

## CHAPTER 7

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### CONCLUDING STATEMENT

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### SUMMARY

The comagmatic siliceous volcanic and high-level intrusive rocks in the Emmaville-Tenterfield region of northwestern New South Wales are now recognized as constituting a volcano-plutonic association. Cauldron structures are relatively simple and lack the complex associations of ash-flow, ash-fall and sedimentary reworked volcanic rocks typical of volcano-plutonic provinces in, for example, western U.S.A. Tin, tungsten, molybdenum and polymetallic sulfide mineralization in the region is not directly related to cauldron formation but is associated with specific high-level leucogranitoids considered to have been generated by partial melting of the same intermediate igneous source rock as that which produced the comagmatic volcanic and barren intrusive rocks.

#### 1) THE VOLCANO-PLUTONIC ASSOCIATION

Late Permian igneous activity in the region commenced with the intrusion of large bodies of siliceous magma to high crustal levels. Doming of the brittle sedimentary rocks overlying individual magma chambers caused arcuate fractures to develop at locations of maximum tension. Fractures which intersected the cupolas of underlying magma chambers were rapidly filled with vesiculated magma which streamed from the arcuate vents and flowed over the Permian land surface to form extensive sheets of ash-flow tuff. The Emmaville Volcanics so formed, probably ranged from south of Wellingrove to north of Wallangarra. The evacuation of magma from the roof zones of several discrete chambers triggered subsidence of overlying sediments and fresh volcanic rocks partly circumscribed by the arcuate fractures, resulting in the formation of a number of cauldron structures.

Subsequent to the first phase of pyroclastic volcanism, large volumes of Dundee Rhyodacite magma were emplaced to upper crustal levels, possibly following pathways generated by the preceding leucocratic magmas. Fluidized Rhyodacite magma was erupted from central vents in the floors of the Dundee, Brassington, Tenterfield, and possibly Bolivia calderas, filling and sometimes overflowing these calderas. The enormous volumes of magma which defluidized within the confines of

the pre-existing cauldron structures developed characteristic microgranular groundmass textures, whereas outflow facies of the Rhyodacite which quenched more rapidly display the microscopic eutaxitic textures of typical ash-flow tuffs.

The ring fracture system partly surrounding the Dundee Caldera was re-activated during or immediately following eruption of the Dundee Rhyodacite, and the ensuing series of relatively small pyroclastic eruptions which produced the pile of ash-flow and rare ash-fall tuffs comprising the Tent Hill Volcanics, represent the waning stages of the second major volcanic episode in the region. Ring fractures associated with the other calderas were apparently not re-activated by the second episode of volcanism and remained plugged by the quenched (porphyritic) remnants of the first volcanic episode.

Unlike Flood et al., (1979) who proposed that the Tent Hill Volcanics or Emmaville Volcanics may, in part, represent the vitric (ash-fall) fraction of the magma erupted during the formation of the Dundee Rhyodacite, this study has revealed no genetic relationship between products of the first and second volcanic episodes.

The second phase of (rhyodacitic) volcanism was apparently short-lived, for many of the volatile-depleted leucocratic magmas related to the first volcanic episode remained sufficiently fluid to intrude to even higher crustal levels, ultimately to reside within the base of the Emmaville Volcanic pile.\* Leucocratic magmas in pristine high-level chambers that were not vented during the first volcanic episode were also able to move to subvolcanic levels. Perhaps it is these magmas which exhibit the greatest potential for the operation of fractionation processes leading to economic concentrations of rare metals. The Mole Granite (Sn, W), Kingsgate Granite (Mo) and the unexposed granitoids presumed linked to the Glen Eden molybdenite and Grampians Range cassiterite stockworks, may be examples of plutons which crystallized from untapped magma chambers.

Small plutons of hornblende-biotite adamellite were also emplaced to subvolcanic levels and are closely spatially associated with the more leucocratic granitoids. Geochemical and mineralogical evidence suggest these more mafic adamellites were derived by higher temperature non-minimum partial melting of the

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\* The lack of intervening strata between high-level plutons and their comagmatic ejecta is a commonly recognized phenomenon characteristic of many volcano-plutonic associations (see Hyndman, 1981), so it must be assumed that residual magmas often have a protracted intrusive history at high crustal levels.

intermediate igneous parent common to the leucogranitoid magmas. Much of the calcic plagioclase and the mafic components of the adamellites may be refractory residua transported from the zone of partial melting, but melt-restite re-equilibration and the mantling of restite by compositionally similar phases crystallizing directly from the melt are processes considered to have operated during emplacement and final consolidation of these magmas.

The steeply dipping arcuate fractures defining individual cauldron blocks were a major control on highest level emplacement of the leucogranitoid and adamellite magmas. The intruding magmas apparently were channelled away from the cauldron blocks and were finally emplaced to very high levels by doming and displacing the sedimentary and volcanic cover rocks between neighbouring calderas. Occasionally cauldron blocks were either pierced by intruding magmas (e.g. the Billyrimba Leucoadamellite and Cottesbrook Adamellite in the Brassington Caldera) or were totally displaced by such magmas (e.g. the deeply eroded Mt. Mackenzie - Nonnington Leucoadamellite cauldron structure) but in neither case is there evidence that this type of intrusion represented a true resurgent phase in the development of the calderas.

## 2) MINERALIZATION IN THE EMMAVILLE-TENTERFIELD REGION

All of the major molybdenum, tungsten, tin and polymetallic vein-style mineralization in the region is associated with, or was derived from, leucogranitoid plutons. Important molybdenite-bismuth pipe deposits occur at the margins of the Mt. Jonblee Leucoadamellite and Kingsgate Granite plutons. Smaller deposits include molybdenite stockwork veinlet (Glen Eden) and Sn-W-Mo greisen types (Glen Elgin, Deepwater deposits).

The principal tungsten deposits occur in the Torrington (roof) Pendant of the Mole Granite pluton. Wolframite-bismuth mineralization occurs as veins and pods of pegmatite associated with small topazite intrusions, and wolframite accompanies cassiterite in quartz-fluorite vein or "bung" deposits near the perimeter of the Torrington Pendant.

Significant cassiterite mineralization is almost exclusively associated with the Mole Granite pluton. Hydrothermal deposits include cassiterite-quartz veins in the apical portions of the pluton; cassiterite-wolframite "bung" deposits at the margins of the Torrington Pendant, and complex Sn-W-Bi mineralized veins within adjacent small porphyritic adamellite intrusives. The Ottery As-Sn Mine and (Halls)

Grampians Range cassiterite stockwork deposit near Emmaville may also be related to the intrusion of the Mole Granite. Erosion of the mineralized roof of the pluton has given rise to Tertiary, Quaternary and Recent stream alluvial deposits which have been a very important economic source of tin in the region.

The Webbs Consols, Collisons Silver and Ottery Mines contain complex polymetallic sulfide mineralization which is also genetically related to evolved granitoid magmas. The primary, dominant sulfide assemblage in these deposits is overprinted by a much later Ag, Bi, Sb mineralization presumed to be derived from a deep crustal source (Herbert, 1981). This second phase of mineralization was of prime economic importance at the Webbs Consols and Collisons Silver Mines. The polymetallic sulfide mineralization spatially associated with metamorphosed basic intrusives at Reids Copper Mine and Hellhole Adit was probably also derived from a nearby granitoid, possibly the Mole Granite.

### 3) PETROGENESIS OF VOLCANIC AND INTRUSIVE SUITES

#### a) Hornblende, Biotite Adamellite-Leucogranitoid Suite (the main series)

Members of the mafic adamellite-leucogranitoid suite display a regular, continuous variation in major element abundances within the range approx. 65-74 wt.% SiO<sub>2</sub>. All but the most incompatible of trace elements also display sympathetic regular variations in abundance with silica content. The "anomalous" concentrations of incompatible elements in some plutons are, however, not considered a reflection of original magma chemistries.

Most, if not all of the minerals comprising the leucogranitoids of the suite, are magmatic in origin but this does not apply to the more mafic members. The adamellites and quartz monzonites display no uniform variation in the modal proportions of hornblende and biotite or regular decrease of mg in these ferromagnesians, which suggest mafic mineral chemistries were not controlled by the composition of successive liquids as would be the case if fractional crystallization was important in the development of the lineage. The observed regular whole-rock geochemical variations coupled with the presence of mafic minerals with compositions displaying little or no correlation with whole-rock chemistry, strongly support a partial melting origin for members of the suite. The leucogranitoids probably crystallized from dominantly liquid minimum or partly non-minimum partial melts, whereas magmas for the more mafic members of the lineage were derived by non-minimum partial melting of the same intermediate igneous source rock. The

cloudy, highly calcic cores of plagioclase crystals, and a significant proportion of the hornblende in many adamellites, may be refractory residue transported from the zone of partial melting.

Flinter et al. (1972) have shown that many leucogranitoids in the Emmaville-Tenterfield region, including both mineralized and barren types, contain moderate background levels of the ore trace elements. These incompatible metals probably partitioned strongly into the first partial melts, being released initially from intergranular or lattice defect sites in minerals of the source rock, and later from dissociated mafic and selected accessory minerals in the parent. Therefore, although only the Mole Granite, Kingsgate Granite and Ruby Creek Adamellite are significantly mineralized, the ore potential of the barren leucogranitoids was probably not a function of low primary trace element abundances inherited from a depleted source rock. Economic concentrations of Sn, W, Mo and other metals in the mineralized granitoids can be attributed to efficient fractionation mechanisms operating in the magmas at high crustal levels and there appears no need to invoke a unique metal-rich source for these magmas.

b) Rhyodacite-Rhyolite Suite

Major and trace element whole-rock data support the field evidence for a comagmatic relationship between rhyodacites and rhyolites of the Emmaville Volcanics, and the leucogranitoid and adamellite members of the intrusive lineage. Mineral chemical and, to some extent, modal data are also compatible. Small differences in the trace alkali metal content of otherwise similar leucogranitoids and rhyolites may be due to component loss during devolatilization of the volcanic members during and after eruption.

c) Andesite - Basic Rhyodacite Group

Andesitic members of the Emmaville Volcanics are of two types; (i) those containing abundant amphibole and biotite but little or no pyroxene, and (ii) those with significant modal pyroxene and only minor biotite and/or amphibole. Type (i) andesites display higher modal proportions of all the mafic phases present in associated more siliceous rhyodacitic volcanics and could therefore be considered to be related to the rhyodacites by fractional crystallization and/or crystal accumulation mechanisms which operated during emplacement. However the relatively incompatible elements Li, Rb, Pb, Zn, Cu and Nb display no regular variation with silica content and there exists no obvious relationship in these elements between members of the group. The limited data available suggest these

volcanics were derived from magmas generated by high-temperature partial melting of intermediate source rocks similar to that which produced the mafic adamellites, but the data fail to elucidate possible relationships between these parent rocks.

The euhedral pyroxene and strongly zoned phenocryst plagioclase characteristic of type (ii) andesites indicate these rocks crystallized from high temperature, largely liquid magmas. The limited data do not justify speculation on the likely composition and mineralogy of the source for these magmas.

d) Dundee Rhyodacite Suite

The presence of euhedral clino and orthopyroxene, amphibole, biotite and strongly zoned plagioclase in addition to mafic microxenoliths best interpreted as being of cumulate origin, are features of the Dundee Rhyodacite suggestive of crystallization from an essentially liquid, high-temperature magma. Rare highly calcic core plagioclase in some microcrystalline mafic xenoliths may be relict indicative of very high magma temperatures, a conclusion supported by pyroxene thermometric data (approx. 850 - 880°C).

Compared with the Dundee Rhyodacite, the more basic whole-rock composition of several analysed samples of the Tent Hill Volcanics may be attributed to the occasional presence of slightly more magnesian pyroxenes and a more calcic zoned plagioclase but the effect of these subtle mineralogical differences was obviously subordinate to physical processes of phenocryst aggregation and separation from groundmass components during eruption. Compositional variation between members of the Dundee Rhyodacite Suite are therefore not due to the production of successively more basic liquids by progressive partial melting of a single source rock. However the source for the Dundee Rhyodacite suite can be assumed to have been of originally intermediate, possibly granodioritic, composition.

4) MECHANISMS OF MAGMA FRACTIONATION

Smith (1979) has suggested that all large bodies of siliceous magma residing in high-level chambers will ultimately evolve a vertical compositional zonation independent of crystal fractionation processes. The theoretical concepts of magma zoning were developed from studies of high-level magmas related to acid pyroclastic volcanism and caldera formation (Shaw et al., 1976), and because of the potential relevance of primary zoning to processes leading to economic concentrations of rare metals (e.g. Hildreth, 1979; Mutschler et al., 1981) the mechanisms of magma zoning

and the related development of magmatic hydrothermal solutions and the speciation of incompatible elements in such magmas and solutions, have been discussed in detail in this thesis.

In the thermogravitational diffusion model (Shaw et al., 1976; Hildreth, 1979) a zoned magma is thought to consist of a volatile- and incompatible element-enriched, relatively depolymerized upper portion, and an underlying, slightly depleted and relatively more polymerized major lower portion. The volatile-enriched upper portion is itself zoned, consisting of a number of stacked, independently convecting magma cells, each less polymerized than the one below. The zonation is thought to develop in response to small but permanent temperature differences between the uppermost and underlying magma in the chamber (i.e. the Soret effect). Once subtle compositional variations are established, the integrity of each compositionally uniform subzone or cell is maintained by convection. The larger the temperature variation experienced within the chamber and the longer the residence time of the magma in the upper crust, the more effective will be the zonation established. Although the thermogravitational diffusion model has now become well accepted (e.g. Westra and Keith, 1981), proof of the validity of the Soret effect in siliceous volatile-undersaturated magmas is required.

Favoured mechanisms of magma zonation culminating in the development of trace element- and volatile-rich hydrothermal solutions also include (i) convection-enhanced diffusion in response to pressure gradients in the magma chamber (c.f. Whitney, 1975a), and (ii) resurgent boiling triggered by either a sudden reduction in hydrostatic pressure or induced by an extreme build-up of volatile components in the residual melts of largely crystallized magmas (Burnham, 1979; Groves and McCarthy, 1978).

The original composition of the magma is also a very important determinant in the initiation of incompatible element zonation and the eventual development of hydrothermal fluids. Peralkaline or mildly sub-alkaline siliceous magmas similar to those evolving ore deposits near Emmaville, are more likely to concentrate fluorine and accompanying ore metals than more calcic magmas of lower silica content (see Bailey<sup>#</sup>, 1977).

The theoretical aspects of magma evolution and the production of hydrothermal and gaseous fluids leading to orebody formation in high-level granitoids may be used as a model for the mineralized plutons in the Emmaville region. The sequential development of the mineralized system may be summarized as follows:



- (A) Once emplaced to a high level in the crust a typically potassic calc-alkaline granitoid magma evolves an alkali- and incompatible element-enriched, relatively depolymerized zone near the top of the chamber. This compositional zonation may be produced by thermogravitational diffusion (Hildreth, 1979) or pressure-induced diffusion enhanced by convection (cf. Whitney, 1975a).
- (B) In some circumstances failure of the roof rocks capping the magma chamber may permit the growth of a cylindrical conduit extending some distance above the primary chamber (Mutschler et al., 1981). The already volatile-enriched magma occupying this conduit establishes a new pattern of compositional zonation, with increased upward enrichment of volatiles and incompatible elements. Although the development of a vertical conduit doubtless dramatically increases the roofward concentration of ore metals, this is not an essential requirement in the evolution of mineralized systems and apparently does not apply to the plutons near Emmaville.
- (C) As cooling and crystallization proceed, localized resurgent boiling is initiated and an alkalic, metal-rich hydrothermal fluid separates from the magma and accumulates at the top of the cupola. An orebody is formed in the cupola by the crystallization of ore minerals directly from the hydrothermal solution and from the vapour resulting from the boiling of this solution.
- (D) The build-up of pressure in the cupola during the hydrothermal stage causes hydrofracturing of the chilled granitic lining, submitting these rocks to the attack of highly corrosive fluids and vapours. Disseminated mineralization may characterise this greissenized region of the cupola. Topazite dyke formation in the Mole Granite pluton may correspond to the latter period of development stage (C) or the early period of stage (D).
- (E) Meteoric water may enter the upper parts of the system during the hydrothermal phase, but there is little to suggest that meteoric waters affected ore deposition in the Mole Granite or other mineralized plutons in the region, although they may have contributed to the magmatic fluids associated with the formation of nearby polymetallic sulfide deposits (e.g. Collisons Silver Mine).
- (F) The final residual fluids associated with the last stages of crystallization of the magma may invade fractures and cooling joints in the overlying mineralized zones, forming greisen veins.

### CONCLUDING STATEMENT

"The variations in the relations between ash-flow sheets and calderas reflect variations in the volumes of magma in the chambers, the tectonic controls on intrusive processes and the timing of major eruptions, and the continuity of magma generation beneath a given area." (Christiansen, 1979, p.40). The object of this study has been to examine such variations specifically within the Emmaville-Tenterfield region of northeastern New South Wales. In addition an attempt has been made to reveal the relationship between volcanic rocks and the mineralized and barren plutons in the area and to elucidate the magmatic processes involved in the generation of granitoid-related orebodies. An important conclusion is that high-level magmas related to comagmatic volcanic rocks are unlikely to later produce large, economic concentrations of mineralization (cf. Elston, 1978).

However, definition of the factors restricting the occurrence of tin, tungsten or molybdenum mineralization to specific leucogranitoids remains a vexing and largely unexplained problem. The possible relationship between the Dundee Rhyodacite and specific I-type granitoids in other parts of northern New England is also the subject of speculation (Flood et al., 1980). For these reasons the Emmaville-Tenterfield area, like so many mineralized volcano-plutonic associations in other parts of the world, will be of continuing interest to mineral explorationists and researchers alike.

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## APPENDIX 1

### ANALYTICAL METHODS

#### (1) WHOLE ROCK CHEMISTRY

Fresh rock material was pulverized to pass a 200 mesh screen using a tungsten carbide siebtechnik ring grinder.

The major elements (Si, Ti, Al, Fe, Mn, Ca, K and P) were determined by X-ray fluorescence spectrometry on fused discs, using the method of linear calibration by dilution (Norrish and Hutton, 1969). A Corning-Eel flame photometer (butane/air flame) was used to measure Na, and K was also determined as a check on results from the XRF. Ferrous iron was determined by titrimetric methods, using ceric ammonium sulphate as a standard. Total H<sub>2</sub>O was determined by weighing the collected condensate from powdered rock samples heated to 1050<sup>o</sup>C for 40 minutes.

Trace elements (V, Ni, Cr, Y, Sr, Rb, Zn, Nb, Ba, Ce, Nd and Pb) were determined by X-ray fluorescence spectrometry on pelletized powder samples (Norrish and Chappell, 1967), using calculated mass absorption coefficients. The elements Li, Cu, Zn and Mg were determined on a Varian Techtron AA-5 Atomic Absorption Spectrophotometer using rock solutions prepared by standard techniques of mixed-acid digestion.

#### (2) MINERAL CHEMISTRY

Minerals were analysed on a TPD electron microprobe using energy dispersive X-ray spectrometry and a Si (Li-drift) X-ray detector. The accelerating voltage was 15 kv with a filament current of 5nA. Detection limits were SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, Na<sub>2</sub>O = 0.1 wt %; K<sub>2</sub>O = 0.06 wt %; CaO, TiO<sub>2</sub> = 0.07 wt % and MnO, FeO = 0.09 wt %. On-line data reduction utilized the ZAF correction procedure.

Major and trace elements, ferrous iron and H<sub>2</sub>O were determined on selected mineral separates using the methods described above.

## APPENDIX 2

### MAJOR AND TRACE ELEMENT DATA

<u>ROCK TYPE</u>	<u>ANALYSIS NOS.</u>
Tent Hill Volcanics	1-11
Dundee Rhyodacite	12-17
Emmaville Volcanics (including Wallangarra Volcanic (41))	18-41*
*Volcanics comagmatic with the Dundee Rhyodacite	21, 25, 31
"Intrusive rhyolites"	42-43
Ring-dyke porphyries	44-48
Undifferentiated granitoids and porphyries	49-58
Stanthorpe Adamellite porphyry	59
Mackenzie Adamellite	60-62
Nonnington Leucoadamellite	63-64
Clive Adamellite	65-66
Bolivia Range Leucoadamellite	67-68
Bungulla Porphyritic Adamellite	69-70
Sandy Flat Adamellite	71-73
Shannonvale Granodiorite	74-76
Diorites	77-78
Mafic xenoliths from the Dundee Rhyodacite	79-80
Xenoliths from Undifferentiated Adamellites	81-84
Xenolith from the Bungulla Porphyritic Adamellite	85

### TRACE ELEMENTS

blank	-	not determined
-	-	below detection limit
(2)	-	at lower limit of detection

## TENT HILL VOLCANICS

Field No.	104	102	113	39	43	44	66F	256B	100	259A	41
UNE Rock No.	46202	46203	46204	46205	46206	42607	46208	46209	46210	46211	46212
Analysis No.	1	2	3	4	5	6	7	8	9	10	11
SiO <sub>2</sub>	64.35	68.20	59.89	68.56	67.35	66.38	59.53	60.36	66.97	70.82	66.22
TiO <sub>2</sub>	0.61	0.47	0.93	0.44	0.49	0.54	0.72	0.93	0.56	0.39	0.54
Al <sub>2</sub> O <sub>3</sub>	15.97	14.73	15.86	14.57	14.76	15.44	17.65	15.76	14.97	14.00	15.30
Fe <sub>2</sub> O <sub>3</sub>	1.56	1.16	0.73	1.48	1.74	1.67	2.03	1.69	0.92	1.19	1.79
FeO	2.88	2.20	5.23	1.68	1.98	2.10	3.55	4.30	2.98	1.62	2.30
MnO	0.09	0.07	0.13	0.07	0.08	0.08	0.12	0.12	0.08	0.06	0.09
MgO	2.02	1.33	3.27	1.26	1.51	1.59	2.48	3.20	1.70	1.01	1.64
CaO	4.18	3.23	5.36	2.77	3.28	3.58	5.75	5.34	3.52	2.39	3.73
Na <sub>2</sub> O	3.50	3.50	3.00	3.30	3.47	3.49	3.88	3.15	3.42	3.37	3.48
K <sub>2</sub> O	3.40	4.00	3.43	4.17	4.00	3.99	2.60	3.49	3.83	4.33	3.65
P <sub>2</sub> O <sub>5</sub>	0.16	0.15	0.34	0.14	0.12	0.16	0.17	0.36	0.15	0.09	0.13
H <sub>2</sub> O total	0.81	0.62	1.11	0.70	0.92	0.83	1.64	1.14	1.08	0.54	0.96
TOTAL	99.53	99.66	99.28	99.14	99.70	99.85	100.12	99.84	100.18	99.81	99.83

## DUNDEE RHYODACITE

	413A	316B	396C	297A
	46213	46214	46215	46216
	12	13	14	15
SiO <sub>2</sub>	65.70	65.23	65.81	69.59
TiO <sub>2</sub>	0.56	0.59	0.63	0.41
Al <sub>2</sub> O <sub>3</sub>	15.65	15.37	15.41	14.57
Fe <sub>2</sub> O <sub>3</sub>	1.37	1.03	1.66	1.20
FeO	2.70	3.13	3.06	1.78
MnO	0.09	0.09	0.10	0.07
MgO	1.71	1.89	2.08	1.13
CaO	3.87	3.95	4.33	2.66
Na <sub>2</sub> O	3.43	3.59	3.68	3.52
K <sub>2</sub> O	3.63	3.61	3.35	4.33
P <sub>2</sub> O <sub>5</sub>	0.10	0.11	0.18	0.13
H <sub>2</sub> O total	0.57	0.81	0.81	0.52
TOTAL	99.38	99.40	100.10	99.91

## MESONORMATIVE MINERALOGY

Q	20.05	23.07	14.91	26.34	22.17	22.68	11.59	13.78	22.40	27.46	21.59	21.29	18.83	17.59	24.83
Or	14.55	21.29	11.69	20.59	21.83	19.33	11.22	15.17	18.00	23.03	18.53	16.97	18.02	17.59	22.68
Ab	31.99	31.96	27.58	30.37	31.77	30.12	35.37	28.81	31.20	30.78	31.83	31.36	32.84	33.45	32.03
An	16.26	10.48	15.37	12.75	10.50	14.74	19.02	13.23	12.09	9.48	13.30	14.91	11.68	11.12	10.14
C															
Bi	9.45	4.40	14.51	7.46	3.64	7.54	7.00	9.34	8.00	4.80	5.51	7.80	5.95	3.91	5.19
Ho	5.69	7.23	14.40	0.60	7.95	3.46	13.24	17.06	6.99	2.99	7.04	5.97	11.34	14.17	3.57
Mt	1.66	1.23	0.78	1.59	1.86	1.78	2.16	1.80	0.98	1.27	1.91	1.46	1.10	1.76	1.27
Ap	0.34	0.32	0.73	0.30	0.26	0.34	0.36	0.77	0.32	0.19	0.28	0.21	0.23	0.38	0.28
TOTAL	99.99	99.98	99.97	100.00	99.98	99.99	99.96	99.96	99.98	100.00	99.99	99.97	99.99	99.97	99.99
D.I.	66.6	76.3	54.2	77.3	75.8	72.1	58.2	57.8	71.6	81.3	72.0	69.6	69.7	68.6	79.5

## DUNDEE RHYODACITE

Field No.	22A	397
UNE Rock No.	46217	46218
Analysis No.	16	17
SiO <sub>2</sub>	64.63	65.03
TiO <sub>2</sub>	0.63	0.62
Al <sub>2</sub> O <sub>3</sub>	15.58	15.81
Fe <sub>2</sub> O <sub>3</sub>	1.67	1.55
FeO	2.80	2.93
MnO	0.10	0.10
HgO	1.94	2.05
CaO	4.07	4.21
Na <sub>2</sub> O	3.68	3.50
K <sub>2</sub> O	3.42	3.47
P <sub>2</sub> O <sub>5</sub>	0.13	0.17
H <sub>2</sub> O total	0.81	0.45
TOTAL	99.46	99.89

## EMMAVILLE VOLCANICS

87A	156	306A	176	253A	291c	291	155	265A	210	169	285	206
46219	46220	46221	46222	46223	46224	46225	46226	46227	46228	46229	46230	46231
18	19	20	21	22	23	24	25	26	27	28	29	30
70.65	61.69	68.39	64.33	69.89	64.80	64.77	66.89	58.63	67.30	65.17	59.74	60.89
0.20	0.91	0.48	0.63	0.34	0.68	0.70	0.51	1.07	0.43	0.60	0.96	0.86
15.02	16.25	16.91	15.14	14.64	15.89	15.80	15.18	15.43	15.86	15.58	15.99	15.99
0.17	1.54	0.40	1.54	1.42	0.72	0.85	1.20	1.43	1.00	1.30	0.63	2.02
1.85	3.44	1.29	3.19	1.42	3.43	3.36	2.53	5.58	1.99	2.91	5.26	3.37
0.06	0.11	0.04	0.10	0.06	0.11	0.10	0.08	0.14	0.07	0.09	0.12	0.10
0.20	2.16	0.22	2.04	0.60	1.61	1.54	1.52	4.20	0.91	1.71	3.19	2.68
1.46	4.56	2.38	4.33	2.05	3.96	3.53	3.42	5.69	2.75	3.81	5.77	4.92
4.05	3.15	4.08	3.45	3.45	3.18	3.18	3.38	2.50	3.80	3.45	3.22	3.00
5.15	4.09	4.66	3.52	5.05	4.44	4.50	3.83	3.35	4.62	3.72	3.78	3.85
0.15	0.34	0.09	0.16	0.04	0.22	0.23	0.15	0.42	0.13	0.13	0.41	0.34
0.95	1.38	0.96	1.23	0.70	1.25	1.19	0.66	1.82	0.54	1.12	1.19	1.60
99.91	99.62	99.90	99.66	99.66	100.29	99.75	99.35	100.26	99.40	99.59	100.26	99.62

## MESONORMATIVE MINERALOGY

Q	18.42	19.82	23.15	16.53	20.56	17.71	30.84	18.82	20.68	23.63	16.44	20.53	20.59	9.51	16.09
Or	17.14	15.68	27.71	17.91	25.23	19.11	18.62	20.90	19.28	17.62	8.53	23.23	17.28	18.09	17.25
Ab	33.64	31.78	36.81	28.97	36.99	31.68	32.15	29.02	29.18	30.98	23.01	34.59	31.65	29.27	27.67
An	12.69	14.77	6.34	16.25	11.33	10.67	10.29	13.97	15.43	14.19	16.92	12.54	14.35	10.22	15.84
C			0.54		1.15		1.73								
Bi	5.50	8.09	4.96	10.96	4.12	3.45	4.75	9.22	12.63	8.77	18.81	7.12	8.30	7.23	9.79
Ho	10.52	7.86		6.99		15.35		6.81	1.40	3.20	13.82	0.65	6.16	24.09	10.45
It	1.78	1.64	0.18	1.65	0.42	1.65	1.54	0.77	0.91	1.28	1.53	1.06	1.39	0.67	2.17
Ap	0.28	0.36	0.32	0.73	0.19	0.34	0.09	0.47	0.49	0.32	0.90	0.28	0.28	0.87	0.73
TOTAL	99.99	100.00	100.01	99.99	99.99	99.96	100.01	99.98	100.00	99.99	99.96	100.00	100.00	99.95	99.99
D.I.	69.2	67.3	87.7	63.4	82.8	68.5	81.6	68.7	69.1	72.2	48.0	78.3	69.5	56.9	61.0

## EMMAVILLE VOLCANICS

INTRUSIVE  
RHYOLITES

Field No.	18	308	264	13B	378B	378E	327B	217	218A	254A	393c	W305	250
UNE Rock No.	46232	46233	46234	46235	46236	46237	46238	46239	46240	46241	46242	46243	46244
Analysis No.	31	32	33	34	35	36	37	38	39	40	41	42	43
SiO <sub>2</sub>	67.11	69.72	57.35	65.25	70.89	71.07	62.51	64.72	67.79	75.70	73.82	72.46	75.39
TiO <sub>2</sub>	0.41	0.29	1.10	0.61	0.23	0.24	0.78	0.43	0.35	0.14	0.13	0.24	0.20
Al <sub>2</sub> O <sub>3</sub>	15.73	15.48	15.69	15.81	15.09	15.14	16.50	17.38	16.11	12.28	13.30	13.84	12.99
Fe <sub>2</sub> O <sub>3</sub>	0.88	0.40	1.43	0.39	0.27	0.32	0.87	0.68	0.47	0.64	1.11	0.76	0.45
FeO	2.10	0.88	4.98	3.51	1.17	1.55	3.84	2.38	2.50	0.85	0.48	1.23	0.82
MnO	0.07	0.02	0.12	0.08	0.06	0.06	0.09	0.06	0.09	0.04	0.05	0.05	0.03
MgO	0.87	0.15	4.00	1.90	0.11	0.12	2.16	0.89	0.29	0.11	0.22	0.34	0.12
CaO	3.11	1.20	6.39	3.96	0.80	0.78	3.52	3.55	1.42	0.72	0.72	1.42	0.50
Na <sub>2</sub> O	3.80	4.10	2.83	3.40	3.42	3.75	3.65	3.84	3.55	3.07	4.05	3.75	3.46
K <sub>2</sub> O	4.50	6.38	3.80	3.61	6.45	6.35	4.21	4.02	5.99	5.30	5.17	4.40	5.03
P <sub>2</sub> O <sub>5</sub>	0.09	0.05	0.50	0.20	0.05	0.01	0.30	0.12	0.09	0.01	0.04	0.01	0.03
H <sub>2</sub> O total	0.63	0.63	1.32	0.99	0.87	0.97	1.26	1.06	1.09	0.65	0.23	1.06	0.63
TOTAL	99.30	99.30	99.51	99.71	99.41	100.36	99.69	99.13	99.74	99.51	99.32	99.56	99.65

## MESONORMATIVE MINERALOGY

Q	18.73	17.42	7.40	21.69	23.30	21.75	17.40	18.64	20.20	34.26	27.01	29.19	33.12
Or	25.23	37.30	19.37	13.57	36.50	35.36	14.67	18.81	31.79	30.81	30.90	24.27	28.96
Ab	34.66	37.18	25.98	31.06	31.22	33.95	33.32	35.15	32.42	28.28	36.87	34.44	31.71
An	10.49	4.42	9.56	16.39	3.70	3.90	15.77	17.16	6.57	3.60	2.42	7.14	2.33
C					1.28	0.75	0.29	0.61	1.58	0.23		0.39	1.13
Bi	2.85	1.25	5.74	13.03	3.60	3.95	17.00	8.65	6.75	2.11	0.13	3.72	2.20
Ho	6.89	1.90	29.28	3.41							1.41		
Mt	0.93	0.42	1.53	0.41	0.29	0.34	0.92	0.72	0.50	0.69	1.18	0.81	0.48
Ap	0.19	0.11	1.07	0.43	0.11		0.64	0.26	0.19	0.02	0.08	0.02	0.06
TOTAL	99.93	100.00	99.93	99.99	100.00	100.00	100.01	100.00	100.00	100.00	100.00	99.98	99.99

D.I. 78.6 91.9 52.7 66.3 91.0 91.1 65.4 72.6 84.4 93.3 94.8

87.9 93.8

## RING-DYKE PORPHYRIES

Field No.	193	196	201	195	192A
UNE Rock No.	46245	46246	46247	46248	46249
Analysis No.	44	45	46	47	48
SiO <sub>2</sub>	67.31	63.56	69.78	77.33	74.32
TiO <sub>2</sub>	0.46	0.53	0.33	0.11	0.17
Al <sub>2</sub> O <sub>3</sub>	16.41	15.06	14.77	12.47	14.18
Fe <sub>2</sub> O <sub>3</sub>	1.21	4.03	1.45	0.93	1.12
FeO	1.55	2.38	1.01	0.25	0.43
MnO	0.08	0.17	0.08	0.02	0.06
MgO	0.86	1.10	0.56	0.06	0.13
CaO	2.84	4.51	2.00	0.65	0.06
Na <sub>2</sub> O	4.30	7.40	3.85	3.90	3.74
K <sub>2</sub> O	4.01	0.09	4.81	4.28	4.95
P <sub>2</sub> O <sub>5</sub>	0.15	0.19	0.10	0.01	0.04
H <sub>2</sub> O total	0.84	0.69	0.54	0.34	0.60
TOTAL	100.02	99.71	99.28	100.35	99.80

## GRANITOIDS

389C	391C	446B	427B	433B	399C	447C	448C	407B	457B
46250	46251	46252	46253	46254	46255	46256	46257	46258	46259
49	50	51	52	53	54	55	56	57	58
68.81	68.30	64.66	69.02	68.63	68.56	70.34	64.43	68.96	67.45
0.39	0.42	0.52	0.47	0.44	0.41	0.34	0.60	0.37	0.49
16.03	16.39	17.91	15.31	14.47	15.97	14.77	17.71	15.38	15.58
1.27	1.09	1.81	0.91	1.33	1.24	0.81	0.82	1.50	1.40
1.40	1.32	1.67	2.28	1.91	1.30	1.70	2.95	1.11	1.99
0.05	0.09	0.04	0.07	0.10	0.12	0.08	0.09	0.06	0.07
0.25	0.65	0.46	0.46	1.28	0.66	0.46	1.36	0.58	1.20
2.15	2.37	4.51	3.00	3.13	2.37	1.81	4.06	2.45	3.34
4.35	4.35	5.05	3.80	3.39	4.45	5.00	4.42	3.60	3.65
4.22	4.24	2.09	3.63	4.25	4.35	3.70	2.70	4.75	3.73
0.06	0.13	0.16	0.14	0.09	0.09	0.12	0.24	0.03	0.17
0.61	0.62	0.54	0.59	0.66	0.54	0.57	0.80	0.60	0.89
99.59	99.99	99.42	99.68	99.68	100.06	99.70	100.18	99.39	99.96

## MESONORMATIVE MINERALOGY

Q	19.87	23.26
Or	19.92	27.25
Ab	38.89	35.17
An	13.21	8.52
C	0.21	
Bi	6.31	2.67
Ho		1.37
Mt	1.27	1.54
Ap	0.32	0.21
TOTAL	100.00	99.99

21.48	20.54	16.10	24.74	22.72	19.46	21.20	18.95	23.17	23.56
23.04	22.00	11.35	17.81	24.57	23.22	20.39	8.71	26.37	17.59
39.51	39.26	45.72	35.05	30.99	40.09	45.19	39.85	32.91	33.28
10.40	10.97	18.91	14.35	8.66	10.39	5.72	18.66	11.82	15.01
0.60	0.71		0.01				0.78		
3.50	5.10	1.77	6.76	1.60	4.12	2.59	11.69	3.54	7.67
		3.91		9.84	1.23	3.80		0.53	1.04
1.34	1.15	1.91	0.98	1.42	1.30	0.85	0.86	1.60	1.49
0.13	0.27	0.34	0.30	0.19	0.19	0.25	0.50	0.06	0.36
100.00	100.00	100.01	100.00	99.99	100.00	99.99	100.00	100.00	100.00

D.I. 78.7 85.7

84.0 81.8 73.2 77.6 78.3 82.8 86.8 67.5 82.4 74.4



GRANITOIDS

Field No.	387A	459	441	464B	461	462	468	469C	470B	472B	370	455B	476B	473B	475
UNE Rock No.	46260	46261	46262	46263	46264	46265	46266	46267	46268	46269	46270	46271	46272	46273	46274
Analysis No.	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73
SiO <sub>2</sub>	68.46	71.40	71.76	72.87	76.45	77.09	76.13	75.26	75.22	73.79	69.37	67.38	73.38	71.19	73.50
TiO <sub>2</sub>	0.45	0.38	0.40	0.39	0.14	0.19	0.15	0.11	0.25	0.20	0.48	0.51	0.22	0.31	0.19
Al <sub>2</sub> O <sub>3</sub>	16.30	14.28	13.86	13.36	13.29	12.17	12.95	12.94	12.80	13.22	14.68	15.54	13.94	14.14	13.65
Fe <sub>2</sub> O <sub>3</sub>	1.25	0.85	0.72	0.80	0.51	0.70	0.27	0.16	0.55	0.55	1.30	1.12	0.55	0.57	0.45
FeO	1.29	1.57	1.71	1.64	0.38	0.46	0.77	0.89	1.25	0.98	1.53	2.16	1.18	1.88	1.21
MnO	0.10	0.06	0.06	0.06	0.03	0.04	0.02	0.02	0.04	0.04	0.07	0.17	0.05	0.09	0.05
MgO	0.67	0.24	0.52	0.59	0.17	0.23	0.07	0.14	0.36	0.26	1.11	1.24	0.44	0.64	0.39
CaO	2.30	1.52	1.80	1.76	1.12	0.74	0.75	0.80	1.06	0.82	2.73	3.34	1.60	2.15	1.52
Na <sub>2</sub> O	4.60	3.80	3.90	3.70	3.29	3.42	3.35	3.55	3.60	3.63	3.65	3.50	3.35	3.77	3.20
K <sub>2</sub> O	4.46	4.77	4.24	4.50	4.32	4.81	4.75	4.81	4.55	4.99	4.22	3.80	5.10	3.78	4.90
P <sub>2</sub> O <sub>5</sub>	0.11	0.08	0.08	0.16	0.05	0.06	0.01	0.04	0.12	0.06	0.17	0.08	0.10	0.11	0.08
H <sub>2</sub> O total	0.61	0.67	0.76	0.55	0.62	0.30	0.83	0.58	0.52	0.61	0.62	0.82	0.52	0.54	0.44
TOTAL	100.60	99.62	99.81	100.38	100.37	100.21	100.05	99.30	100.32	99.15	99.93	99.66	100.43	99.17	99.58

MESONORMATIVE MINERALOGY

Q	18.47	26.42	27.15	28.17	36.23	35.10	34.85	32.77	32.79	30.32	24.24	23.75	29.22	28.87	31.27
Or	23.19	26.05	22.72	24.83	25.12	27.81	27.41	27.49	24.74	28.30	22.43	17.73	27.88	18.69	26.99
Ab	41.17	34.74	35.60	33.59	29.99	31.13	30.68	32.58	32.75	33.34	33.21	32.00	30.38	34.59	29.30
An	10.61	7.15	7.31	5.50	5.31	3.33	3.73	3.79	4.54	3.76	10.13	15.18	7.36	10.17	7.16
C		0.33			1.43	0.15	1.07	0.60	0.35	0.56			0.27	0.23	0.57
Bi	4.94	4.24	4.42	3.30	1.28	1.61	1.96	2.51	4.00	2.99	4.54	8.22	4.10	6.62	4.05
Ho	0.09		1.86	3.41							3.71	1.75			
Mt	1.30	0.90	0.77	0.85	0.54	0.74	0.29	0.17	0.58	0.59	1.38	1.19	0.58	0.61	0.48
Ap	0.23	0.17	0.17	0.34	0.11	0.13	0.02	0.09	0.25	0.13	0.36	0.17	0.21	0.24	0.17
TOTAL	100.00	100.00	100.00	99.99	100.00	100.01	100.01	100.00	100.00	99.99	100.00	99.99	100.00	100.02	99.99

D.I.            82.8    87.2    85.5    86.6    91.3    94.0    92.9    92.8    90.3    92.0    79.9    73.5    87.5    82.1    87.6

## GRANITOIDS

Field No.	12	244B	245B
UNE Rock No.	46275	46276	46277
Analysis No.	74	75	76
SiO <sub>2</sub>	70.39	67.59	66.60
TiO <sub>2</sub>	0.43	0.54	0.55
Al <sub>2</sub> O <sub>3</sub>	14.36	14.90	15.23
Fe <sub>2</sub> O <sub>3</sub>	0.59	1.19	0.13
FeO	2.21	2.61	3.02
MnO	0.07	0.08	0.08
MgO	1.04	1.69	1.71
CaO	2.43	3.38	3.47
Na <sub>2</sub> O	3.32	3.40	3.53
K <sub>2</sub> O	4.40	3.95	3.84
P <sub>2</sub> O <sub>5</sub>	0.07	0.12	0.16
H <sub>2</sub> O total	0.75	0.84	0.87
TOTAL	100.06	100.29	99.19

## DIORITES

	451	445C
UNE Rock No.	46278	46279
Analysis No.	77	78
SiO <sub>2</sub>	60.12	53.18
TiO <sub>2</sub>	1.25	0.93
Al <sub>2</sub> O <sub>3</sub>	16.31	14.40
Fe <sub>2</sub> O <sub>3</sub>	2.01	2.00
FeO	4.49	5.97
MnO	0.18	0.17
MgO	2.54	7.04
CaO	5.35	9.78
Na <sub>2</sub> O	4.30	2.75
K <sub>2</sub> O	1.49	1.56
P <sub>2</sub> O <sub>5</sub>	0.47	0.22
H <sub>2</sub> O total	1.13	2.11
TOTAL	99.64	100.11

## XENOLITHS

	X150A	X97A	X426B	X426A	X445A	X433A	X370A
UNE Rock No.	46280	46281	46282	46283	46284	46285	46286
Analysis No.	79	80	81	82	83	84	85
SiO <sub>2</sub>	56.87	57.95	56.63	56.35	55.49	53.90	57.03
TiO <sub>2</sub>	1.03	1.20	1.20	1.20	0.99	1.27	0.93
Al <sub>2</sub> O <sub>3</sub>	16.67	16.24	18.21	18.56	16.31	17.86	16.66
Fe <sub>2</sub> O <sub>3</sub>	3.11	2.00	1.52	1.56	2.15	3.37	2.99
FeO	5.15	5.14	5.07	5.03	5.21	5.51	3.76
MnO	0.17	0.14	0.16	0.16	0.15	0.20	0.20
MgO	3.26	2.67	2.65	2.71	5.18	3.28	3.00
CaO	6.04	5.70	7.32	7.28	7.76	5.00	5.56
Na <sub>2</sub> O	3.60	3.13	3.97	3.91	3.20	4.32	4.81
K <sub>2</sub> O	3.25	3.62	1.67	1.70	1.78	3.12	3.57
P <sub>2</sub> O <sub>5</sub>	0.11	0.34	0.46	0.42	0.28	0.30	0.39
H <sub>2</sub> O total	1.17	1.43	1.28	1.26	1.62	1.15	1.53
TOTAL	100.43	99.56	100.14	100.14	100.12	99.28	100.43

## MESONORMATIVE MINERALOGY

Q	27.32	22.82	21.94	16.56	0.48	4.34	9.90	4.87	6.12
Or	21.25	19.29	16.92	0.20	9.39	18.35	17.32	10.80	7.60
Ab	30.28	30.92	32.34	39.37	25.15	32.72	28.90	29.50	29.17
An	11.16	11.64	12.84	18.51	4.40	10.35	13.47	8.33	13.32
C									
Bi	8.27	6.97	9.98	14.05		1.74	7.49		4.92
Ho	0.94	6.84	5.49	8.15	55.12	28.90	20.00	43.30	35.90
Wo					2.73			0.19	
Mt	0.63	1.26	0.14	2.14	2.13	3.29	2.15	2.31	2.28
Ap	0.16	0.25	0.34	1.00	0.47	0.23	0.73	0.60	0.59
TOTAL	100.00	99.99	99.99	99.98	99.87	99.92	99.96	99.90	99.90
D.I.	78.9	73.0	71.2	56.1	35.0	55.4	56.1	45.2	42.9

TRACE ELEMENTS ( $\mu\text{g/g}$ )

Analysis No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Li	24	21	21	23	17	21	23	26	28	19	19	22	22	22	26
Cu	10	11	20	11	12	10	15	16	12	9	11	12	10	12	8
Zn	68	53	104	51	60	59	84	84	62	46	79	64	63	70	50
V		63	141	58	65		113	132		63	81	77	76	85	50
Ni		14	23		14		16	22			13	14	14	13	
Cr		26	85		30		51	75			35	32	32	36	
Y	32	31	30	31	30	33	36	29	30	29	30	31	34	32	30
Sr	324	258	421	230	266	285	445	429	274	203	302	299	306	324	218
Rb	142	176	160	178	162	158	103	169	188	189	148	152	151	141	182
Zr	48	173	188	168	172	174	183	212	168	157	181	170	175	236	
Nb		11	8		11		14	13		12	9	6	11	10	
Ba		716	957	694	730		704	982		674	728	720	753	752	686
Ce				64				57							62
Nd				29				53							28
Pb	25		16	29	30	27	14	18	19	31		25	24	23	30
K/Rb	199	189	68	151	205	210	210	171	169	190	205	198	198	197	198

Analysis No.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Li	21	24	27	15	11	23	18	30	36	21	43	21	22	53	17
Cu	10	12	14	12	5	11	5	10	9	11	16	8	12	26	16
Zn	65	76	44	86	65	72	47	91	120	64	82	62	65	87	73
V	83	87	-	108	34	92		77				36	86	135	108
Ni	15	15	12	20	12			16					14	22	18
Cr	34	34	6	53	18			35					35	80	45
Y	30	32	41	32	35	34	34	31	31	30		30	31	33	29
Sr	317	320	81	400	306	331	188	342	341	261		291	301	421	358
RB	319	147	203	155	176	147	187	181	199	160		173	155	179	179
Zr	169	210	300	235	249	193		249	250	188		238	140	209	226
Nb	11	8	13	9	10	10		10					13		6
Ba	782	762	1152	979	1456	750		990				1335	720	1081	941
Ce		55	66	59		60									57
Nd		27	33	34		33									33
Pb	25	26	30	27	31	22	25	60		27		29	27	14	28
K/Rb	204	196	211	219	220	199	224	204	188	199	210	222	199	175	179

## TRACE ELEMENTS (µg/g)

Analysis No.	31	32	33	34	35	36	37	38	39	40	41	42	43
Li	23	8	29	29	15	18	11	24	43	23	28	27	18
Cu	9	7	18	10	6	3	14	8	10	5	7	4	8
Zn	55	111	79	71	45	45	73	63	83	45	60	47	65
V	41	-	158	81	-		87		7		-	8	-
Ni	11	9	22	20	13		21		14			9	
Cr	18	6	100	62	5		53		9			6	
Y	30	29	28	30	40	36	36	23	33		48	42	111
Sr	300	102	443	307	65	80	349	384	149		45	97	48
Rb	151	167	246	156	200	200	215	166	229		208	159	211
Zr	251	451	219	217	380		260	280	474		172	201	142
Nb	10	13	13	10	14		15		12		15	11	12
Ba	1363	1303	929	941	759		1141		2391		479	975	388
Ce		56	37		46			22	29			105	182
Nd		31	58									40	78
Pb	29	26	14	10								19	31
K/Rb	247	317	128	192	268	264	163	201	217		206	230	199

Analysis No.	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58
Li	28	10	21	8	18	22	22	14	19	16	21	23	34	10	28
Cu	5	8	5	5	3	4	4	9	7	5	4	6	11	5	7
Zn	47	48	51	40	42	54	54	33	55	63	51	56	76	70	34
V					-		25	65	38	59	25	13	54	25	52
Ni			11		9	23	10	(2)	10	9	7	6	11	9	11
Cr					6		8	10	14	24	9	9	16	15	16
Y	28	31	32	42	37	36	33	17	38	32	32	44	36	31	30
Sr	357	298	213	33	93	287	309	491	225	250	309	195	445	264	314
Rb	165	-	173	196	182	124	140	36	128	148	145	91	125	168	155
Zr	264		222	144	203	400	311	487	229	149	263	316	299	219	220
Nb			11	11	6	10	12	6	10	11	11	11	15	10	8
Ba				208	947	1934	1733	992	910	717	1577	1308	696	123	755
Ce							32		59			46			
Nd							15		26			25			
Pb			32	33		32	22	11	20	14	22	15	16	56	16
K/Rb						283	251	482	235	238	244	338	179	235	200

TRACE ELEMENTS ( $\mu\text{g/g}$ )

Analysis No.	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73
Li	21	29	40	39	25	34	34	32	83	56	31	29	25	46	33
Cu	8	4	5	3	7	3	5	8	11	6	7	9	5	3	2
Zn	74	45	49	47	18	26	33	21	27	29	48	42	38	68	40
V	23	17		22		(2)	-		9		43		11		
Ni	9	15		16		15	15		17		10		11		
Cr	9	7		11		7	7		11		17		14		
Y	36	49	45	42	24	47	61	80	59	57	21	28	29	37	33
Sr	322	131	146	165	103	70	48	36	86	71	342	311	171	164	124
Rb	132	224	228	227	218	262	231	226	337	298	198	156	222	207	237
Zn	310	209	174	177	64	100	99	101	143	135	215	164		116	95
Nb	11	17		9		16	10		14		6		11		
Ba	2112	557		564		180	256		274		375		404		
Ce				37			57		77		45		48		
Nd				31			38		35		16		25		
Pb	22	25	18	20		25	31	33	17	20	22	17	31		31
K/Rb	280	162	154	165	165	152	171	177	112	139	177	202	191	152	172

Analysis No.	74	75	76	77	78	79	80	81	82	83	84	85
Li	23	22	22	34	20	28	15	28	29	19	28	39
Cu	3	16	6	12	20	29	16	3	6	26	6	11
Zn	45	58	51	111	94	117	107	85	78	92	157	114
V	42	71		139	213	245		148		187	192	43
Ni	10	11		18	41	13		10		27	19	21
Cr	22	31		24	282	15		21		159	20	20
Y	30	33		49	22	32		29	29	40	30	26
Sr	212	268		395	453	386		661	652	630	355	358
Rb	191	157		98	46	139		82	82	54	198	242
Zn	155	171		204	122	112		121	127	53	249	242
Nb	11	13		20	3	15		11		9	14	14
Ba	711	759		475	481	1019		353		511	747	127
Ce				77	30	46		44		56	55	55
Nd				45	17	23		25		35	30	24
Pb	21	31		13	7	19		9		9	12	18
K/Rb	191	209		126	282	241		169	172	274	131	122

UNPUBLISHED CHEMICAL DATA REPRESENTATIVE ANALYSES

Field No.	STANTHORPE ADAMELLITE								RUBY CREEK ADAMELLITE				BOOKOOKOORARA ADAMELLITE		POSTMANS CREEK GRANODIORITE
	11	27M	37	14	16	87M	3B	4	26	2	3	49	1B	2B	41
SiO <sub>2</sub>	67.67	69.09	73.04	68.13	74.00	76.61	75.17	72.97	77.07	75.63	73.91	75.97	72.13	72.94	62.74
TiO <sub>2</sub>	0.56	0.53	0.29	0.54	0.23	0.27	0.16	0.23	0.05	0.14	0.13	0.12	0.13	0.21	0.65
Al <sub>2</sub> O <sub>3</sub>	15.47	14.67	13.54	15.24	13.11	12.19	12.25	13.82	12.35	13.00	12.99	12.43	13.70	14.05	15.77
Fe <sub>2</sub> O <sub>3</sub>	0.44	0.36	0.27	0.45	0.34	0.22	0.37	0.70	0.22	0.31	0.28		0.57	0.46	1.03
FeO	3.28	2.51	1.88	3.16	1.59	0.79	0.87	1.06	0.71	1.03	0.91	1.26*	1.18	0.92	4.62
MnO	0.07	0.06	0.05	0.06	0.02	0.25	0.04	0.07	0.05	0.06	0.04	0.04	0.04	0.05	0.16
MgO	0.99	0.94	0.44	1.09	0.43	0.47	0.26	0.45	0.09	0.43	0.29	0.18	0.65	0.53	2.53
CaO	2.15	2.46	1.12	2.37	0.76	0.63	0.97	1.33	0.43	1.16	1.09	0.88	1.52	1.55	4.89
Na <sub>2</sub> O	4.25	3.67	3.49	4.50	3.44	3.13	3.54	3.75	3.75	3.44	3.59	3.71	3.59	3.89	3.13
K <sub>2</sub> O	4.52	4.32	5.14	5.24	5.27	5.37	4.58	4.63	4.74	4.51	4.24	5.27	4.84	3.72	3.23
P <sub>2</sub> O <sub>5</sub>	0.18	0.18	0.10	0.15	0.11	0.07	0.05	0.11	0.01	0.08	0.05	0.06	0.07	0.09	0.
H <sub>2</sub> O total	0.35	0.24	0.11	0.27	0.22	0.08	0.05	0.28	0.10	0.17	0.08	0.08	0.15	0.12	0.58
TOTAL	99.93	99.03	99.47	101.20	99.52	101.08	98.31	99.40	99.57	99.96	97.60	100.00	98.57	98.53	99.51
Y	44	43	52	44	20	25	42	39	68	29	34		22	54	32
Sr	199	270	90	213	72	30	86	126	4	114	81		232	454	339
Rb	155	141	158	141	137	187	292	197	337	224	204		210	248	124
Zr	311	221	238	291	203	104	117	137	149	113	103		162	107	172
U	4	5	5	4	3	5	8	6	13	5	8		10	14	4
Th	6	25	16	15	10	31	30	19	30	14	24		27	18	12
Pb	20	29	23	21	28	25	30	23	40	28	27		28	18	16

Major elements in weight percent oxide.

Trace elements in µg/g.

\* Total iron as FeO. This analysis from Juniper, 1974.

All others from Thomson, 1976.

APPENDIX 3

## MINERAL CHEMICAL DATA

Electron microprobe analyses of -

Amphiboles

Clinopyroxenes and Orthopyroxenes

Biotites

Magnetites

Ilmenites

Plagioclases (Ca, K, Na components)

## ELECTRON MICROPROBE ANALYSES OF AMPHIBOLES

Analysis No.	150A	150A	16	16	12	12	13	13	15	15	2	2	1	1	5	5	11	11
SiO <sub>2</sub>	46.06	46.76	44.51	45.48	43.83	46.16	46.67	46.62	46.57	46.19	45.91	42.22	46.55	45.44	47.88	46.02	46.58	46.17
TiO <sub>2</sub>	1.56	1.55	1.67	1.68	2.39	1.65	1.60	1.54	1.50	1.58	1.52	2.22	1.52	1.40	1.37	1.3	1.53	1.54
Al <sub>2</sub> O <sub>3</sub>	7.01	7.44	8.33	8.11	10.16	7.71	7.21	7.18	7.31	7.33	7.53	11.13	6.87	7.52	6.25	7.50	7.45	7.48
V <sub>2</sub> O <sub>5</sub>													0.11			0.12		
FeO total	16.39	16.10	17.22	16.77	14.78	15.27	16.17	16.49	16.78	16.74	16.71	15.94	16.07	16.98	15.85	16.38	16.23	16.46
MnO	0.49	0.39	0.43	0.42	0.27	0.40	0.43	0.42	0.40	0.42	0.46	0.43	0.39	0.43	0.40	0.47	0.55	0.46
MgO	12.16	12.49	11.53	12.19	12.24	12.51	12.33	12.44	12.52	12.20	12.23	11.41	12.67	11.98	13.39	12.21	12.53	12.54
CaO	10.86	11.00	11.19	11.18	11.27	11.03	11.14	11.27	11.20	11.09	10.95	11.41	11.02	11.13	11.19	11.00	11.06	11.04
K <sub>2</sub> O	0.73	0.68	0.98	0.79	0.75	0.83	0.74	0.71	0.77	0.82	0.83	0.89	0.77	0.77	0.65	0.69	0.82	0.78
Na <sub>2</sub> O	1.28	1.33	1.59	1.66	1.99	1.46	1.49	1.44	1.30	1.60	1.44	1.85	1.34	1.26	1.21	1.44	1.49	1.42
Cl	0.11	0.10	0.14	0.11	0.07	0.12		0.14	0.12	0.12	0.15	0.11	0.14	0.13	0.11	0.07	0.17	0.13
TOTAL	96.66	96.85	97.58	98.40	97.76	97.55	97.79	98.25	98.47	98.09	97.74	97.60	97.44	97.15	98.29	97.25	98.41	98.01

## Structural formulae based on 23 oxygens

Si	6.949	6.883	6.719	6.771	6.523	6.869	6.942	6.924	6.906	6.889	6.871	6.538	6.957	6.867	7.060	6.900	6.904	6.877
Al <sup>IV</sup>	1.051	1.117	1.281	1.229	1.477	1.131	1.058	1.076	1.094	1.111	1.129	1.462	1.043	1.133	0.940	1.100	1.096	1.123
Al <sup>VI</sup>	0.196	0.201	0.200	0.195	0.305	0.220	0.207	0.181	0.184	0.178	0.200	0.513	0.166	0.202	0.145	0.235	0.205	0.190
Ti	0.177	0.176	0.189	0.188	0.268	0.185	0.179	0.172	0.167	0.177	0.171	0.251	0.170	0.159	0.151	0.153	0.171	0.172
Fe <sup>2+</sup>	2.067	2.025	2.174	2.088	1.840	1.901	2.012	2.049	2.080	2.088	2.091	2.007	2.008	2.141	1.955	2.053	2.012	2.050
Mn	0.063	0.050	0.056	0.053	0.034	0.051	0.052	0.052	0.051	0.053	0.058	0.055	0.049	0.055	0.050	0.059	0.070	0.058
Mg	2.734	2.799	2.594	2.705	2.715	2.863	2.734	2.755	2.767	2.712	2.729	2.561	2.822	2.693	2.944	2.728	2.769	2.783
V													0.013			0.015		
	5.237	5.251	5.213	5.229	5.162	5.220	5.186	5.209	5.249	5.208	5.249	5.387	5.228	5.250	5.245	5.243	5.227	5.253
Ca	1.755	1.772	1.810	1.784	1.797	1.759	1.776	1.794	1.779	1.772	1.756	1.841	1.765	1.797	1.768	1.766	1.757	1.761
K	0.140	0.130	0.189	0.151	0.143	0.157	0.140	0.135	0.146	0.155	0.158	0.172	0.147	0.147	0.122	0.132	0.155	0.149
Na	0.378	0.388	0.465	0.478	0.574	0.422	0.430	0.413	0.373	0.462	0.418	0.540	0.389	0.369	0.345	0.420	0.428	0.409
	2.273	2.290	2.464	2.413	2.514	2.338	2.346	2.342	2.298	2.389	2.332	2.553	2.301	2.313	2.235	2.318	2.340	2.319
Total cations	15.510	15.541	15.677	15.642	15.676	15.558	15.532	15.551	15.547	15.597	15.581	15.940	15.529	15.563	15.480	15.561	15.567	15.572
100.Mg/Mg+Fe	56.9	58.0	54.4	56.4	59.6	60.1	57.6	57.4	57.1	56.5	56.6	56.1	58.4	55.7	60.1	57.1	57.9	57.6

Analysis No.	9	9	4	4	6	6	10	10	28	28	23	23	178A	178A	25	25	21	21
SiO <sub>2</sub>	45.80	45.81	45.80	42.21	46.36	45.05	45.66	46.71	43.84	45.94	43.71	46.91	46.72	43.19	46.15	45.82	46.49	45.38
TiO <sub>2</sub>	1.35	1.52	1.49	2.05	1.47	1.68	1.62	1.53	1.74	0.49	1.21	0.80	1.47	2.39	1.41	1.61	1.48	1.39
Al <sub>2</sub> O <sub>3</sub>	7.50	7.97	6.94	11.30	7.27	8.48	7.76	7.16	7.90	5.33	8.25	5.73	7.17	10.89	7.40	7.47	6.85	7.61
V <sub>2</sub> O <sub>5</sub>												0.11			0.14			
FeO total	16.65	15.17	15.83	15.24	16.74	16.52	17.00	16.55	17.30	22.70	21.51	20.18	16.63	15.22	16.45	16.87	16.35	16.88
MnO	0.39	0.49	0.42	0.31	0.49	0.29	0.53	0.48	0.43	1.24	0.69	0.70	0.40	0.28	0.58	0.58	0.47	0.45
MgO	12.22	12.99	12.29	11.66	12.35	11.89	11.87	12.34	11.33	9.50	7.73	9.45	13.18	12.33	12.22	12.17	12.68	11.88
CaO	10.91	11.17	10.81	11.61	11.09	11.12	11.13	11.03	11.86	10.27	11.72	11.62	11.16	11.43	10.95	11.02	11.02	11.02
K <sub>2</sub> O	0.79	0.87	0.73	1.02	0.80	0.94	0.87	0.76	0.92	0.36	1.01	0.58	0.70	0.70	0.78	0.81	0.71	0.87
Na <sub>2</sub> O	1.28	1.40	1.40	1.89	1.52	1.53	1.44	1.35	2.68	2.17	1.23	0.74	1.23	1.85	1.42	1.43	1.17	1.35
Cl	0.11	0.11	0.25	0.98	0.09	0.10	0.12	0.13			0.47	0.24	0.21	0.06	0.15	0.16	0.08	0.11
TOTAL	97.00	97.50	95.95	97.38	98.18	97.73	98.01	98.02	98.00	98.00	97.80	97.21	98.87	98.34	97.64	97.94	97.42	96.94

## Structural formulae based on 23 oxygens

Si	6.894	6.826	6.956	6.353	6.903	6.748	6.832	6.948	6.640	7.065	6.763	7.166	6.096	6.406	6.905	6.856	6.951	6.859
Al <sup>IV</sup>	1.106	1.174	1.044	1.647	1.097	1.252	1.168	1.052	1.360	0.935	1.237	0.834	1.104	1.594	1.095	1.144	1.049	1.141
Al <sup>VI</sup>	0.225	0.225	0.199	0.348	0.179	0.245	0.200	0.203	0.050	0.032	0.267	0.198	0.144	0.310	0.209	0.173	0.158	0.214
Ti	0.153	0.171	0.170	0.233	0.164	0.190	0.183	0.171	0.198	0.056	0.141	0.092	0.163	0.266	0.159	0.181	0.166	0.158
Fe <sup>2+</sup>	2.095	1.891	2.010	1.919	2.085	2.069	2.127	2.059	2.190	2.919	2.783	2.578	2.053	1.889	2.058	2.110	2.044	2.133
Mn	0.050	0.061	0.054	0.039	0.062	0.037	0.067	0.061	0.056	0.161	0.090	0.090	0.050	0.035	0.074	0.073	0.060	0.058
Mg	2.742	2.886	2.783	2.616	2.741	2.655	2.648	2.735	2.557	2.177	1.783	2.152	2.899	2.726	2.724	2.714	2.826	2.675
V											0.014			0.017		0.014		
	5.265	5.234	5.216	5.165	5.231	5.211	5.225	5.229	5.051	5.345	5.078	5.110	5.309	5.226	5.241	5.251	5.268	5.239
Ca	1.759	1.783	1.759	1.873	1.769	1.785	1.784	1.757	1.924	1.692	1.944	1.901	1.765	1.816	1.755	1.767	1.765	1.784
K	0.151	0.166	0.141	0.196	0.152	0.179	0.166	0.143	0.179	0.070	0.200	0.114	0.131	0.132	0.149	0.155	0.135	0.168
Na	0.374	0.406	0.413	0.553	0.439	0.444	0.418	0.388	0.787	0.646	0.369	0.220	0.353	0.533	0.411	0.415	0.339	0.395
	2.284	2.355	2.313	2.622	2.360	2.408	2.363	2.298	2.890	2.403	2.513	2.235	2.249	2.481	2.315	2.337	2.239	2.347
Total cations	15.549	15.589	15.529	15.787	15.591	15.619	15.593	15.517	15.941	15.753	15.591	15.345	15.558	15.707	15.556	15.588	15.507	15.586
100.Mg/Mg+Fe	56.7	60.4	58.1	57.7	56.8	56.2	55.5	57.0	53.9	42.7	40.7	40.9	58.5	59.1	57.0	56.3	58.0	55.6

Analysis No.	27	27	33	33	31	31	75	75	74	74	72	69	69	58	58	50	50	
SiO <sub>2</sub>	46.06	48.99	51.13	48.22	47.00	46.36	45.13	44.46	47.68	45.16	43.42	43.73	51.83	50.41	48.5	44.32	42.75	47.11
TiO <sub>2</sub>	0.23	0.13	0.64	1.03	1.48	1.60	1.52	1.50	0.96	1.48	1.39	1.49	0.39	0.41	0.78	1.54	2.49	1.38
Al <sub>2</sub> O <sub>3</sub>	6.63	4.02	4.41	6.49	7.14	7.35	7.14	7.13	5.90	7.75	7.80							



ELECTRON MICROPROBE ANALYSIS OF AMPHIBOLS (continued)

Analysis No.	53	53	51	51	55	55	54	54	52	52	79	79	85	85	83	83	81	81
SiO <sub>2</sub>	46.86	47.15	49.54	47.96	47.07	45.75	47.04	45.97	44.67	43.96	45.85	45.12	47.47	46.77	49.60	4.22	47.82	46.42
TiO <sub>2</sub>	1.07	1.52	0.74	1.02	1.26	0.70	1.30	1.60	1.09	0.74	1.58	1.64	1.31	1.48	0.41	0.99	0.95	1.14
Al <sub>2</sub> O <sub>3</sub>	6.49	6.84	4.93	6.03	8.00	6.19	6.53	7.75	7.24	3.05	7.42	7.90	6.86	7.25	4.38	5.74	5.54	6.98
V <sub>2</sub> O <sub>5</sub>				0.11														0.12
FeO total	15.66	15.10	14.37	14.49	26.19	21.61	15.15	15.26	21.70	21.43	17.24	17.39	13.96	14.52	14.09	15.21	13.78	19.49
MnO	0.82	0.89	0.29	0.42	1.30	1.18	0.98	0.92	0.84	0.66	0.56	0.52	0.78	0.86	0.50	0.49	0.54	0.56
MgO	12.53	12.83	14.21	13.85	4.96	8.41	13.08	12.23	3.65	8.61	12.04	11.75	13.54	13.12	13.63	12.60	10.88	9.91
CaO	11.49	11.10	11.98	11.78	10.44	10.96	11.15	10.92	10.85	11.41	11.24	11.13	11.71	11.67	13.19	13.11	11.78	11.92
K <sub>2</sub> O	0.63	0.70	0.43	0.48	1.03	0.64	0.71	0.64	0.85	0.91	0.76	0.86	0.70	0.75	0.24	0.55	0.53	0.74
Na <sub>2</sub> O	1.14	1.59	0.63	0.94	1.89	1.41	1.60	1.69	1.37	1.43	1.34	1.35	1.36	1.33	1.97	2.09	0.92	1.03
Cl	0.17	0.17	0.28	0.28	0.38	0.13	0.11	0.09	0.23	0.22	0.10	0.14					0.09	0.16
TOTAL	96.88	97.91	97.50	97.36	97.53	96.99	97.54	97.05	97.50	97.41	98.13	97.80	97.69	97.95	98.00	98.00	97.83	98.47

Structural Formulae based on 23 oxygens

Si	7.040	6.993	7.294	7.108	6.707	7.080	7.002	6.886	6.894	6.796	6.838	6.785	7.004	6.918	7.115	7.034	7.185	6.987
Al <sup>6</sup>	0.960	1.007	0.706	0.892	1.293	0.920	0.998	1.114	1.106	1.204	1.162	1.215	0.996	1.082	0.885	0.966	0.815	1.013
Al <sup>6</sup>	0.189	0.180	0.157	0.160	0.211	0.209	0.147	0.254	0.211	0.262	0.143	0.186	0.197	0.181	0.099	0.041	0.167	0.225
Ti	0.121	0.170	0.082	0.114	0.151	0.082	0.146	0.180	0.127	0.086	0.177	0.166	0.145	0.164	0.074	0.110	0.107	0.129
Fe <sup>2+</sup>	1.967	1.873	1.770	1.796	3.492	2.797	1.886	1.911	2.801	2.771	2.149	2.187	1.722	1.797	1.893	1.895	2.359	2.453
Mn	0.105	0.111	0.036	0.053	0.176	0.155	0.123	0.116	0.110	0.086	0.071	0.066	0.098	0.108	0.055	0.062	0.069	0.071
Mg	2.806	2.837	3.118	3.059	1.179	1.940	2.901	2.730	1.989	1.984	2.676	2.633	2.978	2.893	2.804	2.797	2.435	2.222
V			0.013															0.015
Ca	5.188	5.180	5.163	5.195	5.209	5.183	5.203	5.191	5.238	5.184	5.216	5.258	5.140	5.143	4.925	4.905	5.137	5.115
K	1.849	1.764	1.891	1.870	1.784	1.817	1.778	1.752	1.794	1.890	1.796	1.793	1.852	1.881	2.063	2.093	1.895	1.921
Na	0.122	0.133	0.081	0.091	0.209	0.127	0.135	0.123	0.167	0.179	0.144	0.165	0.132	0.142	0.073	0.105	0.102	0.142
	0.333	0.458	0.194	0.270	0.585	0.423	0.460	0.490	0.409	0.428	0.389	0.394	0.390	0.382	0.592	0.604	0.269	0.300
	2.304	2.355	2.166	2.231	2.578	2.367	2.373	2.365	2.370	2.497	2.329	2.352	2.374	2.405	2.728	2.802	2.266	2.363
Total cations	15.492	7.535	15.329	15.426	15.787	15.550	15.576	15.556	15.608	15.686	15.545	15.610	15.514	15.548	15.653	15.707	15.403	15.478
100.Mg/Mg+Fe	58.8	60.2	63.8	63.0	25.2	41.0	60.6	58.8	41.5	41.7	55.5	54.6	63.4	61.7	63.3	59.6	50.8	47.5

Analysis No.	84	84	77	77	78	78	Analysis No.	51	53	69	17	78	85
SiO <sub>2</sub>	49.94	49.42	43.45	45.56	47.45	49.27	SiO <sub>2</sub>	49.21	46.98	51.83	45.76	47.45	46.77
TiO <sub>2</sub>	0.65	0.73	2.02	1.63	1.14	0.68	TiO <sub>2</sub>	0.89	1.30	0.39	1.55	1.14	1.48
Al <sub>2</sub> O <sub>3</sub>	4.17	4.77	9.33	7.58	7.70	5.54	Al <sub>2</sub> O <sub>3</sub>	5.07	6.72	3.90	7.44	7.70	7.25
V <sub>2</sub> O <sub>5</sub>				0.15	0.15		Fe <sub>2</sub> O <sub>3</sub>	2.62	1.25	1.92	3.61	1.49	3.77
FeO total	15.19	15.27	19.22	17.16	12.79	12.87	FeO	11.80	14.43	10.35	12.85	11.45	11.13
MnO	1.16	0.96	0.62	0.69	0.30	0.30	MnO	0.34	0.70	0.85	0.37	0.30	0.86
MgO	13.84	13.14	9.74	11.19	14.36	14.99	MgO	14.03	12.82	15.40	12.49	14.36	13.12
CaO	10.73	11.17	11.52	11.24	12.02	12.16	CaO	11.97	11.28	11.68	11.00	12.02	11.87
K <sub>2</sub> O	0.28	0.41	1.01	0.79	0.48	0.31	K <sub>2</sub> O	0.40	0.67	0.51	0.68	0.48	0.75
Na <sub>2</sub> O	0.98	1.04	1.72	1.54	1.17	0.68	Na <sub>2</sub> O	0.63	1.38	0.66	1.33	1.17	1.33
Cl	0.12	0.10	0.13	0.15	0.08	0.11	Cl		0.17		0.10	0.08	
TOTAL	97.06	97.00	98.76	97.68	97.48	97.07	TOTAL	96.96	97.70	97.49	97.20	97.64	98.33

Structural Formulae based on 23 oxygens

Si	7.403	7.344	6.566	6.858	6.956	7.228	Si	7.235	6.980	7.492	6.823	6.931	6.859
Al <sup>6</sup>	0.597	0.656	1.434	1.142	1.044	0.772	Al <sup>6</sup>	0.765	1.020	0.508	1.177	1.069	1.141
Al <sup>6</sup>	0.131	0.180	0.227	0.202	0.286	0.185	Al <sup>6</sup>	0.113	0.156	0.157	0.131	0.256	0.112
Ti	0.073	0.081	0.230	0.185	0.125	0.075	Ti	0.098	0.145	0.043	0.174	0.125	0.163
Fe <sup>2+</sup>	1.883	1.897	2.429	2.160	1.568	1.579	Fe <sup>2+</sup>	0.290	0.139	0.208	0.405	0.163	0.409
Mn	0.145	0.121	0.080	0.099	0.037	0.037	Fe <sup>3+</sup>	1.450	1.792	1.251	1.601	1.399	1.365
Mg	3.058	2.910	2.194	2.510	3.139	3.278	Mg	0.042	0.088	0.104	0.049	0.037	0.107
V				0.018	0.018		Mn	3.075	2.838	3.317	2.775	3.126	2.868
	5.290	5.189	5.160	5.164	5.155	5.172		5.068	5.158	5.080	5.135	5.106	5.024
Ca	1.704	1.778	1.865	1.812	1.808	1.912	Ca	1.835	1.795	1.809	1.756	1.881	1.865
K	0.053	0.078	0.195	0.151	0.090	0.058	K	0.074	0.127	0.094	0.129	0.090	0.141
Na	0.281	0.299	0.503	0.450	0.331	0.194	Na	0.160	0.398	0.184	0.385	0.332	0.379
	2.038	2.155	2.563	2.413	2.309	2.164		2.130	2.320	2.087	2.270	2.303	2.385
Total cations	15.328	15.344	15.723	15.577	15.464	15.336	Total cations	15.207	15.478	15.167	15.405	15.409	15.409
100.Mg/Mg+Fe	61.9	60.5	47.5	53.7	66.7	67.5	100.Mg/Mg+Fe	64.3	59.7	69.8	58.5	66.9	62.3

ELECTRON MICROPROBE ANALYSES OF CLINOPYROXENES

Analysis No.	150A	150A	97A	97A	16	16	16	12	12	13	13	13	15	15	2	2	1	1
SiO <sub>2</sub>	52.17	52.19	52.19	52.03	53.35	51.47	51.96	52.38	52.09	52.36	51.63	51.83	51.96	52.26	52.57	52.14	51.83	52.27
TiO <sub>2</sub>					0.24	0.40				0.40	0.26		0.22	0.14	0.14	0.17	0.17	
Al <sub>2</sub> O <sub>3</sub>	0.83	0.84	0.79	0.76	1.66	2.89	0.88	0.80	1.03	2.18	1.80	0.91	1.24	1.04	0.99	0.99	1.62	
FeO total	12.28	12.11	12.22	11.72	6.37	7.26	12.22	11.89	12.20	7.75	10.15	12.32	12.05	9.94	11.73	12.01	9.84	
MnO	0.78	0.69	0.98	0.74	0.15	0.16	0.82	0.66	0.79	0.16	0.62	0.73	0.56	0.41	0.79	1.03	0.49	
MgO	12.60	12.48	12.21	12.75	17.30	15.60	12.43	12.73	12.38	16.01	13.26	12.38	12.73	13.98	12.46	12.11	13.73	
CaO	21.46	21.61	21.25	21.71	20.94	21.33	21.26	21.54	21.29	20.63	21.79	21.75	21.31	21.74	21.63	21.09	21.67	
K <sub>2</sub> O														0.07				
Na <sub>2</sub> O	0.18	0.26	0.22			0.20	0.25		0.21	0.20	0.33	0.17	0.23	0.28	0.33	0.19		
TOTAL	100.30	100.18	99.86	99.71	100.01	99.31	99.82	100.00	99.89	99.69	99.84	100.09	100.30	100.33	99.89	100.02	99.56	99.98

ELECTRON MICROPROBE ANALYSES OF CLINOPYROXINES (continued)

Analysis No.	3	3	5	5	8	8	6	6	10	10	19	19	25	25	178A	178A	156A	156A
			core	rim	core	rim							core	rim	core	rim	core	rim
SiO <sub>2</sub>	51.38	51.50	52.40	52.02	51.59	51.43	52.66	52.32	51.75	52.29	52.07	51.57	52.30	52.30	52.65	52.20	52.36	52.02
TiO <sub>2</sub>	0.37	0.25			0.28	0.55				0.18	0.33	0.38	0.15				0.28	0.31
Al <sub>2</sub> O <sub>3</sub>	2.03	1.23	0.82	0.92	1.55	2.39	0.82	0.78	0.96	0.91	1.53	2.07	1.30	0.81	0.63	0.70	1.14	1.41
FeO total	11.48	13.36	11.92	12.17	11.86	10.20	9.91	11.92	12.11	11.48	10.38	11.62	10.55	12.06	12.55	12.30	10.96	12.09
MnO	0.28	0.43	0.70	0.88	0.35	0.34	0.43	0.74	0.82	0.41	0.28	0.33	0.38	0.66	0.71	0.80	0.28	0.26
MgO	13.49	12.22	12.41	12.40	13.11	14.19	12.91	12.34	12.36	12.93	14.04	13.42	13.70	12.55	12.53	12.47	13.81	13.64
CaO	20.68	20.79	21.54	21.27	20.71	20.72	22.80	21.26	21.39	21.58	21.21	20.38	21.63	21.40	21.36	21.31	21.16	20.65
K <sub>2</sub> O																		
Na <sub>2</sub> O	0.17	0.22	0.21	0.17	0.19	0.17	0.47	0.20	0.23	0.20	0.17	0.32	0.22	0.22				0.15
TOTAL	99.88	100.00	100.00	99.83	99.64	99.99	99.90	99.56	99.62	99.99	100.01	100.09	100.31	100.00	100.43	99.78	99.99	100.53

Structural Formulae based on 6 oxygens

Si	1.935	1.958	1.982	1.975	1.953	1.925	1.982	1.987	1.970	1.973	1.952	1.940	1.961	1.979	1.986	1.982	1.964	1.952
Al <sup>4</sup>	0.065	0.042	0.018	0.025	0.047	0.075	0.018	0.013	0.030	0.027	0.048	0.060	0.039	0.021	0.014	0.018	0.036	0.048
Al <sup>6</sup>	0.025	0.013	0.018	0.016	0.022	0.031	0.018	0.022	0.013	0.014	0.020	0.032	0.018	0.015	0.014	0.013	0.015	0.014
Ti	0.011	0.007			0.008	0.016				0.005	0.009	0.011	0.004				0.008	0.009
Fe <sup>2+</sup>	0.362	0.425	0.377	0.387	0.376	0.320	0.312	0.379	0.385	0.362	0.325	0.366	0.330	0.382	0.396	0.391	0.341	0.379
Mn	0.009	0.014	0.023	0.028	0.011	0.011	0.014	0.024	0.026	0.013	0.009	0.010	0.012	0.021	0.023	0.026	0.009	0.008
Mg	0.757	0.693	0.700	0.702	0.740	0.792	0.719	0.698	0.702	0.727	0.784	0.752	0.765	0.708	0.704	0.706	0.772	0.763
Ca	0.834	0.847	0.873	0.865	0.840	0.831	0.920	0.865	0.872	0.872	0.852	0.821	0.868	0.868	0.863	0.867	0.850	0.830
K																		
Na	0.012	0.016	0.016	0.012	0.014	0.012	0.034	0.015	0.017	0.015	0.012	0.023	0.016	0.016				0.011
	2.010	2.015	2.014	2.010	2.011	2.013	2.017	2.003	2.015	2.008	2.011	2.015	2.013	2.010	2.000	2.003	1.998	2.014
Total cations	4.010	4.015	4.014	4.010	4.011	4.013	4.017	4.003	4.015	4.008	4.011	4.015	4.013	4.010	4.000	4.003	3.998	4.014
100.Mg/Mg+Fe	67.7	62.0	65.0	64.5	66.3	71.3	69.7	64.8	64.5	66.7	70.7	67.3	69.8	65.0	64.0	64.4	69.2	66.8

ORTHOPYROXINES

Analysis No.	34	34	21	21	33	33	31	30	30	30	30	79	80	80	13	13	74	74
								core	rim	core	rim							
SiO <sub>2</sub>	52.33	51.72	52.01	51.74	52.63	52.09	51.92	50.52	51.71	50.97	50.72	51.81	51.94	51.92	50.84	52.94	51.72	52.46
TiO <sub>2</sub>		0.13	0.11		0.36	0.11		0.90	0.58	0.74	0.37		0.12	0.12	0.15	0.33	0.35	0.24
Al <sub>2</sub> O <sub>3</sub>	0.54	0.63	0.77	0.82	1.98	0.95	1.07	4.18	3.16	3.89	3.95	0.88	0.93	1.05	0.91	1.39	2.03	1.61
FeO total	12.29	13.68	11.77	12.33	6.48	10.68	12.10	7.60	6.93	7.32	12.19	12.31	11.61	12.06	27.86	19.84	22.01	20.14
MnO	0.64	0.46	0.62	0.90	0.18	0.52	0.85		0.12		0.29	0.80	0.80	0.74	1.73	0.41	0.64	0.48
MgO	11.54	11.86	12.80	12.00	15.10	12.19	12.38	15.22	15.79	15.34	14.49	12.50	12.67	12.29	17.34	23.21	21.89	23.48
CaO	22.66	21.45	21.91	21.65	22.59	23.17	20.98	21.25	21.49	21.35	17.69	21.46	21.59	21.58	1.02	2.26	1.49	1.36
K <sub>2</sub> O							0.08				0.08							
Na <sub>2</sub> O		0.19		0.31		0.24	0.25	0.15	0.23	0.24	0.23	0.17	0.35	0.24				
TOTAL	100.00	100.12	99.99	99.74	99.32	99.95	99.63	99.82	100.01	99.85	100.01	99.93	100.01	100.00	99.85	100.38	100.13	99.77

Structural Formulae based on 6 oxygens

Si	1.988	1.971	1.969	1.973	1.945	1.970	1.974	1.872	1.909	1.885	1.899	1.968	1.967	1.969	1.965	1.951	1.931	1.945
Al <sup>4</sup>	0.012	0.029	0.031	0.027	0.055	0.030	0.026	0.128	0.091	0.115	0.101	0.032	0.033	0.031	0.035	0.049	0.069	0.055
Al <sup>6</sup>	0.012		0.003	0.010	0.031	0.013	0.022	0.055	0.047	0.054	0.073	0.008	0.008	0.016	0.007	0.011	0.020	0.015
Ti		0.004	0.003		0.010	0.003		0.025	0.016	0.020	0.010		0.003	0.003	0.004	0.009	0.010	0.007
Fe <sup>2+</sup>	0.390	0.436	0.373	0.393	0.200	0.338	0.385	0.236	0.214	0.226	0.382	0.391	0.368	0.382	0.901	0.612	0.687	0.625
Mn	0.021	0.015	0.020	0.029	0.006	0.017	0.028		0.004		0.009	0.026	0.026	0.024	0.057	0.013	0.020	0.015
Mg	0.654	0.675	0.722	0.682	0.832	0.687	0.702	0.840	0.869	0.846	0.808	0.708	0.715	0.695	0.999	1.275	1.218	1.297
Ca	0.923	0.876	0.889	0.884	0.894	0.939	0.855	0.843	0.850	0.846	0.710	0.874	0.876	0.877	0.042	0.089	0.059	0.054
K							0.004				0.004							
Na		0.014		0.023		0.017	0.019	0.011	0.016	0.017	0.017	0.013	0.025	0.018				
	2.000	2.019	2.010	2.021	1.973	2.014	2.015	2.010	2.016	2.009	2.013	2.020	2.021	2.014	2.010	2.009	2.014	2.013
Total cations	4.000	4.019	4.010	4.021	3.973	4.014	4.015	4.010	4.016	4.009	4.013	4.020	4.021	4.014	4.010	4.009	4.014	4.013
100.Mg/Mg+Fe	62.6	60.7	66.0	63.4	80.6	67.1	64.6	78.1	80.2	78.9	67.9	64.4	66.0	64.5	52.6	67.6	63.9	67.5

ELECTRON MICROPROBE ANALYSES OF BIOTITES

Analysis No.	150A	97A	16	12	13	15	2	1	3	5	11	8	8	9	4	6	10	28
SiO <sub>2</sub>	35.58	35.81	36.20	36.27	35.44	35.94	36.46	35.74	34.55	36.53	36.15	35.82	35.07	36.16	36.29	36.20	36.48	34.11
TiO <sub>2</sub>	4.78	2.72	4.64	3.98	4.97	4.72	4.07	4.75	6.23	5.02	4.75	6.46	6.44	1.00	4.88	5.19	4.71	5.49
Al <sub>2</sub> O <sub>3</sub>	13.36	14.03	13.69	13.78	13.26	13.52	13.49	13.36	13.91	13.61	13.83	14.25	14.40	16.36	13.44	13.56	13.57	13.77
FeO total	19.84	23.32	19.11	20.25	19.21	20.16	19.51	19.27	21.75	18.73	19.46	17.19	21.11	19.92	18.80	19.50	19.48	20.72
MnO	0.30	0.31	0.21	0.27	0.26	0.23	0.28	0.28	0.27	0.28	0.38	0.14	0.14	0.22	0.49	0.27	0.32	0.22
MgO	10.77	9.16	11.55	11.50	11.29	11.14	11.35	11.10	8.53	11.79	11.19	12.52	9.28	11.03	11.39	11.38	11.61	10.51
CaO		0.13	0.09						0.90				0.09					
K <sub>2</sub> O	9.84	9.54	9.36	9.88	9.48	9.60	9.78	9.75	9.15	9.88	9.87	9.01	9.39	10.09	9.53	9.66	9.58	9.47
Na <sub>2</sub> O		0.14	0.38		0.23		0.12					0.35	0.16		0.13	0.51		1.50
Cl	0.20	0.21	0.31	0.22	0.31	0.20	0.21	0.20	0.20	0.18	0.06			0.19	0.21	0.44	0.22	0.20
TOTAL	94.67	95.37	95.54	96.15	94.45	95.51	96.07	94.45	95.29	96.04	95.81	95.80	96.08	94.97	95.16	96.70	95.97	95.99

ELECTRON MICROPROBE ANALYSES OF BIOTITES (continued)

Analysis No.	23	19	156A	170A	25	34	22	29	21	27	33	31	44	46	75	74	72	63
SiO <sub>2</sub>	35.30	35.62	35.73	36.51	35.98	35.85	33.76	36.15	36.67	34.92	36.15	36.57	34.53	36.54	34.00	35.23	34.68	36.38
TiO <sub>2</sub>	3.90	6.33	6.64	5.05	5.04	4.26	4.63	4.04	5.00	5.46	4.00	4.85	4.83	3.06	5.16	4.71	4.77	3.98
Al <sub>2</sub> O <sub>3</sub>	13.41	14.04	14.31	13.56	13.48	13.64	14.54	14.50	13.59	13.37	14.37	13.67	13.31	13.66	13.13	13.10	13.21	13.19
FeO total	22.77	16.64	18.58	19.19	19.07	22.34	22.47	20.41	19.46	23.22	20.79	18.96	21.30	15.94	22.89	22.78	26.53	19.62
MnO	0.23					0.28	0.31		0.19	0.19			0.09	0.82	0.32	0.25	0.97	0.56
MgO	8.79	12.95	11.40	12.32	11.69	9.51	8.37	9.82	11.88	8.31	10.64	11.56	9.39	13.99	9.11	9.22	6.54	11.10
CaO							1.97		0.10									
K <sub>2</sub> O	9.81	8.84	9.15	9.29	9.27	9.58	6.39	9.31	9.19	9.47	9.81	9.49	10.26	9.94	9.98	9.60	9.43	9.97
Na <sub>2</sub> O	0.13	0.32	0.32	0.19	0.30		0.46		0.28				1.37		1.20		0.17	
Cl	0.32		0.05	0.18	0.18	0.41		0.11	0.21	0.24		0.13	0.11		0.20	0.35	0.19	0.10
TOTAL	94.66	94.74	96.18	96.29	95.01	95.87	92.90	94.34	96.57	95.18	95.75	95.57	95.99	94.15	95.99	95.24	96.49	95.90

Structural Formulae based on 22 oxygens

Si	5.592	5.414	5.887	5.539	5.538	5.576	5.359	5.164	5.554	5.492	5.550	5.581	5.414	5.606	5.361	5.543	5.496	5.637
Al <sup>IV</sup>	2.408	2.515	2.547	2.423	2.444	2.424	2.641	2.654	2.426	2.479	2.450	2.419	2.461	2.394	2.441	2.430	2.467	2.363
Ti		0.071	0.058	0.041	0.013			0.182	0.020	0.029			0.125		0.198	0.027	0.037	
Al <sup>VI</sup>	0.095					0.077	0.079				0.132	0.044		0.112				0.046
Ti	0.464	0.653	0.696	0.535	0.583	0.499	0.553	0.290	0.550	0.617	0.462	0.558	0.445	0.353	0.414	0.530	0.532	0.464
Fe <sup>2+</sup>	3.017	2.115	2.346	2.433	2.454	2.906	2.983	2.651	2.464	3.055	2.669	2.423	2.793	2.045	3.019	2.997	3.516	2.542
Mn	0.031					0.037	0.042		0.024	0.026		0.050	0.119	0.107	0.043	0.033	0.130	0.073
Mg	2.074	2.933	2.566	2.783	2.683	2.205	1.981	2.274	2.681	1.949	2.436	2.633	2.195	3.200	2.142	2.161	1.545	2.562
	5.681	5.701	5.608	5.751	5.702	5.724	5.638	5.215	5.719	5.647	5.699	5.708	5.552	5.817	5.618	5.721	5.723	5.637
Ca							0.335		0.016		0.015							
K	1.982	1.713	1.764	1.798	1.820	1.900	1.295	1.843	1.776	1.901	1.921	1.849	2.053	1.945	2.007	1.927	1.906	1.971
Na	0.040	0.094	0.094	0.057	0.088		0.141		0.082				0.416		0.366		0.052	
	2.024	1.807	1.858	1.855	1.908	1.900	1.771	1.843	1.874	1.901	1.936	1.849	2.469	1.945	2.373	1.927	1.958	1.971
Total cations	15.703	15.508	15.466	15.606	15.610	15.624	15.409	15.058	15.593	15.548	15.635	15.557	16.021	15.762	15.991	15.648	15.681	15.658
100. Mg/Mg+Fe	40.7	58.1	5.2.	53.4	52.2	43.1	39.9	46.2	52.1	38.9	47.7	52.1	44.0	61.0	41.5	41.9	30.5	50.2

Analysis No.	61	67	69	66	49	59	56	58	57	50	53	51	55	55	54	52	52	79
SiO <sub>2</sub>	35.98	36.06	36.30	31.81	34.30	36.10	35.46	36.25	37.83	26.20	36.47	36.28	35.50	35.05	35.95	35.45	35.80	36.13
TiO <sub>2</sub>	3.81	3.83	4.79	2.67	2.54	4.63	4.01	3.58	2.34	4.28	3.36	4.10	4.38	4.29	5.14	4.56	1.95	5.01
Al <sub>2</sub> O <sub>3</sub>	12.75	12.42	14.13	16.13	17.56	13.64	15.03	13.50	14.59	13.84	14.17	14.08	13.04	12.97	13.36	13.06	14.17	13.89
FeO total	26.14	26.35	17.53	29.62	24.23	20.16	21.16	20.24	16.09	19.88	19.23	19.41	24.58	27.26	19.22	24.26	23.14	19.50
MnO	0.61	0.60	0.54	0.36	0.52	0.85	0.35	0.34	0.44	0.84	0.50	0.18	0.47	0.49	0.56	0.28	0.29	0.19
MgO	7.15	6.71	11.93	3.45	5.63	10.58	8.73	10.98	14.02	10.90	12.09	11.67	7.98	6.13	10.95	8.38	10.21	11.26
CaO			0.12				0.09				0.20						0.10	
K <sub>2</sub> O	9.60	9.62	9.55	10.03	9.75	9.63	9.83	9.51	9.72	9.84	9.28	9.85	9.48	9.46	9.58	9.47	9.31	9.97
Na <sub>2</sub> O	0.13			0.69	0.20		0.18			0.18	0.15		0.15					
Cl	0.13	0.33	0.06	0.23	0.10	0.12	0.12	0.15	0.05	0.10	0.20	0.15	0.25	0.26	0.19	0.29	0.28	0.23
TOTAL	96.30	95.92	94.95	94.99	94.83	95.71	94.96	94.55	95.08	96.06	95.65	95.72	95.83	95.91	94.95	95.75	95.25	96.18

Structural Formulae based on 22 oxygens

Si	5.674	5.728	5.550	5.244	5.430	5.563	5.530	5.639	5.704	5.557	5.579	5.555	5.591	5.593	5.554	5.575	5.607	5.521
Al <sup>IV</sup>	2.326	2.272	2.450	2.756	2.570	2.437	2.470	2.361	2.296	2.443	2.421	2.445	2.409	2.407	2.433	2.420	2.393	2.479
Ti															0.013	0.005		
Al <sup>VI</sup>	0.043	0.052	0.096	0.378	0.706	0.040	0.292	0.115	0.297	0.060	0.133	0.097	0.010	0.033			0.224	0.022
Ti	0.452	0.457	0.550	0.331	0.302	0.537	0.470	0.419	0.266	0.494	0.386	0.472	0.519	0.515	0.585	0.534	0.229	0.576
Fe <sup>2+</sup>	3.447	3.500	2.242	4.084	3.208	2.598	2.760	2.634	2.029	2.552	2.459	2.485	3.238	3.638	2.484	3.191	3.031	2.492
Mn	0.081	0.081	0.070	0.050	0.070	0.111	0.046	0.044	0.057	0.109	0.064	0.024	0.063	0.066	0.073	0.037	0.039	0.025
Mg	1.681	1.589	2.718	0.849	1.328	2.430	2.030	2.546	3.150	2.493	2.755	2.662	1.873	1.457	2.521	1.963	2.384	2.566
	5.704	5.679	5.676	5.692	5.614	5.716	5.598	5.758	5.799	5.708	5.797	5.740	5.703	5.709	5.663	5.725	5.907	5.681
Ca			0.020				0.014				0.033						0.017	
K	1.932	1.949	1.863	2.109	1.968	1.894	1.955	1.888	1.870	1.927	1.810	1.924	1.904	1.926	1.888	1.900	1.360	1.943
Na	0.040			0.222	0.062		0.055			0.052	0.045		0.047					
	1.972	1.949	1.883	2.331	2.030	1.894	2.024	1.888	1.870	1.979	1.888	1.924	1.951	1.926	1.888	1.900	1.877	1.943
Total cations	15.676	15.628	15.559	16.023	15.644	15.610	15.622	15.646	15.669	15.687	15.685	15.664	7.654	15.635	15.551	15.625	15.784	15.624
100. Mg/Mg+Fe	32.8	31.2	54.8	17.2	29.3	48.3	42.4	49.2	60.8	49.4	52.8	51.7	36.7	28.6	50.4	38.1	44.0	50.7

Analysis No.	80	85	83	81	84	77	78
SiO <sub>2</sub>	35.41	36.29	34.46	35.70	36.25	36.38	36.24
TiO <sub>2</sub>	3.36	4.20	3.86	4.00	4.13	4.21	3.28
Al <sub>2</sub> O <sub>3</sub>	13.81	13.88	14.23	13.81	13.30	14.00	14.57
FeO total	23.90	18.14	20.55	23.74	20.04	21.07	18.61
MnO	0.28	0.44		0.14	0.44	0.36	0.25
MgO	8.87	12.46	10.94	8.69	11.20	10.28	11.98
CaO				0.11		0.34	
K <sub>2</sub> O	9.70	10.05	10.34	9.59	9.92	9.92	9.61
Na <sub>2</sub> O			1.39	0.18		0.15	
Cl	0.17	0.05	0.24	0.25	0.30	0.06	0.22
TOTAL	95.50	95.51	96.01	96.21	95.58	96.43	95.10

Analysis No.	53	51	69	78	17
SiO <sub>2</sub>	36.84	36.28	36.30	36.04	36.02
TiO <sub>2</sub>	3.85	4.10	4.79	2.77	4.36
Al <sub>2</sub> O <sub>3</sub>	13.53	14.08	14.13	14.59	13.51
Fe <sub>2</sub> O <sub>3</sub>	2.98	2.76	1.89	0.33	1.37
FeO	16.58	16.93	15.83	18.45	18.20
MnO	0.45	0.18	0.54		0.20
MgO</					

ELECTRON MICROPROBE ANALYSES OF MAGNETITES

Analysis No.	79	80	85	83	84	150A	12	13	13	15	15	2	2	1	5	11	11	4
TiO <sub>2</sub>	0.48	5.72	0.16	0.17	0.25	1.93	0.20	7.02	4.15	0.20	8.38	2.14	24.92	0.38	0.54	1.83	9.24	0.92
Al <sub>2</sub> O <sub>3</sub>	0.35	0.35	0.21		0.40	0.19	0.17	1.93	0.70	0.22	1.42	0.30	1.18	0.22	0.35	1.01	0.41	0.25
V <sub>2</sub> O <sub>3</sub>	1.03	0.82	0.35	0.58	0.77	0.76	0.48	0.68	0.56	0.77	0.63	0.77	0.33	0.50	0.79	0.60	0.60	0.37
Cr <sub>2</sub> O <sub>3</sub>		0.20		0.13		0.12		0.17		0.16	0.56		0.23		0.15	0.14		0.44
Fe <sub>2</sub> O <sub>3</sub>	66.57	56.48	68.05	67.92	67.22	64.12	67.90	52.65	59.57	67.37	49.92	63.71	18.97	67.46	66.54	63.49	48.89	66.16
FeO	31.57	35.50	31.22	31.21	31.20	32.47	31.25	36.45	34.42	31.28	37.89	32.63	49.05	31.44	31.62	32.69	38.41	31.30
MnO		0.93			0.16	0.41		1.09	0.60		1.20	0.46	5.32		0.24	1.85		
TOTAL	100.00	100.00	99.99	100.01	100.00	100.00	100.00	99.99	100.00	100.00	100.00	100.01	100.00	100.00	100.00	100.00	100.00	99.44

Mag.	98.6	83.6	99.5	99.5	99.1	94.4	99.4	80.1	88.1	99.4	76.1	93.8	29.1	98.9	98.9	94.7	71.8	97.3
Usp.	1.4	16.4	0.5	0.5	0.9	5.6	0.6	19.9	11.9	0.6	23.9	6.2	70.9	1.1	1.1	5.3	28.2	2.7

Rock No.	6	6	10	28	19	19	25	25	21	21	31	30	44	45	46	48	75	74
TiO <sub>2</sub>	4.16	2.39	0.62	7.46	19.88	13.21	9.22	3.72	3.05	26.05	9.06	10.88	0.22	0.15	0.19	0.22	0.77	0.45
Al <sub>2</sub> O <sub>3</sub>	0.38	0.27	0.24	1.30	2.04	2.33	1.41	1.61	2.87	1.18	0.19	0.57	0.53	0.17	0.22	0.23	0.40	0.42
V <sub>2</sub> O <sub>3</sub>	0.48	0.68	0.82	0.71	1.14	1.27	0.66	0.82	0.73	0.47	0.74	0.96	0.33		0.21	0.13	0.75	1.58
Cr <sub>2</sub> O <sub>3</sub>	0.19	0.14		0.20	0.23	0.38	0.22	59.31	0.23	0.40							0.24	0.66
Fe <sub>2</sub> O <sub>3</sub>	59.80	63.19	66.64	52.12	26.82	39.05	48.63	34.64	58.72	17.31	50.53	46.16	67.59	68.48	68.13	68.13	65.99	65.32
FeO	34.38	32.94	31.51	37.24	48.04	42.36	38.31	0.28	34.09	50.74	37.71	40.95	31.04	31.20	31.26	31.29	31.85	31.57
MnO	0.60	0.38	0.17	0.97	1.85	1.40	1.55		0.31	3.85	1.78	0.26	0.30					
TOTAL	99.99	99.99	100.00	100.00	100.00	100.00	100.00	100.38	100.00	100.00	100.01	99.78	100.01	100.00	100.01	100.00	100.00	100.00

Mag.	88.0	93.1	98.2	78.7	44.2	62.7	73.8	89.4	91.3	27.8	74.0	69.9	99.4	99.7	99.5	99.40	97.8	98.7
Usp.	12.0	6.9	1.8	21.3	55.8	37.3	26.2	10.6	8.7	72.2	26.0	31.1	0.6	0.3	0.5	0.60	2.2	1.3

Rock No.	63	67	69	58	57	57	53	51	55	52
TiO <sub>2</sub>	0.16	0.40	0.15	0.21	0.89	0.21	0.12	0.18	0.54	0.13
Al <sub>2</sub> O <sub>3</sub>	0.32	0.27	0.45	1.08	1.51	0.58	0.31	0.36	0.28	0.32
V <sub>2</sub> O <sub>3</sub>	0.27	0.54	0.31	0.34	0.37	0.26	0.53	0.56	0.49	0.54
Cr <sub>2</sub> O <sub>3</sub>				0.18	0.22		0.13			
Fe <sub>2</sub> O <sub>3</sub>	67.99	67.32	67.83	66.79	65.87	67.61	67.69	67.62	67.09	67.79
FeO	31.25	31.47	31.26	31.29	32.14	31.34	31.00	31.06	31.60	31.22
MnO						0.22	0.22			
TOTAL	100.00	100.00	100.00	99.89	100.00	100.00	100.00	100.00	100.00	100.00

Mag.	99.5	98.8	99.6	99.4	97.4	99.4	99.5	99.3	98.4	99.6
Usp.	0.5	1.2	0.4	0.6	2.6	0.6	0.5	0.7	1.6	0.4

ELECTRON MICROPROBE ANALYSES OF ILMENITES

Analysis No.	81	81	84	77	55	54	52	53	63	49	3	3	20	22	29	33	31
TiO <sub>2</sub>	52.71	51.74	56.91	49.57	52.68	51.48	50.15	49.15	51.74	50.44	49.44	52.44	49.28	51.06	51.72	51.82	47.21
Al <sub>2</sub> O <sub>3</sub>	0.13		0.36	0.51	0.13	0.14	0.26	0.13	0.25	0.39	1.06	0.55	0.56	0.21	1.12		0.26
V <sub>2</sub> O <sub>3</sub>											1.22	0.25					
Cr <sub>2</sub> O <sub>3</sub>											0.82						
FeO total	42.68	44.89	36.84	45.47	39.91	32.17	43.92	36.12	34.55	44.28	43.37	41.66	47.71	43.87	44.04	44.23	44.72
MnO	3.86	3.82	5.89	4.51	7.28	16.21	5.67	14.60	13.45	4.89	4.50	5.10	2.45	4.69	3.12	3.95	7.81
TOTAL	99.38	100.45	100.00	100.06	100.00	100.00	100.00	100.00	100.01	100.00	100.01	100.00	100.00	99.83	100.00	100.00	100.00

Ilm.	99.8	97.5	99.5	99.2	99.8	99.8	99.6	99.5	99.6	99.5	92.8	99.3	99.1	99.7	98.3	100.0	99.6
Hem.	0.2	2.5	0.5	0.8	0.2	0.2	0.4	0.5	0.4	0.5	7.2	0.7	0.9	0.3	1.7	0.0	0.4

PLAGIOCLASE COMPOSITIONS (An,Or, Ab end members)

TENT HILL VOLCANICS																				
Analysis No.	2	2	1	1	3	3	5	5	11	11	8	8	9	9	4	4	6	6	10	10
	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim
An	50.1	35.2	45.6	34.1	56.3	43.7	43.1	33.2	54.0	41.7	65.4	37.5	55.8	22.9	38.3	18.3	49.5	37.6	47.7	36.0
Or	0.4	4.5	3.1	5.1	2.5	3.9	3.6	3.9	1.0	1.7	1.3	4.9	2.1	1.4	2.7	1.1	2.5	3.0	3.1	3.2
Ab	49.5	60.3	51.3	60.8	41.2	52.4	53.3	62.9	45.0	56.6	33.3	57.5	42.1	75.7	59.0	80.6	48.0	57.4	49.2	60.8

DUNDEE RHYODACITE														EMMAVILLE VOLCANICS										
Analysis No.	150A	150A	97A	97A	16	16	12	12	13	13	15	15	28	28	23	23	19	19	25	25	34	34	20	20
	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim
An	48.2	34.0	47.1	36.0	52.0	34.2	50.6	33.2	52.3	31.3	40.9	31.3	44.6	38.9	58.9	35.8	65.2	39.9	51.1	37.6	57.5	27.7	52.9	28.1
Or	2.6	2.4	1.9	1.4	2.9	3.4	1.4	2.3	1.9	3.4	3.6	3.7	3.9	5.5	1.0	1.3	2.8	4.4	2.6	4.8	1.0	1.3	3.2	6.6
Ab	43.3	63.6	51.0	62.6	45.1	62.4	48.0	64.5	45.9	65.3	55.5	65.0	51.5	55.6	40.1	62.9	32.0	55.7	46.3	57.6	41.5	71.0	43.9	65.3

EMMAVILLE VOLCANICS																GRANITOIDS								
Analysis No.	22	22	29	29	21	21	27	27	33	33	40	31	31	30	30	178A	156A	75	75	74	74	72	72	
	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim
An	32.1	27.9	57.6	47.8	50.9	34.3	61.1	28.3	62.7	51.0	0.0	47.4	33.3	58.1	30.6	39.6	53.9	47.9	8.5	37.3	22.1	37.4	17.7	
Or	2.2	1.6	0.9	0.8	2.9	3.7	1.5	1.7	0.9	0.8	1.3	2.9	2.5	2.7	1.7	4.1	0.0	2.1	0.9	2.7	2.2	1.5	1.5	
Ab	65.7	70.5	41.5	51.4	46.2	62.0	37.4	70.0	36.4	48.2	98.7	49.7	64.2	39.2	67.7	56.3	46.1	50.0	90.6	60.0	75.7	61.1	80.8	

GRANITOIDS																							
Analysis No.	63	63	61	61	67	69	59	59	56	56	58	58	57	57	50	50	53	53	51	51	55	55	
	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	
An	24.2	9.2	36.3	12.6	13.4	28.8	31.0	20.7	43.5	20.4	40.0	28.0	49.5	34.9	46.7	8.7	77.6	24.3	59.2	15.5	37.1	11.3	
Or	2.6	1.7	1.3	2.5	2.6	1.0	2.6	1.5	1.2	1.3	1.5	0.9	1.1	1.9	0.8	1.3	0.4	1.3	1.2	1.2	0.8	0.8	
Ab	73.2	89.1	62.4	84.9	84.0	70.2	66.4	77.8	55.3	78.3	58.5	71.1	49.4	63.2	52.5	90.0	22.0	74.4	39.6	83.3	62.1	87.9	

GRANITOIDS						DIORITES				MAFIC XENOLITHS											
Analysis No.	54	54	52	52	44	44	78	78	77	77	79	79	80	80	85	83	83	81	81	84	84
	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	
An	47.5	4.4	60.3	19.0	45.6	19.9	82.4	25.4	48.1	25.0	60.4	40.6	80.9	44.3	31.0	68.4	18.6	70.6	24.3	45.1	20.3
Or	0.8	1.1	0.9	1.2	0.0	1.8	0.0	1.6	5.5	2.4	1.5	2.1	0.7	1.0	1.4	0.4	1.6	4.9	0.8	0.8	1.4
Ab	51.7	94.5	38.8	79.8	54.4	78.3	17.6	73.0	46.4	72.6	38.1	57.3	18.4	54.7	67.6	31.2	79.8	24.5	74.9	54.1	78.3

## APPENDIX 4

### METAL COMPLEXES IN MAGMATIC SYSTEMS

A knowledge of the bonding energies and co-ordination geometries of elements in volatile-rich magmas facilitates predictions concerning the relative mobility of these elements across a concentration gradient. As quantitative data are lacking, predictions must be based on basic principles of metal chemistry. For example, the application of ligand field theory (LFT) to the crystal-melt partitioning of many first-period transition metals has been highly successful (e.g. Williams, 1959; Burns and Fyfe, 1964; Walsh et al., 1974; Vaughan and Tossel, 1978). Although LFT can be meaningfully applied only to the transition metals, a short discussion of the theory is warranted because it provides a detailed explanation for the dependence of the stability of metal complexes on the nature of the ligand species, thereby justifying the conclusions made from geological observations that trace element fractionation is strongly linked to the activity of volatiles in a magmatic environment.

In LFT, the effects of overlap of the metal and ligand atomic orbitals in a transition metal complex are considered (Phillips and Williams, 1966; Burns, 1970), thus providing a better understanding of the dependence of metal complex stability on the nature of the ligand. LFT is therefore crystal field theory (CFT) incorporating some of the concepts of molecular orbital theory (MO theory).

The ability of the first series transition metals to form complexes stems from the distribution of electrons in highly directional, unshielded orbitals of the d valence shell. (Zn and Cu are exceptions because formation of  $Zn^{2+}$  and  $Cu^+$  involves removal of electron(s) from the 4s shell.) In the absence of an electrostatic field, the five d orbitals are of equal energy - i.e. they are five-fold degenerate. In the presence of a ligand field this degeneracy is split into higher energy, doubly degenerate  $e_g$  and lower energy, triply degenerate  $t_{2g}$  atomic orbitals. All the transition metals readily form complexes under favourable conditions but the relative stability of a complex depends on the degree of stabilization given to the metal ion by the presence of the ligand field. The energy difference between the  $e_g$  and  $t_{2g}$  atomic orbitals is known as the crystal field splitting parameter  $\Delta_o$ , which is a measure of the crystal field stabilization energy of a metal ion in a particular ligand field.  $\Delta_o$  is dependent on

- (a) the symmetry of the ligands co-ordinated to the metal ion (e.g. octahedral or

tetrahedral co-ordination),

- (b) the charge of the metal ion, and
- (c) the nature of the ligands co-ordinated to the metal ion.

The influence of the bonding characteristics of the ligand on  $\Delta_o$  is of particular importance. For a given metal ion in octahedral co-ordinated complexes, ligands may be arranged in order of increasing  $\Delta_o$  - i.e. the spectrochemical series.\* For ligand species expected to be present in volatile-bearing magmas the sequence may be  $\text{Cl}^- < \text{F}^- < \text{OH}^- \leq \text{H}_2\text{O} (< \text{NH}_3)$  (Burns, 1970).

The spectrochemical series is rarely quoted in the geological literature but may be very useful as an indication of the likely stability of transition metal complexes in magmas containing a number of volatile species. For example, it may be possible to estimate the stage to which a magma must evolve before the efficient migration of metals (as stable complexes) can occur. In a melt at a certain pressure,  $a_{\text{Cl}^-}$  may greatly exceed  $a_{\text{H}_2\text{O}}$  but any transition metal chloride complex formed may not be stable at the prevailing temperature of the melt because of the low crystal field stabilization energy afforded the metal ion by the Cl ligands. However, if at a lower pressure (or a more advanced stage of crystallization of the melt)  $a_{\text{H}_2\text{O}}$  is increased, aquo complexes may form and  $\text{H}_2\text{O}$  will substitute for Cl in surviving chloride complexes. In transition metal complexes the metal-Cl and metal- $\text{H}_2\text{O}$  bonds differ in length. Therefore it may be expected that those metals which favour a distorted electrostatic field (due to the Jahn-Teller effect (Cotton and Wilkinson, 1966)) will form mixed ligand complexes in favourable environments.

The spectrochemical series exists because of variation in the nature of bonding between metal and ligand. A description of this bonding is the realm of MO theory. This theory models the interaction of metal and ligand atomic orbitals which form the  $\sigma$  or  $\sigma$  and  $\pi$  molecular orbitals of the stable complex. The relative energies of the  $\sigma$  and  $\pi$  antibonding, non-bonding and bonding (molecular) orbitals may be referred back to the  $e_g$  and  $t_{2g}$  ("atomic") orbitals of the metal ion described by CFT (Barrett, 1970). Stated simply, the ligand-metal  $\pi$  bonding affects the energy of the "metal"  $e_g$  orbitals, and ligand-metal  $\sigma$  bonding affects the energy of the "metal"  $t_{2g}$  orbitals.

\* For a given ligand species, a similar series also exists for metal ions in octahedral complexes (Kettle, 1970). In silicate minerals the ligand is oxygen and metal ions may be arranged in order of increasing octahedral site preference energy (e.g. Burns and Fyfe, 1964).

The relatively weak crystal field produced by the halide anions may now be explained. For these ligands, two of the filled (atomic) p orbitals in their valence shell will be the orbitals involved in the  $\pi$  bonding (Kettle, 1970). MO theory dictates that for bonding to occur, only two electrons may occupy the same molecular orbital and these electrons must possess opposite spins - i.e. the Pauli exclusion principle. Valence electrons of the metal ion therefore cannot interact with the two already filled p orbitals of the halide anions. The metal-halide bonds in the first series transition metal complexes are simply  $\sigma$  molecular orbitals and lack the extra stability offered by a  $\pi$  bonding component.

The polarizability of ligands, and labels such a " $\sigma$  donor" or " $\pi$  acceptor" given to ligands (Phillips and Williams, 1966), all refer to the ability of partially filled or unfilled atomic orbitals in the ligand to engage in  $\pi$  (as well as  $\sigma$ ) bonding with electrons of the metal ion. A knowledge of the orientation and occupancy of atomic orbitals in the ligand therefore provides for a theoretical understanding of the spectrochemical series not offered by CFT (cf. Burns, 1970).

The cations  $\text{Ni}^{2+}$ ,  $\text{V}^{3+}$  and  $\text{Cr}^{3+}$  exhibit strong octahedral site preference energies (OSPE) (Burns and Fyfe, 1964), and even in volatile-saturated magmas are probably largely bonded to oxygens in the existing aluminosilicate polymers of the melt. However, ions with weak OSPE may be partly co-ordinated to anionic volatile species. Therefore, in the presence of a volatile (and hence melt polymerization) gradient, ions with a high OSPE should remain in the more polymerized fraction of the melt whereas ions with lower OSPE may be more mobile. This concept may also aid in understanding the response of incompatible elements to a volatile gradient (see below).

Actinides and Lanthanides.

The high mobility of U and Th may be attributed partly to incompatibility with melt polymer structures (i.e. co-ordination geometry and ionic radius considerations) and partly to the ability of such ions to form relatively strong bonds with halogens (cf. Pernsteiner and Ikramuddin, 1979) and other volatile species. Although the 5f orbitals of the actinides are considerably more shielded than the unfilled d orbitals of the first series transition metal ions, electrons in the 5f orbitals are also influenced by an electrostatic field, which implies that they may be directly involved in bonding with some ligands. This bonding is important for complexes of U and Th in which the metals are in a high oxidation state (Phillips and Williams, 1966).

The 4f orbitals of the lanthanides are particularly well shielded and they are



commonly not involved in bonding with inorganic ligands - i.e. such ligands produce "outer sphere" complexes. As a result, the relative ligand field stabilization energies of the REE are small ( $\sim 1$  kcal/mole; Moeller, 1972). Fluorine is exceptional in that it forms relatively stable "inner sphere" complexes and REE-F bonds possess a measurable degree of covalency (Choppin, 1971). In aqueous solution the lanthanides are generally surrounded by a hydration sphere which must be broken to permit complexation involving other ligands. The hydration sphere is quite stable because, analogous to F, H<sub>2</sub>O bonds to the metal ion through a small involvement with the 4f orbitals. The 4f orbitals may therefore be partly responsible for the high co-ordination number of REE complexes in aqueous solution.

The REE ions are "A-type" cations or "hard" acids which explains the strong affinity of these metal ions for oxygen (Moeller, 1972). Experimental studies using hydrous silicic rock melts at 1.25 and 4.0 kb (Flynn and Burnham, 1978) showed that the partitioning of REE into the melts varied linearly with the cube of the hydroxyl molality. These authors considered REE partitioning may therefore vary in proportion to the "concentration" of octahedral sites in the melt. Mysen (1979a) has verified the dependence of REE partitioning on melt structure, but proposed that REE have 6-9 nearest oxygen neighbours which is more consistent with the observed co-ordination of REE in minerals, and complexes in aqueous solution (see above).

Although REE-fluoride complexes are readily hydrolysed at 1000°C and low pressure (Waff et al., 1954), the data of Flynn and Burnham (1978) suggest such complexes may in fact be stable under geological conditions (also see Beus, 1958; Bandurkin, 1961; Mineyev, 1963; Mineyev et al., 1966; Kable and Fesq, 1976; Fryer and Edgar, 1977). Balashov and Krigman (1976) proposed complexes of the type M<sup>+</sup>REE F<sub>4</sub> or M<sub>3</sub><sup>+</sup>REE<sub>6</sub> may be stable at magmatic temperatures and that heavy REE form the strongest fluoride complexes. REE F<sub>3</sub> compounds are insoluble (Phillips and Williams, 1966). Many authors have proposed the existence of REE carbonate complexes in hydrothermal solutions and magmas (e.g. Mitchell and Brunfelt, 1975; Mitchell and Bell, 1976; Balashov and Krigman, 1976; Wendlandt and Harrison, 1978), but recent experiments suggest such complexes may not be stable at 800°C and pressures up to 4 kb (Zielinski and Frey, 1974; Flynn and Burnham, 1978). However Harris (1981) has discounted REE-halogen complexing in evolved melts and emphasized the importance of carbonate complexes for transport of REE in the vapour phase.

Flynn and Burnham (1978) also showed that in the presence of Cl, REE partitioning into a vapour-phase co-existing with a dominantly water-saturated siliceous melt was proportional to the cube of the Cl molality, and that light REE

chloride complexes were relatively enriched in the vapour. Although Flynn and Burnham successfully modelled their calculations on the composition  $\text{REE}(\text{Cl})_3$ , this (presumably soluble) molecular species is unlikely to exist in a geological environment because the REE ions would be unfavourably co-ordinated. (In the crystalline stage  $(\text{La to Tb})\text{Cl}_3 = 9$  co-ordinate,  $(\text{Dy to Lu})\text{Cl}_3 = 6$  co-ordinate; Phillips and Williams, 1966). REE trichlorides would be hydrolysed in hydrothermal solutions and aqueous vapours generated by resurgent and first boiling, and in magmas may be partly co-ordinated to oxygens of aluminosilicate polymers.

Holland (1972) showed that Mn, Zn and Pb dichlorides may be abundant in the aqueous vapour phase separating from a volatile-saturated granitic magma. Chlorides of other metals such as Ca and Cu may also be present in the vapour. Flynn and Burnham (1978) predicted cations of high charge may also be very sensitive to halogen concentrations in magmatic environments (also see Buma *et al.*, 1971; Bailey and MacDonald, 1975; Kable and Fesq, 1976) and recommended investigation of the stability of chloride complexes of these elements. Collins *et al.*, (*in press*) have suggested complexes such as  $\text{Na}_3\text{TaF}_8$ ,  $\text{Na}_2\text{NbF}_7$ ,  $\text{Na}_2\text{UF}_6$  and  $\text{KCeF}_4$  may exist in peralkaline, fluorine-rich melts.

#### DISCUSSION: Cation Co-ordination and Mobility in Magmas

The compatibility of a given cation in a melt reflects the degree to which that metal ion has achieved optimum co-ordination with suitable anions. According to Mysen (1979a), the co-ordination numbers of the melt network-modifying cations may be REE = 6 to 9, first period transition metals = 6, alkali metals and alkaline earths =  $\geq 6$ . Other trace cations would have co-ordination numbers of  $\geq 6$ . Any change in the co-ordination of melt polymers will therefore effect the stability of the network-modifying cations (*cf.* Watson, 1976).

In highly silicic melts elements such as Na, K (Rb, Sr and Ba), which stabilize aluminosilicate networks at low P and T, will be largely bonded to oxygens to form three dimensional tetrahedrally co-ordinated polymer structures and may therefore be relatively unaffected by volatile concentration gradients in the melt. Many of the trace cations may achieve optimum co-ordination by bonding to available volatile species in addition to oxygens of nearby melt polymers.

The importance of the composition and hence the degree of polymerization of the melt in permitting LIL elements stable co-ordination, has been recognized by a number of workers. In peralkaline melts Zr forms  $(\text{Na, K})_4 \text{Zr}(\text{SiO}_4)_2$  complexes (Watson, 1979) and Mo may occur as molybdate anions (see Westra and Keith, 1981).

Although F and Cl are abundant in such melts these potential ligands are not involved in bonding; rather their role is to depolymerize the melt whereby it may accommodate bulky complexes (ref. Collins et al., in prep).

The mobility of Li, LIL elements and REE, which are sensitive to polymerization gradients in silicic melts, will be largely dependent on the availability of ligands which may substitute for oxygen to enable the cations to become independent of the aluminosilicate melt polymers (cf. Dunn, 1979). For example, REE trichloride species may require up to six H<sub>2</sub>O "ligands" to maintain cation stability and achieve potentially rapid rates of diffusion through the melt. Incompatible elements requiring low optimum co-ordination numbers may therefore be more easily mobilized at a given volatile activity in the melt.\* However, a major complicating factor may be the relative energies of the metal-(volatile) and metal-oxygen (polymer) bonds; metal-(volatile) bonding must be energetically more favourable than metal-(polymer) bonding for simple metal complexes to form - i.e. the strength of the ligand field must be considered.

Once formed, discrete metal complexes require a "carrier" volatile (fluid) phase to enhance diffusion rates. The rate of diffusion of stable metal complexes across a volatile concentration gradient in a melt may therefore depend on:

- (a) the size of the complex;
- (b) the "viscosity", or degree of polymerization of the melt; and
- (c) the polarizability of the ligands - i.e. if the ligands are highly polarized by bonding with the cation, they may form temporary bonds with other melt components and hence reduce the rate of diffusion of the complex through the melt.

## SUMMARY

1. A fundamental knowledge of the electronic structure and bonding characteristics of metal ions provides a basis for the formulation of mechanisms of trace and major element crystal-liquid, liquid-liquid and liquid-vapour partitioning in a variety of geological environments.
2. Crystal-liquid partitioning of the first series transition metals in polymerized

\* In this case, the availability of appropriately co-ordinated sites in the polymer structures of the melt, has been ignored. At low volatile concentrations such cations may actually prefer to remain in the melt.

magmas can be modelled qualitatively using LFT. Crystal-liquid and liquid-vapour partitioning of these elements in volatile-rich magmas remains poorly understood, but LFT again provides an indication of the speciation of metal ions in melts of known composition and specified volatile activity.

3. In magmas at low pressures the lanthanides may form halogen complexes, and at high pressures  $\text{OH}^-$  or  $\text{H}_2\text{O}$  (Mysen, 1979a) and  $\text{CO}_3^{2-}$  (Wendlandt and Harrison, 1978) may be the ligands in REE complexes. REE phosphate complexes may be stable in basic melts (Ryerson and Hess, 1978). Fractionation of complexed REE is considered possible.
4. Halogen complexes of a large number of di- and polyvalent cations may also exist in magmas under ideal conditions, and fractionation of these cations may be possible.
5. The dual role of the halogens and water (or hydroxide ions) as both ligands and melt depolymerizers is of fundamental importance to the speciation and eventual stability of "incompatible" elements in melts and hydrothermal solutions.
6. Incompatible cation mobility in dry polymerized melts is probably very slow. Cation mobility is enhanced in volatile-bearing melts of the same major element composition due to the combined effects of melt depolymerization and metal complex formation. Under standardized conditions (pressures, convection rates etc.), metal diffusion rates should be directly proportional to the concentration of volatiles in the melt and may vary depending on the affinity of the volatile species for the metal ions, and the solubility of the volatile in the melt. Metals fully co-ordinated with volatile anionic species may require no interaction with oxygen of the melt polymers to maintain stability and may therefore respond strongly to a volatile concentration gradient.