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GEOCHEMICAL STUDY OF THE
MAMAINSE POINT RHYOLITES,
ALGOMA DISTRICT, ONTARIO

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By

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ABSTRACT

A series of shallow intrusive and extrusive silicic volcanic rocks near Mamainse Point, Ontario, were sampled and analyzed for major and trace elements. The rocks are mainly fine grained, silicified rhyolites grading to dacites containing phenocrysts of quartz and feldspar.

The analyses performed (XRF, AAS) indicate that many of these rocks have been altered from the normal igneous spectrum of rocks to potassic keratophyres. An enrichment in potash from potash metasomatism has accompanied low grade, burial metamorphism to produce a secondary mineral assemblage including chlorite, carbonate, and sericite. Local intense alteration of some rocks involved the depletion of mobile alkalis and addition of water and CO_2 to form calcite and kaolin.

The overall field and chemical evidence suggest a single magmatic source for these rocks.

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CHAPTER I

INTRODUCTION

1. GENERAL GEOLOGY

The Mamainse Point study area is located 40 miles north of Sault Ste. Marie and consists of varying rock types of Keweenawan age. These are mainly basaltic flows with interfingerings of rhyolitic rocks and sedimentary rocks (Figure 1).

Most of the outcrops are small, isolated ones along Highway 17 and along the lakeshore (Appendix A); they lie unconformably over rocks of Archean age. The Keweenawan sequences strike northwest and dip west at 20°-60° (Giblin, 1966, 1969). Basaltic rocks make up approximately 70% of the sequence and the remainder is split into roughly equal proportions of rhyolitic rocks and conglomerates.

The basaltic flows average 5-30 feet in thickness but a few are up to 100 feet thick. Most of these appear uniform in lithology throughout the study area.

Sedimentary rocks are mainly conglomerates which consist of poorly sorted granitic and basaltic fragments ranging in size from sand sized particles to large boulders. Irregular to rounded clasts and fragments of diabase, felsite,

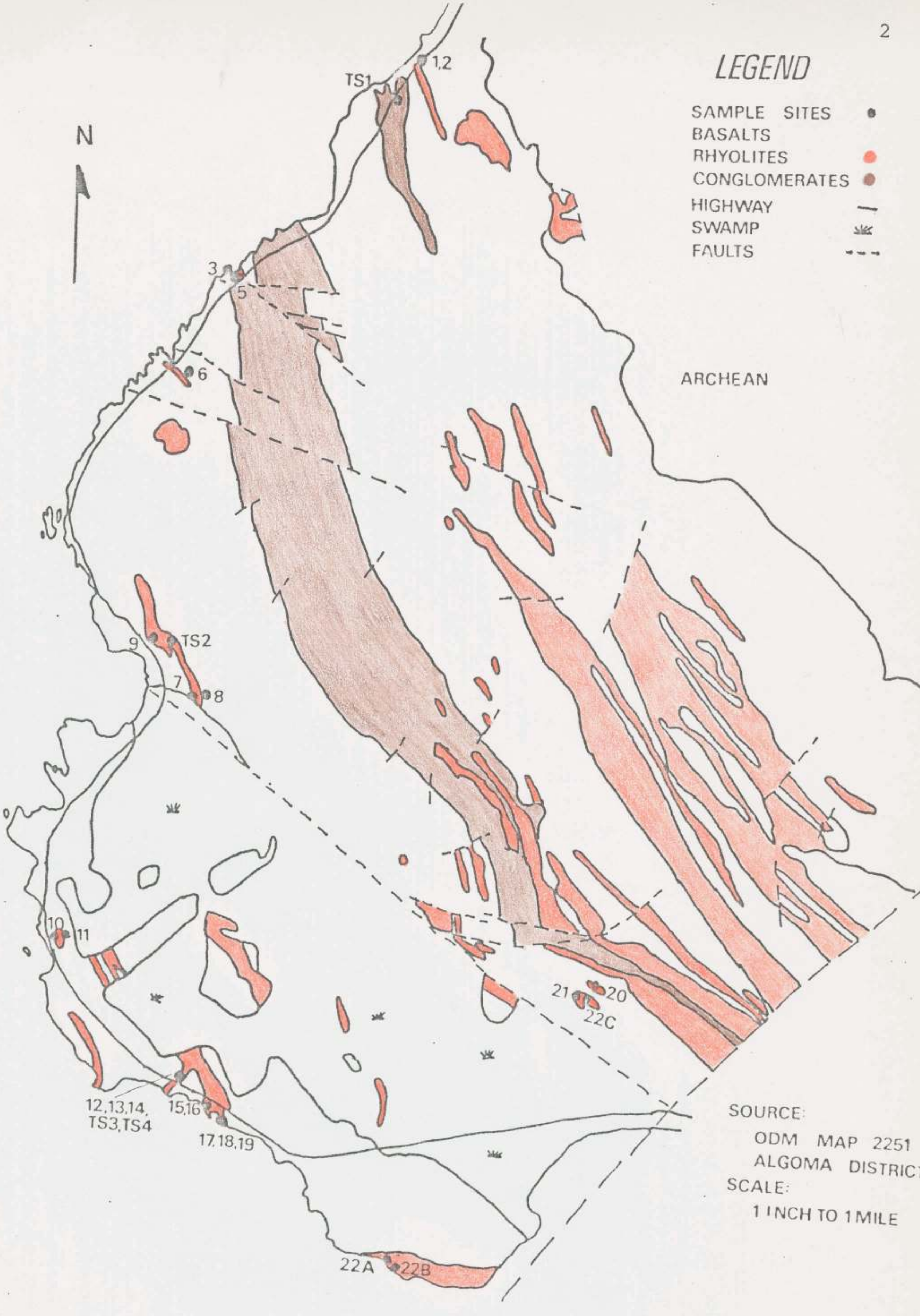

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Figure 1. Sample Location Map

and vein quartz are present as well.

Felsitic or rhyolitic rocks range in colour from light greenish-grey to pinkish-red and contain small quartz and feldspar phenocrysts set in an aphanitic matrix. According to chemical analyses, these range from altered rhyolites to dacites. Many of the felsites are flow laminated and altered in part by carbonate, hematite and kaolin, and show auto-brecciated contact zones with basaltic rocks (Figures 2,3,4,5). Numerous dikes and plugs cross-cut the basalts and conglomerates and are therefore clearly intrusive in origin (Giblin et al., 1974).

2. SPECIFIC PROBLEM

A total of 26 samples were taken for geochemical analyses and petrographic examination. These sample sites are shown in Figure 1 on the sample location map. Accessibility of outcrops was poor, and restricted to highway roadcuts and lakeshore outcroppings.

The various rhyolitic phases were studied chemically and petrographically, and have been classified according to Streckeisen's classification and nomenclature scheme for volcanic rocks (Streckeisen, 1967; Figure 6).

Chemical compositions were obtained to get a bulk-element composition of these rocks to be used in comparison

Figure 2. Flow Banded Rhyolite Contacting Mafic Dike. Rhyolite Shows Autobrecciation-Mafic Fragments, Numerous Fractures, Secondary Alteration.

Figure 3. Autobrecciated Contact Zone A Few Feet From Mafic Contact. Chaotic Accumulation of Rhyolite and Mafic Rock Fragments.


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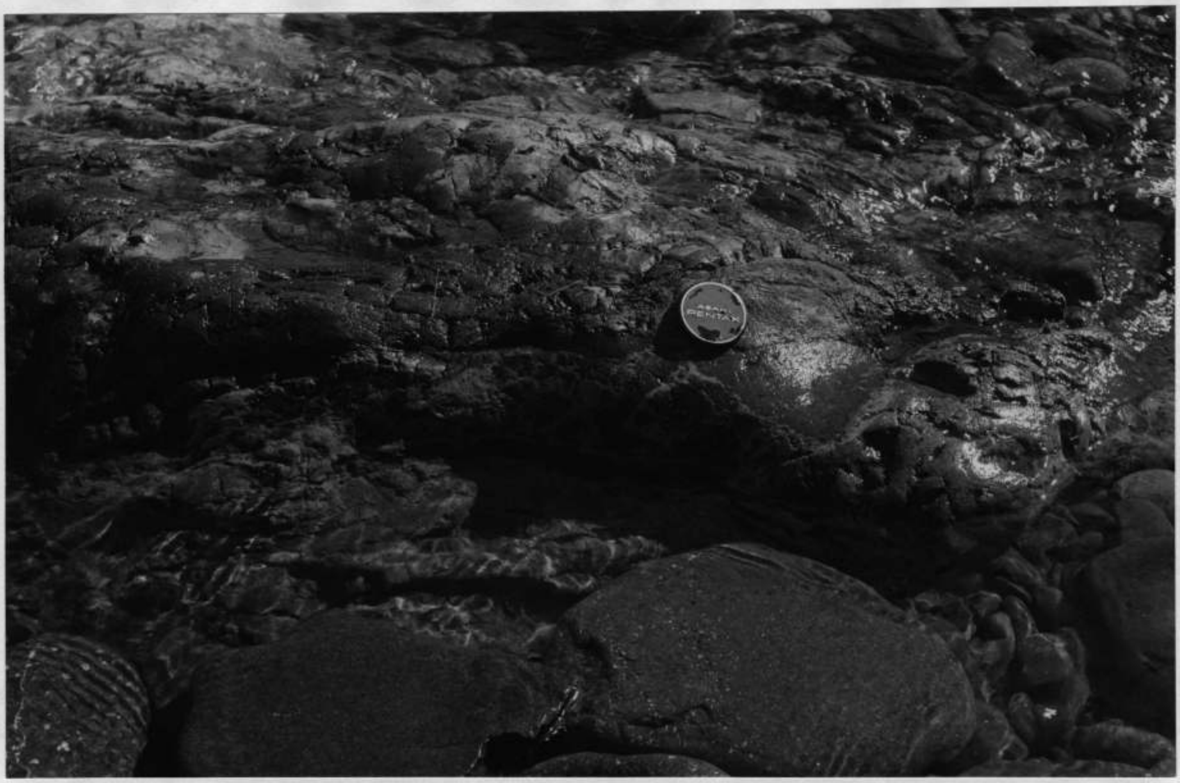
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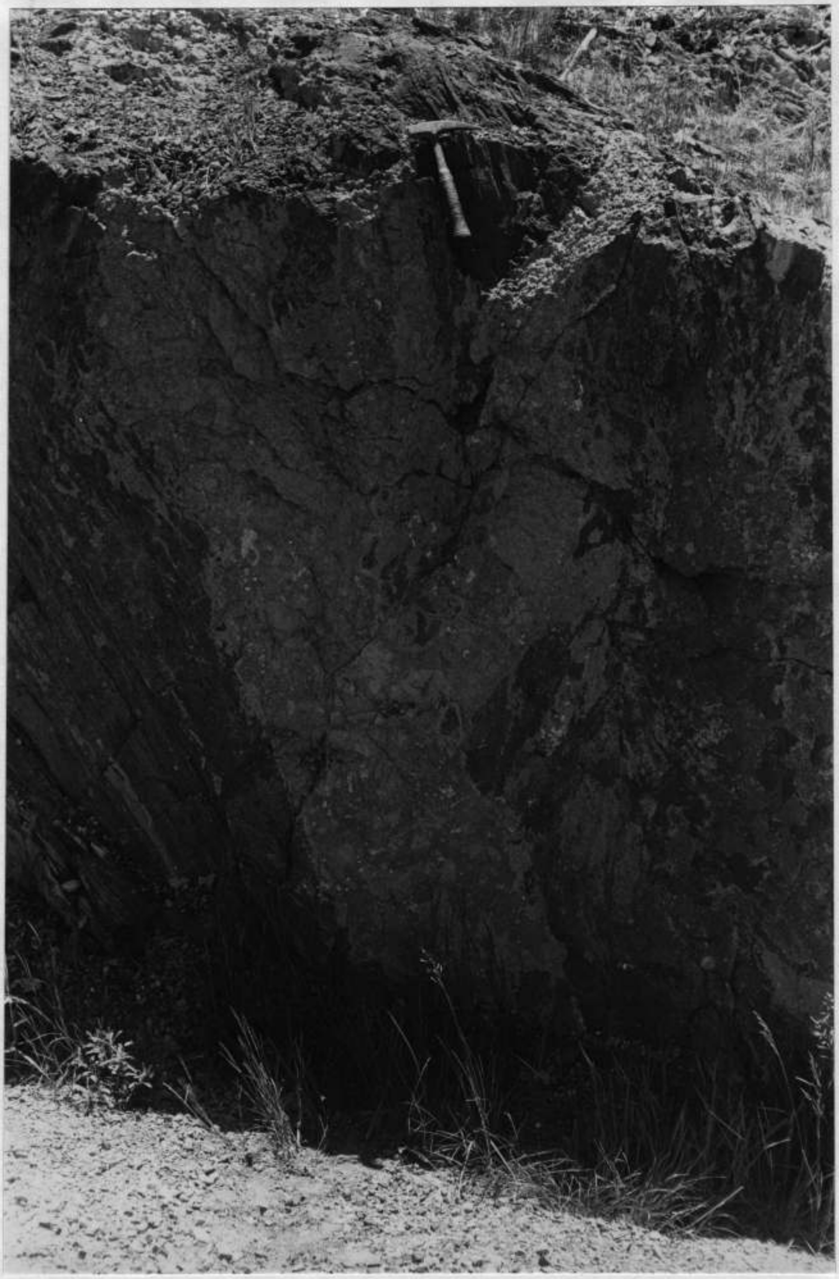

Figure 4. Secondary Alteration of Flow Banded Rhyolite. Greyish-white, Funnel-shaped Intrusion Rich in Calcite with Minor Kaolin and Hematite, Crosscuts Prominent Flow Banded Orientation of the Outcrop.

5. Massive, Altered, Flow Banded Rhyolite. Whitish Patches of Secondary Calcite Invades Along Flow Band Cleavages.

with other rhyolitic (and "keratophyric") rocks. Concentrations, particularly of K, Ba, Sr, Rb, were measured and looked at for elemental zoning variations throughout the study area. For example, are the flows enriched in alkali elements towards the inner zones, and if so, could this be from primary or secondary migration? Anomalous values would probably be explained by local alteration. Ba/Rb ratios, as well as other alkali/Rb ratios, were used to trace the fractionation of potassium-rich feldspars. The ratio should decrease with more differentiation, which, according to other models, should be towards the inner zone.

All of this data has been used here to try to explain alkali variation by late stage migration via liquids and/or volatiles. Chemical compositions of major oxides and trace elements were analyzed to see if the various flows are related by chemistry, and thereby in origin as well. Trace element study has helped in trying to determine whether the rocks all originated from one major magma source or process, or whether they originate from several individual magmatic events.

3. PREVIOUS WORK

The presence of native copper in the basaltic rocks of Mamainse Point has attracted attention to this area as far back as 3,800±500 years according to Drier (1961), at which time Indians were extracting the metal for knives and cooking utensils (from Annells, 1973). White men first entered the area, sinking a number of shafts, in the 18th Century. The first person to study the area geologically was Sir William Logan, in 1863. Macfarlane studied the area in greater detail in 1866 (he had interpreted the reddish, contorted, flow banded rocks as being convoluted, depositional sandstones). The area was mapped by Moore in 1926, and then in greater detail by Thomson in 1953. Giblin extended the detailed mapping of the volcanic sequences over the entire area in 1969. Stratigraphy, petrography, and chemical analyses were done by Annells in 1971 (Annells, 1973).

CHAPTER II

ANALYTICAL METHODS

A number of chemical analytical methods were used to measure abundances of oxides and trace elements for individual samples. The results of these are found in Appendix C. Also, petrographic analyses were undertaken for the individual specimens. These results are found in Table BI.

1. X-RAY FLUORESCENCE

Whole rock and Rb, Sr trace element analyses were done using a Philips Model 1450 AHP x-ray fluorescence spectrometer. A Cr x-ray tube was used for measuring SiO_2, TiO_2, Al_2O_3, Fe_2O_3 (as total Fe), MnO, MgO, CaO, Na_2O, K_2O, P_2O_5. An Mo x-ray tube was used for measuring Rb and Sr.

The powder method was used for measuring concentrations of Rb and Sr according to the method outlined by Marchand (1973). Fusion with lithium tetraborate prior to pelletization was carried out on the samples for major oxides analyses. One sample was repeatedly analyzed, together with the other samples, to act as a drift monitor. Precision of this method was examined by running the same sample three times, and by running three different samples derived from the same rock

(Appendix C, Tables I and II, respectively).

2. ATOMIC ABSORPTION SPECTROMETRY

(i) Solution Preparation

(1) 1.0 gram of sample powder is transferred to teflon crucibles and wetted with H_2O;

(2) 2.0 ml. of HNO_3 are added to crucibles;

(3) 25.0 ml. of an acid mixture (2/3 HF, 1/3 $HClO_4$) are added to crucibles;

(4) evaporate solution on a low heat steambath overnight;

(5) evaporate to low volume on sand bath;

(6) cool; then add 10 ml. $HClO_4$ and 25 ml. H_2O;

(7) quantitatively transfer to vycor beakers and boil to dissolve solute;

(8) transfer to 200 ml. volumetric flasks;

(9) transfer to 250 ml. polyethylene bottles for analysis.

(ii) Standards

Stock standard solutions were prepared for Ba (200, 400, 1000 ppm) and Li (10, 100, 1000 ppm) in order to compare known values with the unknown samples on a relative scale. Other solutions of known Ba and Li concentrations were also used in order to check the precision of the method.

Blank solutions were run to monitor drift.

(iii) Spectrometry

A model 603 Perkin-Elmer spectrometer measured the relative concentrations of Ba and Li by emission.

Sensitivity was approximately 0.4 μg/ml Ba and 0.035 μg/ml Li for 1% absorption. For Ba, this value assumes that sufficient alkali was added to control ionization effects. Linearity was achieved up to about 25 μg/ml in aqueous solution for Ba, and up to 2 μg/ml in aqueous solution for Li. The most sensitive emission wavelengths were 553.6 nm. for Ba and 670.8 nm. for Li. A nitrous oxide-acetylene flame was used, rather than air-acetylene, for better sensitivity.

3. SUBROUTINE NORM CALCULATIONS

Norms were calculated using a subroutine norm computer program (Shaw, pers. comm.). These are listed in Table CVI.

4. INDIVIDUAL DETERMINATIONS FOR FeO

Concentrations of FeO for individual samples were obtained using the dichromate titration method. 0.4 g. of the sample powders were reacted with 5 ml. H_2SO_4, 5 ml HF, and 13 ml O_2 free H_2O under a low bunsen flame for 10 minutes, and then gently mixed with a solution containing 50 ml. boric acid, 330 ml. O_2 free H_2O, and 15 ml. H_2SO_4. At this point, a calomel electrode containing saturated KCl solution and an oxidized platinum electrode were lowered into the solution. Standard dichromate titrant was added until an obvious endpoint was measured on a potentiometer.

5. VOLATILE DETERMINATIONS

CO_2 and H_2O concentrations were approximated by loss on ignition, taking the difference in weight plus the oxygen of the reaction:

$$2FeO + O_2 \rightarrow Fe_2O_3$$

(The factor for converting $FeO \rightarrow Fe_2O_3$ is 1.1114).

The loss in weight of pre-weighed porcelain crucibles containing sample powder at 550°C after 25 minutes represented the loss of H_2O from the sample. The loss in weight at 1000°C after 60 minutes represented the loss of CO_2 from the sample.

This method is at best a rough estimate of the total volatiles driven out of the samples by increased temperatures. Reliability is not very good because:

(1) the correction for the oxidation of FeO is often too high (i.e. oxidation is usually incomplete);

(2) some minerals such as apatite, epidote, and micas are reluctant to give up their water.

6. POINT COUNTING

Modal analyses were performed in conjunction with general textural and mineralogical examinations of thin sections.

Approximately 1000 points were counted for each thin section. It is seen from the modal compositions (Table BI) that the petrographic composition compliments the norm calculations (Table CVI). A high percentage of fine grained, quartzo-feldspathic groundmass accounts for the lower quartz+potash feldspar+albite values that were obtained when comparing the modal results with the normative results.

CHAPTER III

GENERAL PETROGRAPHY

Samples collected throughout the Mamainse Point study area are highly variable in mineralogy, texture, and colour. Most can be termed felsites, containing small quartz and feldspar phenocrysts set in an aphanitic, quartzo-feldspathic matrix with minor amounts of mica, carbonate, chlorite, and opaques. Most of these are altered rhyolites which grade to fresher rhyolites, rhyodacites, and dacites. Many show flow lamination and some, such as those from Cottrell Cove, have highly contorted flow bands and deeply mottled, altered feldspars. In contrast, samples from Hibbard Bay are fresher rhyodacites and dacites which do not show flow lamination. Still others are brecciated, containing angular to rounded fragments of felsite, granite, and basalt.

1. MINERALOGY (PHENOCRYSTS)

The phenocrysts are quartz, potash feldspar (mostly orthoclase with lesser amounts of sanidine and anorthoclase), and albite in highly varying proportions reflecting changes in differentiation and alteration to more potash feldspar-rich sections.

Quartz grains are colourless with low relief and are generally angular, corroded, and embayed in places. Occasionally quartz phenocrysts are quite euhedral in habit lacking any evidence of deformation. Fine grained, rounded, aggregates occur in veins and stringers in some sections. Phenocrystic quartz usually makes up 4-8% of the rock but it ranges up to 34%.

Potash feldspar crystals show good carlsbad twinning in cloudy, mottled grains with an anhedral to euhedral form. They range in size from 0.1-3.0 mm. diameter and make up anywhere from 1-20% of the rock, averaging 4-8%. They are commonly intergrown with albite, which is riddled with carbonate and sericite inclusions.

Albite ranges from 0-20% but is commonly 0-2% of the rock in small, altered grains, averaging 0.5-1.0 mm. in diameter. The crystals are colourless and anhedral to subhedral with some good albite and carlsbad twinning.

Chlorite averages 1% of the sections in colourless to pale green, pleochroic, scaly, acicular prisms which are often bent and show one good cleavage. Biotite is present rarely in deep brown, pleochroic, subhedral to euhedral plates. They are somewhat bent with one good cleavage.

MINERALOGY (GROUNDMASS)

The groundmass is a mixture of microcrystalline alkali feldspar and quartz with carbonate patches and minor accessories. Compositions and textures are quite variable. Graphic intergrowths of quartz and alkali feldspars are common; fine grained, acicular alteration by sericite and carbonate occurs sporadically in the sections along fractures and flow laminations: acicular, alteration minerals define a foliation with the flow bands in the felsic, devitrified matrix.

The opaques occur in highly variable proportions. Both magnetite and hematite usually make up less than 1% but can reach 6-10%, especially hematite in the more altered varieties. Magnetite grains average 0.2-0.3 mm. in diameter and are commonly rimmed by reddish, opaque to translucent hematite. Hematite tends to form in association with secondary mineralization (i.e. with chlorite and kaolin) in irregular grains and aggregates.

Carbonate ranges from 0-29% but is usually 5-6% of the section. It forms mainly along veins and fractures as irregular patches, and commonly pseudomorphs alkali feldspars. It shows extreme birefringence and some rhombohedral cleavage.

2. TEXTURES

Irregular fragments and crystals of altered alkali feldspar and rounded, corroded quartz are set in a fine grained quartzo-feldspathic matrix.

Varying degrees of alteration are seen. Plagioclase is commonly altered to albite, potash feldspar and sericite. Carbonatization and silicification are also common alterations. Mafic minerals such as pyroxene and amphibole have been all but completely replaced by chlorite and carbonate. The latest stage of alteration is represented by the replacement of alkali feldspar by kaolin.

Radiating, fibrous, spherulitic textures around inclusions and quartz grains are commonly preserved as well as perlitic cracks and glassy flow contortions. These latter textural features are outlined by chlorite, sericite, and carbonate. Other terms describing the textures seen are: microlitic, micropoikilitic, devitrified.

CHAPTER IV

GEOCHEMISTRY - DISCUSSION

1. COMPARISON WITH OTHER SILICIC VOLCANICS

An initial comparison was made with Mamainse Point samples and averages of silicic volcanic rocks to get an overall impression of the chemical compositions (Table CVII). From these data it is seen that there are some interesting contrasts between the rocks sampled and those values considered to represent averages of silicic volcanic rocks.

For example, SiO_2, H_2O, CO_2 are all high and CaO, Na_2O, K_2O are all low relative to average silicic volcanics. These differences can be explained by alteration processes that have affected Mamainse Point rhyolites involving low grade metamorphism and metasomatism, which is looked at in more detail in succeeding sections of this chapter.

Normative compositions are also quite different than those for average silicic volcanics. Quartz makes up 45.15%, compared with 19.6 to 31.1% for average silicic volcanics. This is attributed here to silicification. Albite and anorthite are relatively low in abundance at Mamainse Point. This is explained by potash metasomatism involving the

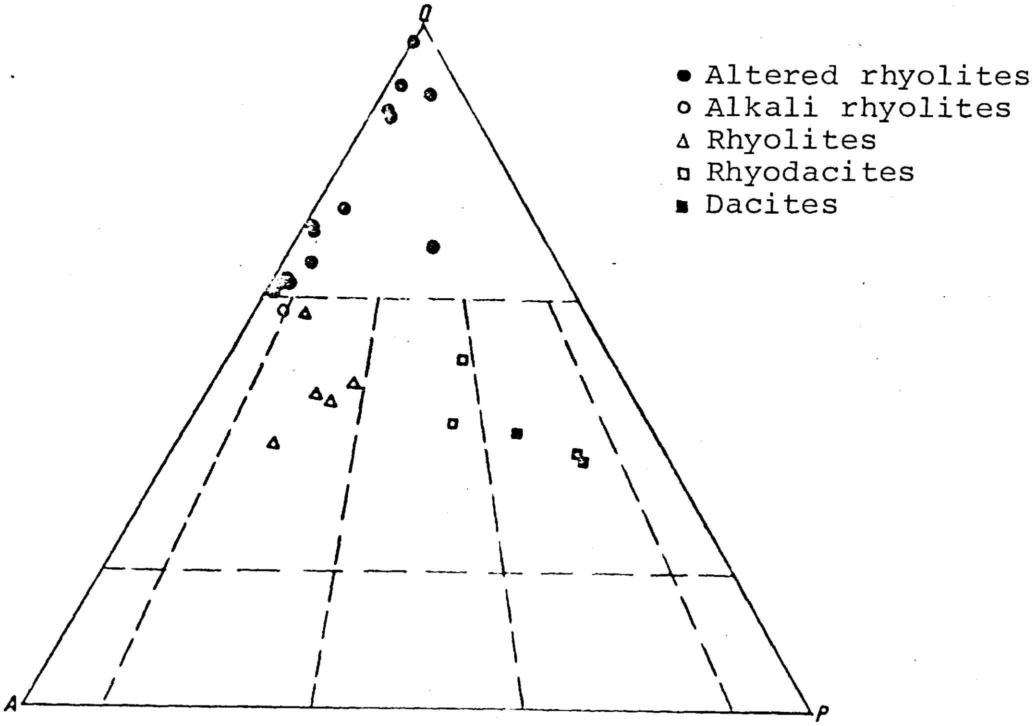

Figure 6. Classification of Volcanic Rocks According to their Quartz-Potash Feldspar-Albite Plagioclase Calculated Mineral Composition (Streckeisen, 1967).

Q = Quartz, A = Potash Feldspar,
P = Albite Plagioclase

enrichment in potash feldspar and depletion in albitic feldspar. The presence of corundum (probably representing kaolin), hematite, and calcite reflects the secondary mineral assemblage formed from alteration processes.

2. THE KERATOPHYRE QUESTION

Keratophyres are low grade, metamorphosed, silicic volcanics (Hughes, 1972) which have a somewhat different chemistry and mineralogy from their primary silicic volcanic equivalents.

Keratophyres are believed to be derived from:

(1) primary processes involving extrusion or shallow intrusion followed by cooling, and/or

(2) secondary processes involving lowest grade metamorphism.

The rocks studied in the Mamainse Point area could be considered to be derived from both primary and secondary processes, with a gradation from fresher varieties influenced mainly by primary processes, to more altered varieties that have undergone low grade metamorphism according to mineral assemblages and textural evidence seen in thin section.

Petrographically, these are quartz-albite-orthoclase volcanic rocks with an aphanitic groundmass of quartz and alkali feldspar. Chlorite, mica, calcite, and opaques are minor constituents. Femic phenocrysts are rare, occurring mostly as small grains in the groundmass which varies from devitrified to a coarser, recrystallized mosaic. Vitrophyric, spherulitic, and microlitic textures are common. The high content of potash feldspar would lead some authors to classify these rocks as "kalikeratophyres" (Lehmann, 1949). This term refers to the high potassium content and occurrence of quartz as phenocrysts in the keratophyre.

Albitization was not the only process of alteration at work on these rocks; silicification, potash enrichment, and enrichment in H_2O and CO_2 have also occurred.

On Hughes' keratophyre diagram (Figure 7), the samples plot outside of Hughes' igneous spectrum for compositions of fresh volcanic rocks, and fall within the potassic keratophyre spectrum. Therefore, these rocks should be termed keratophyres rather than rhyolites (which implies fresher, younger volcanic rocks). The dacites and rhyodacites plot within the igneous spectrum and can be considered fresher rocks that have been affected by secondary processes much less than the potassic keratophyres. The samples all plot on a fairly well defined trend upwards, showing a regular increase in alkalis. As total alkalis increase, potash/soda ratios increase to define spectrums. (Samples falling below the trend from dacite to rhyolite are altered rhyolites which have been depleted in potash and soda). The rocks that lie well off to the right of the igneous spectrum have therefore undergone metasomatism (Hughes, 1972). The suite

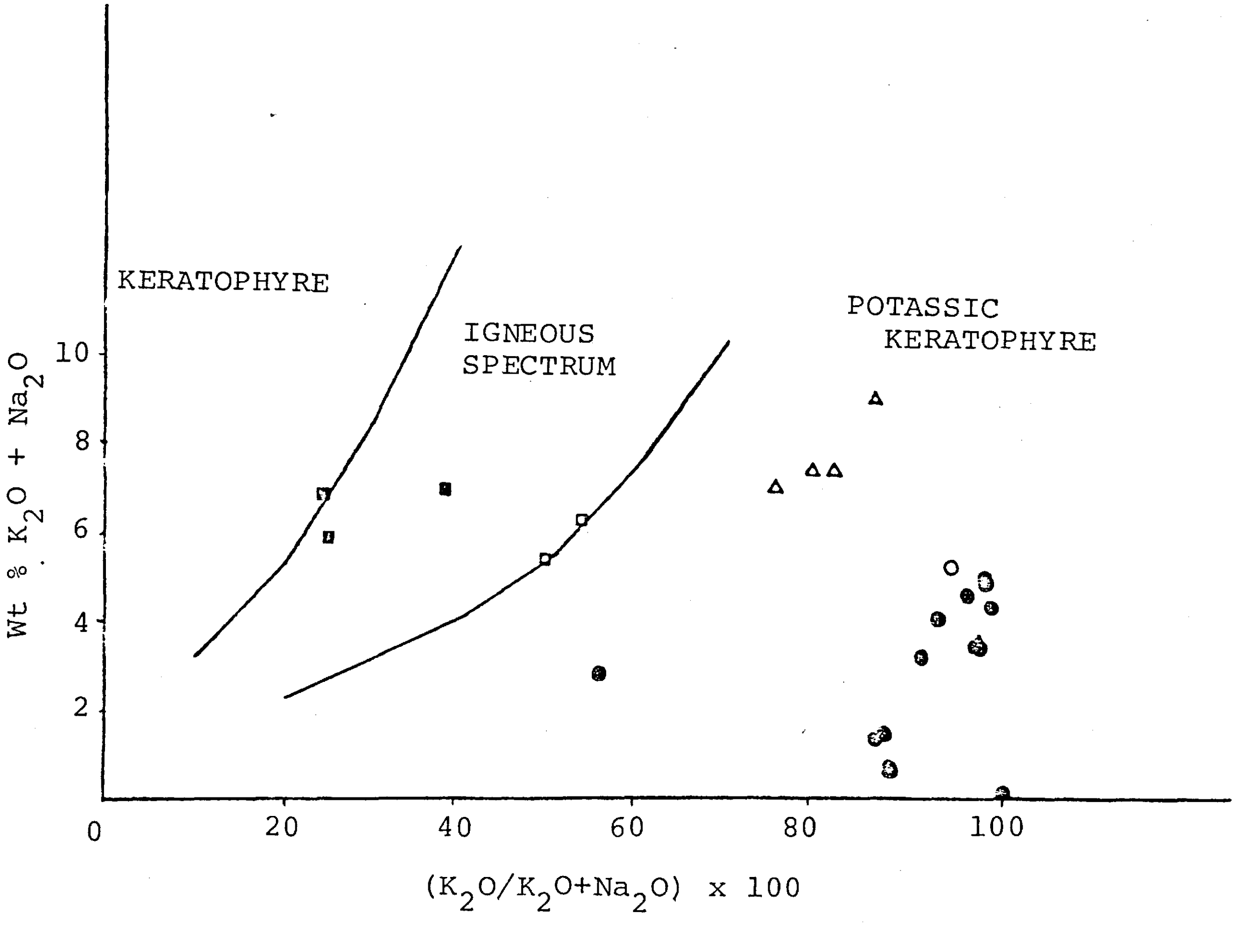

Figure 7. Plots of Alkali Parameters of Analyzed Volcanic Rocks (Hughes, 1972).

Legend same as in Figure 6.

shows a progressive enrichment of potash at the expense of soda in alkali feldspars.

3. TRACE ELEMENT DISTRIBUTION

Ba, Rb, and K show a sketchy regional variation in abundance. No systematic trend in distribution is well defined. The expected trend is a decrease in these elements towards the central or inner zone of the rhyolitic flows (Figure 8). This trend would be due to the inward migration of alkalis and volatiles (Hart et al., 1971) towards the central regions of flows. Ba/Rb ratios should decrease as the fractionation of potassium feldspar increases (Taubeneck, 1967). The general trend that is shown by these trace elements therefore indicates that Ba and Rb follow the general rules for isomorphous replacement of potassium in feldspars (Watkins et al., 1970), and that the movement of alkalis is directly due to differentiation.

Many trace elemental abundances show an anomalous distribution regionally which probably represents local alteration effects.

Trace element variation can also be explained by crystallization involving late stage alkali migration via liquids and/or volatiles.

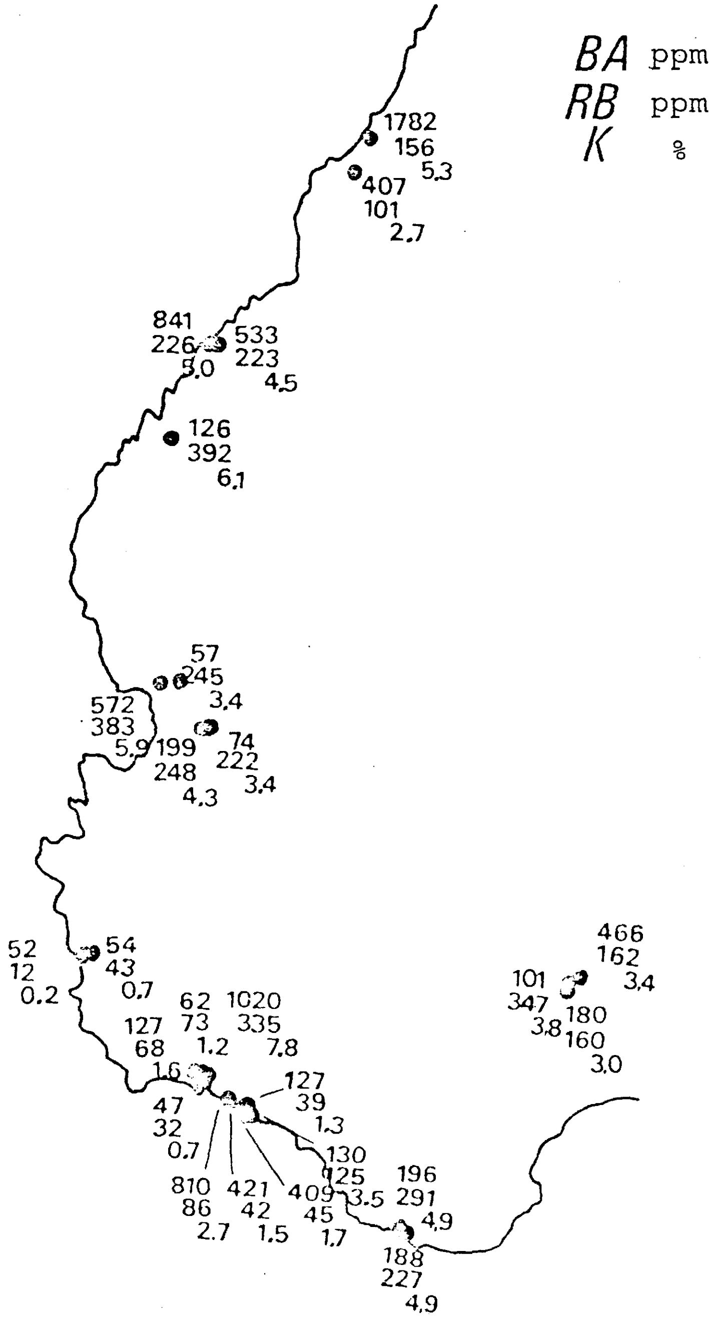

Figure 8. Areal Distribution of Ba, Rb, K (respectively) in Mamainse Point Rhyolites

4. TYPE OF METAMORPHISM

Metamorphic recrystallization is not seen in the field, but can be deduced from strong flow band cleavages. The adjustment of mineralogy that has taken place probably represents retrograde metamorphism, and is dependent upon:

(1) the access of H_2O and CO_2 in pore fluids to form low grade minerals such as chlorite, sericite, and carbonate;

(2) a sufficient rise in temperature to induce these chemical reactions.

A prograde temperature of up to 400°C is not necessary for these chemical reactions to proceed. Eskola found from models in Finland that temperatures as low as 264-331°C may be sufficient to initiate chemical reactions in an already unstable mineral assemblage (from Hughes, 1973). Therefore, keratophyres can be found below as well as within the lowest grade of greenschist facies metamorphism.

5. SINGLE MAGMATIC SOURCE?

This suite of rocks could represent one major magmatic source that underwent subsequent fractional crystallization to produce the various phase changes from dacite to alkali rhyolite.

Points for a Single Source:

(1) From Figure 6 it is seen that there is a gradation from dacite to rhyolite, an enrichment in quartz and a general clustering towards alkali feldspar rather than towards plagioclase feldspar. If alteration influences are ignored, this could be suggestive of a single magmatic source, with the increase in quartz in some samples representing fractional crystallization.

(2) An AFM plot (Figure 9) shows a well defined gradation from acid to less acid members which could be interpreted as being the result of fractional crystallization from a single magma.

(3) Rb is enriched relative to K in these rocks (Figure 10) and fairly good trends are seen by plotting K/Rb, Na/Rb, Sr/Rb vs. Rb (Figures 11,12,13; Table C-V). The ratios of K/Rb, Na/Rb, Sr/Rb increase with respect to Rb from rhyolites to rhyodacites to dacites as alteration of these rocks decreases. The ratios decrease and fall from the general trend for rhyolites which have been extremely altered. The overall trends would also seem to be consistent with the idea of a differentiated magma produced by a single magmatic source (Dostal, 1973).

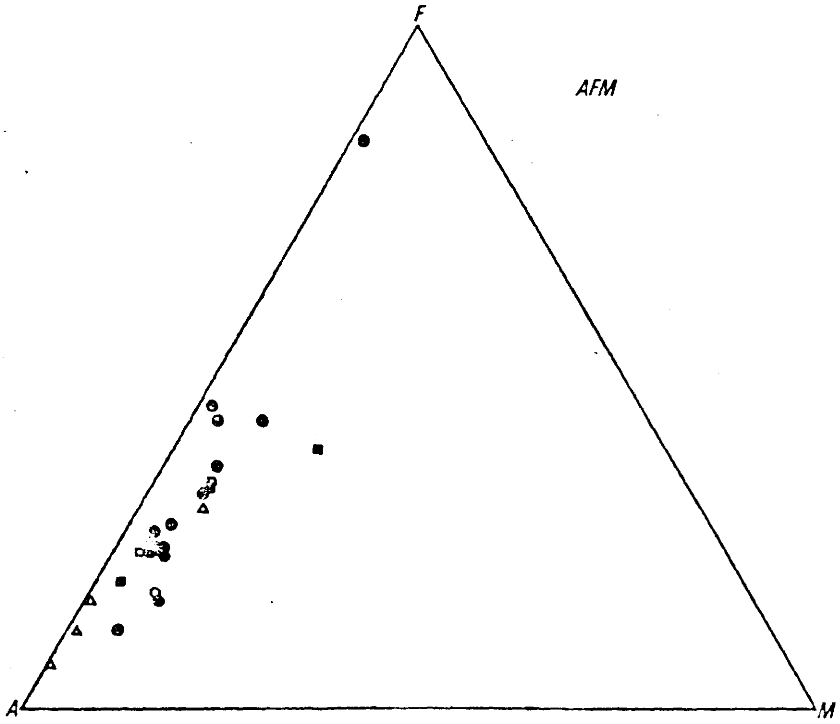

Figure 9. AFM Plot

$A = Na_2O + K_2O$, $F = FeO + Fe_2O_3$, $M = MgO$

Legend same as in Figure 6

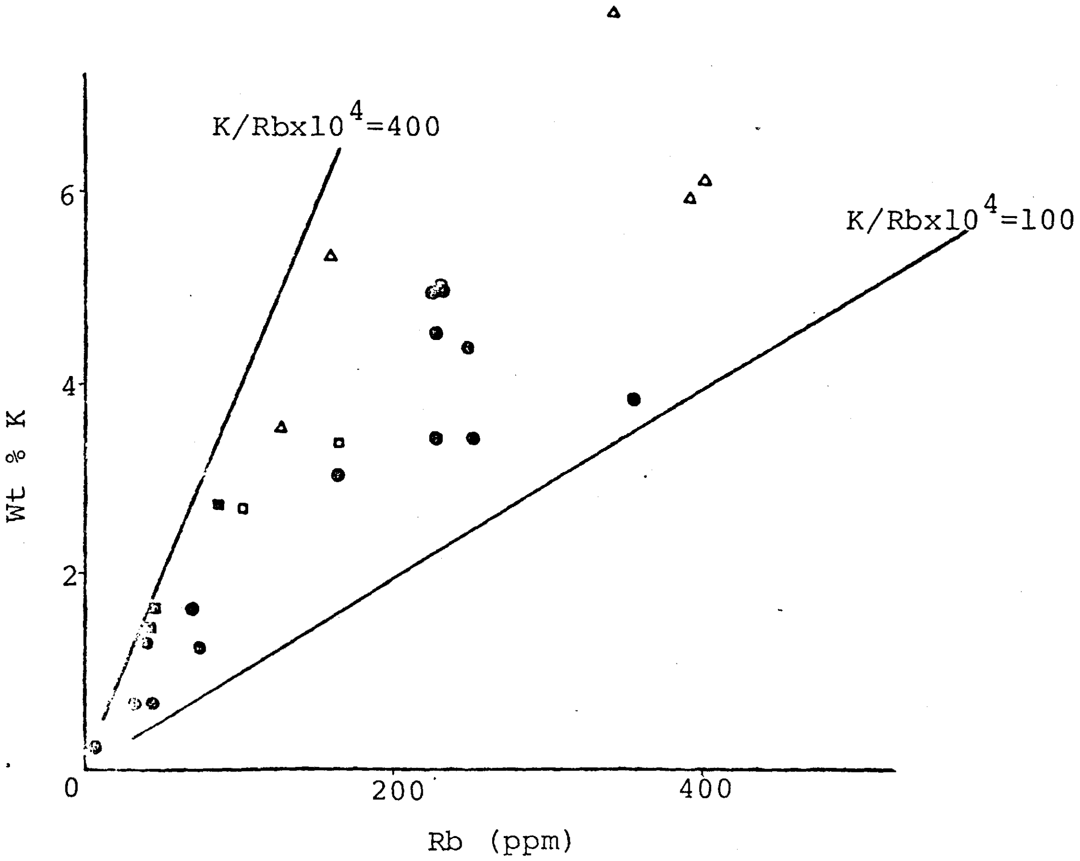

Figure 10. K versus Rb

Legend same as in Figure 6

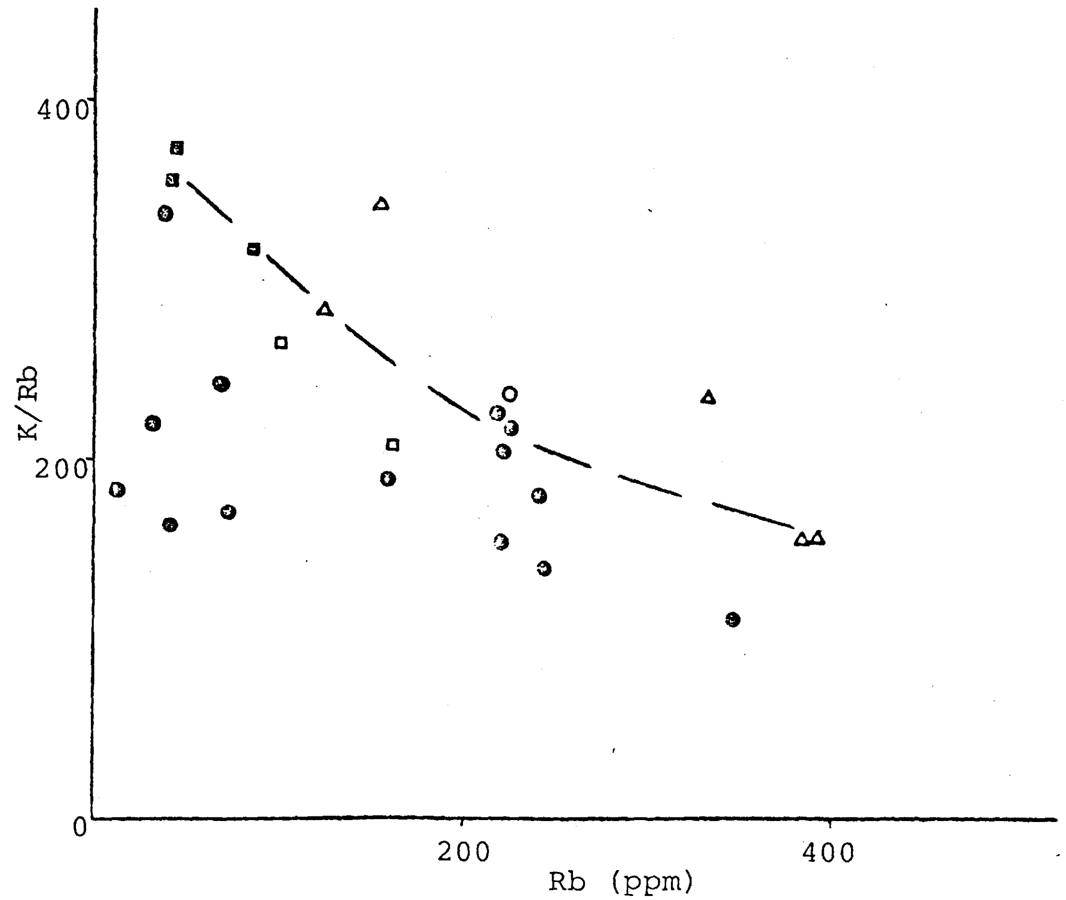

Figure 11. K/Rb versus Rb

Legend same as in Figure 6

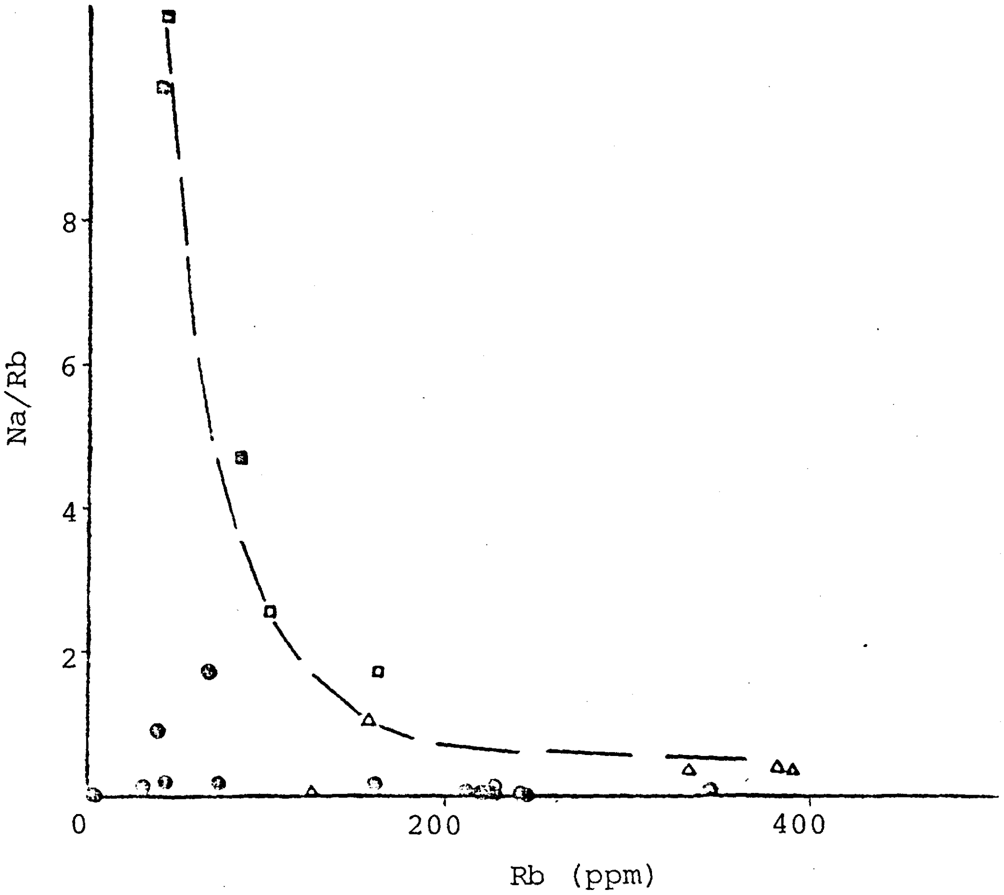

Figure 12. Na/Rb versus Rb

Legend same as in Figure 6

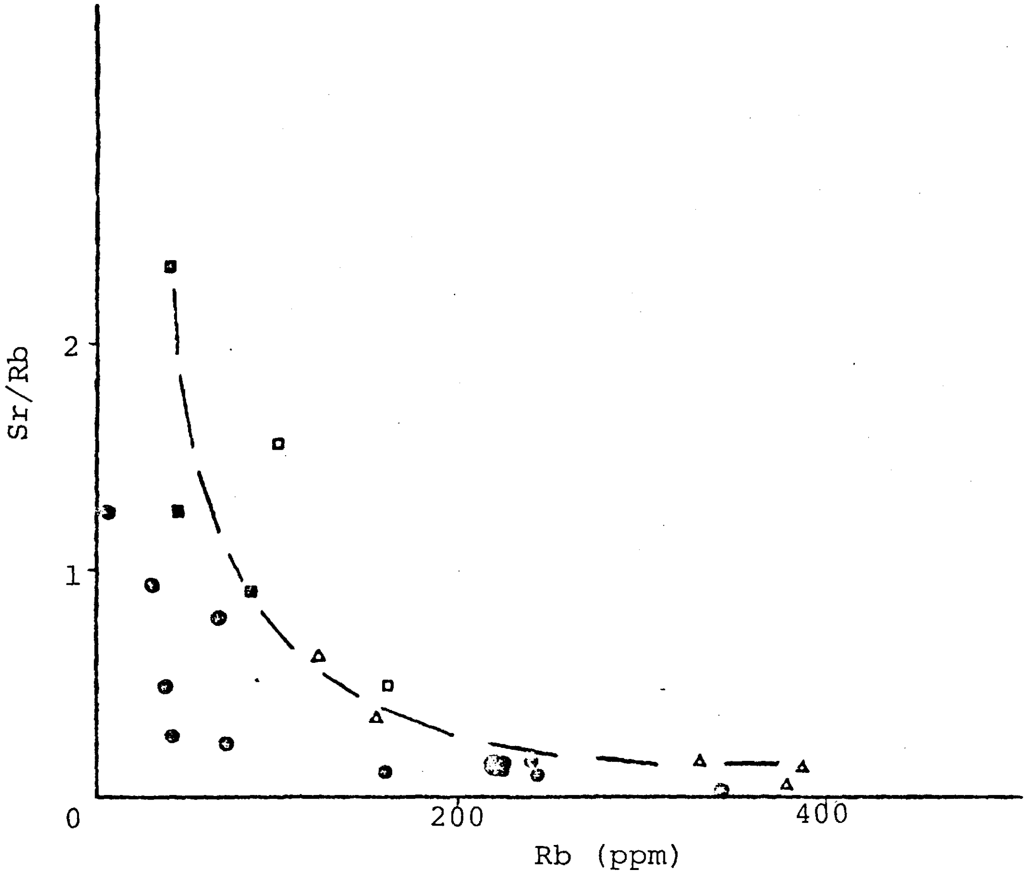

Figure 13. Sr/Rb versus Rb

Legend same as in Figure 6

Points Against a Simple Single Source Theory:

(1) The increase in quartz in some samples is probably due to alteration processes involving silicification. The clustering of feldspars towards alkali feldspar rather than plagioclase feldspar is probably the result of an enrichment in alkali elements via metasomatic migration.

(2) Through chemical analyses it is seen that the alkali elements were relatively mobile and that metasomatism must have had an important role in transforming these rocks. CaO, Na_2O, K_2O are commonly quite variable from one sample location to the next, which are quite close in proximity. There must have been, then, a highly variable influx and outflux of alkali elements over short distances. Therefore, there are more problems involved than just a simple, single, magmatic source.

(3) The relatively high K/Rb values and other alkali ratio trends are probably defining patterns of alteration from one rock type to the next, such as the enrichment of potassium forming potash feldspar and sericite.

From these points it is concluded that, although a single magmatic source is very probable, other important factors are involved in differentiation. Metasomatism must be looked at in order to try to sort out the sources and processes involved in the differentiation of this suite of rocks.

6. METASOMATISM

Original textures are preserved to some extent in these rocks. However, they are Proterozoic in age, and volcanic rocks almost always undergo significant changes in chemical composition over time. Therefore, it becomes difficult to classify these rocks in terms of original composition. The rhyodacites and dacites are much less altered than the more acid varieties though. This is probably partly due to their:

(1) occurrence in larger plutonic rock bodies relative to spot outcrops (i.e. MJR-15,16 in Figure 1);
(2) somewhat coarser grain size;
(3) lesser amounts of fine grained groundmass and glass, which readily react to form more potassium in other more acid varieties.

Chemical alteration involves albite pseudomorphing of a more calcic plagioclase, and chlorite pseudomorphing of clinopyroxene (Batley, 1955). Calcium is being released in this process to form secondary minerals. Therefore, calcium is highly mobile. Silica and alkalis are also extremely mobile (i.e. they show a high variation from sample to sample over small distances). For example, the following equation, first proposed by Goldschmidt in 1921, could represent late stage crystallization of these rocks involving the hydrolysis of orthoclase and an enrichment in potash:

$$3\text{Or} + 2H_2O \rightarrow 2\ \text{Musc.} + 2\ \text{Potash} + 12\ \text{Silica}$$ (from Billings, 1938)

Intense local alteration involved the depletion of alkalis and the addition of water and CO_2 to form kaolin (i.e. sample MJR-11).

It is therefore evident that these rocks have undergone metamorphism with accompanying metasomatism after extrusion and/or shallow intrusion followed by cooling. However, this may be too much of an over-generalization because:

(1) there may have been important additional metasomatism during the cooling of the flow units;

(2) there may have been a series of closely spaced magmatic events since metasomatism does not affect all of these rocks to the same extent. Indeed, some rocks appear to be completely unaffected by metasomatism according to their chemistry and and mineralogy (i.e. MJR-15 in Appendix C).

Given the field occurrences and chemical observations, the rocks probably belong to the same magmatic suite in general. They represent a sequence of silicic extrusive and shallow intrusive rocks that have been buried to a sufficient depth where a temperature of from 200-400°C has generated recrystallization and limited alkali and lime mobility. Equilibrium was approached under relatively low temperatures with the introduction of H_2O and CO_2 via pore fluids and/or volatiles.

CHAPTER V

SUMMARY AND CONCLUSIONS

(1) Field evidence indicates that these are largely shallow intrusive rocks; some are probably extrusive as well.

(2) Mineralogy, textures, and chemistry show that these rocks are potassic keratophyres: low grade metamorphosed silicic volcanics.

(3) There has been a significant enrichment in potash as a result of potash metasomatism.

(4) Relative mobility of the alkali elements represents magmatic differentiation in general and late stage migration via liquids and/or volatiles specifically. Local enrichment and depletion in these elements suggests intense local alteration.

(5) Low grade, retrograde metamorphism has accompanied metasomatism due to:

- (a) a significant rise in temperature during burial;
- (b) introduction of H_2O and CO_2 in pore fluids forming a secondary mineral assemblage (chlorite, carbonate, sericite).

(6) A single magmatic source is probable; there may have been a series of closely spaced magmatic events, but if so, they would have to be considered to be strongly related to a single magma source.

SUGGESTIONS FOR FURTHER WORK

(1) A more detailed investigation of elements, particularly with respect to alteration processes, is needed in order to more fully understand the processes forming potash feldspar, kaolin, etc.

(2) Better control on regional trends of trace elements and other mobile alkali elements could be attained with a much larger, concentrated sampling procedure.

(3) Sr^{87}/Sr^{86} dating could be used to correlate the age and source of these keratophyres with their associated spilites.

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APPENDIX A

FIELD OCCURRENCES

See Figure 1 for sample locations

MJR-1,2:	Kincaid Location 6, Kincaid Township. Quartz porphyry dike; small, isolated, poorly exposed spot outcrop.
MJ-TS-1:	Kincaid Location 7, Kincaid Township. Rhyolitic tuff; small, isolated, poorly exposed and badly weathered spot outcrop.
MJR-3:	Mamainse Point Area (north). Shallow intrusive felsite; flow banded, brecciated near mafic contact.
MJR-5:	Mamainse Point Area (north) Shallow intrusive felsite; massive whitish-grey portion.
MJR-6:	Munising Wood Products Sawmill (along stream), northwest of "Lutz" vein, Mamainse Point Area (north). Shallow intrusive felsite; massive, reddish to dark red, relatively fresh.
MJR-7,8:	Due east of Hibbard Bay, Mamainse Point Area. Shallow intrusive felsite; grades from whitish-pink to greyish-green in colour, poorly exposed along bush road.

MJR-9: Due west of Silver Creek Zone, Mamainse Point Area. Shallow intrusive felsite; fresh, brittle, pinkish-red.

MJ-TS-2: Due west of Silver Creek Zone, Mamainse Point Area. Shallow intrusive felsite; near basaltic contact, greyish-green, poorly exposed and badly weathered.

MJR-10: Rousseau ld. kaolin trenches near Coppermine Pt. on the old highway, Maminse Point Area. Shallow intrusive felsite; large exposure of white to grey to pink rock, crumbly outcrop, kaolinized and hematized in part.

MJR-11: Rousseau ld. kaolin trenches near Coppermine Pt. on the old highway, Mamainse Point Area. Shallow intrusive felsite; highly altered: extremely soft, crumbly outcrop, hematized, whitish-grey patches of kaolin.

MJR-12: Cottrell Cove North, Mamainse Point Area. Shallow intrusive felsite; massive portion of a large plug outcrop.

MJR-13: Cottrell Cove North, Mamainse Point Area. Shallow intrusive felsite; extremely flow banded and altered section of a large plug outcrop.

MJ-TS-3: Cottrell Cove North, Mamainse Point Area.
Shallow intrusive felsite; autobrecciated zone contacting basaltic rocks.

MJ-TS-4: Cottrell Cove North, Mamainse Point Area.
Shallow intrusive felsite; copper sulphide mineralization zone within the large plug outcrop.

MJR-14: Cottrell Cove North, Mamainse Point Area.
Felsite dike; adjacent to felsite plug, cross-cuts basaltic lavas, secondary mineralization and autobrecciation.

MJR-15,16: Cottrell Cove (near the Black Forest Motel), Mamainse Point Area.
Shallow intrusive felsite; fresh, pinkish-red, coarser grained variety.

MJR-17: Cottrell Cove South, Mamainse Point Area.
Shallow intrusive felsite; contorted flow banded central portion of outcrop.

MJR-18: Cottrell Cove South, Mamainse Point Area.
Shallow intrusive felsite; autobrecciated contact zone of felsite outcrop near the basaltic contact.

MJR-19:	Cottrell Cove South, Mamainse Point Area. Shallow intrusive felsite; funnel-shaped, brecciated, highly altered vein within a large outcrop.
MJR-20:	Micro-wave Relay Tower, Due North of Pancake Bay, Ryan Township. Shallow intrusive felsite (possibly extrusive); pinkish-red, relatively fresh, near basaltic contact.
MJR-21,22c:	Micro-wave Relay Tower, Due North of Pancake Bay, Ryan Township. Extrusive felsite; concordant contact with conglomerate unit, shows chill skin surface and vesicular top.
MJR-22a, 22b:	Sawpit Bay, Ryan Township. Shallow intrusive felsite; crumbly, flow banded, reddish variety grading to whitish-grey variety.

APPENDIX B

SELECTED PETROGRAPHIC DESCRIPTIONS AND SKETCHES OF DISTINCT MINERALOGICAL AND TEXTURAL PHASES

SAMPLE MJ-TS-1

FIELD NAME:	WELDED TUFF
CHEMICAL CLASSIFICATION:	RHYODACITE

DESCRIPTION:

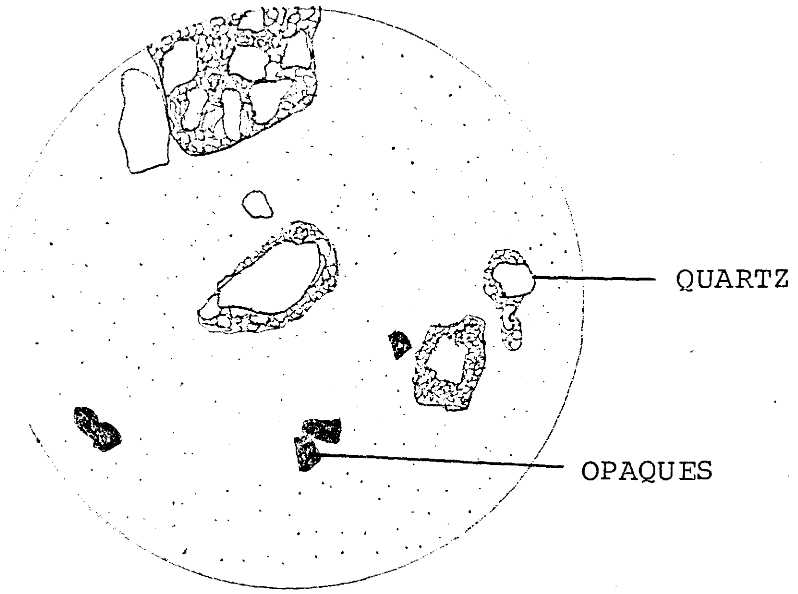
Some quartz crystals and aggregates are cemented with patches of matrix, which suggests a pyroclastic origin. The quartzofeldspathic matrix is highly altered to carbonate and sericite giving the rock a dark, aphanitic appearance.

SAMPLE MJR-1,2

FIELD NAME:	QUARTZ-FELDSPAR PORPHYRY
CHEMICAL CLASSIFICATION:	RHYOLITE

DESCRIPTION:

Quartz crystals are corroded, embayed, and very irregular in habit. Potash feldspar phenocrysts are cloudy, subhedral to anhedral in form, and altered to sericite and carbonate in part. Potash feldspars are also intergrown with and included by albite, and are intergrown with quartz in graphic intergrowths.



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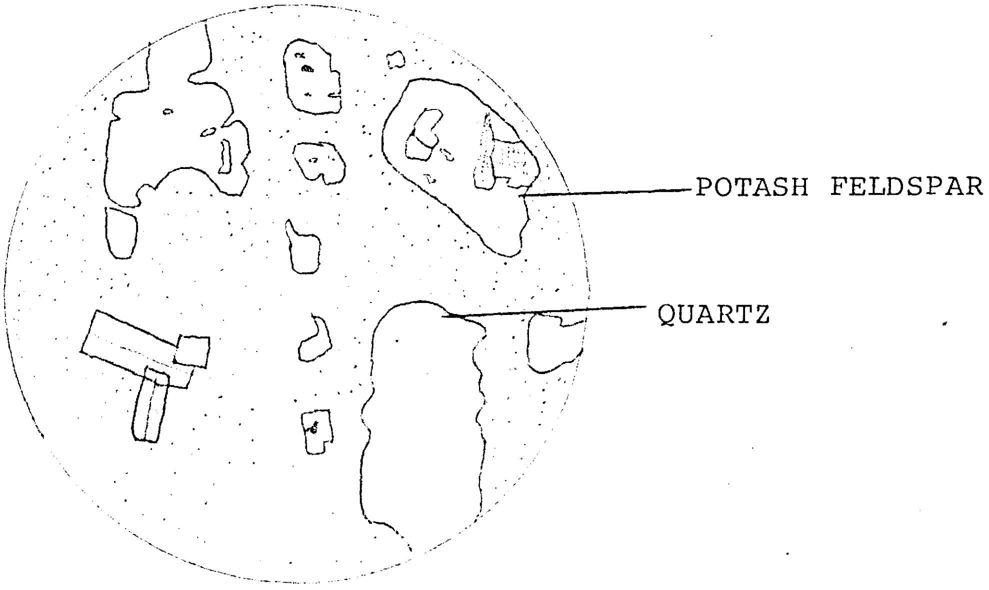

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SAMPLE MJR-5

FIELD NAME: FLOW BANDED RHYOLITE

CHEMICAL CLASSIFICATION: ALTERED RHYOLITE

DESCRIPTION:

This sample contains irregular, corroded, and embayed quartz fragments set in a flow banded, aphanitic, quartzofeldspathic matrix. The glassy flow bands are somewhat contorted and highly altered to sericite and carbonate.

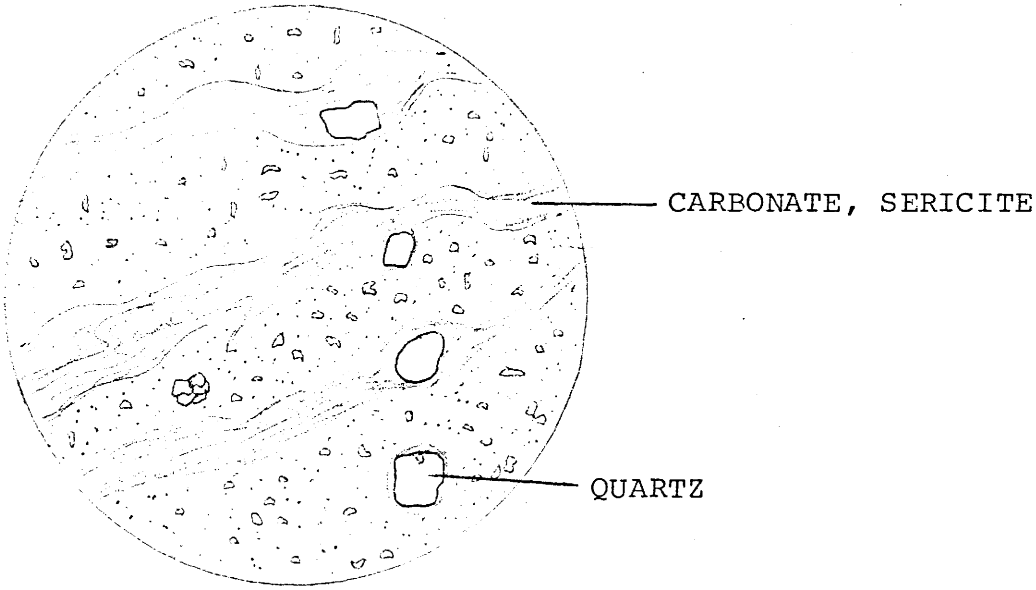
SAMPLE MJR-7

FIELD NAME: FLOW BANDED RHYOLITE

CHEMICAL CLASSIFICATION: ALTERED RHYOLITE

DESCRIPTION:

This sample contains large embayed and included quartz phenocrysts as well as numerous aggregates of partially altered, well rounded quartz grains. The flow bands are much thinner and more parallel than those in sample MJR-5, and highly altered to sericite and carbonate like those in sample MJR-5.



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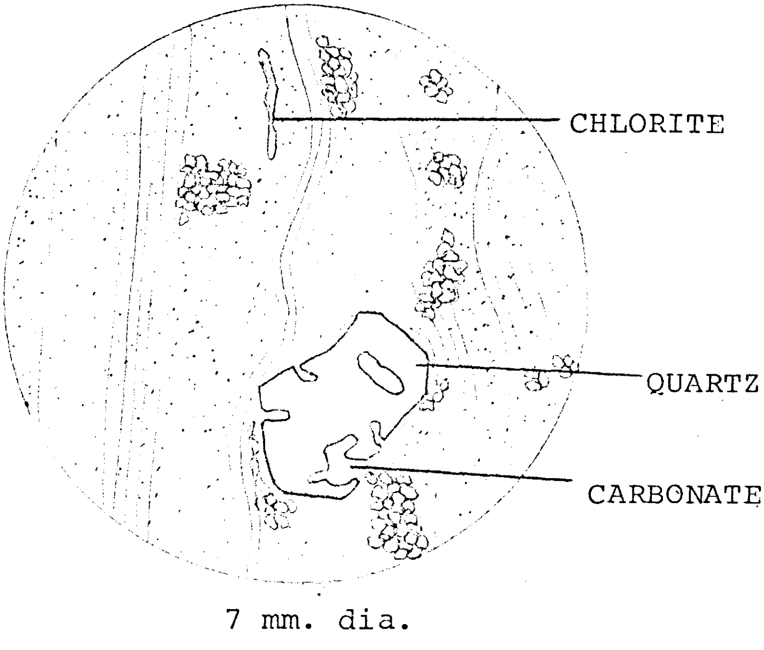

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SAMPLE MJR-11

FIELD NAME: ALTERED, KAOLINIZED RHYOLITE

CHEMICAL CLASSIFICATION: ALTERED RHYOLITE

DESCRIPTION:

Large, irregular patches of calcite are altered and rimmed by hematite and kaolin, and included by these secondary minerals in places along fractures and veins cut into the calcite. The matrix is rich in fine grained quartz, sericite, and carbonate; a few remnants of alkali feldspar grains are just slightly recognizeable.

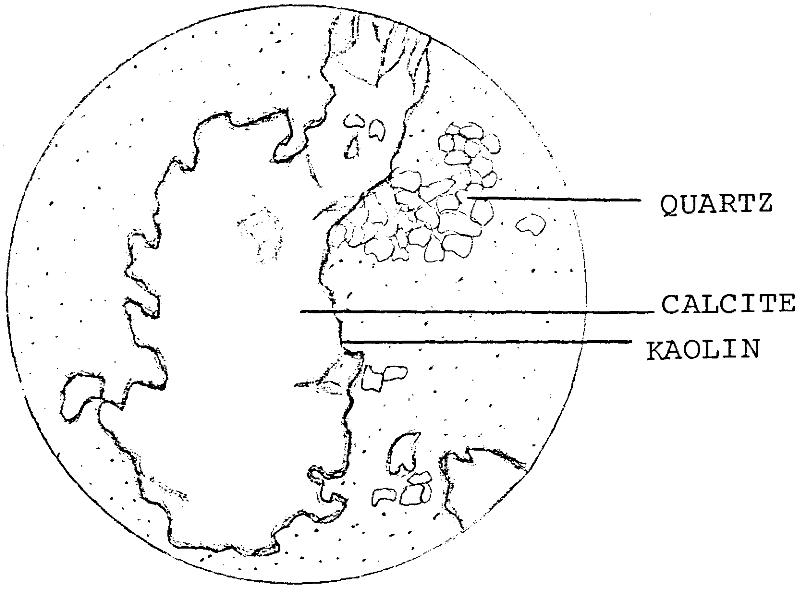
SAMPLE MJR-15

FIELD NAME: RELATIVELY FRESH RHYOLITE

CHEMICAL CLASSIFICATION: DACITE

DESCRIPTION:

Zoned, albite phenocrysts are intergrown with lesser amounts of potash feldspar in chequered textures. There are also common graphic intergrowths of quartz and feldspar. Sericite and carbonate replace and totally pseudomorph some feldspars.



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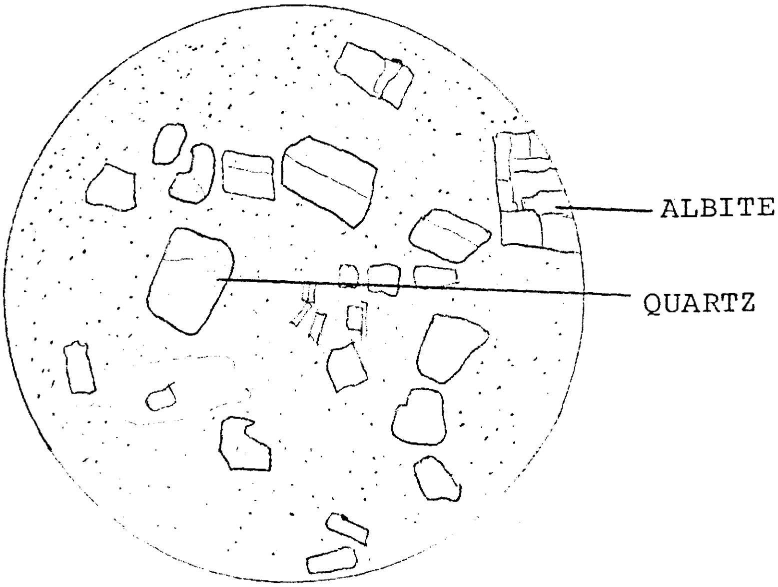


7 mm. dia.

SAMPLE MJ-TS-4

FIELD NAME: COPPER MINERALIZED RHYOLITE

CHEMICAL CLASSIFICATION: NOT ANALYZED

DESCRIPTION:

An oriented patchwork of veins, stringers, and disseminations of copper sulphides cut through the highly altered, quartzofeldspathic matrix. A few scattered quartz phenocrysts are seen, some of which show deformational textures (i.e. numerous fractures and microfaults).

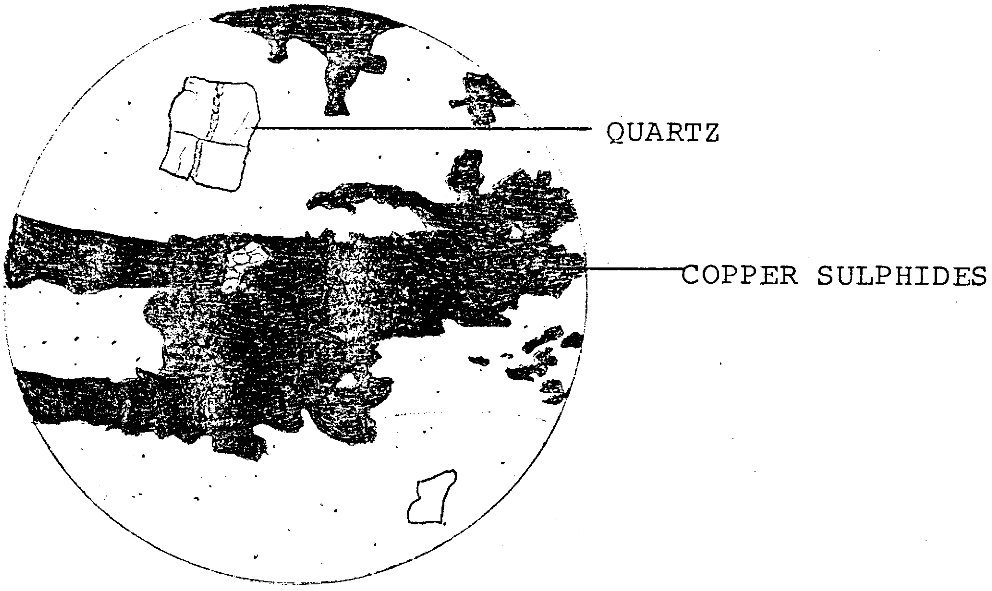
SAMPLE MJ-TS-3

FIELD NAME: RHYOLITE BRECCIA

CHEMICAL CLASSIFICATION: ALTERED RHYOLITE

DESCRIPTION:

Basaltic and rhyolitic rock fragments measuring 0.5 to 5.0 mm. in diameter are set haphazardly in a quartzofeldspathic matrix. The rock fragments have been largely altered to carbonate.



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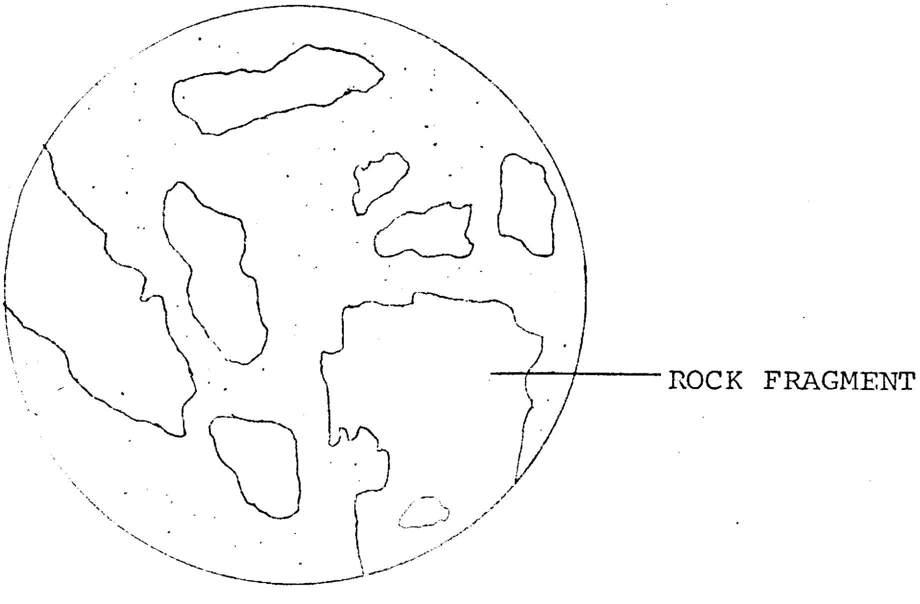

7 mm. dia.

Table B-I. Modal Analyses %

	ALTERED RHYOLITES														ALKALI RHYOLITE	RHYOLITES					RHYODACITES		DACITES		
	MJR-5	MJR-7	MJR-8	MJR-10	MJR-11	MJR-12	MJR-13	MJR-17	MJR-21	MJR-22a	MJR-22b	MJR-22c	MJ-TS2	MJ-TS3	MJR-3	MJR-1,2	MJR-6	MJR-9	MJR-14	MJR-19	MJR-20	MJ-TS	MJR-15	MJR-16	MJR-18
PHENOCRYSTS:																									
Quartz	8	8	14	30	20	22	2	4	17	4	5	9	7	4	6	34	5	6	5	5	9	8	6	8	8
Potash Feldspar	2	2	5	4		5		2	8	6	7	4	2	2	2	13	2	3	3	10	16	14	5	4	7
Albite																5				16	10	8	13	11	21
Carbonate	7	8	5	16	29	10	2	13	18	2	2	15	11	22	21		5	8	7	14	8	14	2	7	6
Chlorite		1	1	1	1	1		2	1	2	2			1			1	1	1	1			2	2	1
Magnetite		1	1	1	1	1		1	2					5		1	1	2	2	1	2	1	2	4	1
Hematite		1	1	2	2	3		4	2	1	1	1	1	2	1			1	1	2	1	2	1	2	5
QUARTZO-FELDSPATHIC MATRIX	83	79	73	46	47	58	96	74	52	85	83	71	79	67	70	47	86	79	81	51	54	53	69	62	51

APPENDIX C

GEOCHEMICAL DATA

Tables C-I & II. XRF Precision

Table C-I

	MJR-6(1)	MJR-6(2)	MJR-6(3)
SiO_2	76.39	76.53	76.52
TiO_2	0.11	0.11	0.10
Al_2O_3	12.67	12.79	12.69
Fe_2O_3*	1.47	1.41	1.46
MnO	0.03	0.03	0.03
MgO	0.12	0.12	0.10
CaO	1.18	1.12	1.16
Na_2O	1.42	1.42	1.41
K_2O	6.46	6.40	6.39
P_2O_5	0.00	0.00	0.00
Total	99.85	99.83	99.86

Table C-II

	MJR-6(1)	MJR-6(2)	MJR-6(3)
SiO_2	76.39	76.49	76.26
TiO_2	0.11	0.09	0.11
Al_2O_3	12.67	12.79	12.84
Fe_2O_3*	1.47	1.40	1.44
MnO	0.03	0.03	0.03
MgO	0.12	0.11	0.12
CaO	1.18	1.24	1.15
Na_2O	1.42	1.33	1.51
K_2O	6.46	6.51	6.31
P_2O_5	0.00	0.00	0.00
Total	99.85	99.99	99.77

*Fe_2O_3 as total iron

Table C-III. AAS Precision

Ba	expected	experimental	Li	expected	experimental
ON-64	.031	.023	ON-64	21.8	23.0
SY-2	.051	.047	SY-2	86.0	85.2
BCR-1	.068	.073	BCR-1	12.8	12.4

Table C-IV. Major Oxide and Trace Element Variation*

	ALTERED RHYOLITES														ALKALI RHYOLITE	RHYOLITES					RHYODACITES		DACITES		
	MJR-5	MJR-7	MJR-8	MJR-10	MJR-11	MJR-12	MJR-13	MJR-17	MJR-21	MJR-22a	MJR-22b	MJR-22c	MJ-TS2	MJ-TS3	MJR-3	MJR-1,2	MJR-6	MJR-9	MJR-14	MJR-19	MJR-20	MJ-TS1	MJR-15	MJR-16	MJR-18
SiO_2	72.33	74.85	75.55	75.25	72.34	69.92	79.35	81.94	76.62	79.59	77.60	81.76	75.56	56.65	75.30	76.32	75.67	78.16	76.03	50.76	72.77	71.60	76.89	67.89	73.31
TiO_2	0.10	0.11	0.12	0.08	0.34	0.07	0.11	0.15	0.07	0.13	0.13	0.12	0.09	0.52	0.10	0.31	0.11	0.08	0.09	0.17	0.24	0.44	0.16	0.50	0.35
Al_2O_3	11.81	12.52	12.02	11.04	13.32	11.36	10.18	9.56	12.12	11.74	12.38	10.27	11.45	10.34	11.11	12.27	12.56	12.03	12.41	13.38	14.06	13.25	12.17	12.52	13.14
Fe_2O_3	0.90	1.11	1.13	1.15	0.37	2.20	0.96	0.41	2.81	0.60	1.84	1.45	1.15	2.41	0.98	1.44	1.02	0.68	0.49	1.25	1.15	2.45	0.90	2.10	3.14
FeO	0.13	0.30	0.23	0.09	0.06	0.15	0.11	0.10	0.80	0.06	0.09	0.15	0.11	1.85	0.10	0.93	0.44	0.10	0.12	0.41	0.82	0.64	0.79	3.14	0.57
MnO	0.04	0.04	0.04	0.03	0.04	0.04	0.03	0.03	0.05	0.03	0.04	0.03	0.04	0.05	0.04	0.04	0.03	0.30	0.03	0.08	0.04	0.05	0.05	0.13	0.04
MgO	0.59	0.25	0.20	0.00	0.09	0.11	0.13	0.13	0.82	0.40	0.43	0.38	0.35	0.13	0.56	0.40	0.12	0.09	0.08	0.48	0.32	0.65	0.34	2.52	0.90
CaO	1.04	2.61	3.04	4.72	4.72	6.10	2.92	2.03	0.15	0.29	0.27	0.20	3.31	13.30	2.18	0.21	1.17	0.38	0.69	14.55	1.61	2.36	0.64	2.07	0.35
Na_2O	0.22	0.14	0.11	0.00	0.10	1.26	0.16	0.19	0.30	0.10	0.06	0.32	0.07	0.05	0.31	1.77	1.40	1.60	1.32	0.07	2.94	2.75	4.38	4.47	5.31
K_2O	4.45	4.28	3.37	0.22	0.68	1.61	1.24	1.29	3.77	4.87	4.88	2.98	3.36	0.68	4.90	5.28	6.03	5.86	7.78	3.40	3.33	2.64	2.72	1.47	1.67
P_2O_5	0.00	0.01	0.00	0.00	0.02	0.00	0.01	0.03	0.00	0.01	0.02	0.01	0.01	0.05	0.00	0.04	0.00	0.01	0.00	0.14	0.06	0.09	0.03	0.07	0.05
H_2O	1.35	1.07	0.94	0.49	2.48	1.76	2.04	1.55	0.77	1.06	0.99	1.34	0.93	2.23	1.98	0.46	0.68	0.35	0.38	2.25	0.74	0.63	0.31	1.04	0.50
CO_2	1.63	2.78	3.33	7.03	5.68	5.60	3.22	2.70	1.77	1.16	1.33	1.05	3.65	12.25	2.45	0.55	0.81	0.65	0.59	12.60	1.95	2.48	0.65	2.14	0.68
Total	100.09	100.07	100.08	100.10	100.24	100.18	100.46	100.11	100.05	100.04	100.06	100.06	100.08	100.51	100.01	100.02	100.04	100.29	100.01	100.54	100.03	100.03	100.03	100.06	100.01
Li ppm	43	75	78	99	74	197	87	872	26	50	49	213	20	88	41	11	24	8	36	201	15	9	39	54	39
Ba ppm	533	199	74	52	54	127	62	127	101	196	188	180	57	47	841	1782	126	572	1020	130	466	407	810	421	409
Rb ppm	223	242	222	12	43	68	73	39	347	219	227	160	245	32	226	156	392	383	335	125	162	101	86	42	45
Sr ppm	29	39	38	15	12	55	18	20	10	33	37	17	25	31	30	55	51	19	53	80	83	156	81	99	57

*weight percent

Table C-V. Alkali Ratio Variation

	Li/Rb	Ba/Rb	Na/Rb	K/Rb	Sr/Rb
ALTERED RHYOLITES					
MJR-5	0.19	2.4	9.9	203.1	0.13
MJR-7	0.31	0.82	5.8	178.9	0.16
MJR-8	0.35	0.33	5.0	153.2	0.17
MJR-10	8.3	4.3	0	183.3	1.3
MJR-11	1.7	1.3	23.3	162.8	0.28
MJR-12	2.9	1.9	189.7	241.2	0.81
MJR-13	1.2	0.85	21.9	169.9	0.25
MJR-17	22.4	3.3	48.7	335.9	0.51
MJR-21	0.07	0.29	8.6	109.5	0.03
MJR-22a	0.23	0.90	4.6	224.7	0.15
MJR-22b	0.21	0.83	2.6	217.2	0.16
MJR-22c	1.3	1.1	20.0	188.8	0.11
MJ-TS2	0.08	0.23	2.9	138.4	0.10
MJ-TS3	2.8	1.5	15.6	218.8	0.97
ALKALI RHYOLITE					
MJR-3	0.18	3.72	14.2	234.5	0.13
RHYOLITES					
MJR-1,2	0.071	11.42	114.10	339.74	0.35
MJR-6	0.06	0.32	36.0	154.9	0.13
MJR-9	0.02	1.5	41.8	153.5	0.05
MJR-14	0.11	3.1	39.4	233.1	0.16
MJR-19	1.6	1.0	5.6	281.6	0.64
RHYODACITES					
MJR-20	0.09	2.9	182.7	207.4	0.51
MJ-TS1	0.09	4.0	274.3	263.4	1.6
DACITES					
MJR-15	0.45	9.4	510.5	317.4	0.94
MJR-16	1.3	10.0	1076.2	354.8	2.4
MJR-18	0.87	9.1	1186.7	373.3	1.3

Table C-VI. Norm Calculations %

	ALTERED RHYOLITES														ALKALI RHYOLITE	RHYOLITES					RHYODACITES		DACITES		
	MJR-5	MJR-7	MJR-8	MJR-10	MJR-11	MJR-12	MJR-13	MJR-17	MJR-21	MJR-22a	MJR-22b	MJR-22c	MJ-TS2	MJ-TS3	MJR-3	MJR-1,2	MJR-6	MJR-9	MJR-14	MJR-19	MJR-20	MJ-TS1	MJR-15	MJR-16	MJR-18
Qtz	49.14	46.67	50.39	59.58	53.26	45.75	62.86	65.34	48.89	50.85	48.29	59.18	50.97	41.31	47.29	39.62	38.11	41.15	34.55	33.80	33.78	36.48	35.70	25.69	30.11
Or	27.70	26.40	20.80	1.35	4.25	9.90	7.65	8.10	23.35	30.15	30.30	18.65	20.70	4.20	30.45	32.15	36.75	35.59	47.10	20.75	20.10	15.97	16.25	8.81	9.96
Ab	2.05	1.30	1.00	0.00	0.95	11.85	1.50	1.80	2.80	0.95	0.55	3.00	0.65	0.45	2.96	16.41	13.72	14.72	12.10	3.95	26.90	25.27	39.73	40.61	48.11
Cor	7.65	8.74	9.35	12.30	14.34	8.59	9.77	9.10	8.66	7.23	8.02	7.57	8.79	10.97	6.09	4.11	3.90	3.44	2.05	9.51	6.25	6.55	2.24	3.94	2.86
Hyp	1.78	0.78	0.64	0.04	0.32	0.38	0.44	0.44	2.44	1.18	1.30	1.16	1.06	0.44	1.68	0.09	0.34	0.30	0.10	1.38	0.96	0.16	0.95	8.63	1.33
Mgt	0.30	0.48	0.27	0.03	0.00	0.21	0.03	0.00	1.80	0.00	0.00	0.09	0.06	2.90	0.12	1.56	0.88	0.14	0.16	0.00	1.30	0.70	0.95	2.22	0.69
Ilm	0.14	0.16	0.18	0.12	0.30	0.10	0.16	0.19	0.10	0.14	0.16	0.18	0.14	0.76	0.14	0.44	0.16	0.11	0.13	0.77	0.34	0.62	0.22	0.71	0.49
Hem	0.39	0.49	0.64	0.82	0.27	1.46	0.68	0.31	0.85	0.44	1.35	1.01	0.80	0.00	0.70	0.00	0.15	0.39	0.24	0.90	0.00	1.28	0.00	0.00	1.75
Ap	0.00	0.02	0.00	0.00	0.04	0.00	0.02	0.07	0.00	0.02	0.04	0.02	0.02	0.11	0.00	0.09	0.00	0.02	0.00	0.29	0.13	0.19	0.06	0.15	0.11
Ct	10.85	14.96	16.73	25.76	26.27	21.76	16.89	14.65	11.11	9.04	9.99	9.14	16.81	38.86	10.57	5.53	5.99	4.14	3.57	28.65	10.24	12.78	3.90	8.62	4.59

Table C-VII. Averages of Silicic Volcanic Rocks (Nockolds, 1954)

	ALKALI RHYOLITES (21)	RHYOLITES (22)	RHYODACITES (115)	DACITES (50)	MAMAINSE PT. VOLCANICS (25)
OXIDES (wt.%)					
SiO_2	74.57	73.66	66.27	63.58	74.71
TiO_2	0.17	0.22	0.66	0.64	0.23
Al_2O_3	12.58	13.45	15.39	16.67	12.11
Fe_2O_3	1.30	1.25	2.14	2.24	1.39
FeO	1.02	0.75	2.23	3.00	0.50
MnO	0.05	0.03	0.07	0.11	0.05
MgO	0.11	0.32	1.57	2.12	0.42
CaO	0.61	1.13	3.68	5.53	2.90
Na_2O	4.13	2.99	4.13	3.98	1.18
K_2O	4.73	5.35	3.01	1.40	3.35
P_2O_5	0.07	0.07	0.17	0.17	0.03
H_2O	0.66	0.78	0.68	0.56	1.15
CO_2	*	*	*	*	2.97
Li ppm[a]	51±12	*	*	*	98
Ba ppm[b]	118	1127	1210	629	359
Rb ppm[c]	*	217	*	97	168
Sr	*	*	*	*	46
NORMATIVE COMPOSITION (%)					
Qtz	31.1	33.2	20.8	19.6	45.15
Or	27.8	31.7	17.8	8.3	20.93
Ab	35.1	25.1	35.1	34.1	10.93
An	2.0	5.0	14.5	23.3	-
Cor	-	0.9	-	-	7.28
$CaSiO_3$	0.1	-	1.3	1.3	1.13
$MgSiO_3$	0.3	0.8	3.9	5.3	
$FeSiO_3$	0.6	-	1.3	2.8	
Mgt	1.9	1.9	3.0	3.3	
Ilm	0.3	0.5	1.4	1.2	0.28
Hem	-	-	-	-	0.60
Ap	0.2	0.2	0.3	0.3	0.06
Ct	-	-	-	-	13.66

a. Beus, 1964; b. Wedepohl, 1969; c. Heier and Adams, 1964

* Values not available

Number of samples in parentheses