W content is more similar to that of a peridotite. Before suggesting that kimberlites are concentrating dispersed elements (Ukhanov et al., 1973) more data should be gathered.

Table 5.37 Some major oxides (%), trace elements (ppm) and correlation coefficients (r) for tungsten with each of these variables for four kimberlites

Samples Variables	KB-1	KB-2	KB-3	KB-4	r^+
SiO_2	36.95	41.53	21.50	40.00	-.45
TiO_2	2.50	3.79	.87	3.15	-.29
CaO	14.57	12.39	11.02	4.04	.64
Na_2O	.12	1.04	.22	.07	.64
K_2O	.85	.53	.09	1.59	-.95
Rb	33	60	4	67	-.51
Sr	605	257	2133	1265	-.04
Ni	455	1227	376	1189	-.27
Y	21	6	21	18	-.38
Zr	384	81	604	395	-.12
Nb	176	89	238	335	-.71
W	.42	.81	.81	.10	1.00

$^+$ values of r .950 are significant at the .05 level (Brooks, 1972)

5.4.4 Summary

The continental basalts, including 30 alkaline and subalkaline rocks, contain about 1.11 ppm W. However, when these rocks are subdivided into an alkaline and a subalkaline group the following facts must be considered:

(1) The alkaline basalts contain about 1.29 ppm W, which is about twice the content of equivalent rocks of ocean islands. The range of W distribution is much larger for continental rocks. When, however, comparing the alkaline rocks from the southwestern U.S.A. with the ocean island equivalents, these differences almost disappear (0.50 ppm W and 0.60 ppm W, respectively).

(2) The subalkaline basalts contain about 0.36 ppm W which is similar to the content of subalkaline ocean islands. The same is true for the range of W distribution.

(3) A correlation between W and any other late stage elements, if existing at all, seems much less conspicuous than in rocks from other environments. The group of samples (group I) in which partial fusion seems to have been an important mechanism, shows a strong negative correlation between Si and W, of which W correlates positively with the other 'late stage' elements.

CHAPTER VI

CONCLUSIONS

In this Chapter an attempt will be made to reach some general conclusions on the behaviour of tungsten in basalts and andesites. It will be necessary, therefore, to repeat some of the conclusions drawn in previous sections. It always has been the feeling of this author that many more data should be gathered despite the fact, however, that in the past so often conclusions were drawn, the importance (and persistence) of which was inversely related to the number of available data.

(1) Values obtained in this study for the various types of rocks are given in Table 6.1. These values are represented graphically in Figure 6.1. Median values were calculated as well, because they are less affected by the presence of a few anomalous values (e.g. AU in the ocean floor basalts) in a set of samples and therefore are believed to represent better the real picture.

From these data the following can be concluded:

- alkaline basalts generally have higher tungsten contents than subalkaline basalts. Their range of distribution is also wider;

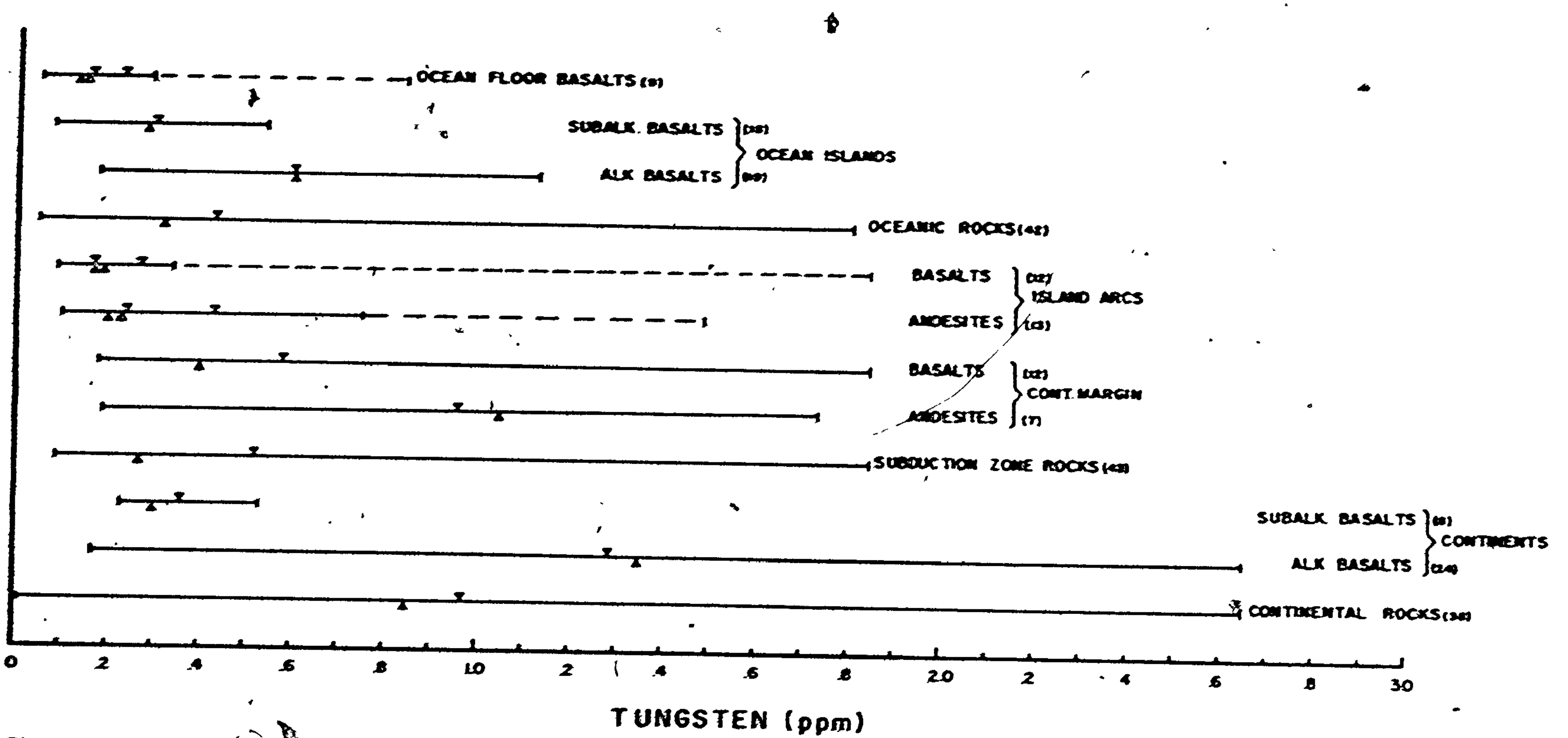

Fig. 6.1 Mean (▼), median (▲) and range of distribution of tungsten (full line) in rocks of various areas. The empty triangles represent mean (▽) and median (△) values for a range enlarged (dashed line) with some anomalous values (see text). The range of distribution for "ROCKS" includes also samples other than basalts or andesites (X) indicates number of samples involved.

Table 6.1 Distribution of tungsten (ppm) in basalts and andesites obtained in this study

Samples and no.	Mean	Median	Range
I. Oceanic environment			
Ocean floor basalts 8(9)*	0.16 (0.23)	0.13 (0.15)	0.05 - 0.29 (0.84)
Subalk. ocean island basalts 18	0.30	0.28	0.08 - 0.54
Alk. ocean island basalts 10	0.60	0.60	0.18 - 1.13
All oceanic rocks** 42	0.43	0.32	0.05 - 1.81
II. Subduction zone environment			
Island arc basalts 9(12)*	0.17 (0.27)	0.17 (0.19)	0.09 - 0.34 (0.67)
Island arc andesites 11(13)*	0.24 (0.43)	0.20 (0.23)	0.10 - 0.75 (1.49)
Cont. margin basalts 12	0.58	0.40	0.18 - 1.85
All subduction zone rocks** 43	0.52	0.27	0.09 - 1.85
III. Continental environment			
Subalkaline basalts 6	0.36	0.30	0.23 - 0.53
Alkaline basalts 24	1.29	1.35	0.17 - 2.65
All continental rocks** 38	0.97	0.85	0.01 - 2.65

*Values in parentheses refer to a set of rocks that include anomalous rocks (see Chapter V), i.e. AU for ocean floor samples; TL-3,4,5 for island arc basalts; TL-1,2 for island arc andesites.

**Values for 'rocks' include felsic differentiates, ultramafics, etc. whenever available.

- ocean floor basalts and island arc basalts have similar tungsten contents which are among the lowest recorded;
- island arc andesites contain less tungsten than subalkaline ocean island basalts, which are indiscernible from continental equivalents. This may be an indication of the immobility of tungsten, and hence its inability to contaminate;
- continental margin andesites seem to have higher tungsten contents than their island arc equivalents. This conclusion, however, should be considered with caution because of the involvement of rocks which underwent alteration.

(2) - The average content of tungsten in all basalts (91 samples) and andesites (22 samples), without considering any further discrimination because of chemistry or environment, is below any previously suggested value (Table 6.2).

The large discrepancy between mean and median values, however, suggest some discrimination. Such a discrimination produces median values of a particular group of samples, and in some cases this difference even disappears. In this study preference is given to median values because it is believed that these values are closer to reality without ignoring anomalous values.

A content of 0.32 ppm W is suggested for all oceanic rocks. This group is made up predominantly of subalkaline

Table 6.2 Comparison of the tungsten contents (ppm) of this study with earlier suggested values

Authors	Mean	Median
Basalts		
This work	0.61 (±0.57)	0.36
Vinogradov (1962)	1.10	-
Turekian et al. (1961)	0.70	-
Wiendl (1968)	1.17	-
Andesites		
This work	0.60 (±0.52)	0.29
Vinogradov (1962)	1.10	-
Wiendl (1968)	1.10	-

Values in parentheses are standard deviations

basalts (Ronov et al., 1969), but also includes a small number of more felsic differentiates and alkaline basalts. The W content of oceanic basalts should lie between 0.15 ppm (ocean floor basalts) and 0.28 ppm (ocean island basalts), and is likely to be closer to the lower limit. However, the range of variation is small and both groups overlap.

W values of 0.17 ppm and 0.20 ppm are suggested for island arc basalts and andesites, respectively. The values for equivalent rocks from continental margins are significantly higher, i.e. 0.40 ppm and 1.05 ppm, respectively. It should be kept in mind, however, that several of these rocks, particularly the Chilean ones, were extensively altered, whereas N.W. Sardinia may eventually turn out to be a W-enriched province. It is interesting that the W contents of the Guatemalan basalts are similar to island arc basalts.

A W content of 0.85 ppm for continental basalts is likely to be too high, particularly because of the strong influence of the highly alkaline rocks with high W contents from France. It is believed that a value of 0.30 ppm W is much closer to reality.*

(3) Vinogradov et al. (1958) and Vinogradov (1962) suggested and later revised a crustal average of 2 ppm W and 1.3 ppm W, respectively. The latter figure refers to a standard crust made up by two parts of felsic rocks and one part of mafic rock. Taylor (1964) suggests on the basis of a 1:1 mixture of granite and basalt abundances, a crustal content of 1.5 ppm W. The much lower values of this study for mafic rocks certainly would reduce drastically previous suggested values. Moreover, Simon (unpublished Ph.D. thesis, 1972), in a detailed study of the southern California batholith, calculated a weighted average of 0.44 ppm W, which may, despite its

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*Simon (1972) reports a mean W content of 0.32 ppm for seven gabbros of the southern California batholith.

locality, be of significance. Until more data are available on more felsic material, despite the preponderance of basaltic rocks, to suggest new values for a crust, either continental or earth's crust, would seem to be premature.

(4) Vinogradov et al. (1958) mention a tendency towards higher tungsten contents in mafic volcanics, as compared to their plutonic equivalents. Wiendl (1968) "hazards a guess" (op. cit. Krauskopf, 1970) in extending this tendency in more felsic rocks including granites and rhyolites. These tendencies are not substantiated nor repudiated by this study by the mere fact that no plutonic rocks were investigated. It should be mentioned, however, that most of the basalts of this study have tungsten contents below the lowest content of the intrusives of Vinogradov et al. (1958). The extension (of higher W contents in extrusives) towards more felsic rocks needs no more discussion because of lack of data (one andesite? and one rhyolite), particularly when considering the low values obtained for many andesites (Table 6.1, Figure 6.1).

(5) The so-called good correlation that seems to exist between tungsten and silica (Vinogradov et al., 1958; Sandell, 1946) has been confirmed in a few cases, i.e. a single differentiation sequence or when rocks are involved which show large interval increments of silica, i.e. from ultramafic towards granitic rocks. On a smaller scale, i.e. within a

group of basalts this correlation can be non-existent or even negative, when correlations of tungsten with other trace elements can still be good. A somewhat similar observation was made by Simon with respect to some granites of Sandell (Table 12, p.51 *in* Simon, 1972).

(6) Conclusions drawn on a detailed search for possible correlations that may exist between tungsten and other elements can be summarized as follows:

- the more coherent a set of samples, the more obvious the close association between tungsten and a whole series of late stage elements such as Na, K, P, Li, Rb, Sr, Ba, Y, Zr, Nb, Pb, U and Th becomes;
- in cases where sampling has been less systematic (?) tungsten may show good-to-fair correlation or even none at all with some or all of these elements. Striking, however, is the fact that the negative correlations between tungsten and early stage elements, such as Mg, Ni, Co, Cr, often is more clear-cut that with its late stage 'associates';
- tungsten seems to fall among the elements that go over into the liquid fraction very early when partial melting takes place. Some indications exist that its enrichment factor in such a liquid may lie between K and Rb. More data should be

gathered with respect to this enrichment, before this speculation can be substantiated.

- also interesting are the low tungsten contents for andesites from various island arcs, a characteristic coinciding with the low Nb contents as well.

Many "mythical" characteristics have been ascribed to tungsten, some rightly but often without substantiation, others incorrectly. Very much remains to be done; nevertheless it is the hope and the wish of the present author to have contributed, albeit an infinitesimal part, to the unravelling of the "Tungsten Story".

Krauskopf (1968) in his philosophical reflections on "A Tale of Ten Plutons" commented "To appeal to a random element in nature is, in a sense, to admit defeat" ... and further, "We try to see relations that do not exist, to find order in processes that are largely random. Further study can give us more data, more correlations, more understanding of details, but the central questions will forever elude us - because the questions themselves are meaningless. In much the same way that physicists find questions about the exact location and speed of a particular electron meaningless, perhaps we are asking the wrong questions about the separation and movements of the units that make up a batholith". Maybe, in a way, the same is valid for the "Tungsten Story", not so much with reference to the data, since they are still glittering by their absence, but with respect to the questions asked.

The next question? Maybe ... tungsten in greywackes? (Massey, personal discussion)!!

REFERENCES

ABBEY, S., 1973. Studies in 'standard samples' of silicate rocks and minerals. Part 3: 1973 extension and revision of 'usable' values. Geol. Surv. Canada Paper 73-36, 1-25.

ALVAREZ, W., 1972. Rotation of the Corsica-Sardinia microplate. Nature Phys. Sci., 235, 103.

ALVAREZ, W., COCOZZA, T. and WEZEL, F.C., 1974. Fragmentation of the Alpine orogenic belt by microplate dispersal. Nature, 248, 309-314.

AMIRUDDIN, A. and EHMANN, W.D., 1962. Tungsten abundances in meteoritic and terrestrial materials. Geochim. Cosmochim. Acta, 26, 1011-1022.

ASSUNCAO, C.T. de, MACHADO, F. and SERRALHEIRO, A., 1968. New investigations on the geology and volcanism of the Cape Verde Islands. XXIII Int. Geol. Congress, 2, 9-16.

AUMENTO, F., 1969. The Mid-Atlantic ridge near 45°N. V. Fission track and ferro-manganese chronology. Can. Jour. Earth Sci., 6, 1431-1440.

AUMENTO, F., 1971. Uranium content of Mid-Oceanic basalts. Earth Planet. Sci. Lett., 11, 90-94.

AUMENTO, F., 1973. Petrology, chronology and paleomagnetism of basalts drilled from the floor of the Median Valley of the M.A.R. at 45°N. EOS, 54, 132.

AUMENTO, F., LONCAREVIC, B.D. and ROSS, D.I., 1971. Regional studies. IV. Hudson geotraverse: part of the Mid-Atlantic ridge at 45°N. Phil. Trans. Roy. Soc. Lond., A.268, 623-650.

AUMENTO, F. and LOUBAT, H., 1971. The Mid-Atlantic ridge near 45°N. XVI. Serpentinized ultramafic intrusions. Can. Jour. Earth Sci., 8, 631-663.

AUMENTO, F., MITCHELL, W.S., FRATTA, M., DOSTAL, J. and GUSTAJTIS, A., 1975. Interaction between sea water and oceanic layer two as a function of time and depth. Geol. Soc. Amer., N.C. Section, 7, 713.

AUZENDE, J.M. and OLIVET, J.L., 1974. Structure of the western Mediterranean Basin, in The Geology of Continental Margins (ed. C.A. Burk and C.L. Drake), Springer-Verlag, N.Y. pp.723-731.

ATKINS, D.H.F. and SMALES, A.A., 1960. The determination of tantalum and tungsten in rocks and meteorites by neutron activation analysis. Anal. Chim. Acta, 22, 462-478.

BAKER, P.E., 1968. Comparative volcanology and petrology of the Atlantic island arcs. Bull. Volc., 32, 189-206.

BARBERI, F., GASPARINI, P., INNOCENTI, F. and VILLARI, L., 1973. Volcanism of the southern Tyrrhenian Sea and its geodynamic implications. Jour. Geophys. Res., 78, 5221-5232.

BLAKE, D.H., 1968. Post Miocene volcanoes on Bougainville Island, territory of Papua and New Guinea. Bull. Volc., 32, 1, 121-138.

BROOKINS, D.G., CARDEN, J.R. and LAUGHLIN, A.W., 1975. Additional note on the isotopic composition of strontium in McCarty's flow, Valencia county, New Mexico. Earth Planet. Sci. Lett., 25, 327-330.

BROOKS, R.R., 1972. Geobotany and Biogeochemistry in Mineral Exploration. Harrow and Row, N.Y., pp.1-290.

BROWN, G.C., HUGHES, D.J. and ESSON, J., 1973. New X.R.F. data retrieval techniques and their application to U.S.G.S. standard rocks. Chem. Geol., 11, 223-229.

BRUNFELT, A.O. and STEINNES, E., 1971. A neutron-activation scheme developed for the determination of 42 elements in lunar material. Talanta, 18, 1197-1208.

CARDEN, J.R. and LAUGHLIN, A.W., 1974. Petrochemical variations within the McCarty's basalt flow, Valencia county, New Mexico. Geol. Soc. Amer. Bull., 85, 1479-1484.

CARMICHAEL, I.S.E., TURNER, F.J. and VERHOOGEN, J., 1974. Igneous Petrology. McGraw-Hill, Toronto, pp.1-739.

CHAN, K.M. and RILEY, J.P., 1967. Determination of vanadium, molybdenum and tungsten in the new series of U.S. Geological Survey analysed samples. Chem. Geol., 2, 171-172.

CHASE, C.G., 1971. Tectonic history of the Fiji plateau. Geol. Soc. Amer. Bull., 82, 3087-3110.

CHAYES, F., 1971. Ratio Correlation. A Manual for Students of Petrology and Geochemistry. Univ. Chicago Press, Chicago, pp.1-99.

CHRISTENSEN, N.I., FREY, F., MACDOUGALL, D., MELSON, W.G., PETERSON, M.N.A., THOMPSON, G. and WATKINS, N., 1973. Deep Sea Drilling Project: Properties of igneous and metamorphic rocks of the oceanic crust. EOS, 54, 972-981.

CHRISTIANSEN, R.L. and LIPMAN, P.W., 1972. Cenozoic volcanism and plate tectonic evolution of the western United States. II. Late Cenozoic. Phil. Trans. Roy. Soc. Lond., A.271, 249-284.

CHYI, L.L., 1972. Distribution of some noble metals in sulfide and oxide minerals in Strathcona mine, Sudbury. Unpub. Ph.D. Thesis, McMaster Univ., Ontario, pp.1-183.

CLOUD, P.E., Jr., SCHMIDT, R.G. and BURKE, H.W., 1956. Geology of Saipan, Mariana Islands. Chapter A. General Geology. U.S.G.S. Prof. Paper 280-A, pp.1-126.

COULON, C., BAQUE, L. and DUPUY, C., 1973. Les andésites cénozoiques et les laves associées en Sardaigne Nord-Occidentale (Provinces du Logudoro et du Bosano) - caractères minéralogique et chimiques. Contr. Mineral. and Petrol., 42, 125-139.

COULON, C. and DUPUY, C., 1975. Évolution spatiale des caractères chimiques du volcanisme andésitique de la Sardaigne (Italie). Earth Planet. Sci. Lett., 25, 170-176.

COX, A. and DALRYMPLE, G.B., 1966. Paleomagnetism and K-Ar ages of some volcanic rocks of the Galápagos Islands. Nature, 209, 776-777.

CROCKET, J.H., 1970. Neutron activation analysis for noble metals in geochemistry. In Proc. NATO Advanced Study Inst. Activation Analysis in Geochemistry and Cosmochemistry (eds. A.O. Brunfelt and E. Steinnes). Kjeller, Norway, pp.339-351.

DARWIN, C., 1846. Geological Observations on Volcanic Islands. Smith, Elder and Co., London, pp. 1-674.

DAVIS, J.C., 1973. Statistics and Data Analysis in Geology. John Wiley and Sons, Inc., Toronto, pp.1-550.

DE JONG, K.A., MANZONI, M., STAVENGA, T., VAN DIJK, F., VAN DER VOO, R. and ZIJDERVELD, J.D.A., 1973. Paleomagnetic evidence for rotation of Sardinia during the Early Miocene. Nature, 243, 281-283.

DE LAETER, J.R. and ABERCROMBIE, I.D., 1970. Mass spectrometric isotope dilution analyses of rubidium and strontium in standard rocks. Earth Planet. Sci. Lett., 9, 327-330.

DE LA ROCHE, H. and GOVINDARAJU, K., 1971. Tables of recommended or proposed values (major, minor and trace elements) for the ten geochemical standards of the Centre de Recherches Pétrographiques et Géochimiques and the Association Nationale de la Recherche Technique. Meth. Phys. Analyse (GAMS) Paris, 7, 314-322.

DENISON, B.A., 2070. In The Gods Themselves, Asimov I. Fawcett Publications, Inc., Greenwich, Conn., pp.1-288.

DENGO, G., 1973. Estructura geológica, historia tectónica y morfología de America Central, Icaiti, Guatemala. Guatemala , pp.1-52.

DE ROEVER, W.P. and DE BOORDER, H., 1975. Belts with scattered leucite occurrences indicate direction of dip of coeval subduction zones. Pétrologie, I, 37-42.

DE SOETE, D., GIJBELS, R. and HOSTE, J., 1972. Neutron Activation Analysis. Wiley-Interscience, Toronto, pp.1-836.

DOELL, R.R. and DALRYMPLE, G.B., 1973. Potassium-argon ages and paleomagnetism of the Waianae and Koolau volcanic series, Oahu, Hawaii. Geol. Soc. Amer. Bull., 84, 1217-1242.

DOSTAL, J., 1973. Geochemistry and petrology of the Loon Lake pluton, Ontario. Unpub. Ph.D. Thesis, McMaster Univ., Ontario, pp.1-328.

DUPUY, C. and LEFEVRE, C., 1972. Le fractionnement du strontium et du nickel dans les basaltes des Causses et du Bas-Languedoc (Hérault). C.R. Acad. Sci. Paris, 2556-2559.

DUPUY, C., MCNUTT, R.H. and COULON, C., 1974. Détermination de Sr-87/Sr-86 dans les andésites cénozoïques et les laves associées de Sardaigne Nord-Occidentale (Italie). Geochim. Cosmochim. Acta, 38, 1287-1296.

DUPUY, C., VERNIERES, J., DOSTAL, J. and COULON, C., 1975. Li, Rb, Sr, Ba and R.E. in some calc-alkaline rocks of Logudoro and Bosano (N.W. Sardinia). EOS, 56, 164.

ENGEL, A.E.J. and ENGEL, C.J., 1966. The rocks of the ocean floor. In Proc. 2nd Int. Oceanic Congress, Moscow, 161-187.

FISHER, G., 1951. Granit und Sial. Geol. Rundschau, 39, 32-77.

FLANAGAN, F.J., 1969. U.S. Geological Survey standards - II. First compilation of data for the new U.S.G.S. rocks. Geochim. Cosmochim. Acta, 33, 81-120.

FLANAGAN, F.J., 1973. 1972 values for international geochemical reference samples. Geochim. Cosmochim. Acta, 37, 1189-1200.

FOSTER, R.P., 1972. Experimental geochemistry of tungsten. National Environment Research Council, Pub. Series D, No. 2, 51-52. London.

FREY, F.A., BRYAN, W.B. and THOMPSON, G., 1974. Atlantic ocean floor: geochemistry and petrology of basalts from Legs 2 and 3 of the Deep-Sea Drilling Project. Jour. Geophys. Res., 79, 5507-5527.

FULLARD, H. (ed.), 1956. Philips' Modern School Atlas, 50th edition. George Philip and Son Ltd., London.

GARRETT, R.G., 1971. Molybdenum, tungsten and uranium in acid plutonic rocks as a guide to regional exploration, S.E. Yukon. Can. Mining Jour., April, 1-4.

GAST, P.W., 1968. Trace element fractionation and the origin of tholeiitic and alkaline magma types. Geochim. Cosmochim. Acta, 32, 1057-1086.

GEZE, B., 1955. Le volcanisme des Causses et du Bas-Languedoc (France). Bull. Volc., 17, 73-89.

GEZE, B., 1962. Relations entre volcans et plutons dans la Montagne Noire, Les Causses et le Bas-Languedoc (Sud de la France). Bull. Volc., 24, 87-91.

GIGNOUX, M., 1955. Stratigraphic Geology. Freeman and Co., San Francisco, pp.1-682.

GILL, J.B., 1970. Geochemistry of Viti Levu, Fiji and its evolution as an island arc. Contr. Mineral. and Petrol., 27, 179-203.

GOMBERG, D.N., BANKS, P.O. and MCBIRNEY, A.R., 1968. Guatemala: Preliminary zircon ages from Central Cordillera. Science, 162, 121-122.

GUNN, B., 1975. X.R.F. A.S.C.I. Newsletter, May, No. 4, 1-18.

GUNN, B.M., ABRANSON, C.E., NOUGIER, J., WATKINS, N.D. and HAJASH, A., 1971. Amsterdam Island, an isolated volcano in the southern Indian Ocean. Contr. Mineral. and Petrol., 32, 79-92.

GUNN, B.M., COY-ILL, R., WATKINS, N.D., ABRANSON, C.E. and NOUGIER, J., 1970. Geochemistry of an oceanite-ankaramite-basalt suite from East Island, Crozet Archipelago. Contr. Mineral. and Petrol., 28, 319-339.

GUNN, B.M., WATKINS, N.D., TRZCIENSKI, W.E., Jr. and NOUGIER, J., 1975. The Amsterdam-St. Paul volcanic province, and the formation of low Al tholeiitic andesite. Lithos, 8, 137-149.

HARMAN, H.H., 1967. Modern Factor Analysis, 2nd edition. Univ. Chicago Press, Chicago, pp.1-473.

HART, R.A., 1973. A model for chemical exchange in the basalt-seawater system of oceanic Layer II. Can. Jour. Earth Sci., 10, 799-816.

HAYES, D.E., 1966. The Peru-Chile trench. Proc. Int. Upper Mantle Project Symp. on Continental Margins and Island Arcs (ed. W.H. Poole), Geol. Soc. Amer. Paper 66-15, 238-243.

HEATH, R.L., 1964. Scintillation spectrometry: gamma ray spectrum catalogue 2nd edition. U.S. Atomic Energy Commission, Idaho Operations Office, Vol. 2.

HEATH, R.L., 1968. Table of the isotopes. In Handbook of Chemistry and Physics (ed. R.C. Weast). 49th edition, The Chemical Rubber Co., Cleveland, Ohio, pp.B-4 to B-92.

HELSEN, J.N.W., 1970. Geochemistry of tungsten. Unpub. M.Sc. Thesis, McMaster University, Ontario, pp.1-50.

HÖLL, R., 1969. Scheelitprospektion und Scheelitvorkommen im Bundesland Salzburg/Österreich. Chemie der Erde, 28, 185-203.

HÖLL, R., MAUCHER, A. and WESTENBERGER, H., 1972. Synsedimentary-diagenetic ore fabrics in the strata- and time-bound scheelite deposits of Kleinarltal and Felbertal in the eastern Alps. Mineral. Deposita, 7, 217-226.

HORN, M.K. and ADAMS, J.A.S., 1966. Computer-derived geochemical balances and element abundances. Geochim. Cosmochim. Acta, 30, 279-297.

IRVINE, T.N. and BARAGAR, W.R.A., 1971. A guide to the chemical classification of the common volcanic rocks. Can. Jour. Earth Sci., 8, 523-548.

IVANOVA, G.F. and KHODAKOVSKIY, I.L., 1968. Transport of tungsten in hydrothermal solutions. Geochemistry International, 5, 779-780.

JEFFERY, P.G., 1959. The geochemistry of tungsten, with special reference to the rocks of the Uganda Protectorate. Geochim. Cosmochim. Acta, 16, 278-295.

JENKINS, R. and DE VRIES, J.L., 1970. Worked examples in X-ray spectrometry. Philips Technical Library, distributed by Springer-Verlag, N.Y., pp.1-129.

JOHANSEN, O. and STEINNES, E., 1970. Determination of Co, Cu, Fe, Ga, W and Zn in rocks by neutron activation and anion-exchange separation. Talanta, 17, 407-414.

JOHNSON, T. and MOLNAR, P., 1972. Focal mechanisms and plate tectonics of the south west Pacific. Jour. Geophys. Res., 77, 5000-5032.

KARIG, D.E., 1971. Origin and development of marginal basins in the western Pacific. Jour. Geophys. Res., 76, 2542-2561.

KAY, R., HUBBARD, N.J. and GAST, P.W., 1970. Chemical characteristics and origin of ocean ridge volcanic rocks. Jour. Geophys. Res., 75, 1585-1613.

KEEN, M.J., 1975. The oceanic crust. Geoscience Canada, 2, 36-43.

KEMPE, D.R.C., 1973. Basalts from the southern Indian Ocean: DSDP Leg 26. EOS, 54, 1008-1011.

KLERKX, J., DEUTSCH, S. and DE PAEPE, P., 1974. Rubidium, strontium content and strontium isotopic composition of strongly alkalic basaltic rocks from the Cape Verde Islands. Contr. Mineral. and Petrol., 45, 107-118.

KOZLOV, V.D., SHEREMET, Ye.M. and YANOVSKIY, V.M., 1974. Geochemical characterization of the Mesozoic Plumasite leucocratic granites of the Trans-Baykalia tin-tungsten belt. Geochemistry International, 11, 997-1008.

KRAUSKOPF, K.B., 1953. Tungsten deposits of Madera, Fresno, and Tulare counties, California. Calif. Div. Mines, Special Rept. 35, pp.1-83.

KRAUSKOPF, K.B., 1956. Factors controlling the concentrations of thirteen rare metals in sea water. Geochim. Cosmochim. Acta, 9, 1-32.

KRAUSKOPF, K.B., 1967. Source rock for metal-bearing fluids. In Geochemistry of Hydrothermal Ore Deposits (ed. H.L. Barnes). Holt, Rinehart and Winston, N.Y., pp.1-33.

KRAUSKOPF, K.B., 1968. A tale of ten plutons. Geol. Soc. Amer. Bull., 79, 1-17.

KRAUSKOPF, K.B., 1970. Tungsten (Wolfram). In Handbook of Geochemistry (ed. K.H. Wedepohl), Chapter 74, Vol. II/2, Springer-Verlag, Berlin.

KRAUSKOPF, K.B., 1971. The source of ore metals. Geochim. Cosmochim. Acta, 35, 643-659.

LAHUSEN, L., 1972. Schicht- und Zeitgebundene Antimonit-Scheelit -Vorkommen und Zinnober-Vererzungen in Kärnten und Osttirol/Österreich. Mineral. Deposita, 7, 31-60.

LAPP, R.E. and ANDREWS, H.L., 1963. Nuclear Radiation Physics, 3rd edition. Prentice-Hall, Inc., New Jersey, pp.1-413.

LAUGHLIN, A.W., BROOKINS, D.G. and CAUSEY, J.D., 1972a. Late Cenozoic basalts from the Bandera lava field, Valencia county, New Mexico. Geol. Soc. Amer. Bull., 83, 1543-1552.

LAUGHLIN, A.W., BROOKINS, D.G. and CARDEN, J.R., 1972b. Variations in the initial strontium ratios of a single basalt flow. Earth Planet. Sci. Lett., 14, 79-82.

LEFEVRE, C. and DUPUY, C., 1972. Sur la présence de basaltes a hypersthène normatif dans les volcans du Bas-Languedoc (Hérault). C.R. Acad. Sci. Paris, 274, 2616-2619.

LE PICHON, X., 1968. Sea-floor spreading and continental drift. Jour. Geophys. Res., 73, 3661-3705.

LE PICHON, X. and FOX, P.J., 1971. Marginal offsetts, fracture zones and the early opening of the North Atlantic. Jour. Geophys. Res., 76, 6294-6308.

LE PICHON, X., PAUTOT, G., AUZENDE, J.-M. and OLIVET, J.-L., 1971. La Méditerranée occidentale depuis l'oligocène - schema d'évolution. Earth Planet. Sci. Lett., 13, 145-152.

LIPMAN, P.W., PROSTKA, H.J. and CHRISTIANSEN, R.L., 1972. Cenozoic volcanism and plate-tectonic evolution of the western United States. I. Early and Middle Cenozoic. Phil. Trans. Roy. Soc. Lond., A.271, 217-248.

LYAKHOVICH, V.V. and BALANOVA, T.T., 1969. Mean contents of W, Mo, Sn, Ta, Nb and Zn in sphene and ilmenite from granites. Geochemistry International, 6, 281-287.

MACDONALD, G.A., 1960. Dissimilarity of continental and oceanic rock types. Jour. Petrol., 1, 172-177.

MACDONALD, G.A. and ABBOTT, A.T., 1970. Volcanoes in the sea, the geology of Hawaii. Univ. Hawaii Press, Honolulu, 1-44.

MACDONALD, G.A. and KATSURA, T., 1964. Chemical composition of Hawaiian lavas. Jour. Petrol., 5, 82-133.

MACGREGOR, I.D., 1969. The system MgO-SiO_2-TiO_2 and its bearing on the distribution of TiO_2 in basalts. Amer. Jour. Sci., 267-A, 342-363.

MARCHAND, M., 1970. Ultramafic nodules from Ile Bizard, Quebec. Unpub. M.Sc. Thesis, McGill Univ., Montreal, pp.1-73.

MARCHAND, M., 1973. Determination of Rb, Sr, and Rb/Sr by XRF. Tech. Memo 73-2, McMaster University, pp. 1-16.

MAUCHER, A., 1972. Time and strata bound ore deposits and the evolution of the earth. XXIV Int. Geol. Congress, 4, 83-87.

MAUCHER, A. and HÖLL, R., 1968. Die Bedeutung geochemisch-stratigraphischer Bezugshorizonte für die Alterssstellung der Antimonitlagerstätte von Schlaining im Burgenland, Österreich. Mineral. Deposita, 3, 272-285.

MCBIRNEY, A.R., 1967. Genetic relations of volcanic rocks of the Pacific Ocean. Geol. Rund., 57, 21-33.

MCBIRNEY, A.R., 1969. Compositional variations in Cenozoic calc-alkaline suites of Central America. Internat. Upper Mantle Proj. Sci. Rep. 16, 185-189.

MCBIRNEY, A.R. and AOKI, K., 1966. Petrology of the Galápagos Islands, in The Galápagos. Proc. Symp. Galápagos Internat. Sci. Project (ed. R.I. Bowman), Univ. Calif. Press, Los Angeles, 71-77.

MCBIRNEY, A.R. and WILLIAMS, H., 1969. Geology and Petrology of the Galápagos Islands. Geol. Soc. Amer. Mem., No. 118, pp.1-197.

MCDOUGALL, I., 1964. Potassium-argon ages of lavas from the Hawaiian islands. Geol. Soc. Amer. Bull., 75, 107-128.

MCMANUS, D.A., VON DER BORCH, C., GOLL, R., MILOW, E.D., OLSSON, R.K., VALLIER, T. and WESER, O., 1970. Initial Reports of the Deep Sea Drilling Project, Volume V. U.S. Government Printing Office, Washington, D.C., 203-254.

MCNUTT, R.H., CROCKET, J.H., CLARK, A.H., CAELLES, J.C., FARRAR, E., HAYNES, S.J. and ZENTILLI, M., 1975. Initial Sr-87/Sr-86 ratios of plutonic and volcanic rocks of the Central Andes between latitudes 26° and 29° South. Earth Planet. Sci. Lett., 27, 305-313.

MITTCHELL-THOMÉ, R.C., 1972. Outline of the geology of the Cape Verde Archipelago. Geol. Rund., 61, 1087-1109.

MUIR, I.D. and TILLEY, C.E., with chemical analyses by SCOON, J.H., 1964. Basalts from the northern part of the Rift Zone of the Mid-Atlantic ridge. Jour. Petrol., 5, 409-434.

MURATA, K.J. and RICHTER, D.H., 1966. Chemistry of the lava of the 1959-60 eruption of Kilauea volcano, Hawaii. U.S. Geological Survey Prof. Paper 537-A, pp.1-26.

PETERSEN, U., 1970. Metallogenic provinces of South America. Geol. Rund., 59, 834-897.

PETERSEN, M.N.A. et al., 1970. Initial reports of the Deep Sea Drilling Project, Volume II. U.S. Government Printing Office, Washington, D.C., 117-248.

PICHLER, H. and ZEIL, W., 1969. Quartäre 'Andesit' - Formation in der Hochkordillere Nord-Chiles. Geol. Rund., 58, 866-903.

PICHLER, H. and ZEIL, W., 1972. The Cenozoic rhyolite-andesite association of the Chilean Andes. Bull. Volc., 35, 424-452.

POWERS, H.A., 1955. Composition and origin of basaltic magma of the Hawaiian Islands. Geochim. Cosmochim. Acta, 7, 77-107.

PUSHKAR, P., 1968. Strontium isotope ratios in volcanic rocks of three island arc areas. Jour. Geophys. Res., 73, 2701-2713.

PUSHKAR, P., STEUBER, A.M., TOMBLIN, J.F. and JULIAN, G.M., 1973. Strontium isotopic ratios in volcanic rocks from St. Vincent and St. Lucia, Lesser Antilles. Jour. Geophys. Res., 78, 1279-1287.

RAFF, A.D., 1968. Sea-floor spreading - another rift. Jour. Geophys. Res., 73, 3699-3705.

RICHTER, D.H. and MURATA, K.J., 1966. Petrography of the lavas of the 1959-60 eruption of Kilauea volcano, Hawaii. U.S.G.S. Prof. Paper 357-D, pp.1-12.

RODDA, P., 1967. Outline of the geology of Viti Levu. N.Z. Jour. Geol. Geophys., 10, 1260-73.

RONOV, A.B. and YAROSHEVSKY, A.A., 1969. Chemical composition of the earth's crust. In The Earth's Crust and Upper Mantle (ed. P.J. Hart), Amer. Geophys. Union, Geophys. Mono. 13, Washington, D.C., 37-57.

ROWE, R.B., 1973. Porphyry deposits of the Canadian Cordillera. Can. Mining Jour., 94, 11, 35-41.

RUTTEN, M.G., 1969. The Geology of Western Europe. Elsevier Pub. Co., Amsterdam, pp.1-520.

SAMPSON, P. and JENNRICH, R.I., 1972. BMD08M factor analysis. In BMD Biomedical Computer Programs (ed. W.J. Dixon), Univ. Calif. Press, Berkeley, 255-268.

SANDELL, E.B., 1946. Abundance of tungsten in igneous rocks. Amer. Jour. Sci., 244, 643-648.

SCHILLING, J.G., 1973a. Iceland mantle plume. Geochemical evidence along Reykjanes ridge. Nature, 242, 565-571.

SCHILLING, J.G., 1973b. Iceland mantle plume. Nature, 246, 141-143.

SCHMIDT, R.G., 1957. Geology of Saipan, Mariana Islands, Chapter B: Petrology of the volcanic rocks. U.S.G.S. Prof. Paper 280-B, 127-175.

SHAW, D.M., DUPUY, C., FRATTA, M. and HELSEN, J., in press. An application of factor analysis to basic volcanic rock geochemistry. Bull. Volc.

SHUMWAY, G. and CHASE, T.E., 1961. Bathymetry in the Galápagos region. Calif. Acad. Sci., Occasional Paper 44, 11-19.

SIMON, F.O., 1972. The distribution of chromium and tungsten in the rocks and minerals from the southern California batholith. Unpub. Ph.D. Thesis, Univ. Maryland, pp.1-130.

SIMON, F.O. and ROLLINSON, C.L., 1975. Determination of tungsten in geologic materials by neutron activation analysis. Jour. Research, U.S. Geological Survey, 3, 475-478.

SKAARUP, P., 1974. Strata-bound scheelite mineralization in skarns and gneisses from the Bindal area, northern Norway. Mineral. Deposita, 9, 299-308.

SPENCER, D.W., 1966. Factor Analysis. Woods Hole Ocean. Inst., Mass., Ref. 66-39, pp.1-25.

SPOONER, E.T.C. and FYFE, W.S., 1973. Sub-sea-floor metamorphism, heat and mass transfer. Contr. Mineral. and Petrol., 42, 287-304.

STEINNES, E., 1970. Epithermal neutron activation analysis of geological material. In Activation Analysis in Geochemistry and Cosmochemistry, Proc. NATO Advanced Institute, Kjeller, Norway, 113-128.

STOIBER, R.E. and CARR, M.J., 1974. Quaternary volcanic and tectonic segmentation of Central America. Bull. Volc., 37, 304-325.

SUPKO, P.R. and PERCH-NIELSEN, C., 1975. Deep Sea Drilling Project. Geotimes, 20, 1, 19-20.

SWANSON, F.J., BAITIS, H.W., LEXA, J. and DYMOND, J., 1974. Geology of Santiágo, Rábida, and Pinzón Islands, Galápagos. Geol. Soc. Amer. Bull., 85, 1803-1810.

TAYLOR, S.R., 1964. Abundance of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta, 28, 1273-1285.

TAYLOR, S.R., CAPP, A.C., GRAHAM, A.L. and BLAKE, D.H., 1969. Trace element abundances in andesites. II. Saipan, Bougainville and Fiji. Contr. Mineral. and Petrol., 23, 1-26.

TAYLOR, S.R. and WHITE, A.J.R., 1966. Trace element abundances in andesites. Bull. Volc., 29, 177.

THE WORLD ATLAS, 1967 (ed. S.I. Shurov). Chief Administration of Geology and Cartography under the Council of Ministers of the U.S.S.R., 2nd edition, Moscow.

THORARINSSON, S., STEINTHÓRSSON, S., EINARSON, Th., KRISTMANNSDÓTTIR, H. and OSKARSSON, N., 1973. The eruption on Heimaey, Iceland. Nature, 241, 372-375.

TOMBLIN, J.F., 1974. Lesser Antilles. In Mesozoic and Cenozoic Orogenic Belts (ed. A.M. Spencer), Scottish Academic Press, Edinburgh, 663-670.

TONG, S.L., 1971. Mass-yield variations in the thermal and epithermal fission of Pu-239. Unpub. Ph.D. Thesis, McMaster Univ., Ontario.

TOURNON, J., 1969. Les roches basaltiques de la province de Gérone (Espagne), basanites à leucite et basanites à analcime. Bull. Soc. fr. Min. Crist., 92, 376-382.

TUREKIAN, K.K. and WEDEPOHL, K.H., 1961. Distribution of the elements in some major units of the earth's crust. Geol. Soc. Amer. Bull., 72, 175-192.

UKHANOV, A.V. and RASSKAZOVA, V.S., 1973. New data on the tungsten content of basic rocks. Geochemistry International, 6, 716.

VINOGRADOV, A.P., 1962. Average contents of chemical elements in the principal types of igneous rocks of the earth's crust. Geochemistry, No. 7, 641-664.

VINOGRADOV, A.P., VAINSHTEIN, E.E. and PAULENKO, L.I., 1958. Tungsten and molybdenum in igneous rocks (as related to the geochemistry of tungsten). Geochemistry, No. 5, 497-509.

WAGNER, G., MAUTHE, F. and MENSINK, H., 1971. Salzstock von Cardona in Nordostspanien. Geol. Rund., 60, 970-996.

WÄNKE, H., 1975. Korrelierte Elemente. Die Naturwissenschaften, 62, 264-271.

WESTPHAL, M., BARDON, C., BOSSERT, A. and HAMZEH, R., 1973. A computer fit of Corsica and Sardinia against Southern France. Earth Planet. Sci. Lett., 18, 137-140.

WEYL, R., 1961. Die Geologie Mittelamerikas. Gebrüder Borntraeger, Berlin, pp.1-226.

WEYL, R., 1966. Geologie der Antillen. Gebrüder Borntraeger, Berlin, pp.1-410.

WEYL, R., 1967. Volcanoes and volcanic rocks in Central America and the West Indies. Bull. Volc., 31, 3-12.

WIENDL, U., 1968. Zur Geochemie und Lagerstättenkunde des Wolframs. Unpub. Ph.D. Thesis, Univ. Clausthal, West Germany, pp.1-295.

WILLIAMS, H., 1966. Geology of the Galápagos Islands. Proc. Symp. Galápagos Internat. Sci. Project (ed. R.I. Bowman), Univ. Calif. Press, 65-70.

WILLIAMS, H., MCBIRNEY, A.R. and DENGO, G., 1964a. Geologic reconnaissance of southeastern Guatemala. Univ. Calif. Publ. Geol. Sci., 50, 1-56.

WILLIAMS, H. and MCBIRNEY, A., 1964b. Petrologic and structural contrast of the Quaternary volcanoes of Guatemala. Bull. Volc., 27, 61.

WILLIS, J.P., ERLANK, A.J., GURNEY, J.J., THEIL, R.H. and AHRENS, L.H., 1972. Major, minor, and trace element data for some Apollo 11, 12, 14 and 15 samples. Proc. Third Lunar Sci. Conf., Vol. 2, 1269-1273.

WILSON, J.T., 1963. Evidence from islands on the spreading of ocean floors. Nature, 197, 536-538.

WRIGHT, J.B., 1971. The phonolite-trachyte spectrum. Lithos, 4, 1-5.

WRIGHT, R.L., 1971. Mn and S^{34} partitioning in sulphides - a comparison of two geothermometers. Unpub. B.Sc. Thesis, McMaster University, Ontario.

YAROSLAVSKIY, R.I. and SKORNYAKOVA, I.V., 1974. Tungsten in rocks and minerals of the granulite facies of the northern Nuratinsk Range (Southern Tien Shan). Geochemistry International, 11, 1104.

YULE, H.P., 1969. Section 5 - Calculations in activation analysis - computation of experimental results in activation analysis. In Modern Trends in Activation Analysis. U.S. Nat. Bureau Standards, Spec. Pub. 312, Vol. II, 1155-1204.

YULE, H.P., 1970. Computer data reduction in activation analysis. In Activation Analysis in Geochemistry and Cosmochemistry, Proc. NATO Advanced Inst., Kjeller, Norway, 145-166.

ZEIL, W., 1964. Geologie von Chile. Gebrüder Borntraeger, Berlin, pp.1-233.


H.Kh.

APPENDIX I

COMPILATION OF GENERAL NON-GEOCHEMICAL INFORMATION

Some 125 samples from all over the world are presented in Table A.1.1. This table divides the rocks used for this research into various subgroups according to their geographical origin. For the sake of simplicity new shorter identification numbers were given to the samples. The original field number is shown in brackets in the table.

Because many samples from various donors were involved, each donor classifying the rocks according to his own criteria, a uniform system of classification was needed. For this purpose norms were calculated and names given according to the classification of volcanic rocks proposed by Irvine and Baragar (1971). If the proposed new name differs markedly from the donor's name the latter is given in brackets.

Table A.1.1 shows also the name of the donor and the analyst of the samples, as well as the sample localities and some references for further details, if needed.

Table A.1.1 The samples investigated in this study. The references refer to publications as well as pers. or written communications, publications in press, etc.

	Sample		Name of Rock		Donor/ Analyst	Locality	References
	This study	(Donor)	This study	(Donor)			
						Standard Rocks	
1	W-1	(USGS W-1)	Diabase		DMS/	Centerville, Va.	Flanagan
2	AGV	(USGS AGV-1)	Andesite			Guano Valley, Oreg.	(1973)
3	BCR	(USGS BCR-1)	Basalt			Colorado R. group, Wash.-Oreg.	
4	PCC	(USGS PCC-1)	Peridotite			Cazadero ultramafics, Calif.	
5	DTS	(USGS DTS-1)	Dunite			Twin Sisters area, Wash.	
						Hawaiian Islands	
6	Ha-1	(B-I-A)	Tholeiite		JHC/JM	Late phase 1960 Kilauea eruption	Crocket
7	Ha-2	(B-I-D)	Tholeiite		JHC/	1881 flow, Mauna Loa	(pers. comm.)
8	Ha-3	(B-I-F)	Tholeiite		JHC/JM	West slope, Mauna Kea	
9	Ha-4	(B-I-H)	Tholeiite		JHC/	Waianae Range, Oahu Island	
10	Ha-5	(B-I-J)	Tholeiite		JHC/	Wailuku Volc. series, West Maui	
11	Ha-6	(Ha-10)	Calc. alk. basalt		DMS/JM	Kohala Mountains	
						Deep Sea Drilling Project	
12	D-1	(2-10-20-1)	Tholeiite	(ol. tholeiite)	RJF/JM	32°51'73"N/52°12'92"W	Peterson et al
13	D-2	(2-11a-7-1)	Tholeiite	(ol. tholeiite)		29°56'58"N/44°44'80"W	(1970)
14	D-3	(3-15-11-1)	Tholeiite	(ol. tholeiite)		30°53'38"S/17°58'99"W	Frey et al.
15	D-4	(3-18-7-1)	Calc. alk. basalt	(ol. tholeiite)		27°58'72"S/08°00'70"W	(1974)
16	D-5	(3-19-12-1)	Calc. alk. basalt	(ol. tholeiite)		28°32'08"S/23°40'63"W	
17	D-6	(5-36-14-1)	Calc. alk. basalt	(ol. tholeiite)		40°59'08"N/130°06'58"W	
18	BR-1	(CRPC BR)	Nephelinite	(basalt)	DMS/JM	Essey-La-Côte (Lorr.) France	de la Roche et al. (1972)
19	Au	(197-7)	Tholeiite		FA/JM	Mid Atlantic Ridge (45°N)	Aumento et al. (1971)
						Crozet Archipelago	
20	Ce-1	(CE-0203)	Alk. ol. basalt		BMG/BMG	Ile de l'est	Gunn et al.
21	Ce-2	(CE-0340)	Alk. ol. basalt			Ile de l'est	(1970)
22	Ce-3	(CE-0384)	Ankaramite			Ile de l'est	
23	Ce-4	(CE-0411)	Alk. picrite basalt	(oceanite)		Ile de l'est	
24	Ce-5	(CE-0421)	Ankaramite	(aphyr. basalt)		Ile de l'est	
						Amsterdam Island	
25	Na-1	(Na-0500)	Tholeiite		BMG/BMG	SE Indian Ocean Ridge System	Gunn et al.
26	Na-2	(Na-0900)	Calc. alk. basalt			SE Indian Ocean Ridge System	(1971)
27	Na-3	(Na-1100)	Tholeiite			SE Indian Ocean Ridge System	
28	Na-4	(Na-1200)	Calc. alk. basalt			SE Indian Ocean Ridge System	
						Cabo Verde Archipelago	
29	VM-1	(VM-0152)	Alk. ol. basalt		BMG/BMG	Maio Island	Gunn
30	VM-2	(VM-0171)	Alk. ol. basalt	(ankaramitic basalt)		Maio Island	(written comm.)
31	VS-1	(VS-0033)	Ankaramite	(oceanite)		Sal Island	
32	VS-2	(VS-0093)	Alk. ol. basalt			Sal Island	
33	VS-3	(VS-0113)	Phonolite			Sal Island	

	Sample		Name of Rock		Donor/ Analyst	Locality	References
	This study	(Donor)	This study	(Donor)			
						France (Herault)	
34	He-1	(H-2)	Alk. ol. basalt		CD/CD	I St. Thibéry	Lefèvre and
35	He-2	(H-3)	Hawaiite			St. Thibéry	Dupuy (1972)
36	He-3	(H-4)	Hawaiite			St. Thibéry	Dupuy and
37	He-4	(H-6)	Alk. ol. basalt			Agde	Lefèvre (1972)
38	He-5	(H-7)	Calc. alk. basalt	(alk. basalt)		Agde	
39	He-6	(H-9)	Hawaiite			Agde	
40	He-7	(H-10)	Calc. alk. basalt	(alk. basalt)		Agde	
41	He-8	(H-13)	Calc. alk. basalt	(alk. basalt)		Roque-Haute	
42	He-9	(H-26)	Trachybasalt			III Ladève	
43	He-10	(H-27)	Hawaiite			Ladève	
44	He-11	(H-32)	Hawaiite			Ladève	
45	He-12	(H-33)	Hawaiite			Ladève	
46	He-13	(H-38)	Nephelinite			Ladève	
47	He-14	(H-39)	Trachybasalt			Ladève	
						Italy	
48	S-1	(1528)	Calc. alk. basalt	(basic andesite)	CD/CD	Sardegna Island	Dupuy et al.
49	S-2	(1532)	Calc. alk. basalt	(high-Al basalt)		Sardegna Island	(1974,1975)
50	S-3	(1560)	Andesite			Sardegna Island	
51	S-4	(1569)	Andesite			Sardegna Island	
52	S-5	(1583)	Andesite			Sardegna Island	
53	S-6	(1587)	Calc. alk. basalt	(andesite)		Sardegna Island	
						South Pacific Ocean	
54	G-1	(69-818)	Tholeiite		SRT/JDG	Fiji Islands	Gill
55	G-2	(69-876)	Andesite			Fiji Islands	(written comm.)
56	G-3	(71-390)	Andesite			Fiji Islands	
57	T-1	(151)	Hawaiite	(low-Si andesite)	SRT/SRT	Mt. Bagana, Bougainville	Taylor et al.
58	T-2	(122)	Andesite	(low-Si andesite)		Mt. Bagana, Bougainville	(1969)
59	T-3	(148)	Andesite	(low-Si andesite)		Mt. Bagana, Bougainville	
60	T-4	(44)	Andesite	(high-K andesite)		Malabita Hill, Bougainville	
61	T-5	(1022)	Andesite	(andesite)		Taroka Volc., Bougainville	
62	T-6	(S-15)	Andesite	(low-K andesite)		North Central Saipan (N.Pacific Oc.)	
						North Atlantic Ocean	
63	IC-1		Hawaiite		MM/HB	Heymay (Feb. 1973)	Marchand (pers.comm.)
64	IC-2	(TR101 31D9C)	Tholeiite		JGS/JGS	60°44'N/28°25'W Reykjanes Ridge	Schilling
65	IC-3	(IC-43)	Tholeiite			63°59'N/21°26'W Reykjanes Ridge	(1973a)
						Gerona, NE Spain	
66	H-1	(He-71-01)	Hawaiite		JNH/JM	Castellfullit de la Roca	
67	H-2	(He-71-02)	Alk. ol. basalt		AM/JNH	Olot	

	Sample		Name of Rock		Donor/		
	This study	(Donor)	This study	(Donor)	Analyst	Locality	References
						New Mexico and Arizona	
68	WL-1	(AWL-10-70)	Tholeiite		WLL/WLL	McCartys Flow, Grants	Laughlin et al.
69	WL-2	(AWL-40-70)	Tholeiite			Laguna Flow, Grants	(1972 a,b)
70	WL-3	(AWL-28-71)	Alk. ol. basalt			Bandera Crater	
71	WL-4	(AWL-33-71)	Tholeiite			Blue Water Flow, Grants	
72	WL-5	(AWL-33-72)	Tholeiite			Fence Lake Basalt, Fence Lake	
73	WL-6	(AWL-48-72)	Hawaiite	(tholeiite)	WLL/HB	Unnamed flow, Springerville, Ariz.	
74	WL-7	(AWL-58-72)	Tholeiite		WLL/WLL	Unnamed flow, Springerville, Ariz.	
75	WL-8	(B-5)	Alk. ol. basalt			Cinders, Bandera Crater	
76	WP-1	(FD-8-72)	Alk. ol. basalt		WLL/FD	Paxton Springs Flow	
77	WP-2	(FD-85-72)	Alk. ol. basalt			Paxton Springs Flow	
78	WP-3	(FD-112-72)	Ankaramite	(alk. basalt)		Cerro Colorado Flow	
79	WP-4	(FD-157b-72)	Alk. ol. basalt			Cerro Colorado Flow	
						North Pacific Ocean, Mariana Islands	
80	US-1	(USGS S-135)	Tholeiiticandesite	(low-K andesite)	PDP/S&B	NW Saipan	Schmidt
81	US-2	(USGS P-6)	Calc. alk. basalt	(ol. au. basalt)		Pagan	(1957)
82	US-3	(USGS AL-7)	Tholeiite	(ol. au. basalt)		Alamagan	
83	US-4	(USGS AG-4)	Calc. alk. basalt	(au. basalt)		Agrihan	
84	US-5	(USGS P-8)	Tholeiite	(ol. au. basalt)		Pagan	
						Guatemala	
85	M-1	(G-4)	Andesite		PDP/KA	Volcán Santiaguito	Pushkar
86	M-2	(McB-G-37)	Andesite			Volcán Toliman	(1968)
87	M-3	(McB-G-652)	Calc. alk. basalt			Volcán Obrejuelo	
88	M-4	(McB-G-726)	Calc. alk. basalt	(andesite)		Volcán Pacaya (1961)	
						Lesser Antilles	
89	TL-1	(L00005)	Andesite	(cpx. dacite)	JFT/JFT	Dome, St. Lucia	Tomblin
90	TL-2	(L00038)	Andesite			Qualibu volc., St. Lucia	(written comm.)
91	TL-3	(L00083)	Calc. alk. basalt			Dauphin Bay, St. Lucia	Pushkar et al.
92	TL-4	(L00153)	Calc. alk. basalt			Qualibu volc., St. Lucia	(1973)
93	TL-5	(L00251)	Calc. alk. basalt			Qualibu volc., St. Lucia	
94	TV-1	(V27097)	Andesite			NE of Soufrière Crater, St. Vincent	
95	TV-2	(V27713)	Calc. alk. basalt			W of Soufrière Crater, St. Vincent	
96	TV-3	(V37311)	Tholeiite			Black Point, St. Vincent	
97	TV-4	(V37454)	Calc. alk. basalt			Jumby Point, St. Vincent	
98	TV-5	(V37457)	Andesite			New Sandy Bay, St. Vincent	
99	TV-6	(V37460)	Basalt			Biabou Church, St. Vincent	
						Galapagos Islands	
100	BH	(DH-8H)	Tholeiitic andesite	(Icelandite)	HB/HB	Flow Sequence A, Pinzón	Baitis
101	BI	(DH-8I)	Tholeiitic andesite	(Icelandite)		(= Duncan) Island	(pers.comm.)
102	BJ	(DH-8J)	Tholeiite	(Icelandite			
103	BK	(DH-8K)	Tholeiite	(Icelandite)			
104	BL	(DH-8L)	Tholeiite	(ol. tholeiite)			
105	BM	(DH-8M)	Tholeiite	(ol. tholeiite)			
106	BN	(DH-8N)	Tholeiite	(ol. tholeiite)			
107	BO	(DH-8O)	Calc. alk. basalt	(ol. tholeiite)			
108	BP	(DH-8P)	Dacite	(trachyte)		Flow Sequence B, Pinzón	
109	BR	(DH-8R)	Dacite			(= Duncan) Island	
110	BS	(DH-8S)	Tholeiite	(ferro basalt)			
111	BT	(DH-8T)	Tholeiite	(ferro basalt)			

	Sample		Name of Rock		Donor/ Analyst	Locality	References
	This study	(Donor)	This study	(Donor)			
112	GA	(721104-4)	Gabbro		DMS/HB		Shaw (pers.comm.)
						Atacama, Chile	
113	Z-1	(Z-S-123)	Tholeiite		MZ/JNH	28°03'S/70°02'W	Zentilli (written comm.)
114	Z-2	(Z-507)	Tholeiite			Quebrada Paipote	
115	Z-3	(Z-545-B)	Hawaiite			27°48'S/70°05'W	
116	Z-4	(Z-558)	Hawaiite			Quebrada Paipote	
117	Z-5	(Z-565)	Hawaiite			27°16'S/69°59'W, Quebrada Paipote	
118	Z-6	(Z-571)	Hawaiite			Quebrada Paipote	
119	Z-7	(Z-684)	Tholeiitic andesite			26°49'S/69°22' Quebrada Vicuñita	
120	Z-8	(Z-753A)	Calc. alk. basalt			Quebrada Salamanca	
121	Z-9	(JC-77A)	Tholeiite			27°23'S/66°19'W, Mi vida Cu-deposit (Arg.)	
122	KB-1	(W-R-7)	Kimberlite		MM/MM	Ile Bizard, Québec, Canada	Marchand (pers.comm.)
123	KB-2	(P-10)	Kimberlite			Premier Mine, Pretoria, S.Africa	
124	KB-3	(70-213)	Kimberlite			Du Toitspan Mine, Kimberley, S.A.	
125	KB-4	(70-219)	Kimberlite			Bells Bank Main Fissure, NW of Kimberley, S. Africa	

Donor/Analyst Abbreviations

DMS	D.M. Shaw	JGS	J.G. Schilling
JHC	J.H. Crocket	JNH	J.N. Helsen
JM	J.R. Muysson	AM	A. Mir
RJF	R.J. Fiske III	WLL	W.L. Laughlin
FA	F. Aumento	FD	F. Dellechaie
BMG	B.M. Gunn	PDP	P.D. Pushkar
CD	C. Dupuy	S&B	L. Shapiro and S.M. Berthold
SRT	S.R. Taylor		
JBG	J.B. Gill	KA	K. Aoki
MM	M. Marchand	JFT	J.F. Tomblin
HB	H. Baitis	MZ	M. Zentilli

APPENDIX II

COMPILATION OF THE DATA

All the geochemical data available on the rocks under investigation in this study are compiled in Table A.2.1. These data include major oxides, trace elements, norms and some element ratios.

Table A.2.1 Major oxides (%), trace elements (ppm), norms and ratios for the rocks investigated in this study

	W-1	AGV	BCR	PCC	DTS	HA-1	HA-2
SIO2	52.64	58.97	54.50	41.87	40.45	50.00	52.05
TIO2	1.07	1.08	2.20	.02	.02	3.00	3.52
AL2O3	15.00	17.01	13.61	.65	.25	13.63	12.12
FE2O3	1.40	4.51	3.68	2.84	1.21	2.76	3.19
FEO	8.72	2.04	8.80	5.14	6.79	9.06	8.87
MNO	.17	.09	.18	.12	.12	.17	.11
MGO	6.62	1.49	3.46	43.56	49.80	7.36	7.43
CAO	10.96	4.98	6.92	.53	.15	10.19	10.12
NA2O	2.15	4.33	3.27	.05	.04	3.05	2.25
K2O	.64	2.89	1.70	.01	.02	.62	.35
P2O5	.14	.48	.36	.01	.01	.33	.25
H2O +	.53	.81	.77	4.70	.46	.06	.25
H2O -	.16	1.33	.80	.47	.09	0.06	.07
CO2	.06	.05	.03	.12	.07	0.00	0.00
S	.01	.31	.03	.01	0.00	-0.00	-0.00
SUM	100.27	99.79	100.31	100.10	99.75	100.33	100.17
LI	14.50	12.10	12.80	2.80	2.00	6.30	4.20
RB	22.60	69.00	48.60	0.00	0.00	12.90	5.50
SR	180.00	654.00	332.00	0.00	0.00	332.00	288.00
BA	160.00	1206.00	675.00	1.00	2.00	367.00	179.00
CR	114.00	12.00	18.00	2730.00	4000.00	240.00	376.00
CO	47.00	14.00	38.00	112.00	133.00	-0.00	-0.00
NI	84.00	19.00	16.00	2460.00	2513.00	153.00	107.00
CU	110.00	60.00	18.00	11.00	7.00	-0.00	-0.00
Y	19.50	18.00	33.50	0.00	0.60	29.10	28.20
ZR	92.70	235.20	191.00	0.00	0.00	203.00	105.20
NB	6.00	11.60	11.30	0.00	10.40	20.50	3.20
ZN	79.00	81.50	117.90	42.20	50.70	109.10	87.10
PB	13.20	41.00	21.30	11.20	11.60	8.50	8.90
U	[illegible]	4.20	1.30	0.00	0.00	4.00	6.40
TH	5.70	9.10	10.10	0.00	0.00	4.10	3.80
W	.60	.89	.52	.01	.02	.36	.80
QZ	3.67	9.78	8.39	0.00	0.00	0.00	7.46
OR	3.84	17.30	10.04	.06	.13	3.69	2.11
AB	19.59	39.86	33.51	.42	.32	27.82	20.64
AN	29.83	18.32	18.13	1.69	.21	21.87	22.42
NE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DI	19.22	2.29	11.32	0.00	0.03	21.56	21.76
HY	20.41	6.21	12.58	20.42	.89	16.18	17.72
OL	0.00	4.66	0.00	75.57	96.84	1.15	4.30
MT	1.48	2.73	4.00	1.42	1.12	2.91	3.36
IL	1.51	1.54	3.18	.03	.02	4.33	5.01
AP	.30	1.13	.78	.02	.02	.70	.53
CT	.15	.13	.08	.28	.16	0.00	0.00
K2O/NA2O	.30	.67	.52	.20	.50	.20	.16
FE2O3/FEO	.16	2.21	.42	.57	.18	.30	.36
SR87/SR86	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
RB/SR	.120	.106	.146	0.000	0.000	.033	.019
K/RB	235.03	344.71	290.39	0.00	0.00	339.99	528.20
TH/K	10.73	3.77	7.16	0.00	0.00	7.97	13.08
U/K	6.59	1.75	2.34	0.03	0.00	7.77	22.03

Major oxides and trace elements: -0.00 = not determined; 0.00 = below detection limit

	HA-3	HA-4	HA-5	HA-6	O-1	O-2	O-3
SIO2	47.32	49.65	46.74	48.06	39.63	49.39	48.71
TIO2	2.52	2.61	2.27	3.31	1.41	1.40	1.86
AL2O3	12.73	14.37	14.61	17.13	13.61	16.21	15.61
FE2O3	3.37	2.98	3.58	3.70	2.88	4.57	7.05
FEO	8.39	8.16	8.54	7.86	3.26	5.22	5.11
MNO	.17	.17	.19	.17	.14	.17	.23
MGO	10.71	7.41	9.56	6.07	4.53	6.27	5.65
CAO	11.27	10.47	10.74	9.61	21.64	12.19	11.10
NA2O	2.10	2.03	1.61	3.29	2.17	2.59	2.76
K2O	.54	.30	.22	.59	1.65	.39	.65
P2O5	.26	.25	.20	.56	.22	.13	.18
H2O +	.16	.70	1.11	.80	.58	.73	1.62
H2O -	.04	.34	.60	.36	.41	.60	.76
CO2	0.00	.01	0.34	.01	9.23	.10	.03
S	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
SUM	99.51	99.94	99.85	99.35	100.05	99.96	100.69
LI	9.20	2.80	3.70	7.00	9.30	6.60	8.40
RB	12.20	6.40	1.83	5.90	-0.00	9.20	-0.00
SR	464.00	349.00	236.00	568.00	-0.00	115.00	-0.00
BA	365.00	335.00	246.00	564.00	170.00	45.00	36.00
CR	582.00	464.00	575.00	89.30	264.00	301.00	212.60
CO	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
NI	289.00	115.00	258.00	-0.00	-0.00	97.00	-0.00
CU	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
Y	24.00	26.20	20.20	34.40	-0.00	30.20	-0.00
ZR	157.80	130.14	133.30	338.20	-0.00	82.00	-0.00
NB	15.90	8.03	4.70	32.20	-0.00	9.80	-0.00
ZN	86.30	96.83	36.10	134.50	-0.00	79.80	-0.00
PB	9.50	0.04	7.60	11.60	-0.00	6.70	-0.00
U	0.00	3.33	0.06	18.30	-0.00	3.30	-0.00
TH	5.20	3.81	4.40	7.20	-0.00	3.36	-0.00
W	.32	.22	.18	.52	.23	.05	.11
QZ	0.00	3.72	.89	1.65	.07	.29	6.63
OR	3.22	2.36	1.22	3.61	6.69	2.35	3.98
AB	19.07	18.44	14.83	30.63	19.14	23.76	23.67
AN	23.95	31.38	33.31	31.20	23.87	32.15	27.61
NE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DI	24.63	16.06	16.41	11.44	18.20	22.54	22.41
HY	11.31	26.65	26.85	11.35	4.26	13.34	13.01
OL	10.49	0.00	0.00	0.00	0.00	0.30	.57
MT	3.56	3.26	3.85	4.91	2.98	3.07	3.60
IL	3.54	3.45	3.26	4.70	1.93	1.99	2.68
AP	.55	.54	.45	1.22	.45	.28	.39
CT	0.00	0.00	0.00	.33	22.93	.26	.08
K2O/NA2O	.26	.13	.14	.18	.46	.15	.24
FE2O3/FEO	.40	.37	.42	.47	.92	.88	1.38
SR87/SR86	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
RB/SR	.026	.018	.006	.010	0.000	.080	0.00
K/RB	367.45	432.31	922.43	830.16	0.00	351.92	0.00
TH/K	11.60	9.31	26.54	14.73	0.00	18.13	0.00
U/K	0.00	16.40	0.30	20.83	0.00	13.19	0.00

	D-4	D-5	D-6	BR-1*	AU	CE-1	CE-2
SIO2	46.99	46.95	47.72	38.65	50.69	47.35	47.09
TIO2	.67	1.23	.81	2.76	1.24	3.34	3.03
AL2O3	18.08	19.66	17.92	10.04	16.20	15.69	14.08
FE2O3	4.12	4.54	2.73	5.45	1.31	3.46	12.73
FEO	3.69	2.63	6.61	6.66	7.77	8.15	-0.00
MNO	.13	.21	.19	.24	.16	.16	.17
MGO	7.47	2.61	8.77	13.15	7.67	5.69	7.29
CAO	13.63	11.25	12.33	13.57	11.65	10.92	11.11
NA2O	1.91	2.91	1.92	3.02	2.49	3.24	2.74
K2O	.19	1.02	.17	1.33	.13	1.50	1.32
P2O5	.07	.29	.33	1.05	.11	.55	.45
H2O +	1.05	1.64	.35	1.79	.38	-0.00	-0.00
H2O -	1.63	1.65	.71	.65	.16	-0.00	-0.00
CO2	.64	.38	.05	.76	.03	-0.00	-0.00
S	-0.00	-0.00	-0.00	-0.30	-0.00	-0.00	-0.00
SUM	99.90	99.54	99.97	99.02	99.90	100.30	100.01
LI	14.46	11.66	11.22	13.70	5.65	-0.00	-0.00
RB	-0.00	11.54	3.56	49.60	3.75	36.40	34.10
SR	-0.00	134.00	142.00	1326.00	95.00	630.30	542.00
BA	27.00	72.60	45.00	1285.00	66.00	326.30	255.00
CR	397.00	396.00	376.00	397.30	40.00	92.30	200.00
CO	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
NI	-0.00	119.00	179.00	280.00	163.30	65.00	106.00
CU	-0.00	-0.00	-0.00	-0.00	-0.00	95.00	76.00
Y	-0.00	28.00	15.76	25.00	26.25	26.00	23.00
ZR	-0.00	69.86	34.66	269.25	59.95	278.30	247.86
NB	-0.00	0.35	3.00	131.84	0.00	61.90	49.75
ZN	-0.00	119.30	64.10	147.30	86.00	97.60	98.30
PB	-0.00	9.16	6.00	11.60	19.66	9.16	11.40
U	-0.00	3.66	4.47	11.80	0.03	6.45	6.50
TH	-0.00	3.24	5.06	15.30	3.60	10.76	9.90
W	.35	.25	.11	2.12	.84	.82	.83
QZ	0.00	6.70	0.00	0.00	0.30	0.00	0.00
OC	1.15	6.39	1.31	0.00	.77	0.97	7.95
AB	17.62	24.96	17.41	0.00	22.21	24.71	25.16
AN	41.31	41.34	38.41	10.39	33.14	24.11	22.68
NE	0.00	0.00	0.00	16.56	0.00	2.83	0.00
DI	18.78	12.29	17.06	33.05	19.26	21.63	24.44
HY	13.07	7.33	12.38	0.00	20.74	0.00	.74
OL	2.98	2.20	0.53	19.90	.52	8.26	9.80
MT	2.20	2.32	2.42	4.41	1.30	3.66	4.02
IL	.96	1.77	1.14	3.03	1.60	4.73	4.31
AP	.09	.66	.11	2.26	.23	1.17	.96
CT	1.77	.21	.13	1.96	.08	0.00	0.00
K2O/NA2O	.10	.33	.09	.44	.05	.46	.48
FE2O3/FEO	1.12	4.26	.41	.82	.17	.42	0.00
SR87/SR86	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
RB/SR	0.000	.087	.025	.037	.039	.058	.063
K/RB	0.00	729.77	443.22	222.63	291.60	342.15	321.35
TH/K	0.00	4.51	35.43	13.86	33.36	8.39	9.03
U/K	0.00	4.47	30.47	16.69	0.00	5.14	5.93

*add 6.40% Lc, 1.57% Ln

	CE-3	CE-4	CE-5	NA-1	NA-2	NA-3	NA-4
SIO2	47.31	45.81	46.02	48.75	49.12	49.73	49.97
TIO2	2.54	1.66	2.65	1.21	1.63	2.07	1.67
AL2O3	13.19	8.32	13.32	15.49	18.26	14.43	17.60
FE2O3	4.73	2.35	3.45	9.86	10.36	13.81	10.74
FEO	7.01	8.66	7.90	-0.00	-0.00	-0.00	-0.00
MNO	.16	.16	.17	.15	.15	.19	.15
MGO	10.33	18.09	8.03	8.81	5.83	6.19	4.98
CAO	10.54	10.72	13.03	13.27	12.03	11.06	11.70
NA2O	2.58	1.60	2.37	1.89	2.57	2.45	2.44
K2O	1.24	.74	1.19	.45	.67	.71	.65
P2O5	.48	.26	.41	.12	.19	.22	.17
H2O +	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
H2O -	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
CO2	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
S	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
SUM	99.99	99.39	100.01	100.00	100.60	100.00	99.99
LI	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
RB	34.16	18.24	33.66	11.93	18.00	17.40	17.40
SR	349.00	317.00	472.00	288.00	352.00	287.00	324.00
BA	249.00	186.00	272.00	152.00	218.00	218.00	194.00
CR	374.00	1628.00	159.30	143.06	40.00	51.00	69.00
CO	-0.00	-0.00	-0.00	49.00	41.34	37.70	43.00
NI	238.06	551.60	139.30	88.30	46.03	38.00	47.04
CU	79.04	81.00	123.00	83.66	69.00	87.00	44.00
Y	24.30	17.64	22.40	16.60	20.30	26.10	22.10
ZR	273.04	145.66	216.35	81.30	110.20	142.70	120.98
NB	59.16	20.30	45.64	17.90	22.90	28.56	24.00
ZN	94.24	79.36	80.27	59.20	67.00	89.66	74.40
PB	9.70	9.04	10.03	9.20	7.36	13.30	8.20
U	6.43	4.30	5.60	3.34	0.03	4.00	4.00
TH	10.36	6.30	9.04	4.60	4.50	5.10	4.20
W	.77	.18	.42	.32	.42	.46	.45
QZ	0.00	0.00	0.00	0.00	.37	1.91	2.57
OC	7.33	4.23	7.11	2.60	4.02	4.31	3.92
AB	23.17	11.35	17.03	17.10	23.46	22.60	22.37
AN	28.76	14.35	22.04	32.71	36.93	27.01	35.91
NE	0.04	1.36	2.23	0.00	0.00	0.00	0.00
DI	22.16	28.40	32.22	26.27	17.99	22.06	17.79
HY	1.25	0.00	0.03	11.58	11.27	14.86	11.33
OL	16.55	34.22	9.23	4.07	0.03	0.00	0.00
MT	4.22	2.19	4.13	2.05	3.20	3.02	3.37
IL	3.54	2.55	4.02	1.73	2.27	2.98	2.30
AP	1.01	.53	.87	.25	.46	.47	.36
CT	0.00	0.00	0.36	0.00	0.03	0.00	0.00
K2O/NA2O	.48	.47	.53	.24	.26	.29	.27
FE2O3/FEO	.67	.27	.43	0.00	0.00	0.00	0.00
SR87/SR86	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
RB/SR	.067	.057	.065	.041	.051	.061	.054
K/RB	301.00	319.29	322.04	313.93	309.00	338.74	318.12
TH/K	10.01	10.33	9.72	12.31	8.09	8.65	7.78
U/K	6.22	7.40	5.67	8.83	0.00	6.79	7.41

	VM-1*	VM-2	VS-1**	VS-2	VS-3***	ME-1	ME-2
SIO2	45.85	41.65	39.36	46.36	54.53	46.02	46.89
TIO2	4.42	6.96	3.43	2.47	.56	2.19	2.87
AL2O3	15.12	13.13	9.66	13.67	22.22	12.74	12.43
FE2O3	11.73	15.63	13.04	12.94	3.18	2.06	1.75
FEO	-0.00	-0.00	-0.00	-0.00	-0.00	8.56	8.28
MNO	.24	.17	.22	.16	.13	.20	.20
MGO	5.65	6.31	16.35	10.03	.40	10.16	10.84
CAO	11.77	13.18	13.51	12.02	2.36	11.02	9.47
NA2O	3.29	3.35	2.87	3.31	10.92	3.42	3.69
K2O	1.17	1.39	1.23	.91	6.06	1.44	1.37
P2O5	.64	.88	.78	.30	.06	.77	.69
H2O +	-0.00	-0.00	-0.00	-0.00	-0.00	.33	.02
H2O -	-0.00	-0.00	-0.00	-0.00	-0.00	.26	.25
CO2	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
S	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
SUM	100.01	100.01	100.01	100.01	100.00	99.84	99.76
LI	-0.00	-0.00	-0.00	-0.00	-0.00	7.50	7.00
RB	17.64	42.34	32.24	19.50	196.70	-0.00	-0.00
SR	1141.00	1011.04	992.00	518.66	1091.06	-0.00	-0.00
BA	837.00	665.40	676.00	233.00	624.00	615.00	650.00
CR	28.00	47.06	534.00	327.33	6.06	-0.00	-0.00
CO	42.24	52.32	70.24	76.90	38.06	-0.00	-0.00
NI	38.00	63.06	425.04	189.03	6.06	-0.00	-0.00
CU	133.00	108.00	81.05	53.30	4.00	51.00	51.00
Y	27.74	25.64	25.26	21.10	18.70	-0.00	-0.00
ZR	343.00	416.36	243.73	172.78	593.30	-0.00	-0.00
NB	133.56	114.14	35.50	42.78	116.50	-0.00	-0.00
ZN	142.20	94.64	83.40	91.63	96.40	-0.00	-0.00
PB	9.16	11.16	12.16	5.63	13.90	-0.00	-0.00
U	3.16	6.09	6.26	8.16	6.53	-0.00	-0.00
TH	9.30	11.73	9.30	5.43	18.30	-0.00	-0.00
W	.64	1.13	.43	.25	1.01	1.78	1.03
QZ	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OR	7.07	8.23	0.00	5.44	35.83	8.51	8.25
AB	26.54	4.33	0.00	16.03	13.11	18.35	13.53
AN	23.71	15.76	0.55	23.37	0.00	15.04	13.65
NE	2.05	17.45	15.27	2.96	40.27	7.39	9.72
DI	24.32	37.53	26.33	27.78	3.95	23.72	22.19
HY	0.00	0.00	0.00	0.00	0.03	0.00	0.00
OL	2.05	.36	25.83	15.87	0.00	18.37	18.00
MT	3.49	6.03	5.87	4.16	0.00	3.01	3.79
IL	6.30	6.78	4.71	3.45	.73	3.30	2.07
AP	1.06	1.71	1.61	.64	.12	1.61	1.44
CT	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K2O/NA2O	.36	.36	.43	.39	.58	.42	.44
FE2O3/FEO	0.00	0.00	0.00	0.00	0.00	.00	.45
SR87/SR86	0.0003	0.0000	0.0003	0.0300	0.0330	0.0000	0.00
RB/SR	.015	.042	.034	.038	.188	0.000	0.00
K/RB	551.87	272.79	238.57	387.41	255.76	0.00	0.00
TH/K	9.78	10.31	9.76	7.15	3.64	0.00	0.00
U/K	9.37	5.09	0.33	3.38	1.29	0.00	0.00

*add 0.99% Hm
**add 5.73% Lc, 5.36% La
***add 5.39% Ac, 2.28% Wo, 0.53% Ns

	ME-3	ME-4	ME-5	ME-6	ME-7	ME-8	ME-9
SIO2	46.29	44.73	50.93	46.89	51.35	50.54	44.23
TIO2	2.87	3.72	1.29	2.36	1.88	1.33	2.99
AL2O3	12.46	13.44	13.51	13.70	13.40	12.84	14.31
FE2O3	3.39	5.61	4.28	3.71	4.25	3.64	4.43
FEO	8.25	7.39	6.29	7.89	6.00	7.18	7.56
MNO	.20	.19	.16	.17	.15	.17	.22
MGO	10.74	7.43	8.46	8.00	8.91	6.40	6.85
CAO	9.74	9.53	8.49	9.15	8.56	9.03	9.37
NA2O	3.55	3.89	3.47	3.05	3.55	3.20	4.33
K2O	1.52	2.27	1.52	1.05	1.35	1.00	2.79
P2O5	.74	.95	.49	.78	.49	.43	.77
H2O +	.85	1.12	.85	.29	.37	.35	.72
H2O -	.23	.17	.33	.31	.28	.23	.29
CO2	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
S	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
SUM	99.33	99.10	99.11	99.70	100.23	99.17	98.81
LI	7.34	10.54	7.16	9.50	6.03	6.06	10.50
RB	41.00	68.71	37.84	45.60	32.03	21.00	76.40
SR	781.00	1021.30	683.04	836.00	610.03	586.00	1167.00
BA	634.00	886.34	538.06	664.00	648.00	305.30	1843.60
CR	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
CO	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
NI	232.30	151.16	236.00	146.30	200.04	226.06	85.00
CU	47.00	37.00	46.03	44.86	43.03	67.46	38.09
Y	24.74	27.76	18.63	25.20	16.30	28.50	28.70
ZR	222.36	324.16	210.24	240.10	190.03	155.70	624.30
NB	32.70	133.35	75.76	95.83	62.63	46.30	166.10
ZN	106.43	116.76	91.80	104.60	85.20	137.66	133.60
PB	12.76	9.31	18.34	10.83	8.00	9.38	15.10
U	11.00	5.65	5.70	6.73	5.38	3.30	11.10
TH	12.50	12.00	8.26	10.30	8.50	6.30	16.80
W	2.89	1.78	1.88	1.39	1.35	.96	2.65
QZ	0.00	0.00	3.03	0.12	0.00	0.06	0.00
OR	8.97	13.71	8.33	10.35	7.95	5.97	16.83
AB	30.36	15.32	31.36	25.51	31.68	29.74	9.63
AN	13.56	12.34	16.91	13.69	16.64	17.54	12.52
NE	0.04	11.08	0.00	0.41	0.00	0.00	16.92
DI	23.08	23.31	17.91	21.17	18.46	19.94	24.61
HY	0.00	0.00	6.86	0.00	9.81	13.99	0.00
OL	19.08	11.42	12.25	15.25	6.50	5.61	8.91
MT	3.64	4.69	2.92	3.09	3.52	3.66	4.72
IL	2.08	4.16	1.81	3.29	2.61	2.72	4.25
AP	1.55	2.01	.37	1.64	.83	.89	1.64
CT	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K2O/NA2O	.43	.58	.44	.47	.38	.38	.64
FE2O3/FEO	.42	.66	.68	.47	.71	.50	.59
SR87/SR86	0.0000	0.0000	0.0000	0.0004	0.0300	0.0000	0.00
RB/SR	.054	.067	.055	.055	.052	.045	.065
K/RB	381.06	274.36	333.32	336.40	350.22	380.81	303.16
TH/K	9.91	6.37	6.33	6.71	7.58	7.59	7.35
U/K	8.72	2.65	6.52	4.36	6.73	3.98	4.79

	MC-10	MC-11	MC-12	MC-13	MC-14	S-1	S-2
SIO2	45.28	48.56	49.49	41.97	46.78	52.92	48.70
TIO2	2.85	3.31	2.97	3.14	2.75	.71	1.83
AL2O3	14.33	15.23	14.31	11.97	14.21	18.85	18.95
FE2O3	3.36	4.79	5.12	3.75	3.49	8.35	11.00
FEO	6.86	5.19	5.87	6.97	7.32	-0.00	-0.00
MNO	.19	.17	.26	.26	.19	.15	.20
MGO	7.37	6.23	8.20	12.12	7.16	4.97	5.38
CAO	9.89	7.23	10.36	10.86	8.90	8.23	9.95
NA2O	4.39	5.63	3.81	3.98	4.29	2.71	2.83
K2O	1.09	1.45	1.01	.85	3.12	2.04	1.00
P2O5	.65	.05	.64	.78	.73	.21	.19
H2O +	1.37	1.44	1.16	.36	.37	1.63	.16
H2O -	.20	.21	.35	.24	.05	.30	.16
CO2	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
S	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
SUM	98.96	99.17	99.55	98.80	99.21	99.6[illegible]	100.10
LI	8.56	9.06	7.56	6.56	9.05	-0.00	-0.00
RB	121.40	128.35	92.75	38.30	83.93	-0.00	-0.00
SR	1216.00	1226.00	1058.43	932.00	1081.00	-0.00	-0.00
BA	958.00	998.00	853.00	845.30	933.00	-0.00	-0.00
CR	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
CO	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
NI	122.00	97.00	138.00	249.10	38.00	-0.00	-0.00
CU	41.00	27.00	49.00	45.00	36.00	-0.00	-0.00
V	25.20	26.76	27.56	26.40	26.00	-0.00	-0.00
ZR	379.20	453.34	332.40	329.00	416.70	-0.00	-0.00
NB	161.00	108.14	129.26	139.83	134.83	-0.00	-0.00
ZN	111.40	114.00	106.30	91.76	112.40	-0.00	-0.00
PB	12.36	12.26	11.20	18.40	12.66	-0.00	-0.00
U	3.60	5.16	6.76	7.33	9.83	-0.00	-0.00
TH	13.78	14.34	12.90	14.23	14.74	-0.00	-0.00
W	1.30	1.37	1.57	1.34	2.40	1.00	23.70
QZ	0.00	0.00	4.36	0.00	0.00	3.82	0.00
OR	6.36	8.70	6.08	5.16	17.92	12.45	6.01
AB	22.93	34.09	21.84	0.06	14.37	33.14	24.04
AN	10.54	14.99	18.49	12.36	10.65	32.11	37.63
NE	10.41	7.06	8.28	16.27	14.67	0.00	0.00
DI	23.41	16.51	23.64	29.45	23.27	6.91	9.09
HY	0.00	0.00	0.00	0.00	0.00	15.85	12.23
OL	10.16	16.00	12.12	17.18	10.17	0.30	6.54
MT	4.29	4.00	4.73	4.85	3.66	2.34	2.64
IL	4.04	3.27	4.21	4.40	3.85	1.02	1.42
AP	1.39	1.38	1.37	1.64	1.53	.45	.41
CT	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K2O/NA2O	.25	.23	.27	.21	.73	.75	.38
FE2O3/FEO	.47	.32	1.05	.95	.48	0.00	0.00
SR87/SR86	0.0000	0.0000	0.0000	0.0000	0.0000	.7583	.7047
RB/SR	.100	.121	.088	.099	.078	0.000	0.00
K/RB	74.54	81.45	90.95	72.06	298.82	0.00	0.00
TH/K	15.14	12.36	15.99	20.12	5.86	0.00	0.00
U/K	5.64	4.24	7.99	11.20	3.79	0.00	0.00

	S-3	S-4	S-5	S-6	G-1	G-2	G-3
SIO2	55.17	61.35	59.81	54.46	50.04	55.43	60.64
TIO2	.86	.64	.72	.85	.74	.82	.62
AL2O3	16.67	17.10	16.41	18.86	15.53	18.85	17.08
FE2O3	8.20	4.76	6.67	8.67	11.65	8.83	5.92
FEO	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
MNO	.16	.09	.12	.17	.13	.13	.11
MGO	3.68	1.85	2.76	3.85	6.73	4.26	2.18
CAO	7.65	4.35	5.83	7.94	12.25	8.36	5.74
NA2O	2.47	3.81	2.93	2.86	2.12	3.42	4.47
K2O	2.27	3.01	2.45	1.43	.59	1.28	2.89
P2O5	.21	.19	.11	.20	.15	.23	.34
H2O +	1.33	.66	1.33	.00	-0.00	-0.36	-0.00
H2O -	.72	.19	.75	.60	-0.00	-0.00	-0.00
CO2	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
S	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
SUM	99.42	99.48	99.57	99.31	99.99	100.31	99.99
LI	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
RB	66.00	-0.00	89.46	-0.00	18.26	19.16	54.00
SR	335.85	-0.00	225.30	-0.00	396.00	447.00	1315.00
BA	-0.00	-0.00	-0.00	-0.00	271.00	426.30	550.00
CR	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
CO	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
NI	14.00	-0.00	12.00	-0.00	49.00	10.00	10.00
CU	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
V	21.60	-0.00	25.40	-0.00	14.90	13.20	13.90
ZR	141.80	-0.00	153.46	-0.00	40.83	74.30	157.90
NB	5.06	-0.00	7.96	-0.00	8.00	0.00	8.00
ZN	58.16	-0.00	44.46	-0.00	76.33	52.10	52.00
PB	17.00	-0.00	16.70	-0.00	9.90	8.76	9.30
U	3.70	-0.00	9.06	-0.00	4.90	8.70	8.70
TH	11.60	-0.00	11.36	-0.00	4.20	3.86	4.90
W	.90	.19	1.30	.31	.89	.17	.25
QZ	9.15	12.53	15.13	7.78	0.00	5.06	8.42
OR	13.47	31.16	13.82	8.71	3.53	7.61	17.09
AB	23.13	35.17	27.50	25.28	19.39	30.91	40.18
AN	29.47	19.61	25.18	33.31	31.71	30.36	18.06
NE	0.00	0.00	0.00	0.00	0.00	0.35	0.00
DI	6.25	3.81	3.27	4.59	23.36	7.92	6.69
HY	13.24	5.64	10.17	15.19	10.83	13.35	3.07
OL	0.00	0.03	0.00	0.00	.21	0.00	0.00
MT	2.40	2.21	2.36	2.43	2.37	2.43	2.21
IL	1.16	.86	1.04	1.22	1.83	1.15	.86
AP	.46	.31	.26	.43	.32	.48	.71
CT	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K2O/NA2O	.92	.35	.83	.50	.28	.37	.65
FE2O3/FEO	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SR87/SR86	.7064	.7082	.7066	.7063	0.0000	0.0000	0.00
RB/SR	.197	0.000	.397	0.000	.046	.043	.041
K/RB	285.52	0.00	227.50	0.00	269.12	554.34	444.29
TH/K	6.16	0.00	5.56	0.00	9.19	3.58	2.04
U/K	1.90	0.00	0.00	0.00	10.00	6.49	3.63

	T-1	T-2	T-3	T-4	T-5	T-6	IC-1
SIO2	56.88	55.26	56.50	58.81	62.73	57.72	48.25
TIO2	.87	.56	.58	.81	.63	.62	1.81
AL2O3	16.38	17.58	17.73	16.98	15.84	18.56	13.31
FE2O3	5.35	3.23	2.93	3.93	3.95	2.38	15.38
FEO	6.60	3.65	6.60	2.93	.67	2.26	-0.00
MNO	.15	.17	.17	.15	.12	.08	.24
MGO	4.35	3.80	3.30	3.73	2.26	2.46	9.21
CAO	8.28	7.78	7.85	6.73	6.35	8.38	7.57
NA2O	3.24	4.33	4.15	3.98	4.35	2.76	5.08
K2O	1.01	1.63	1.67	2.75	1.95	.74	1.07
P2O5	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	.41
H2O +	.83	.00	.15	.72	.51	1.30	-0.00
H2O -	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
CO2	-0.30	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
S	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
SUM	99.65	99.47	99.36	99.58	99.64	99.32	100.53
LI	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
RB	27.40	26.35	26.60	-0.00	30.22	12.60	24.90
SR	830.00	822.00	799.00	-0.00	740.00	160.00	342.00
BA	260.00	225.00	280.00	180.00	380.00	92.00	-0.00
CR	33.00	-0.00	-0.00	19.00	19.00	22.00	-0.00
CO	30.00	23.00	21.30	19.30	13.00	17.30	-0.00
NI	37.00	16.30	13.30	[illegible]	13.00	11.00	13.00
CU	70.00	36.60	41.00	150.00	42.00	38.00	-0.00
Y	15.00	17.80	16.95	-0.00	14.00	19.40	46.20
ZR	74.50	82.50	89.71	-0.00	97.93	47.20	293.60
NB	8.00	4.50	0.00	-0.00	7.30	8.30	44.00
ZN	69.50	79.30	71.10	-0.00	53.80	52.30	121.10
PB	10.50	10.44	8.00	-0.00	9.13	6.30	9.00
U	6.70	8.85	5.90	-0.00	7.50	8.00	8.00
TH	4.85	4.65	3.60	-0.00	4.63	3.10	6.20
W	.25	.13	.15	.75	.23	.17	.56
QZ	8.08	1.33	3.45	8.14	14.86	14.59	0.00
OC	5.43	9.76	9.93	15.73	11.63	4.53	6.53
AB	27.63	36.72	37.02	32.68	37.15	23.63	37.52
AN	16.77	23.65	25.12	21.26	21.34	36.07	16.07
NE	3.15	0.53	0.00	0.30	0.00	0.00	3.29
DI	19.66	11.23	11.54	0.70	0.17	5.32	15.50
HY	0.00	11.20	13.73	9.74	3.73	10.02	0.00
OL	9.22	6.06	0.85	0.00	0.00	0.36	9.30
MT	1.83	2.21	1.77	2.23	2.23	2.26	4.70
IL	.37	3.24	.56	[illegible]	.89	.89	4.26
AP	0.00	0.00	0.00	0.30	4.83	0.00	.87
CT	0.00	0.30	0.30	0.00	0.00	0.00	0.00
K2O/NA2O	.31	.38	.41	.76	.48	.27	.21
FE2O3/FEO	.85	1.16	.64	1.34	6.37	2.16	0.00
SR87/SR86	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
RB/SR	.033	.032	.033	0.000	.051	.075	.073
K/RB	601.78	514.71	521.17	0.00	423.77	407.22	356.74
TH/K	3.59	3.40	2.66	0.30	2.84	4.85	6.98
U/K	4.64	6.34	4.26	6.30	6.63	0.00	0.00

	IC-2	IC-3	M-1	M-2	WL-1	WL-2	WL-3
SIO2	49.54	47.64	49.93	46.62	50.50	50.82	45.90
TIO2	1.53	1.36	2.15	2.66	1.33	1.57	2.55
AL2O3	16.20	16.85	15.22	15.68	14.90	15.16	15.50
FE2O3	.69	3.54	3.02	13.20	-0.00	-0.00	-0.00
FEO	10.16	10.16	7.33	-0.00	10.42	11.43	12.45
MNO	.21	.20	.17	.19	.17	.18	.17
MGO	7.64	7.58	7.32	8.37	7.64	8.92	8.12
CAO	11.66	11.65	8.33	9.86	9.19	9.75	8.53
NA2O	1.83	1.80	4.07	3.16	2.74	2.80	3.77
K2O	.06	.23	1.83	1.93	.72	.80	2.08
P2O5	.12	.22	.43	.91	-0.00	-0.00	-0.00
H2O +	.34	.32	.15	-0.00	-0.00	-0.00	-0.00
H2O -	-0.00	-0.00	.06	-0.00	-0.00	-0.00	-0.00
CO2	.05	.05	.81	-0.00	-0.00	-0.00	-0.00
S	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
SUM	99.47	99.62	99.82	100.26	98.82	100.41	99.18
LI	-0.00	-0.00	5.66	8.68	-0.00	-0.00	-0.00
RB	-0.00	-0.00	45.90	48.03	15.50	14.90	23.50
SR	-0.00	-0.00	931.00	904.00	297.00	348.00	833.00
BA	-0.00	-0.00	591.00	756.00	-0.00	-0.00	-0.00
CR	224.00	262.30	246.00	197.00	-0.00	-0.00	-0.00
CO	60.00	53.50	-0.00	-0.00	-0.00	-0.00	-0.00
NI	-0.00	-0.00	126.00	120.00	131.00	160.00	120.00
CU	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
Y	-0.00	-0.00	23.66	26.50	19.86	26.70	20.00
ZR	-0.00	-0.00	233.30	248.00	102.63	128.10	268.10
NB	-0.00	-0.00	67.54	90.00	4.75	12.96	52.40
ZN	-0.00	-0.00	93.60	97.90	82.00	84.10	115.60
PB	-0.00	-0.00	7.90	11.60	10.76	11.06	10.90
U	-0.00	-0.00	2.96	7.70	4.14	4.86	6.30
TH	-0.00	-0.00	8.14	18.70	4.50	4.30	6.80
W	.15	.22	1.09	1.28	.29	.27	.99
QZ	0.10	6.06	2.36	0.00	0.00	0.06	0.00
OC	.36	1.36	10.78	11.58	4.33	4.65	12.82
AB	16.74	16.76	31.87	15.72	23.47	24.97	13.86
AN	36.58	37.77	17.82	23.14	26.56	26.27	19.72
NE	0.00	0.00	2.75	7.99	0.00	0.00	10.78
DI	16.58	14.53	15.53	14.35	15.93	11.54	18.64
HY	24.36	26.30	0.00	0.00	21.86	19.82	0.00
OL	1.31	4.73	14.10	15.24	.58	2.40	19.55
MT	.52	1.19	3.13	4.37	3.17	2.19	4.23
IL	1.52	2.33	2.93	[illegible]	2.53	2.17	[illegible]
AP	.26	.47	.94	1.00	0.00	0.00	0.00
CT	.13	.13	.03	0.00	0.00	0.00	0.00
K2O/NA2O	.03	.13	.45	.62	.26	.29	.53
FE2O3/FEO	.05	.14	.41	0.00	0.00	0.00	0.00
SR87/SR86	0.0000	0.0086	0.0000	0.0000	.7044	.7033	0.00
RB/SR	0.000	0.028	.066	.054	.052	.044	.028
K/RB	0.00	0.00	331.98	320.32	385.62	445.72	706.52
TH/K	0.00	0.00	5.33	6.60	7.36	5.67	5.10
U/K	0.00	0.00	1.91	4.49	6.86	7.23	5.00

	M-1	M-2	*M-3	M-4	TL-1	TL-2*	TL-3
SIO2	63.31	59.95	52.11	50.46	63.05	59.13	50.49
TIO2	.90	.73	1.39	1.24	.57	.50	.67
AL2O3	17.59	17.60	17.11	20.77	16.95	18.28	17.30
FE2O3	2.17	3.16	2.37	2.77	.76	.85	2.74
FEO	2.49	3.59	6.49	5.90	3.71	3.62	5.78
MNO	.13	.13	.17	.14	.10	.08	.18
MGO	1.73	2.39	6.00	3.75	1.86	7.86	5.37
CAO	4.96	5.39	9.39	9.69	6.90	7.36	11.51
NA2O	4.74	3.39	3.37	3.41	2.41	2.37	2.57
K2O	1.59	1.39	1.23	.83	1.31	1.42	.56
P2O5	.34	.37	.35	.23	.17	.12	.13
H2O +	.26	.77	.37	.29	.66	1.31	1.02
H2O -	.13	.30	.06	.17	.21	2.34	.64
CO2	-0.02	-0.33	-0.02	-0.16	.17	.58	-0.00
S	-0.02	-0.33	-0.02	-0.00	-0.00	-0.02	-0.00
SUM	99.30	99.81	99.62	99.76	98.75	100.62	99.28
LI	-0.00	-0.46	-0.00	-0.00	-0.00	-0.00	-0.00
RB	37.73	72.73	-0.00	-0.00	77.93	63.30	14.50
SR	477.00	463.03	-0.00	-0.00	327.03	299.00	238.00
BA	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
CR	-0.00	-0.46	-0.00	-0.00	-0.03	-0.00	-0.00
CO	-0.00	-0.40	-0.00	-0.00	-0.00	-0.00	-0.00
NI	-0.00	18.00	-0.00	-0.00	0.00	0.00	45.00
CU	-0.00	-0.33	-0.00	-0.00	-0.00	-0.00	-0.00
Y	14.00	18.33	-0.00	-0.00	16.00	17.55	17.73
ZR	164.34	173.05	-0.00	-0.00	159.96	117.16	55.60
NB	4.00	6.03	-0.00	-0.00	2.94	6.00	0.03
ZN	65.00	68.37	-0.00	-0.00	93.00	89.16	61.60
PB	9.00	13.62	-0.00	-0.00	21.93	17.60	10.60
U	3.00	4.70	-0.00	-0.00	3.13	3.30	5.20
TH	4.00	6.14	-0.00	-0.00	9.91	11.16	5.70
K	1.74	1.35	.22	.18	1.42	1.69	.67
QZ	15.20	11.66	1.47	.84	21.82	18.44	2.30
OR	9.56	11.03	7.47	4.95	6.83	8.39	3.43
AB	23.08	24.07	27.87	31.11	26.07	21.79	23.96
AN	22.11	25.00	27.20	37.24	30.04	33.92	33.70
NE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DI	9.85	9.55	13.90	9.53	2.71	0.93	19.07
HY	9.27	16.21	19.46	12.53	8.77	12.83	13.98
OL	0.00	0.00	0.36	3.33	0.04	0.00	0.00
MT	2.05	2.35	2.19	3.45	.58	.93	3.00
IL	.65	1.53	1.92	1.69	.79	.73	1.00
AP	.38	.36	.53	.49	.33	.28	.28
CT	0.00	0.00	0.00	0.00	.18	1.26	0.00
K2O/NA2O	.34	.53	.41	.24	.47	.62	.23
FE2O3/FEO	.88	.61	.34	.46	.12	.23	.44
SR87/SR86	.7038	.7042	.7037	.7039	.7080	.7092	.7054
RB/SR	.080	.115	0.000	0.030	.238	.218	.061
K/RB	407.39	314.72	0.00	0.00	139.64	184.34	328.61
TH/K	3.68	3.71	0.30	0.30	9.13	9.22	12.26
U/K	2.88	2.86	0.33	0.33	2.85	3.24	11.19

* add 1.00% Co

	TL-4*	TL-5	TV-1	TV-2	TV-3	TV-4	TV-5
SIO2	51.73	52.35	55.70	50.51	47.74	52.72	56.29
TIO2	1.03	1.17	.84	.83	1.36	.86	.77
AL2O3	16.23	18.27	18.54	17.52	15.87	18.18	18.26
FE2O3	1.68	1.98	2.71	3.18	3.89	1.66	2.43
FEO	7.52	6.71	5.47	5.83	7.88	6.33	4.93
MNO	.28	.13	.17	.16	.18	.18	.17
MGO	4.28	3.73	3.33	7.28	11.99	6.85	4.29
CAO	7.57	9.26	7.75	11.27	11.38	9.71	7.01
NA2O	3.59	3.36	3.47	2.09	2.21	2.35	3.71
K2O	.47	.79	.64	.43	.63	.66	.75
P2O5	.11	.15	.13	.13	.09	.08	.12
H2O +	1.86	1.14	.87	.57	.16	.76	.67
H2O -	1.55	.34	.23	.12	.28	.39	.50
CO2	2.87	.21	-0.02	-0.32	-0.00	-0.00	-0.00
S	-0.00	-0.02	-0.02	-0.30	-0.00	-0.00	-0.00
SUM	100.49	100.40	100.38	99.69	100.55	100.33	99.90
LI	-0.00	-0.05	-0.06	-0.30	-0.00	-0.36	-0.00
RB	13.06	16.65	13.72	11.90	9.96	10.50	12.00
SR	261.00	233.00	224.30	237.00	241.30	369.00	238.00
BA	-0.00	-0.00	-0.00	-0.30	-0.00	-0.00	-0.00
CR	-0.00	-0.30	-0.30	-0.00	-0.00	-0.00	-0.00
CO	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
NI	11.36	21.00	15.30	78.00	199.00	25.00	71.00
CU	-0.00	-0.00	-0.30	-0.33	-0.00	-0.30	-0.00
Y	27.50	26.33	25.33	21.20	17.93	19.33	23.10
ZR	79.74	113.37	36.75	73.72	68.93	61.70	89.50
NB	4.03	6.67	9.33	0.30	0.83	0.00	0.00
ZN	166.14	84.03	77.22	77.00	60.44	62.70	78.82
PB	8.83	14.13	8.90	6.10	6.53	9.20	8.10
U	2.90	3.35	4.15	5.37	0.96	4.85	6.40
TH	3.83	5.05	4.33	3.67	3.73	4.66	3.90
K	.31	.33	.23	.17	.12	.34	.27
QZ	8.52	5.61	8.13	1.56	0.06	3.34	7.67
OR	2.84	4.37	3.84	2.57	3.63	3.56	4.48
AB	33.03	29.27	31.61	18.36	19.01	23.82	33.87
AN	22.31	32.87	32.24	37.35	30.99	36.61	31.23
NE	0.00	0.00	0.23	0.20	.25	0.00	0.00
DI	0.09	5.21	0.20	14.62	19.16	7.85	2.92
HY	20.27	15.32	11.75	20.72	0.00	22.56	16.16
OL	0.00	0.04	0.05	0.00	23.45	0.00	0.00
MT	2.69	2.14	2.47	2.43	1.94	1.73	2.38
IL	1.47	1.61	1.13	1.17	1.45	1.20	1.88
AP	.24	.33	.20	.21	.19	.17	.25
CT	6.98	2.33	0.00	0.00	0.00	0.00	0.00
K2O/NA2O	.13	.23	.18	.21	.28	.24	.20
FE2O3/FEO	.59	.29	.51	.55	.27	.27	.49
SR87/SR86	.7048	.7043	.7041	.7036	.7040	.7039	.7037
RB/SR	.065	.083	.361	.049	.027	.028	.058
K/RB	304.13	344.07	387.01	310.71	804.22	474.38	518.85
TH/K	9.74	7.92	7.53	16.63	7.13	9.24	6.26
U/K	7.43	6.18	7.72	14.85	0.30	9.64	18.20

* add 2.06% Co

Small print

	WL-4	WL-5	WL-6	WL-7	WL-8	WF-1	WF-2
SIO2	54.67	49.60	50.65	52.01	45.71	45.56	46.20
TIO2	1.32	1.19	3.32	1.49	2.06	2.09	2.20
AL2O3	14.75	15.97	13.47	14.02	15.60	15.76	15.10
FE2O3	-0.00	12.73	14.97	-0.01	-0.07	-0.05	-0.63
FEO	9.23	-0.69	-0.65	11.28	18.90	10.30	10.93
MNO	.15	.17	.23	.15	.23	.21	.23
MGO	7.09	7.30	3.67	8.37	8.97	9.91	9.90
CAO	9.35	9.83	7.18	7.90	9.22	9.71	9.48
NA2O	3.07	3.12	4.69	2.85	3.08	3.62	2.84
K2O	.47	.39	1.96	.07	1.71	1.64	1.59
P2O5	-0.20	.17	.77	-0.30	-0.03	-0.05	-0.03
H2O +	-0.00	-0.47	-0.45	-0.30	-0.87	-0.05	-0.50
H2O -	-0.06	-0.44	-0.40	-0.00	-0.01	-0.05	-0.50
CO2	-0.36	-0.46	-0.05	-0.36	-0.06	-0.05	-0.03
S	-0.00	-0.36	-0.00	-0.00	-0.06	-0.00	-0.03
SUM	100.20	100.25	100.27	98.97	98.85	99.14	97.46
LI	-0.00	-0.10	-0.04	-0.00	-0.06	-0.05	-0.07
RB	0.20	12.24	26.73	21.05	20.13	-0.05	-0.05
SR	253.04	252.07	374.00	238.03	658.06	-0.00	-0.00
BA	-0.06	-0.06	-3.06	-0.00	-0.03	-0.06	-0.00
CR	-0.00	-0.00	-0.36	-0.30	144.30	142.06	80.00
CO	-0.00	-0.18	-3.06	-3.33	-0.04	-0.05	-0.60
NI	[illegible]	209.08	23.15	169.33	222.07	-0.05	-0.05
CU	-0.00	-0.00	-0.05	-0.00	75.02	77.06	153.06
Y	17.60	26.10	54.03	23.90	23.30	-0.00	-0.00
ZR	86.70	69.04	366.05	133.73	206.70	-0.00	-0.00
NB	3.50	8.07	79.16	10.73	42.53	-0.05	-0.00
ZN	61.03	36.30	113.74	76.74	88.27	-0.05	-0.00
PB	9.10	12.37	17.53	11.84	9.14	-0.05	-0.00
U	3.00	2.96	3.74	5.14	10.10	-0.06	-0.00
TH	5.00	6.32	16.15	5.83	6.97	-3.35	-0.00
W	.33	.36	.17	.23	.47	.62	.34
QZ	3.41	6.04	0.42	1.15	0.03	0.36	0.00
OC	3.26	5.34	11.32	3.19	10.06	9.36	8.37
AB	27.17	27.39	43.36	25.53	14.46	13.82	20.37
AN	25.09	28.27	11.26	23.33	28.84	21.51	24.50
NE	0.00	0.00	0.03	0.06	12.13	11.11	3.38
DI	15.03	11.49	10.12	13.03	19.82	21.17	18.53
HY	20.03	10.46	4.36	26.55	0.33	0.06	3.06
OL	0.04	5.37	1.67	0.06	14.73	16.35	17.51
MT	2.33	3.13	5.18	3.15	4.32	4.33	3.97
IL	2.83	1.34	4.70	2.10	3.63	3.73	3.27
AP	0.03	.38	1.74	6.12	0.04	0.06	0.00
CT	0.00	0.00	3.30	0.12	0.03	0.06	0.00
K2O/NA2O	.15	.12	.42	.31	.44	.47	.48
FE2O3/FEO	0.00	6.00	0.00	0.00	0.03	0.30	0.00
SR87/SR86	0.7040	0.7030	0.7026	0.7030	0.7036	0.7403	0.00
RB/SR	.036	.053	.065	.073	.031	0.000	0.00
K/RB	424.10	352.13	666.05	311.30	706.26	0.00	0.00
TH/K	12.03	13.14	9.33	8.03	4.06	0.00	0.00
U/K	10.03	6.24	2.27	7.06	7.11	0.00	0.20

	WF-3	WF-4	US-1	US-2	US-3	US-4	US-5
SIO2	46.13	44.96	57.24	56.99	53.04	53.52	56.07
TIO2	2.25	2.12	.54	.97	.81	1.04	.95
AL2O3	14.54	14.63	16.35	16.90	16.23	16.94	15.46
FE2O3	-0.00	-0.00	2.23	3.39	4.52	2.70	4.32
FEO	10.34	11.34	5.93	8.29	4.71	8.59	8.32
MNO	.18	.18	.14	.21	.14	.22	.21
MGO	11.26	16.14	4.65	4.74	6.04	5.37	5.35
CAO	9.76	9.42	8.35	10.43	10.25	10.79	10.64
NA2O	2.71	3.37	2.50	2.96	2.57	2.68	2.63
K2O	1.32	1.67	.68	.78	.88	.76	.71
P2O5	-0.00	-0.06	.16	.24	.25	.18	.24
H2O +	-0.04	-0.14	.37	.06	.67	.85	.02
H2O -	-0.02	-0.54	.56	.30	.43	.13	.24
CO2	-0.02	-0.34	-0.32	-0.44	-0.06	-0.32	-0.00
S	-0.00	-0.06	-0.00	-0.00	-0.03	-0.06	-0.00
SUM	98.34	97.43	100.33	99.88	99.97	99.93	100.04
LI	-0.00	-0.04	-0.02	-0.46	-0.04	-0.30	-0.00
RB	-0.04	-0.04	12.06	-0.00	18.23	14.40	13.00
SR	-0.36	-0.04	262.34	-0.33	281.03	344.34	333.00
BA	-0.06	-0.04	-0.02	-0.00	-0.03	-0.32	-0.00
CR	76.04	75.36	-0.30	-0.06	-0.06	-0.00	-0.00
CO	-0.04	-5.06	-0.00	-0.06	-0.06	-0.00	-0.00
NI	-0.06	-5.54	24.34	-0.06	57.03	13.00	14.00
CU	164.36	153.03	-0.36	-0.00	-0.03	-0.32	-0.00
Y	-0.06	-6.54	22.30	-0.04	20.06	17.22	19.80
ZR	-0.04	-6.36	81.74	-0.06	75.03	56.06	52.80
NB	-0.06	-5.46	0.43	-0.06	6.63	0.06	8.20
ZN	-0.00	-6.33	59.33	-0.30	78.10	80.50	96.60
PB	-0.00	-6.34	8.55	-0.06	18.96	9.60	8.90
U	-0.06	-0.04	4.14	-0.36	4.64	3.80	3.60
TH	-0.06	-0.36	3.74	-0.00	3.64	5.40	4.30
W	.32	.38	.13	.16	.21	.11	.17
QZ	0.06	6.06	12.54	.76	3.95	.84	.42
OC	7.01	5.30	4.07	4.69	3.26	4.55	4.27
AB	18.36	12.36	22.04	25.49	23.34	24.39	24.02
AN	23.56	19.24	31.35	31.57	30.64	32.39	28.78
NE	3.03	11.97	0.27	0.30	0.06	3.06	0.06
DI	20.05	22.92	8.27	13.38	15.11	16.35	18.66
HY	0.06	0.37	16.61	18.07	17.63	17.67	19.39
OL	19.71	17.37	2.36	0.30	0.06	0.06	0.00
MT	1.91	3.70	2.16	2.62	2.42	2.69	2.60
IL	3.17	2.93	.77	1.37	1.33	1.47	1.35
AP	0.00	0.04	.77	.51	.53	.38	.51
CT	0.00	0.30	0.36	0.06	0.03	0.00	0.00
K2O/NA2O	.49	.47	.27	.27	.34	.28	.27
FE2O3/FEO	0.06	0.06	.36	.41	.96	.31	.53
SR87/SR86	0.0006	0.0003	.7033	.7067	.7045	.7032	.7034
RB/SR	0.000	0.030	.069	0.068	.065	.142	.039
K/RB	0.07	0.30	441.02	0.00	461.43	438.14	453.40
TH/K	0.06	0.36	6.55	0.00	4.93	6.56	7.30
U/K	0.00	0.36	6.35	0.03	6.33	6.32	6.11

	TV-6	BH	BI	BJ	BK	BL	BM
SIO2	51.29	54.83	53.66	47.12	48.36	47.62	48.80
TIO2	[illegible]	2.21	2.64	2.94	2.46	2.66	[illegible]
AL2O3	19.93	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
FE2O3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
FEO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
MNO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
MGO	[illegible]	[illegible]	[illegible]	5.30	[illegible]	6.36	[illegible]
CAO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
NA2O	[illegible]	[illegible]	[illegible]	[illegible]	2.93	2.55	[illegible]
K2O	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	.47	[illegible]
P2O5	.13	.66	[illegible]	.38	.26	.28	[illegible]
H2O +	[illegible]	.30	.67	[illegible]	[illegible]	.58	[illegible]
H2O -	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CO2	-0.00	[illegible]	-0.33	[illegible]	-0.03	[illegible]	-0.00
S	-0.00	[illegible]	[illegible]	[illegible]	-0.03	-0.00	-0.00
SUM	100.51	100.32	100.57	100.24	100.34	100.12	100.52
LI	-6.00	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.00
RB	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	7.00
SR	[illegible]	282.00	[illegible]	[illegible]	311.00	306.00	304.00
BA	[illegible]	[illegible]	[illegible]	130.30	[illegible]	[illegible]	[illegible]
CR	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	70.00
CO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
NI	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CU	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
ZR	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
NB	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
ZN	70.00	125.60	130.30	[illegible]	[illegible]	[illegible]	[illegible]
PB	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
U	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
TH	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
W	.24	.71	.57	.32	.24	.28	.19
QZ	.87	[illegible]	[illegible]	[illegible]	0.00	[illegible]	0.00
OR	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
AB	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
AN	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
NE	0.00	[illegible]	0.00	0.00	[illegible]	0.00	0.00
DI	5.77	[illegible]	[illegible]	[illegible]	19.86	[illegible]	19.13
HY	16.43	[illegible]	9.73	13.34	14.89	16.30	11.85
OL	0.00	0.00	[illegible]	6.03	1.56	[illegible]	1.51
MT	[illegible]	3.97	[illegible]	4.60	[illegible]	[illegible]	[illegible]
IL	[illegible]	[illegible]	[illegible]	4.80	[illegible]	[illegible]	[illegible]
AP	.27	1.63	1.30	.78	.56	.61	.58
CT	0.00	[illegible]	0.30	0.00	[illegible]	0.00	0.00
K2O/NA2O	.17	.36	.34	.21	.14	.19	.11
FE2O3/FEO	[illegible]	[illegible]	0.00	0.00	0.83	[illegible]	0.00
SR87/SR86	.7043	[illegible]	0.0000	0.0000	0.0000	[illegible]	0.00
RB/SR	[illegible]	.306	.079	.042	.022	.025	.026
K/RB	[illegible]	[illegible]	488.23	[illegible]	[illegible]	[illegible]	[illegible]
TH/K	[illegible]	[illegible]	6.16	10.73	9.64	12.56	16.26
U/K	0.00	[illegible]	0.03	10.97	9.03	11.20	19.21

	BN	BO	BP	BR	BS	BT	GA
SIO2	[illegible]	[illegible]	62.20	64.66	48.06	[illegible]	49.53
TIO2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
AL2O3	[illegible]	17.36	14.73	[illegible]	[illegible]	15.76	[illegible]
FE2O3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
FEO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
MNO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
MGO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CAO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
NA2O	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
K2O	[illegible]	[illegible]	2.09	[illegible]	[illegible]	[illegible]	[illegible]
P2O5	.28	[illegible]	.27	.20	.35	.32	[illegible]
H2O +	[illegible]	.30	1.77	[illegible]	[illegible]	.72	[illegible]
H2O -	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CO2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.00
S	[illegible]	[illegible]	-0.00	-0.00	-0.00	-0.00	-0.00
SUM	99.90	99.33	100.47	99.36	100.09	100.99	99.91
LI	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.00	-0.00
RB	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	7.90	[illegible]
SR	366.00	[illegible]	[illegible]	262.00	[illegible]	[illegible]	1414.00
BA	[illegible]	[illegible]	[illegible]	[illegible]	90.00	80.00	-0.00
CR	67.00	[illegible]	[illegible]	[illegible]	29.00	50.00	-0.00
CO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.00
NI	[illegible]	[illegible]	[illegible]	10.00	[illegible]	64.00	157.00
CU	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.00
ZR	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
NB	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
ZN	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
PB	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
U	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
TH	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
W	.18	.14	1.05	.29	.54	.28	.05
QZ	[illegible]	[illegible]	14.22	10.60	.86	.79	0.00
OR	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
AB	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
AN	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
NE	[illegible]	[illegible]	[illegible]	[illegible]	0.00	[illegible]	.93
DI	[illegible]	17.47	[illegible]	9.13	[illegible]	[illegible]	42.24
HY	12.56	9.53	5.23	[illegible]	[illegible]	[illegible]	[illegible]
OL	1.39	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	9.27
MT	[illegible]	[illegible]	[illegible]	2.43	4.90	[illegible]	2.63
IL	3.77	[illegible]	1.23	1.17	[illegible]	[illegible]	[illegible]
AP	[illegible]	.52	.39	.72	.76	.67	.29
CT	0.00	[illegible]	0.36	0.00	0.00	[illegible]	0.00
K2O/NA2O	.14	.12	[illegible]	.35	.17	.14	.24
FE2O3/FEO	[illegible]	[illegible]	[illegible]	0.00	0.00	[illegible]	[illegible]
SR87/SR86	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.0000	[illegible]
RB/SR	.027	[illegible]	.198	[illegible]	[illegible]	[illegible]	.003
K/RB	[illegible]	397.54	[illegible]	533.44	411.47	441.35	987.38
TH/K	16.70	[illegible]	6.11	5.31	10.14	14.34	0.00
U/K	[illegible]	23.38	3.57	2.05	12.05	13.46	24.60

	Z-1	Z-2*	Z-3	Z-4	Z-5	Z-6	Z-7
SIO2	53.38	53.27	52.63	53.71	52.97	47.07	53.49
TIO2	1.22	.85	1.10	1.12	1.01	1.15	1.44
AL2O3	15.72	15.57	16.75	17.00	18.08	15.77	14.55
FE2O3	8.35	8.57	9.94	9.31	9.98	13.48	9.38
FEO	-0.06	-0.05	-0.34	-0.30	-0.04	-0.03	-0.00
MNO	.15	.15	.16	.15	.15	.23	.20
MGO	9.05	7.30	7.72	3.15	2.99	5.73	5.85
CAO	8.97	13.33	6.63	8.28	11.50	12.25	11.38
NA2O	3.27	2.33	3.93	3.32	3.90	4.61	2.39
K2O	.94	1.22	2.25	1.52	1.15	.22	1.02
P2O5	.18	.14	.13	.21	.19	.13	.21
H2O +	-0.00	-0.00	-0.32	-0.30	-0.33	-3.00	-0.00
H2O -	-0.00	-0.00	-0.30	-0.00	-0.03	-3.00	-0.00
CO2	-0.00	-0.00	-0.00	-0.00	-0.33	-3.00	-0.00
S	-0.00	-0.00	-0.30	-0.30	-0.33	-0.30	-0.00
SUM	100.60	99.73	100.50	99.89	100.21	100.23	99.83
LI	-0.03	-0.00	-0.00	-0.03	-0.03	-0.00	-0.00
RB	15.76	18.35	33.37	20.89	13.35	3.36	14.10
SR	631.04	958.32	820.05	560.03	453.35	467.34	328.60
BA	-0.00	-0.32	-0.00	-0.00	-0.03	-0.00	-0.00
CR	-0.00	-0.32	-0.30	-0.34	-0.00	-0.00	-0.00
CO	-0.00	-6.97	-0.35	-0.35	-0.00	-0.08	-0.00
NI	212.00	14.32	28.42	24.33	21.00	28.08	27.00
CU	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
Y	23.00	12.64	14.35	15.23	13.27	14.35	29.00
ZR	173.08	49.13	138.00	46.80	78.03	47.35	209.10
NB	8.08	0.00	8.00	8.00	0.60	0.35	8.00
ZN	71.34	32.33	365.23	64.53	45.90	33.35	109.30
PB	11.40	8.00	28.33	12.43	11.54	25.85	15.56
V	7.37	7.76	3.33	3.94	8.63	3.56	7.00
TH	7.35	6.05	4.75	3.94	3.93	3.86	11.30
U	.33	.25	.54	.36	.39	.96	1.26
QZ	8.94	4.87	0.00	0.80	0.04	6.05	6.49
OR	5.23	7.37	13.08	9.03	6.87	1.35	6.07
AB	28.09	26.07	40.66	28.92	33.49	20.77	20.97
AN	24.41	26.37	15.70	23.62	23.24	21.81	26.95
NE	0.04	0.00	1.79	0.00	0.03	12.44	0.03
DI	13.53	28.03	4.62	13.14	27.17	30.62	24.09
HY	17.63	0.00	0.00	9.36	2.77	0.06	9.49
OL	5.22	0.00	13.38	3.31	.06	0.53	0.00
MT	3.05	2.35	2.97	2.53	2.63	2.71	3.13
IL	1.97	1.35	1.33	1.57	1.43	1.54	2.05
AP	.78	.26	.33	.44	.34	.27	.49
CT	0.00	0.00	0.00	0.03	0.00	0.00	0.00
K2O/NA2O	.28	.52	.56	.17	.22	.05	.43
FE2O3/FEO	0.00	0.60	0.30	0.30	0.02	0.00	0.00
SR87/SR86	0.0000	0.0000	0.0000	0.0003	0.0000	0.0000	0.00
RB/SR	.023	.019	.075	.033	.030	.011	.043
K/RB	475.83	553.44	335.33	474.38	707.39	344.59	658.34
TH/K	9.64	6.06	2.32	3.03	4.39	20.81	11.34
U/K	5.76	7.30	1.71	0.03	0.06	24.64	8.27

*Add 1.18% Wo

	Z-8	Z-9	K3-1	KB-1	K3-2	KB-3	KB-4
SIO2	54.02	51.47	33.59	36.95	41.53	21.50	40.00
TIO2	1.38	1.25	2.27	2.30	3.79	.87	3.15
AL2O3	15.94	15.55	6.93	7.48	2.01	2.82	1.76
FE2O3	11.79	11.33	13.20	12.46	10.71	15.16	11.66
FEO	-0.04	-0.07	-0.34	-0.30	-0.03	-0.06	-0.00
MNO	.18	.17	-0.04	.13	.15	.20	.17
MGO	4.47	6.25	20.38	23.47	26.75	41.09	34.96
CAO	6.25	11.34	12.69	14.37	12.39	11.02	4.04
NA2O	3.54	2.50	.15	.12	1.84	.22	.07
K2O	.61	2.33	.77	.85	.53	.09	1.59
P2O5	.23	.42	1.18	1.27	.17	6.01	1.92
H2O +	-0.00	-0.46	8.76	-0.36	-0.00	-0.06	-0.00
H2O -	-0.00	-0.40	-0.06	-0.00	-0.00	-0.00	-0.03
CO2	-0.00	-0.30	0.30	-0.30	-0.06	-0.06	-0.00
S	-0.00	-0.03	-0.30	-0.00	-0.00	-0.06	-0.00
SUM	99.65	100.00	99.82	99.42	99.37	99.72	99.32
LI	-0.06	-0.00	-0.03	-0.30	-0.00	-0.03	-0.03
RB	15.56	71.37	33.37	33.10	60.04	4.20	67.00
SR	327.04	567.32	633.37	633.30	257.03	2133.36	1265.00
BA	-0.04	-0.00	-0.30	-0.00	-0.00	-0.06	-0.00
CR	-0.00	-0.00	-0.30	-0.30	-0.03	-0.06	-0.00
CO	-0.01	-0.07	-0.35	-0.00	-0.00	-0.00	-0.00
NI	15.04	36.00	445.30	445.03	1227.00	376.06	1109.00
CU	-0.30	-0.00	-0.30	-0.30	-0.06	-0.06	-0.00
Y	28.16	23.50	20.70	20.76	6.40	21.36	14.49
ZR	112.73	126.12	384.30	384.30	88.83	667.00	395.00
NB	9.03	7.66	173.64	173.60	88.70	238.06	334.90
ZN	77.34	37.30	76.16	76.16	70.14	66.66	58.70
PB	9.34	12.30	10.36	10.36	6.93	16.56	39.30
V	5.15	4.03	8.97	8.76	8.00	19.20	15.90
TH	4.18	5.30	13.14	13.10	7.43	45.60	66.60
U	.41	1.83	.42	.42	.81	.81	.18
QZ	7.54	5.05	0.30	0.03	-17.44	-12.49	0.00
OR	3.73	15.03	4.50	0.00	0.03	0.06	0.04
AB	32.73	24.13	0.00	0.00	0.00	0.00	.20
AN	23.77	22.10	3.70	6.00	6.19	0.35	0.00
NE	0.06	0.90	.93	4.56	.93	0.22	0.00
DI	3.08	21.30	34.27	46.93	0.03	0.30	3.63
HY	20.92	4.34	3.36	0.43	0.06	0.06	15.55
OL	0.03	7.30	35.34	38.36	89.15	32.03	57.94
MT	3.07	2.34	8.05	4.91	2.23	2.29	4.47
IL	1.94	1.76	3.97	5.16	1.65	1.15	4.15
AP	.43	.82	3.37	.35	10.56	12.45	3.00
CT	0.00	0.32	0.32	0.00	0.03	0.00	0.00
K2O/NA2O	.17	.94	4.29	7.08	.51	.41	22.71
FE2O3/FEO	0.04	0.40	0.36	0.06	0.00	0.00	0.00
SR87/SR86	0.0360	0.0003	.7042	.7342	0.0000	0.0003	0.00
RB/SR	.035	.124	.355	.355	.233	.002	.053
K/RB	443.35	294.31	133.12	213.18	73.33	177.69	197.01
TH/K	8.14	2.54	20.49	18.56	16.82	610.32	58.46
U/K	18.07	1.32	16.73	9.78	8.06	256.90	12.85

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APPENDIX III

X-RAY FLUORESCENCE METHODS

X-ray fluorescence (XRF) spectrometry was used in this study for the determination of major oxides and some trace elements. The methods used are described below.

A.3.1 Determination of major oxides

The major oxide data for the majority of all rocks were obtained from donor or analyst generally in the form of a personal or written communication or were taken from publications. For only 11 rocks (samples IC-1, H-2 and Z-1 to 9) were these data missing at the time. For this reason pellets were pressed from these rock powders, using 3 g of -200 mesh powder. The major oxides were then determined on a Phillips PW-1450 automatic XRF spectrometer. Both technique and computer program needed for the major oxide determination were developed by Brownet al. (1973). This technique, however, shows a strong enhancement of Mg by Al and consequently led to controversial results. This enhancement was later confirmed by Gunn (1975). Marchand (written comm.), dealing with this problem in more detail, considers MgO values below 2% as reliable to fair, but still usable. For rocks with MgO contents above 2% the error becomes significant. Obviously this error must become very important in more mafic rocks or rocks with high MgO contents, as was experienced without any doubt in these altered Chilean rocks. As a result of this flaw it was realized that fusion techniques are recommended for future analyses.

A.3.2 Determination of trace elements with XRF

The trace element data as obtained from the various donors show such a variety in elements analyzed that hardly any use could be made of them for any correlation study. Consequently, as many rocks as possible (more than 80%) were analyzed with XRF for the following elements: Rb, Sr, Ni, Cu, Y, Zr, Nb, Zn, Pb, U, Th. The Cu values were rejected because of contamination due to corrosion of some mechanical parts of the spectrometer. Pellets similar to the ones mentioned above were used for this determination.

The XRF spectrometer was programmed by Marchand and much of the information needed for the determination of these trace elements is taken from Marchand (written comm., 1973). In short, background, background curvature, deadtime and peak overlap corrections were made for the fluorescent peak intensities of each element. The mass absorption correction was applied using the Mo-Compton scattered radiation peak (Marchand, written comm.), whereas the detection limits were calculated according to Jenkins et al. (1970, p.52).

Computer programs were used for the subsequent reduction of the raw data. Table A.3.1 shows additional information on the trace element determination.

Accuracy can be judged from Table A.3.2 in which the donors' data are compared with data obtained in this work. In this table the donors' data are indicated by adding a 'D' to each element, e.g. RBD. The elements otherwise refer to results of this study.

Analytical precision for these trace elements is given in Table A.3.3.

Table A.3.1 XRF analytical conditions for trace elements

Element	Standard rock	Calibration value (ppm)	Source for calibration values
	Molybdenum tube+ - 60 KV - 30 Ma		
Rb	BCR	48	De Laeter et al. (1970)
Ni	BR	270	Abbey (1973)
Zn	BCR	120	Abbey (1973)
Pb	GSP	58.7	Peterman et al. (in Flanagan, 1969)
U	NIM-G	14	Abbey (1973)
Th	GSP	106	Peterman et al. (in Flanagan, 1969)
	Tungsten tube+ - 90 KV - 25 Ma		
Sr	BCR	332	De Laeter et al. (1970)
Y	BCR	33.4	Willis et al. (1972)
Zr	BCR	192	Willis et al. (1972)
Nb	BCR	11.3	Willis et al. (1972)

+ Analysing crystal: LiF(100); fine collimator; scintillation counter; counting time is 40 seconds

Table A.3.2 COMPARISON OF TRACE ELEMENTS BY DIFFERENT INVESTIGATORS

	RBO	RB	SRO	SR	NIO	NI	ZNO	ZN	PBO	PB	THO	TH
W-1	21.0	22.6	190.	180.	76.	84.	86.0	79.3	7.0	13.2	2.4	5.7
AGV	67.0	69.6	657.	654.	19.	19.	84.0	81.5	35.1	41.0	7.0	9.1
BCR	46.6	48.6	336.	332.	16.	18.	120.0	117.9	17.6	21.3	6.0	10.1
PCC	.1	0.0	5.	0.	2339.	2460.	36.0	43.2	13.3	11.2	.0	0.0
DTS	.1	0.0	6.	0.	2269.	2513.	45.0	50.7	14.2	11.6	.0	0.0
BR-1	48.0	49.6	1435.	1326.	-0.	288.	-0.0	147.3	-0.0	11.6	-0.0	15.3
MA-1	12.0	12.9	406.	392.	-0.	159.	-0.0	109.1	-0.0	8.5	-0.0	4.1
MA-2	6.4	5.5	296.	281.	-0.	107.	-0.0	87.1	-0.0	8.9	-0.0	3.0
MA-3	11.0	12.2	490.	464.	-0.	209.	-0.0	86.3	-0.0	9.5	-0.0	5.2
MA-4	8.2	6.4	364.	349.	-0.	119.	-0.0	96.0	-0.0	8.0	-0.0	3.0
MA-5	2.7	1.8	334.	296.	-0.	258.	-0.0	36.1	-0.0	7.6	-0.0	4.4
MA-6	5.5	5.9	517.	565.	-0.	47.	-0.0	108.5	-0.0	11.6	-0.0	7.2
D-1	14.6	-0.0	249.	-0.	-0.	-0.	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
D-2	9.1	9.2	116.	115.	-0.	97.	-0.0	79.4	-0.0	6.7	-0.0	3.3
D-3	18.3	-0.0	126.	-0.	-0.	-0.	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
D-4	1.8	-0.0	173.	-0.	-0.	-0.	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
D-5	11.0	11.6	143.	134.	-0.	119.	-0.0	119.0	-0.0	9.1	-0.0	3.9
D-6	4.0	3.5	148.	142.	-0.	179.	-0.0	84.1	-0.0	6.0	-0.0	5.0
AU	2.7	3.7	99.	95.	-0.	183.	-0.0	86.0	-0.0	19.6	-0.0	3.6
CE-1	34.4	36.4	621.	630.	65.	65.	-0.0	97.6	3.0	9.1	9.5	10.7
CE-2	32.1	34.1	536.	542.	115.	106.	-0.0	98.3	1.0	11.4	5.5	9.9
CE-3	31.0	34.1	495.	569.	221.	238.	-0.0	94.2	.0	9.7	6.1	10.3
CE-4	15.6	18.2	302.	317.	387.	551.	-0.0	79.3	.5	9.0	3.0	6.0
CE-5	27.9	30.6	475.	472.	98.	139.	-0.0	88.2	-0.0	10.0	6.1	9.6
NA-1	13.2	11.9	264.	280.	92.	88.	-0.0	59.2	2.6	9.2	.6	4.6
NA-2	17.1	18.0	332.	352.	44.	46.	-0.0	67.8	2.9	7.3	.5	4.5

	RBO	RB	SRO	SR	NIO	NI	ZNO	ZN	PBO	PB	THO	TH
NA-3	17.1	17.4	274.	287.	44.	38.	-0.0	89.6	4.9	13.3	-0.0	5.1
NA-4	16.5	17.4	303.	324.	44.	47.	-0.0	74.4	3.0	8.2	.7	4.2
VM-1	15.0	17.6	1214.	1141.	41.	38.	-0.0	132.2	.2	9.1	10.1	9.5
VM-2	41.5	42.3	1077.	1011.	59.	63.	-0.0	34.6	1.2	11.1	4.0	11.9
VS-1	31.0	34.2	982.	992.	390.	425.	-0.0	85.4	1.7	12.1	7.7	9.9
VS-2	18.4	19.5	495.	560.	197.	189.	-0.0	31.4	-0.0	5.4	-0.0	5.4
VS-3	192.0	194.7	1153.	1391.	9.	8.	-0.0	98.4	5.2	13.9	12.6	18.3
ME-1	29.5	-0.0	794.	-0.	279.	-0.	144.0	-0.0	-0.0	-0.0	-0.0	-0.0
ME-2	36.5	-0.0	903.	-0.	289.	-0.	136.0	-0.0	-0.0	-0.0	-0.0	-0.0
ME-3	35.5	41.0	818.	784.	291.	232.	137.0	186.4	-0.0	12.7	-0.0	12.5
ME-4	64.5	68.7	1103.	1021.	182.	151.	138.0	116.7	-0.0	9.6	-0.0	12.0
ME-5	32.0	37.0	696.	683.	263.	236.	121.0	91.0	-0.0	10.3	-0.0	8.2
ME-6	48.5	43.6	874.	836.	199.	146.	141.0	164.6	-0.0	10.8	-0.0	10.3
ME-7	28.5	32.6	621.	644.	252.	240.	165.6	85.2	-0.0	8.0	-0.0	8.5
ME-8	19.5	21.0	583.	480.	284.	226.	130.0	167.0	-0.0	9.3	-0.0	6.3
ME-9	78.5	76.4	1210.	1167.	180.	85.	161.0	133.6	-0.0	15.1	-0.0	16.0
ME-10	113.0	121.4	1236.	1210.	139.	122.	136.0	111.4	-0.0	12.3	-0.0	13.7
ME-11	130.0	148.5	1243.	1220.	117.	97.	128.0	114.4	-0.0	12.2	-0.0	14.9
ME-12	84.6	92.7	1055.	1056.	170.	138.	127.0	106.3	-0.0	11.2	-0.0	12.9
ME-13	98.0	94.0	593.	592.	296.	249.	124.0	91.7	-0.0	10.0	-0.0	14.2
ME-14	78.0	83.9	1108.	1081.	134.	90.	141.6	112.4	-0.0	12.6	-0.0	14.7
S-1	59.0	-0.0	744.	-0.	-0.	-0.	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
S-2	36.0	-0.0	449.	-0.	-0.	-0.	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
S-3	71.0	64.0	326.	335.	-0.	14.	-0.0	50.1	-0.0	17.0	-0.0	11.6
S-4	119.0	-0.0	377.	-0.	-0.	-0.	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
S-5	96.0	89.4	246.	225.	-0.	12.	-0.0	44.4	-0.0	16.7	-0.0	11.3
S-6	40.6	-0.0	342.	-0.	-0.	-0.	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
G-1	16.0	10.2	402.	395.	44.	49.	-0.0	76.3	2.0	9.9	.5	4.5

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Table A.3.2/continued

	RBO	RB	SRO	SR	NIO	NI	ZNO	ZN	PBO	PB	THO	TH
G-2	14.0	19.1	553.	447.	7.	11.	-0.0	52.1	4.0	8.7	1.5	3.0
G-3	52.0	54.0	1356.	1314.	6.	18.	-0.0	52.0	.1	9.3	4.3	4.9
T-1	26.0	27.0	836.	818.	13.	17.	-0.0	69.4	2.0	10.5	1.0	4.0
T-2	24.0	26.3	816.	822.	7.	16.	-0.0	79.3	3.1	18.4	1.6	4.0
T-3	25.0	26.0	790.	793.	5.	12.	-0.0	71.1	2.0	8.0	1.4	3.6
T-4	69.0	-0.0	956.	-0.	13.	-0.	-0.0	-0.0	6.0	-0.0	4.0	-0.0
T-5	35.0	38.2	718.	748.	7.	12.	-0.0	53.0	2.0	9.1	1.9	4.6
T-6	12.0	12.6	160.	168.	9.	11.	-0.0	62.3	4.5	6.3	0.6	3.1
IC-1	-0.0	24.9	-0.	342.	-0.	13.	-0.0	121.1	-0.0	9.0	-0.0	6.2
IC-2	-0.0	-0.0	-0.	-0.	-0.	-0.	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
IC-3	-0.0	-0.0	-0.	-0.	-0.	-0.	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
N-1	46.6	45.9	769.	691.	-0.	126.	-0.0	93.6	-0.0	7.9	-0.0	8.1
N-2	37.5	48.4	1049.	984.	-0.	120.	-0.0	97.9	-0.0	11.6	-0.0	10.7
WL-1	13.0	15.5	187.	297.	-0.	131.	-0.0	82.0	-0.0	18.7	-0.0	4.4
WL-2	-0.0	14.9	-0.	346.	-0.	160.	-0.0	84.1	-0.0	11.0	-0.0	4.3
WL-3	-0.0	23.5	-0.	833.	-0.	128.	-0.0	115.0	-0.0	10.9	-0.0	6.0
WL-4	-0.0	9.2	-0.	253.	-0.	149.	-0.0	81.0	-0.0	9.1	-0.0	5.0
WL-5	-0.0	13.2	-0.	250.	-0.	239.	-0.0	98.6	-0.0	10.3	-0.0	6.2
WL-6	-0.0	24.4	-0.	374.	-0.	23.	-0.0	111.7	-0.0	17.5	-0.0	16.0
WL-7	-0.0	21.0	-0.	298.	-0.	169.	-0.0	78.7	-0.0	11.0	-0.0	5.0
WL-8	-0.0	20.1	-0.	656.	96.	222.	182.6	88.2	-0.0	9.1	-0.0	6.9
WF-1	-0.0	-0.0	-0.	-0.	97.	-0.	186.0	-0.0	-0.0	-0.0	-0.0	-0.0
WF-2	-0.0	-0.0	-0.	-0.	189.	-0.	86.0	-0.0	-0.0	-0.0	-0.0	-0.0
WF-3	-0.0	-0.0	-0.	-0.	115.	-0.	71.0	-0.0	-0.0	-0.0	-0.0	-0.0
WF-4	-0.0	-0.0	-0.	-0.	111.	-0.	94.0	-0.0	-0.0	-0.0	-0.0	-0.0
US-1	11.0	12.0	250.	262.	26.	24.	-0.0	59.3	4.0	8.5	1.3	3.7
US-2	-0.0	-0.0	-0.	-0.	-0.	-0.	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
US-3	-0.0	18.2	-0.	201.	-0.	57.	-0.0	78.1	-0.0	18.9	-0.0	3.6

	RBO	RB	SRO	SR	NIO	NI	ZNO	ZN	PBO	PB	THO	TH
US-4	-0.0	14.4	-0.	344.	-0.	13.	-0.0	80.5	-0.0	9.6	-0.0	5.4
US-5	-0.0	13.6	-0.	333.	-0.	38.	-0.0	96.6	-0.0	8.9	-0.0	4.3
N-1	-0.0	32.4	-0.	477.	-0.	8.	-0.0	65.6	-0.0	9.0	-0.0	4.6
N-2	-0.0	52.9	-0.	461.	-0.	18.	-0.0	68.3	-0.0	13.6	-0.0	6.1
N-3	-0.0	-0.0	-0.	-0.	-0.	-0.	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
N-4	-0.0	-0.0	-0.	-0.	-0.	-0.	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
TL-1	-0.0	77.9	-0.	327.	-0.	6.	-0.0	93.6	-0.0	21.9	-0.0	9.9
TL-2	-0.0	65.3	-0.	293.	-0.	7.	-0.0	84.1	-0.0	17.6	-0.0	11.1
TL-3	-0.0	14.5	-0.	238.	-0.	45.	-0.0	63.0	-0.0	18.6	-0.0	5.7
TL-4	-0.0	13.6	-0.	201.	-0.	11.	-0.0	136.1	-0.0	8.0	-0.0	3.0
TL-5	-0.0	16.6	-0.	281.	-0.	21.	-0.0	84.0	-0.0	10.1	-0.0	5.0
TV-1	-0.0	13.7	-0.	224.	-0.	15.	-0.0	77.2	-0.0	8.9	-0.0	4.0
TV-2	-0.0	11.5	-0.	237.	-0.	78.	-0.0	77.0	-0.0	6.1	-0.0	3.0
TV-3	-0.0	6.4	-0.	241.	-0.	199.	-0.0	60.4	-0.0	6.5	-0.0	3.7
TV-4	-0.0	18.5	-0.	369.	-0.	24.	-0.0	62.7	-0.0	9.2	-0.0	4.6
TV-5	-0.0	12.0	-0.	230.	-0.	71.	-0.0	78.0	-0.0	8.1	-0.0	3.9
TV-6	-0.0	18.3	-0.	235.	-0.	15.	-0.0	78.6	-0.0	9.1	-0.0	3.4
BH	-0.0	24.2	-0.	282.	-0.	16.	-0.0	125.6	-0.0	8.1	-0.0	5.6
BI	-0.0	22.3	-0.	283.	-0.	14.	-0.0	138.3	-0.0	8.3	-0.0	6.6
BJ	12.0	12.4	301.	297.	39.	53.	-0.0	185.4	-0.0	18.3	2.0	6.0
BK	6.0	6.9	320.	311.	-0.	89.	-0.0	96.0	-0.0	8.0	.9	3.2
BL	-0.0	7.0	-0.	380.	-0.	81.	-0.0	185.7	-0.0	7.4	-0.0	4.9
BM	8.0	7.0	310.	304.	-0.	85.	-0.0	161.0	-0.0	7.9	1.1	5.0
BN	7.0	8.3	312.	305.	-0.	74.	-0.0	96.7	-0.0	7.5	1.1	6.1
BO	5.0	7.1	349.	350.	-0.	68.	-0.0	88.1	-0.0	8.6	.9	5.1
BP	44.0	39.3	196.	198.	-0.	11.	-0.0	98.7	-0.0	8.4	7.1	18.6
BR	-0.0	33.0	-0.	202.	-0.	18.	-0.0	66.9	-0.0	5.1	-0.0	9.7
BS	11.3	11.5	308.	303.	-0.	52.	-0.0	108.7	-0.0	18.2	1.5	4.0

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Table A.3.2/continued

	RBO	RB	SRO	SR	NIO	NI	ZNO	ZN	PBO	PB	THO	TH
BT	9.8	7.9	324.	333.	-0.	64.	-0.0	103.9	-0.0	9.0	1.3	5.0
GA	-0.0	4.3	-0.	1414.	-0.	157.	-0.0	53.6	-0.0	7.0	-0.0	0.0
Z-1	-0.0	15.7	-0.	691.	-0.	212.	-0.0	71.3	-0.0	13.4	-0.0	7.2
Z-2	-0.0	18.3	-0.	958.	-0.	14.	-0.0	32.3	-0.0	6.8	-0.0	0.0
Z-3	-0.0	61.2	-0.	826.	-0.	28.	-0.0	345.2	-0.0	20.3	-0.0	4.7
Z-4	-0.0	24.6	-0.	586.	-0.	24.	-0.0	64.5	-0.0	12.4	-0.0	3.9
Z-5	-0.0	13.5	-0.	453.	-0.	21.	-0.0	44.0	-0.0	11.5	-0.0	3.9
Z-6	-0.0	5.3	-0.	467.	-0.	26.	-0.0	38.1	-0.0	25.0	-0.0	3.0
Z-7	-0.0	14.1	-0.	328.	-0.	27.	-0.0	189.2	-0.0	11.5	-0.0	11.3
Z-8	-0.0	11.5	-0.	327.	-0.	15.	-0.0	77.2	-0.0	9.3	-0.0	4.1
Z-9	-0.0	78.0	-0.	563.	-0.	36.	-0.0	37.5	-0.0	12.1	-0.0	5.3
KB-1	-0.0	33.1	-0.	683.	-0.	445.	-0.0	96.1	-0.0	18.3	-0.0	13.1
KB-2	-0.0	64.6	-0.	257.	-0.	1227.	-0.0	53.1	-0.0	6.9	-0.0	7.4
KB-3	-0.0	4.2	-0.	2133.	-0.	376.	-0.0	68.8	-0.0	18.5	-0.0	45.6
KB-4	-0.0	67.0	-0.	1265.	-0.	1109.	-0.0	58.7	-0.0	39.3	-0.0	66.6

-0.00= not determined; 0.00 = below detection limit;
detection limits (ppm) are: Rb=0.95; Sr=1.79; Ni=5.67; Zn=2.38; Pb=2.37; Th=2.13

COMPARISON OF TRACE ELEMENTS BY DIFFERENT INVESTIGATORS

	YO	Y	ZRO	ZR	NBO	NB	UO	U
W-1	25.0	19.4	105.	93.	9.5	6.2	.6	3.5
AGV	21.3	18.0	225.	235.	15.0	11.6	1.9	4.2
BCR	37.1	33.5	190.	192.	13.5	11.3	1.7	3.3
PCC	5.6	0.0	7.	0.	2.0	0.0	.0	0.0
DTS	.1	0.0	3.	0.	3.0	16.4	.0	0.0
BR-1	27.0	25.0	248.	263.	-0.0	131.0	-0.0	11.0
G-1	19.0	14.9	39.	41.	-0.0	0.0	.2	4.9
G-2	22.0	13.2	87.	74.	-0.0	3.0	.5	6.9
G-3	17.0	15.9	136.	150.	-0.0	0.0	1.7	6.7
T-1	20.0	15.0	96.	79.	4.3	2.0	.4	6.2
T-2	23.0	17.6	96.	83.	4.0	4.0	.6	0.0
T-3	28.0	16.4	185.	98.	5.1	0.0	.3	5.9
T-4	24.0	-0.0	178.	-0.	-0.0	-0.0	1.9	-0.0
T-5	20.0	14.0	116.	186.	4.3	0.0	.7	7.5
T-6	25.0	19.0	88.	47.	.2	0.0	0.0	0.0
US-1	24.0	22.0	95.	82.	.4	0.0	.4	0.0
BJ	-0.0	34.5	243.	236.	-0.0	18.0	-0.0	6.1
BP	-0.0	50.3	596.	613.	-0.0	42.3	-0.0	6.2
BT	-0.0	30.7	190.	189.	-0.0	14.7	-0.0	4.7

-0.00 = not determined; 0.00 = below detection limit;
detection limits (ppm) are: Y=2.05; Zr=1.68; Nb=2.03; U=2.57

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Table A.3.3 Coefficients of variation (%) for trace element determinations in various rocks

Rock Element	AGV (6)°	BCR (10)	NIM-G (3)	He-12 (3)	He-13 (3)	He-14 (3)
Rb	1.0	1.5	.3	.1	.8	.3
Ni	5.7	17.8	8.5	1.9	.5	.8
Zn	2.4	2.3	1.3	1.3	3.7	1.5
Pb	1.0	4.6	1.5	4.9	3.8	4.1
U	38.1	48.8	10.2	24.4	9.6	7.4
Th	3.8	5.3	1.9	8.5	5.7	4.5

Rock Element	He-8 (3)	He-9 (3)	He-10 (3)
Sr	.5	.6	.2
Y	2.4	1.5	4.3
Zr	.6	.3	.6
Nb	2.3	1.1	2.0

° Number of replicate analyses