

FC
573

ROLE OF TRACE ELEMENT PARTITION COEFFICIENTS
IN MODELS OF ANDESITE GENESIS

GL03774

James B. Gill

Earth Sciences Board
University of California, Santa Cruz, California 95064

UNIVERSITY OF UTAH
RESEARCH INSTITUTE
EARTH SCIENCE LAB.

ABSTRACT

Orogenic andesite magmas probably evolve at 1100 to 900°C, have between 1 and 5 wt. % H₂O and f_{O₂} above the NiNiO buffer during phenocryst precipitation, and may be saturated with a second fluid phase prior to eruption. Consequently, many solid/liquid trace element partition coefficients appropriate to andesites are higher than for basalts, perhaps due to the presence of fewer octahedrally coordinated sites in andesite liquids as well as to lower temperatures.

Simple quantitative interpretation of trace element concentration data for orogenic andesites in general or for most specific suites is not possible using available partition coefficients. Fractional crystallization models involving magnetite or amphibole or both seem less at odds with available data than do models invoking equilibration with subducted oceanic crust or overlying peridotite. Critical choices between simple models, or identification of supplementary or more complex processes, require a more rigorous data base than presently available.

INTRODUCTION

Andesite origins remain unsatisfactorily explained in part because possible hypotheses typically fail when their ability to account for trace element concentrations in andesites is tested quantitatively or semiquantitatively (e.g. TAYLOR, 1969; GILL, 1974; LOPEZ-ESCOBAR *et al.*, 1976). No general model of andesite genesis accounts for all the trace element characteristics of orogenic andesites discussed below. Indeed, there are no specific andesite suites with $\Delta \text{SiO}_2 > 5$ wt. % in which the behavior of most trace elements can be explained quantitatively. This discrediting role of trace element studies is due in part to uncertainties in the numerical value, the variation, and the applicability of partition coefficients (D), which are discussed elsewhere in this volume. However, failure to account for trace element data also reflects the simplicity of testable models and the practical difficulties in setting up even these tests.

For example, tests of fractional crystallization require choice of parent-daughter pairs and of an appropriate degree of crystallization. Stratigraphic, geochronologic, and petrologic data sufficient for establishing a realistic context in which to make these choices generally are not available for andesite volcanoes. Consequently, most tests of andesite genesis use analyses of rocks collected, at best, from a given volcano or volcanogenic formation but without benefit of a detailed context for sampling. This procedure would suffice if all ejecta produced within the lifespan of a given volcano were monogenetic, but apparently this is not always or even often the case. There can be sizeable changes within the volcanic pile in trace element concentrations (e.g. the depletion of K, Rb, and Ba but enrichment of Sr and Eu in lavas from the Shastina vent, Shasta volcano, USA; CONDIE and SWENSON, 1973) or isotopic composition (e.g. the increase in ⁸⁷Sr/⁸⁶Sr at Qualibu volcano, St. Lucia, Antilles; PUSHKAR *et al.*, 1973) without sufficient change in overall composition or mineralogy to alert the unwary.

A related matter is evaluation of the mass fraction solidified (F) during generation of daughter from parental magma. This fraction can be estimated by a least squares method utilizing the major element composition of rocks and

UNIVERSITY OF UTAH LIBRARIES

constituent minerals, and evaluated in light of the modal proportion of minerals present as phenocrysts, in inclusions, or in relevant experimental charges (e.g. EWART *et al.*, 1973). Alternatively, $D(i)_{\text{bulk}} = 0$ can be assumed for a trace element i , and F calculated for any parent (P)-daughter (A) pair by $F = 1 - c_i^P/c_i^A$ where c is the concentration of i in parent or daughter. Zr often is the best choice of i for andesites because Zr should be incompatible and is non-volatile, relatively immobile during alteration, and present in high enough concentrations (50-150 ppm) to be easily determined. However, no studies yet have demonstrated that Zr is uniformly distributed within andesite flows. Moreover, F 's calculated by the two methods cited above frequently disagree, with F (least squares) typically exceeding F (Zr) by $> 25\%$ (e.g. data of EWART *et al.*, 1973).

Similar but inherently less tractable problems affect partial fusion models as they require assumptions about source composition and refractory mineralogy as well as the degree of fusion. None of the hypotheses in which andesites are treated as primary partial melts are sufficiently detailed petrologically to significantly constrain trace element calculations. A quasi-exception is the analysis by GILL (1974) of eclogite fusion, based on GREEN'S (1972) experimental study.

Finally, the presence of 20 to 50 vol.% phenocrysts in most andesites poses the problem of whether analyzed samples were once liquid. Because decompression of hydrous liquid causes precipitation unless the liquid is superheated, aphyric andesites also will be atypical. Indeed, REE patterns can be less regular in aphyric than porphyritic andesites (FUJIMAKI, 1975). Only demonstration of mineralogical disequilibrium, therefore, can unambiguously identify samples whose compositions may not be that of a liquid.

Thus, while better knowledge of partition coefficients and their behavior will help, this knowledge alone is unlikely to solve the andesite problem. The premier tasks are acquisition of field, age, petrographic, and isotopic data to constrain sample selection for trace element analysis, and study of ejecta from single eruptions to constrain the extent of, and reasons for, differences in elemental concentrations in magma at one point in time.

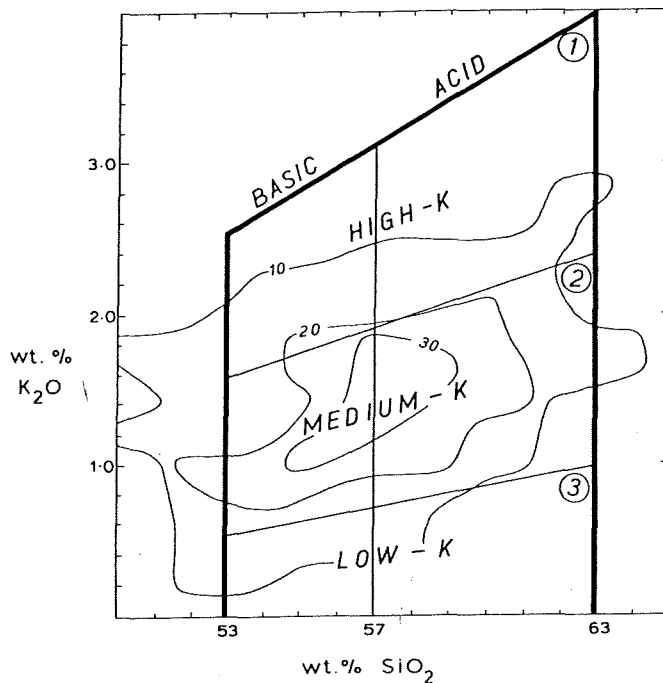


Figure 1. Nomenclature of orogenic andesites. Equations of lines 1, 2 and 3 are, respectively: $K_2O = .145 (SiO_2) - 5.135$; $K_2O = .0818 (SiO_2) - 2.754$; $K_2O = .0454 (SiO_2) - 1.864$. Contours enclose the number of nominal andesites (by namer's definition) whose analyses are stored in datafile RKOC76.

Follow:
normat:
sites:
1). Th
dites,
the app
by 1976
in K_2O
where c
and hig
be furt
iron-en
and FeO
63% of
the cri
ure 2),
using M

The str
diate b
ratio o
for exa
andesit
straine
the liq
ture of
andesit
content
suggest

log
 fO_2

ASPECTS OF OROGENIC ANDESITE MAGMA RELEVANT TO CHOICE AND USE OF PARTITION COEFFICIENTS

Following TAYLOR (1969) and others, I shall define andesites as hypersthene-normative volcanic rocks with 53 to 63% SiO₂, and shall define orogenic andesites as andesites with < 1.75% TiO₂ and K₂O < (0.145 x SiO₂ - 5.135) (Figure 1). This definition of orogenic andesite excludes most rocks called icelandites, trachy-something, latites, or shoshonites, while including over 70% of the approximately 2500 rocks originally called andesite by someone and stored by 1976 in F. Chayes' databank RKOC76. The bivariant frequency distribution in K₂O-SiO₂ space of these 2500 nominal andesites is included in Figure 1 where orogenic andesites are subdivided rather arbitrarily into low, medium, and high-K as well as basic and acid types. Each of these six subdivisions can be further described as tholeiitic or calcalkaline depending on their level of iron-enrichment, and there is a crude inverse correlation between K₂O contents and FeO*/MgO ratios of suites (see JAKES and GILL, 1970). For example, about 63% of the low-K orogenic andesites of Figure 1 are tholeiitic according to the criteria of MIYASHIRO (1974, Figure 1) or IRVINE and BARAGAR (1971, Figure 2), whereas only 35% of the medium and high-K andesites are tholeiitic using Miyashiro's criterion or only 13% using Irvine and Baragar's.

The structure of liquids having these bulk compositions probably is intermediate between that of basalt and rhyolite in degree of polymerization and ratio of octahedral to tetrahedral sites. Si/O ratios and alkali contents, for example, usually are 0.32±.01 and 3 to 5 mole %, respectively, in orogenic andesites. The pre-eruption water content of these magmas is poorly constrained. However, the apparent co-existence of plagioclase and a pyroxene on the liquidus of most andesites (EWART, 1976a), the differences between temperature of eruption and the dry liquidus temperature at 1 atm of the same andesites (EGGLER, 1972; ARAMAKI and KATSURA, 1973), and the estimated volatile content of andesite glass inclusions in phenocrysts (ANDERSON, 1974), all suggest water contents between 1 and 5 wt. % during phenocryst precipitation.

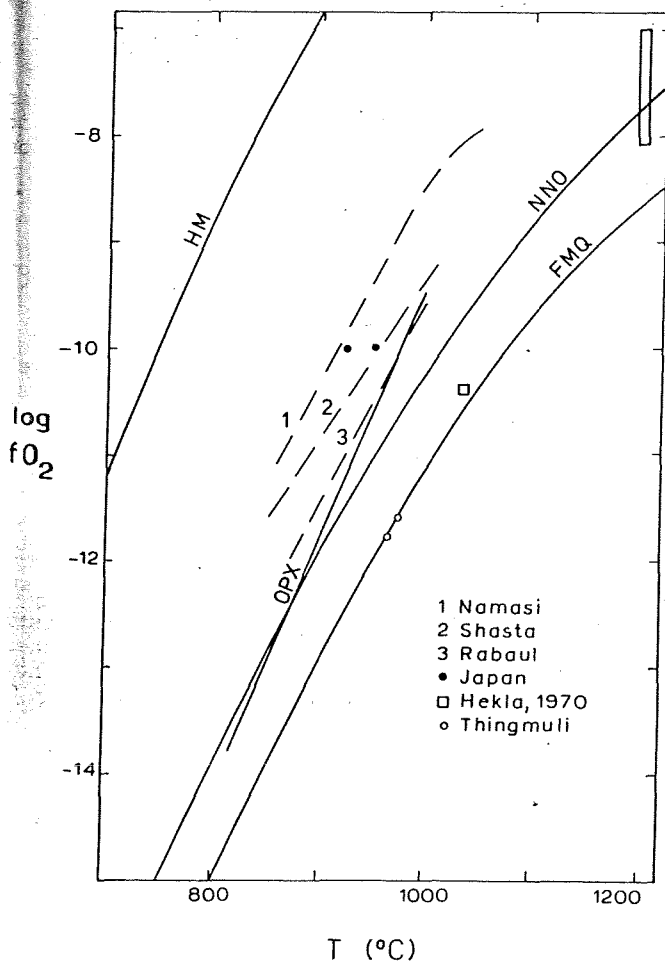


Figure 2. Plot of f_{O_2} vs. T for various andesites and f_{O_2} buffers. Lines 1, 2 and 3 and the solid circles are for orogenic andesites. Data sources: Namosi, Fiji (GILL and TILL, in prep); Shasta (A.T. ANDERSON, written comm., 1976); Rabaul (HEMING and CARMICHAEL, 1973); Japan (BUDDINGTON and LINDSLEY, 1964); OPX (CARMICHAEL, 1967a); Hekla (BALDRIDGE *et al.*, 1973); Thingmuli (CARMICHAEL, 1967b). Rectangle at 1200°C encloses experimental results of FUDALI (1965) for an orogenic andesite. All results are based on the same extrapolation by I.S.E. Carmichael of BUDDINGTON and LINDSLEY'S (1964) experimental data for co-existing Fe-Ti oxides.

UNIVERSITY OF UTAH LIBRARIES

Oxygen fugacities of orogenic andesites have not been measured *in situ* but sometimes can be estimated from the composition of coexisting oxide minerals. This method is limited in andesites by the infrequency and high R_2O_3 contents of ilmenite phenocrysts, as well as calibration problems. However, at least one temperature calculated using similar data for a non-orogenic andesite erupted during 1970 from Hekla volcano, Iceland (BALDRIDGE *et al.*, 1973) agrees to within 15°C with a temperature measured during the eruption (THORARINSSON and SIGVALDASON, 1972). Results for orogenic andesites are summarized in Figure 2. Oxygen fugacities (fO_2) are approximately parallel to, but up to one log unit above the NiNiO buffer, and substantially above the estimated fO_2 of non-orogenic andesite magmas at comparable temperatures. Based on FUDALI'S (1965) experiments at 1200°C, the Fe_2O_3/FeO ratio is ~ 0.3 in medium-K acid andesite magma in which fO_2 is near or above the NiNiO buffer; this ratio will increase as alkali contents increase.

Various methods of estimating the temperature of orogenic andesite magma upon eruption or during phenocryst precipitation suggest about 1100°C for pyroxene basic andesites and 900 to 1000°C for hornblende acid andesites (e.g. Figure 2). Viscosities at the liquidus of anhydrous acid andesite magma have been determined experimentally to be 10^3 to 10^4 poise within the crust (e.g. KUSHIRO *et al.*, 1976); the viscosity of magma beneath Trident volcano, Alaska was estimated to be 10^8 poise (MATUMOTO, 1971); and the viscosity of an acid andesite upon eruption from Santiaguito dome, Guatemala was observed to be 5×10^8 poise (ROSE, 1973).

The time elapsed between magma formation and eruption bears on kinetic studies of element distribution, but is essentially unknown. However, the time necessary for an andesite stratovolcano to go through a crude cycle of cone construction, caldera collapse, and resurgence, is about 10^4 to 10^5 years (e.g. ROSE *et al.*, 1977; KATSUI *et al.*, 1975). This also approximates the interval between formation of basalt and eruption of andesite from Irazu volcano, Costa Rica (ALLEGRE and CONDOMINES, 1976), but is much longer than the period of months estimated for 30% crystallization and resulting fractionation of basalt magma erupted from Fuego volcano, Guatemala (ROSE *et al.*, in press).

Few solid/liquid trace element partition coefficients have been determined experimentally at the T-X- fO_2 - fH_2O conditions described above. Thus, application of partition coefficients to andesite genesis requires either generalization of coefficients so as to be independent of liquid and solid composition, or reliance on data from natural phenocryst/matrix pairs for andesites. Because the former is not yet possible in most instances, a summary of the latter is given in Table 1.

A final issue is the spatial and temporal extent to which andesite liquid coexists with another fluid phase as well as with crystals, thus requiring knowledge of fluid/fluid as well as solid/liquid partition coefficients. Water-saturation (retrograde boiling) will occur atop shallow chambers and within dikes during and sometimes before eruption of most orogenic andesites, but is unlikely at depths > 4 km if water contents are < 5 wt. %. Thus, water-saturation may affect the concentration of volatile elements such as alkalis in an indeterminate volume fraction of magma without being a realistic condition during magmatic differentiation if differentiation occurs primarily at depths > 4 km. In contrast, widespread saturation of orogenic andesite magma with CO_2 or S is possible (MYSEN *et al.*, 1975; ANDERSON, 1974).

SELECTED TRACE ELEMENT CHARACTERISTICS OF OROGENIC ANDESITES

This summary is restricted to a few aspects of orogenic andesite geochemistry which can be evaluated with available partition coefficients; data for other elements and for related rock types are omitted. Emphasis is on accounting for trace element systematics which constrain genetic relationships within andesite suites, rather than on comparisons between average andesites and basalts.

Concentrations of K, Rb, Cs, Sr, and Ba in orogenic andesites cover a wide range, reaching from levels near those of mid-ocean ridge basalts and extending to those of granites. This is illustrated for Rb and Sr in Figure 3. All these elements except Sr correlate positively with silica in andesites and usually increase about two-fold in concentration between 53 and 63% SiO_2 . If $D = 0$ for these elements, their rate of increase implies an average of 5% crystallization for each 1 wt. % increment in SiO_2 . Alternatively, the variation in alkali concentrations requires a factor of two difference in percent fusion to generate the spread in SiO_2 of andesites.

Table 1. Phenocryst/matrix partition coefficients from orogenic andesite whole rocks.

† Data source

1. SCHN
2. PHII
3. EWAF
4. EWAF
5. ANDR
6. IWAS

Gar

Mt

Bt

Hb

Ol

Opx

Aug

Pl

Table 1. Phenocryst/matrix partition coefficients from orogenic andesite whole rocks.

	Pl	Aug	Opx	Ol	Hb	Bt	Mt	Gar
K	* .02-.20 ^{2,3,4†} .11**	.01-.03 ⁷ .02	.01-.02 ² .01	.01 ⁹	.33 ²	-	-	-
Rb	.02-.19 ² .07	.01-.04 ² .02	.01-.03 ² .02	.01 ⁹	.05 ²	3.3 ⁹	-	-
Sr	1.3-3.2 ^{2,3,4} 1.8	.06-.09 ^{2,3} .08	.01-.04 ^{2,3}	.01 ⁹	.19-.26 ^{2,3} .23	.12 ⁹	-	.02 ⁹
Ba	.05-.21 ^{2,3,4} .16	.01-.15 ^{2,3} .02	.01-.06 ^{2,3} .02	.01 ⁹	.08-.10 ^{2,3} .09	6.4 ⁹	-	.02 ⁹
Ce	.06-.30 ^{1,12} .20	.04-.51 ¹ .25	.03-.04 ¹ .03	.01 ⁹	.09 ¹	.04 ⁹	-	-
Sm	.03-.20 ^{1,12} .11	.09-.95 ¹ .57	.05-.10 ¹ .06	.01 ⁹	.34 ¹	.06 ⁹	-	1.3 ¹¹
Eu	.06-.73 ^{1,15} .31	.09-.68 ¹ .47	.06-.08 ¹ .07	.01 ⁹	.36 ¹	.14 ⁹	-	1.6 ¹¹
Yb	.02-.30 ¹ .07	.09-1.3 ¹ .76	.24-.67 ¹ .46	.01 ⁹	.46 ¹	.18 ⁹	-	56 ¹¹
Ni	-	3.5-8 ^{3,4} 6	5-9 ^{3,4} 8	-	7-8 ^{3,5} 8	13 ⁵	4-19 ^{4,7}	0.6 ¹⁰
Co	-	2-8 ^{3,4} 2	3-12 ^{3,4} 6	-	7-19 ^{3,5} 13	25 ⁵	6-11 ^{4,6} 8	2 ¹¹
Cr	-	10-70 ^{3,4} 30	7-23 ^{3,4} 13	-	23-36 ^{3,5} 30	17 ⁵	1-58 ^{4,7} 32	22 ¹⁰
V	-	0.9-18 ^{3,4} 1.1	0.5-7.2 ^{3,4} 1.1	-	18-45 ^{3,5} 32	50 ⁵	24-63 ^{4,6,7} 30	8 ¹⁰
Sc	-	2.5-17 ^{3,4} 3	1.4-7.5 ^{3,4} 3	-	12.5 ³	-	1-3 ⁴ 2	4 ¹¹

* Range of reported values

** Suggested value (a weighted mean)

† Data sources for Table 1.

- | | |
|--|--|
| <ol style="list-style-type: none"> 1. SCHNETZLER and PHILPOTTS (1970) 2. PHILPOTTS and SCHNETZLER (1970) 3. EWART and TAYLOR (1969) 4. EWART et al. (1973) 5. ANDRIAMBOLOLONA et al. (1975) 6. IWASAKI et al. (1962) | <ol style="list-style-type: none"> 7. DUNCAN and TAYLOR (1969) 8. NAGASAWA and WAKITA (1968) 9. ARTH (1976); recommended value 10. GILL (1974); recommended value 11. IRVING and FREY (1977) 12. EWART (1976b) |
|--|--|

Sr contents typically remain approximately constant in orogenic andesites, implying $D(\text{Sr})_{\text{bulk}} \sim 1$, although Sr correlates positively with silica in some high-K suites and correlates negatively with silica in the acid portion of some high-K suites (Figure 3). Also, Rb-Sr covariance is similar regardless of whether or not Rb/Sr ratios correlate positively with initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios thereby yielding pseudoisochrons. Such similarity is more compatible with addition of Rb and ^{87}Sr by contamination than with equilibration between each andesite melt and old upper mantle, as required by the proposal of JAMES *et al.* (1976).

K/Rb ratios correlate negatively with % K when orogenic andesites as a whole are considered (Figure 4), defining a region above but roughly parallel to the main trend of SHAW (1968). Within individual suites, however, frequently there is < 20% change in K/Rb ratios, and sometimes ratios increase as K and Si contents increase. Within specific volcanic arcs both K and Rb contents in orogenic andesites increase relative to silica as the distance between the site of their eruption and the convergent plate boundary increases (e.g. lines 9 and 10, Figure 4). Rb contents increase more than K, causing K/Rb ratios to fall across volcanic arcs (JAKES and WHITE, 1970).

Light REE contents also vary widely between low and high-K orogenic andesites, from < 10 to > 100 times chondritic levels, and correlate positively with silica within suites (Figure 5a). In contrast, there is consistently less variation in heavy REE or Y contents which are about 8 to 15 times chondritic levels and 20 to 25 ppm, respectively (Figure 5b).

Positive correlation between Yb and Si is the norm, although there is less change than for La and several instances are known in which a negative correlation occurs. Except for Osima-osima volcano in the Sea of Japan, all these instances occur in andesites which ascended through relatively thick continental margins or interiors.

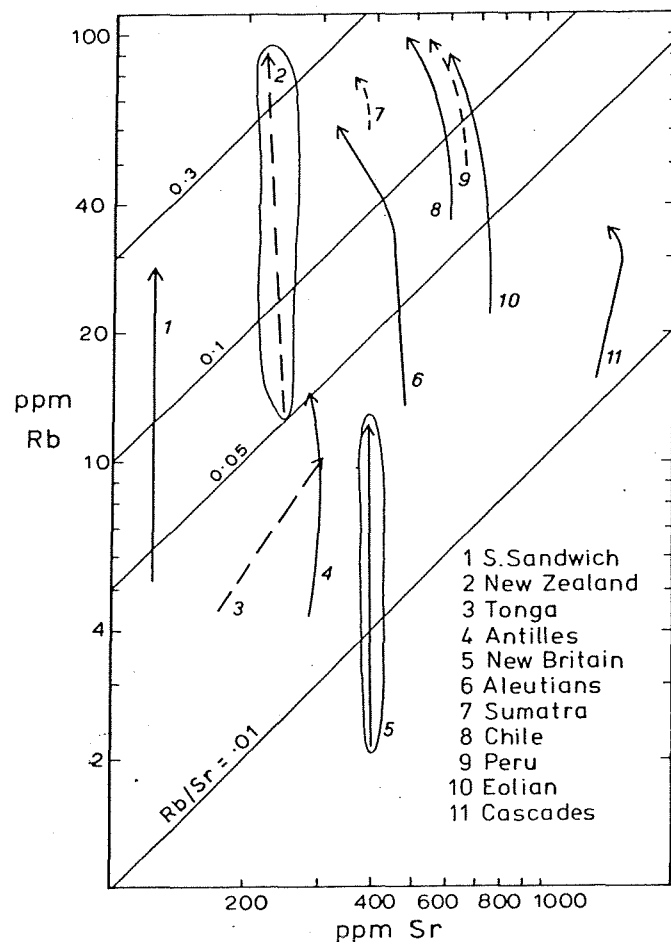


Figure 3. Rb vs. Sr contents in selected orogenic andesite suites. Lines are informal best-fits to data; data typically lie within limits which are shown for two examples. Arrows point in the direction of increasing SiO_2 contents. Dashed lines indicate data populations yielding pseudoisochrons. Data sources: 1. BAKER (in press); 2. EWART and STIPP (1968); 3. EWART *et al.* (1973); 4. BROWN *et al.* (1977), St. Kitts; 5. BLAKE and EWART (1974); 6. DELONG (1974), Semisopochnoi; 7. WHITFORD (1975), Merapi; 8. ROOBBIE *et al.* (1976); 9. JAMES *et al.* (1976); 10. KELLER (1974); 11. CHURCH and TILTON (1973).

K/

La rock / La chondrites

Yb rock / Yb chondrites

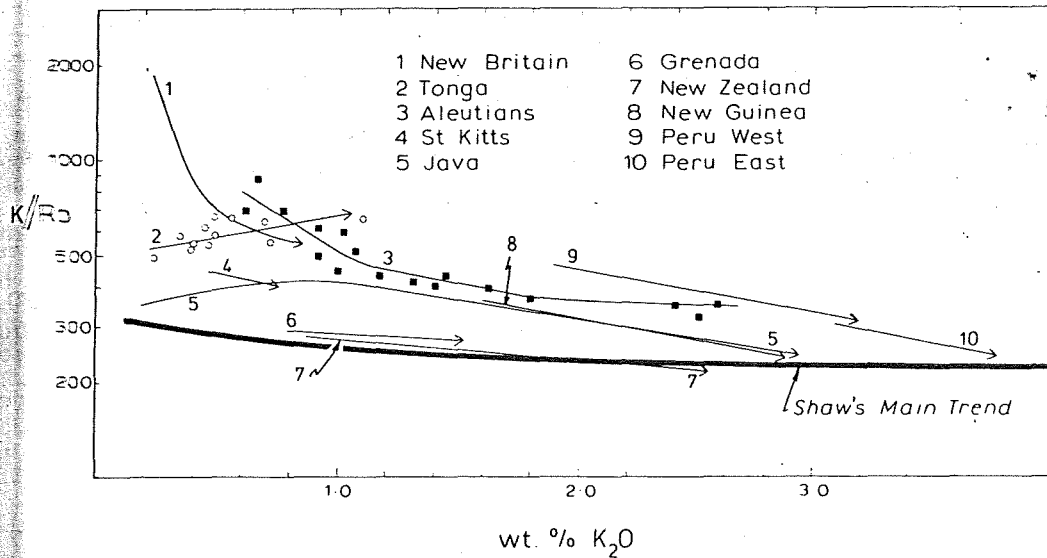


Figure 4. K/Rb ratios vs. K_2O contents in selected orogenic andesite suites. Lines are informal best-fits to data, examples of which are shown for two suites. Arrows point in the direction of increasing SiO_2 contents. Heavy line is from SHAW (1968). Other data sources are: 1. BLAKE and EWART (1974); 2. EWART *et al.* (1973); 3. DELONG (1974), Semisopchnoi; 4. and 6. BROWN *et al.* (1977); 5. WHITFORD (1975); 7. EWART and STIPP (1968); 8. MACKENZIE (1976); 9. and 10. DUPUY and LEFÈVRE (1974). Lines 9 and 10 refer to volcanoes closer to and further from, respectively the Peru-Chile trench.

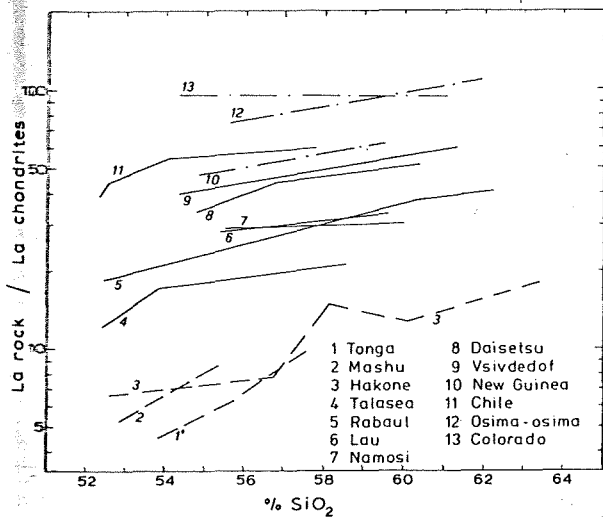
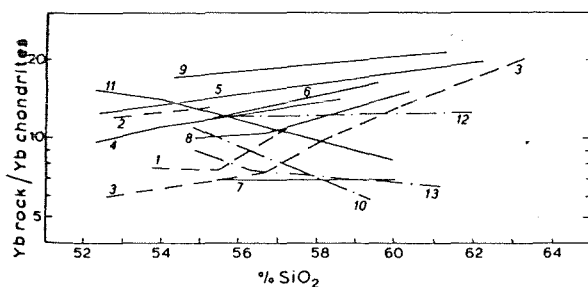


Figure 5. La (a) and Yb (b) enrichments vs. SiO_2 contents in selected orogenic andesite suites. Lines drawn as in previous diagrams. Dashed lines are low-K andesites according to Figure 1; solid lines are medium-K; dash-dot lines are high-K. Chondritic La and Yb values used are 0.30 and 0.17 ppm, respectively. Data sources are: 1. EWART *et al.* (1973); 2., 8., and 12. MASUDA *et al.* (1975); 3. FUJIMAKI (1975); 4. and 5. ARTH (1974); 6. GILL (1976); 7. GILL (1974); 9. KAY (1977); 10. JAKES and GILL (1970); 11. LOPEZ-ESCOBAR *et al.* (1976), Ancud; 13. ZIELINSKI and LIPMAN (1976).



Often REE concentrations differ by only 20 to 50% between basic and acid orogenic andesites, or between basic andesites and associated basalts. That is, REE and especially heavy REE are significantly more compatible than alkalis in andesite magmas. Eu anomalies > 10% are uncommon despite the ubiquity of plagioclase phenocrysts. Positive Eu anomalies, suggesting plagioclase accumulation, do occur but are as common in aphyric as porphyritic samples (e.g. YAJIMA *et al.*, 1972). Negative anomalies are restricted largely to acid orogenic andesites (e.g. FUJIMAKI, 1975; LOPEZ-ESCOBAR *et al.*, 1976), but are much smaller than in icelandites or trachytes of similar silica contents. The detailed internal shape of REE patterns for orogenic andesites is not well known due to insufficiently precise or complete data. However, maxima occur at Nd-Sm in some (e.g. KAY, 1977) while minima occur between Eu and Er in others (e.g. ARTH, 1974; GILL, 1976).

Ni contents of orogenic andesites vary by an order of magnitude between suites (Figure 6). In part, this variation reflects differences between suites in degree of differentiation relative to silica contents (HEDGE, 1971; MIYASHIRO and SHIDO, 1976, but differences exist even in rocks having similar MgO

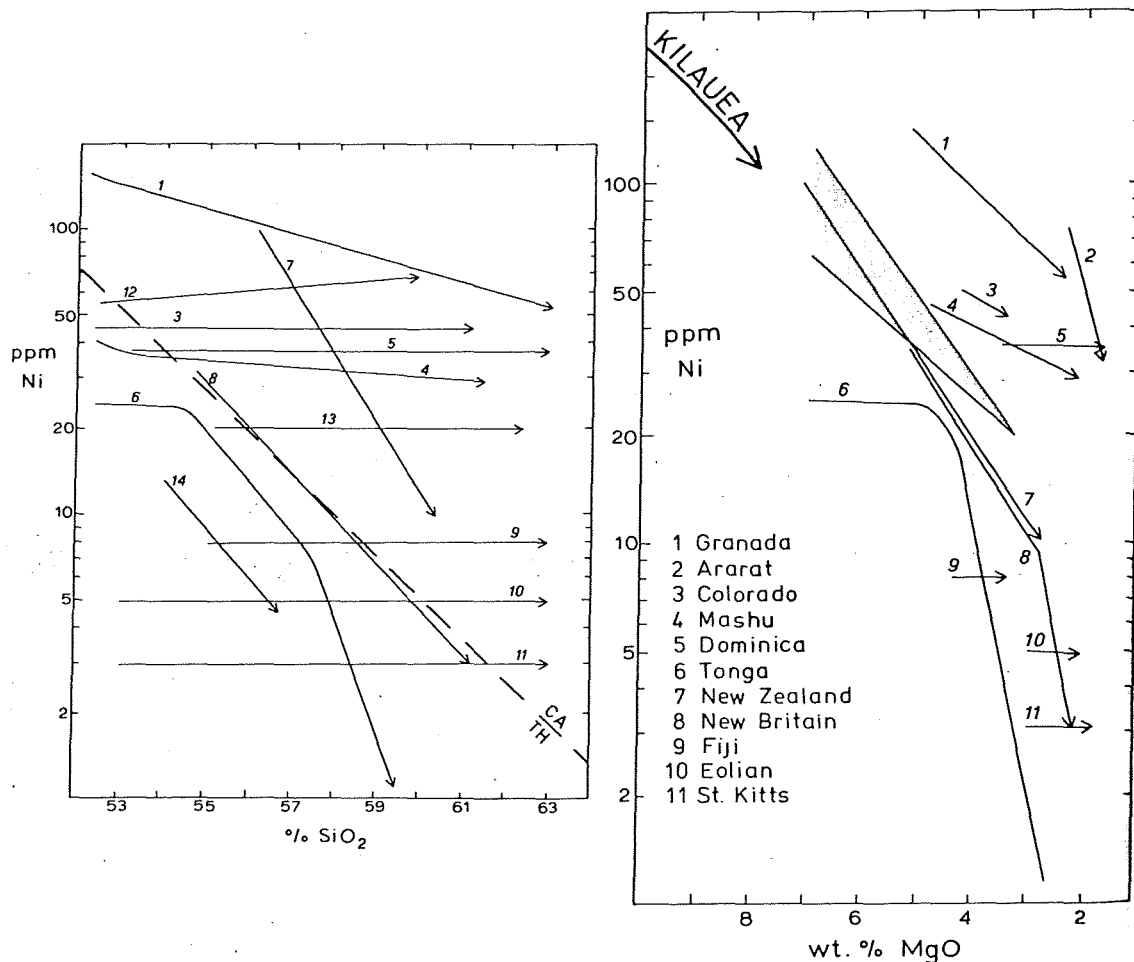


Figure 6. (a) Ni vs. SiO₂ contents in selected orogenic andesite suites. Lines drawn as in previous figures. The CA-TH dashed line separates calcalkaline (CA) from tholeiitic rocks according to MIYASHIRO and SHIDO (1976). (b) Ni vs. MgO contents for some of the same suites. The Kilauea trend is from GUNN (1971). The stipled field is from HEDGE (1971) for island arc high-alumina basalts. Other data sources for both 6(a) and (b) are: 1, 5, 11. BROWN *et al.* (1977); 2. LAMBERT *et al.* (1974); 3. ZIELINSKI and LIPMAN (1976); 4. ANDO (1975); 6. EWART *et al.* (1973); 7. COLE (in press); 8. BLAKE and EWART (1974); 9. GILL and TILL (in prep.); 10. KELLER (1974); 12. LOPEZ-ESCOBAR *et al.* (1976), Ancud; 13. CONDIE and SWENSON (1973), Rainier; 14. TAYLOR *et al.* (1969), Bagana.

contents of FeO^*/MgO ratios. In general, however, Ni contents are low: rarely > 100 ppm, usually < 40 ppm, and frequently < 10 ppm. In addition to the variation within this range between suites, a second striking feature of Figure 6 is the surprising consistency of average Ni contents within suites.

V generally follows Fe^{2+} and Ti in orogenic andesites, remaining constant or going through a maximum in suites showing much Fe-enrichment, but decreasing steadily in suites lacking much Fe-enrichment (Figure 7). In some cases, the sudden drop in V contents seen in Figure 7 is associated with the first modal appearance of magnetite phenocrysts. However, the kinks in Figure 7 connect disparate populations, as shown for the Tonga and Mashu data, which could reflect pooling of genetically unrelated rocks (see Introduction) as well as changes in coexisting phases along a liquid line of descent. In general, there is a two to three-fold decrease in V, Cr, Co, and Sc contents between 53 and 63% SiO_2 .

Cu contents have been determined in over 30 suites of orogenic andesites, range from 10 to 150 ppm, and have an average of about 60 ppm which is several times more than in most icelandites or trachytes having similar SiO_2 contents. In most suites, Cu contents decrease irregularly with increasing silica (e.g. GILL, 1976), but remain relatively constant in others (e.g. CONDIE and SWENSON, 1973). A maximum between 55 and 60% SiO_2 occurs in some suites characterized by rapid Fe-enrichment (e.g. EWART *et al.*, 1973). There is no correlation between Cu and Ni contents in andesites as would be expected if silicate-sulfide liquid immiscibility were an important genetic factor.

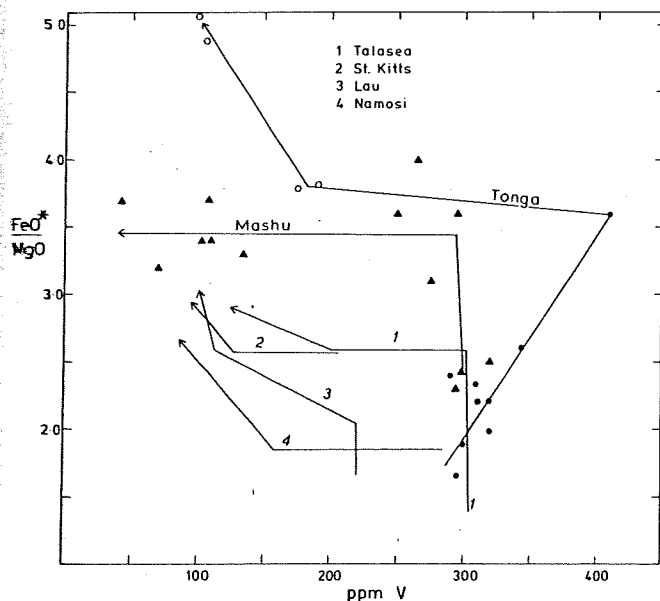


Figure 7. V contents vs. FeO^*/MgO ratios in selected orogenic andesite suites. Lines drawn as in previous figures. Solid triangles are data for Mashu; circles are for Tonga, with filled circles used for samples lacking magnetite phenocrysts and open circles used for those containing magnetite. Arrows point in the direction of increasing SiO_2 . FeO^* = total Fe as FeO . Data sources: 1. LOWDER and CARMICHAEL (1970); 2. BAKER (1968); 3. GILL (1976); 4. GILL and TILL (in prep.); Tonga, EWART *et al.* (1973); Mashu, ANDO (1975).

ROLE OF PARTITION COEFFICIENTS IN MODELS OF ANDESITE GENESIS

Solid/liquid partition coefficients can be used to test simple models in which orogenic andesites are considered to be primary partial melts or products of fractional crystallization of something. Specifically, the trace element characteristics described above might reflect equilibration over a melting interval with refractory phases in subducted oceanic crust (GREEN, 1972) or in overlying and hydrated peridotite (KUSHIRO, 1972). Alternatively, these trace element characteristics may result from fractional crystallization of basalt due to separation of anhydrous minerals (KUNO, 1968) or of amphibole (CAWTHORNE and O'HARA, 1976). However, solid/liquid partition coefficients are not yet as useful in evaluating other likely explanations of these trace element characteristics, such as crustal contamination (WILCOX, 1956), magmatic mixing (EICHELBERGER, 1975), or fluid/fluid fractionation. Because my scope here is more concerned with partition coefficients than trace element aspects of andesite genesis, these latter alternatives will not be discussed.

1. Orogenic andesites as partial melts of subducted oceanic crust

The refractory mineralogy and resulting bulk distribution coefficients appropriate to this model are a function of the depth to which oceanic crust is subducted before fusion. Depth to the Benioff Zone beneath active volcanoes at various convergent plate boundaries is 136 ± 41 km (1 σ), although this figure may decrease by 10 to 20 km as lateral heterogeneities in velocity structure beneath island arcs are taken into account when locating earthquake foci (e.g. ENGDAHL, 1973). If Benioff Zone earthquake foci beneath andesite volcanoes lie either at the slab/mantle boundary or < 25 km below the top of the slab within the colder, more brittle interior (ENGDAHL, 1973), then subducted oceanic crust is > 110 km beneath the volcanoes. At such depth, refractory phases during melting of a basaltic composition will be mostly clinopyroxene and garnet rather than amphibole. Potential accessories include phlogopite or orthoclase, kyanite, sphene, rutile, apatite, and sulfides, but their effect cannot be predicted quantitatively because of lack of partition coefficients and lack of constraints on their mass fraction in the residue. Estimates of the degree of fusion necessary to produce andesitic bulk compositions are 20 to 40%, but are weakly based (GILL, 1974).

The requirement that $D(\text{Sr})_{\text{bulk}} \sim 1$ within orogenic andesite suites is incompatible with an eclogite residuum, even if the residuum contains minor refractory apatite. Also, K, Rb, Cs, and especially Ba contents in andesites are higher than expected in products of 20 to 40% fusion of even altered ocean floor basalt, but this is a problem concerning source materials rather than partition coefficients. In contrast, the negative correlation between K/Rb ratios and K contents across island arcs has been attributed to variations in partition coefficients or percent fusion. JAKES and WHITE (1972) appealed to a changing refractory assemblage containing amphibole ($D(\text{K/Rb})_{\text{amph}} \sim 3$) at shallow depths but phlogopite ($D(\text{K/Rb})_{\text{phl}} \sim 0.3$) at greater depths. However, this explanation is invalid if the K/Rb ratio of the material being fused remains constant because the $D(\text{K/Rb})_{\text{bulk}}$ of the residuum must increase with depth to explain the pattern observed. Alternatively, BESWICK (1976) showed that repeated fusion of the same source, leaving refractory phlogopite each time, could account for the K and Rb distribution. However, successive fractional fusions of a common source are thermally unlikely, and this explanation also requires phlogopite to be more refractory at high degrees of fusion than low. Thus, the K-Rb distribution remains unexplained and may reflect variations in source composition rather than in partition coefficients or percent fusion.

REE provide three sensitive tests of this model (GILL, 1974; THORPE et al., 1976; LOPEZ-ESCOBAR et al., 1976; DOSTAL et al., 1977). First, if the source initially had a flat REE pattern with 10 to 15 times chondritic concentrations, if garnet and clinopyroxene alone constitute the residuum, and if the partition coefficients of Table 1 pertain, then at $< 40\%$ fusion the light REE concentrations of a partial melt will be two to three times higher than observed in low or medium-K orogenic andesites, and the heavy REE will be two to three times lower than in all but a very few orogenic andesites. Secondly, magmas should become increasingly heavy REE-enriched as percent fusion increases; i.e. eclogite melting should lead to a negative correlation between heavy REE and silica. Such negative correlation occasionally occurs (lines 10 to 13, Figure 5b), but is not a general feature and seems mostly restricted to magmas erupted through > 30 km of crust. Finally, if the source material is light REE-depleted, then some characteristics of that depletion (e.g. $\text{La} < \text{Ce}$) will be preserved in partial melts, but are not observed in natural orogenic andesites. The three conclusions listed above are valid if: $D(\text{La})_{\text{gar}} < 0.1$ whereas $D(\text{Yb})_{\text{gar}} > 5$; $D(\text{La})_{\text{cpx}} < 0.2$ whereas $D(\text{Yb})_{\text{cpx}} > 0.5$; accessory minerals with $D(\text{Yb}) \sim 0$ constitute $< 20\%$ of the residuum; and garnet constitutes $> 25\%$ of the residuum.

Both absolute and relative concentrations of some fourth period transition metals also are problematical. For example, if subducted oceanic crust has 100 ppm Ni, if both $D(\text{Ni})_{\text{cpx}} < 3$ and $D(\text{Ni})_{\text{gar}} < 1$ at 1100 to 1200°C, and if garnet constitutes $> 25\%$ of the residuum, then any partial melt will have > 40 ppm Ni. However, IRVING (1977) reported $D(\text{Co})_{\text{gar}} = 9.0$ at 950°C and 30 kb for dacite. If $D(\text{Ni})_{\text{gar}} > D(\text{Co})_{\text{gar}}$, as expected for octahedral coordination, then garnet may be a Ni sink, thereby removing this objection to eclogite fusion. However, garnet also is a Sc sink according to IRVING (1977), with $D(\text{Sc})_{\text{gar}} = 28$ under the conditions mentioned above. Because most orogenic andesites have > 20 ppm Sc, which requires $D(\text{Sc})_{\text{bulk}} < 3.5$ if subducted oceanic crust contained 60 ppm Sc, Irving's experiment clearly adds a serious problem for eclogite fusion models while possibly removing another. Finally, the two to

thr
be
and

Thus
the
may
tics
with
Ni a
et a

2.

Neit
the
by i
or a
cabl
be m
with
bole
bole
chon

Secor
equil
LEEMA
by DA
% MgC
ene c

Thir
cent
(Fig
riod
fO₂,
inter
and V
fract

3. O
m

Varia
quent
miner
CARM
cent
talli
As no
mated
alkal
or at
tuiti
Beacu
model
some

First
phases
quired
on exp
WEILL
lead
anom
Howev
ratio
3.3 fo
SCHNE
each I
D(REE)

three-fold decrease in V contents within orogenic andesites (Figure 7) cannot be explained by fusion of bimineralec eclogite at nearly constant temperature and fO_2 is the partition coefficients of Table 1 are a guide.

Thus, available D_{cpx} and D_{gar} values for Sr, REE, Ni and Sc are unfavorable to the eclogite fusion hypothesis as a general explanation. However, the model may explain the origin of atypical andesites having the following characteristics: strong positive correlation between Sr and silica; steep REE patterns with $Yb < 1$ ppm, $Y < 20$ ppm, and $La/Yb > 20$; < 10 ppm Sc; and probably > 40 ppm Ni and > 300 ppm V. Possible examples have been described by LOPEZ-ESCOBAR *et al.* (1977) and KAY (in press).

2. Orogenic andesites as partial melts of hydrated peridotite

Neither the trace element composition of the source, the percent fusion, nor the refractory assemblage appropriate to this hypothesis have been specified by its proponents, so there are few quantitative trace element arguments for or against it. Three issues which depend on partition coefficients are applicable, however. First, the REE patterns of individual orogenic andesites can be modelled satisfactorily by postulating $< 5\%$ fusion of a lherzolite source with two to three times chondritic REE contents and without refractory amphibole or mica (LOPEZ-ESCOBAR *et al.*, 1976, 1977). Presence of refractory amphibole would require concomitant REE-enrichment of the source above three-times chondritic levels.

Second, the low Ni contents of most orogenic andesites require $D(Ni)_{ol} > 50$ for equilibration with upper mantle olivine. Although the value of 30 reported by LEEMAN and LINDSTROM (1977) for olivine/basalt equilibration at $1100^\circ C$, and by DAVIS and HART (1977) for olivine equilibration with magma containing 4 wt. % MgO helps avoid this problem, fractional crystallization of olivine or pyroxene during ascent seems necessary for andesites containing < 60 ppm Ni.

Third, equilibration with a refractory lherzolite assemblage during a few percent melting can explain neither the diversity of V distributions observed (Figure 7) nor the two to three-fold drop in concentration of most fourth period transition metals within andesite suites. That is, neither temperature, fO_2 , nor refractory mineral weight fractions vary enough within the melting interval to produce such a variation in partition coefficients. Both the Ni and V arguments suggest that orogenic andesites are more likely related by fractional crystallization than partial fusion.

3. Orogenic andesites as products of crystal fractional involving anhydrous minerals

Variations in major element composition within orogenic andesite suites frequently can be approximated by addition or subtraction of anhydrous phenocryst minerals using least squares calculations (e.g. EWART *et al.*, 1973; LOWDER and CARMICHAEL, 1970). These calculations typically indicate that each one percent increment in SiO_2 content of the liquid is accompanied by 12 to 14% crystallization of basic andesite or 8 to 10% crystallization of acid andesite. As noted earlier, these degrees of crystallization are higher than those estimated using the distribution of incompatible trace elements such as Zr or alkalis. Thus, either the fractional crystallization hypothesis is incorrect or at least incomplete and the successful least squares calculations are fortuitous, or the elements are more compatible than suggested in Table 1. Because choice between these alternatives is not yet possible, unequivocal models of fractional crystallization are not available for testing. However, some general principles can be noted.

First, plagioclase typically constitutes 50 to 65% of the mass of crystalline phases removed in least squares solutions. This is consistent with the requirements that $D(Sr)_{bulk} \sim 1$ and increases as fractionation proceeds, based on experimental determinations of $D(Sr)_{pl}$ by SUN *et al.* (1974) and DRAKE and WEILL (1975). Although such extensive plagioclase involvement should also lead to positive Eu anomalies upon plagioclase accumulation or negative Eu anomalies upon plagioclase removal, neither is common in orogenic andesites. However, if $\log fO_2$ is -8.0 at $1100^\circ C$ (Figure 2), then the predicted Eu^*/Eu^3 ratio is ~ 4 (WEILL and DRAKE, 1973) which compares favorably with $Eu^*/Eu^3 = 3.3$ for plagioclase phenocrysts separated from andesites (PHILPOTTS and SCHNETZLER, 1970). This Eu^*/Eu^3 ratio will produce only a 3% Eu anomaly for each 10% plagioclase added or subtracted because of the generally low $D(REE)_{pl}$.

Secondly, magnetite typically constitutes 5 to 10% of the solids removed to prevent Fe-enrichment in least squares solutions. If it constitutes 10%, then $D(v)_{\text{bulk}}$ will be > 3 which, for example, is consistent with values between 3 and 4 calculated by the method of ALLEGRE *et al.* (1977) using data of EWART *et al.* (1973) for Fonualei volcano, Tonga, and data of BAKER (1968) for Mt. Misery volcano, Antilles, assuming $D(\text{Zr})_{\text{bulk}} = 0$.

Thirdly, the REE seem to behave more compatibly in some orogenic andesites than predicted by the partition coefficients of Table 1 (e.g. GILL, 1976; LOPEZ-ESCOBAR *et al.*, 1976), but data are insufficient to quantify this argument. Two explanations are possible. First, the $D(\text{REE})_{\text{px}}$ of Table 1 may be too low for andesite magmas. For example, DRAKE and HOLLOWAY (1977) found $D(\text{Sm})_{\text{aug}} \sim 1$ at 1000°C for an acid andesite. Alternatively, apparent compatibility may reflect precipitation of accessory apatite which is included in the phenocrysts of some andesites. Apatite stability may differ amongst orogenic andesites due to variable halogen and water fugacities and this difference may, in turn, explain why P_2O_5 correlates positively with silica in relatively Fe-enriched suites but negatively in more calcalkaline ones (ANDERSON and GOTTFRIED, 1971). If so, greater incompatibility of REE is predicted in more tholeiitic (Fe-enriched) orogenic andesites. Such contrasting compatibility is suggested by data of YAJIMA *et al.* (1972) for the pigeonitic and pher-sthenic rock series of central Honshu, Japan, although their samples are from several different volcanoes.

Finally, relatively constant Ni contents within suites are inconsistent with this model if pyroxenes and magnetite constitute $> 1/3$ of the crystallizing phases and have $D(\text{Ni}) > 3$. Clearly the role of olivine fractionation is restricted and, significantly, no andesite suites containing olivine phenocrysts have constant Ni contents.

Thus, trace element data, except Ni in many cases, are least at odds with fractional crystallization models involving anhydrous minerals. However, there are few instances where analyses of incompatible and key compatible trace elements and analyses of minerals all are available for enough representatives of a possibly cogenetic suite to test models rigorously, much less to test whether the variations in trace element distributions can be attributed to variations in the mineral proportions being separated.

4. Orogenic andesites as products of crystal fractionation involving amphibole

Hornblende provides an alternative to magnetite as a phase whose fractionation would produce Si-enrichment but relatively little Fe-enrichment. Because the bulk composition of hornblende approximates that of a mixture of plagioclase, pyroxenes, and magnetite, least squares calculations such as those referred to above also yield satisfactory results when hornblende is included as a possible crystallizing phase (e.g. ARCULUS, 1976). The percent crystallization necessary for each one wt. % increment in liquid SiO_2 content is similar to that in anhydrous solutions, but the weight fractions of plagioclase and magnetite decrease slightly when amphibole is included; amphibole typically constitutes 30 to 40% of the crystallizing phases.

Hornblende crystallization would help rationalize the apparent compatibility of alkalis and REE in orogenic andesites. However, separation of equal masses of hornblende and plagioclase would cause K/Rb ratios to drop by a factor of 2 to 3 if $F = 0.5$ and $D(\text{K/Rb})_{\text{hb}} \sim D(\text{K/Rb})_{\text{pl}} = 2$ to 4; such a drop is not observed (Figure 3). Similarly if $D(\text{Ba})_{\text{hb}} > D(\text{La})_{\text{hb}}$ or $D(\text{Ba})_{\text{hb}} > D(\text{Rb})_{\text{hb}}$ as suggested by ALLEGRE *et al.* (1977) and ARTH (1976), then hornblende fractionation should cause significant drops in Ba/Rb and Ba/La ratios. Equilibration with hornblende also could account for orogenic andesites whose REE patterns have a minimum near Dy.

However, consistent Ni contents within suites are an equal or greater problem than in the fractionation of anhydrous minerals if $D(\text{Ni})_{\text{hb}} > D(\text{Ni})_{\text{px}}$ (Table 1). Similarly, if $D(\text{V})_{\text{hb}} \gg D(\text{V})_{\text{px}}$, then the mass fraction of hornblende which can be removed is very restricted. Finally, the hornblende/dacite pairs analyzed by ANDRIAMBOLOLONA *et al.* (1975) suggest that $D(\text{Ni})_{\text{hb}} < D(\text{Co})_{\text{hb}}$ and $D(\text{Cr})_{\text{hb}} < D(\text{V})_{\text{hb}}$, in contrast to prediction for octahedral coordination of these transition metals. If true, then hornblende crystallization would cause a positive correlation between silica contents and Ni/Co or Cr/V ratios, which is not observed.

Thus, partition coefficients may help distinguish cases of anhydrous versus hydrous mineral fractionation events. Examples of the latter involving hornblende will be characterized by: rapidly dropping K/Rb and possibly Ba/Rb and Ba/La ratios as well as Ni and V contents with increasing silica contents; nearly constant or decreasing heavy REE and Y contents with a REE minimum near Dy; and possibly by a positive correlation between Ni/Co or Cr/V ratios and silica contents. No clear examples with these characteristics are known to me.

CONCLUSIONS

The origin of most orogenic andesites probably reflects a combination of one or more of the four models discussed above, together with other processes less testable using solid/liquid partition coefficients. However, before invoking more complex hypotheses one must try to demonstrate that failure of a given model to account for observed trace element characteristics is not a function of the samples chosen, the degree of crystallization assumed, or the partition coefficients used. Reconnaissance studies have not provided adequate data with which to make this demonstration; future trace element studies need to be accompanied by more thorough field, petrographic, and isotopic work than has been common heretofore. Such accompaniment may lead to families of fractional crystallization models, or to multi-stage genetic hypotheses invoking the mixing of partial melts of different sources or the additive effects of partial melting, crystal and liquid/liquid fractionation, and magma mixing. Present versions of such multi-stage schemes can be successful in modelling specific andesites (e.g. LOPEZ-ESCOBAR *et al.*, 1977; DOSTAL *et al.*, 1977), but are non-unique and *ad hoc*, and await criteria for their selection. Successful explanation of the trace element characteristics of orogenic andesites probably requires models of such complexity.

ACKNOWLEDGEMENTS

Roy Harris of the University of Auckland drafted the figures. Felix Chayes generously supported my use of his datafile, which was made possible by a travel grant from the Faculty Research Committee, UCSC. Preparation of this review was supported by NSF grant EAR76-84065.

REFERENCES

- ALLEGRE C.J. and CONDOMINES M. (1976) Fine chronology of volcanic processes using ^{238}U - ^{230}Th systematics. *Earth Planet. Sci. Letters* **28**, 395-406.
- ALLEGRE C.J., TREUIL M., MINSTER J.-F., MINSTER B., and ALBAREDE F. (1977) Systematic use of trace element in igneous process. Part I: Fractional crystallization processes in volcanic suites. *Contr. Mineral. and Petrol.* **60**, 57-75.
- ANDERSON A.T. (1974) Chlorine, sulfur, and water in magmas and oceans. *Geol. Soc. America Bull.* **85**, 1485-1492.
- ANDERSON A.T. and GOTTFRIED D. (1971) Contrasting behavior of P, Ti, and Nb in a differentiated high-alumina olivine tholeiite and a calcalkaline andesitic suite. *Geol. Soc. America Bull.* **82**, 1929-1942.
- ANDO S. (1975) Minor element geochemistry of the rocks from Mashu Volcano, eastern Hokkaido. *J. Fac. Sci. Hokkaido Univ., Ser. IV*, **16**, 553-566.
- ANDRIAMBOLOLONA R., LEFÈVRE C., and DUPUY C. (1975) Coefficient de partage des éléments de transition dans les minéraux ferro-magnésiens extraits des dacites. *C. R. Acad. Sc. Paris, Série D*, **281**.
- ARAMAKI S. and KATSURA T. (1973) Petrology and liquidus temperature of the magma of the 1970 eruption of Akita-Komagatake Volcano, northeastern Japan. *J. Japan. Assoc. Min. Petr. Econ. Geol.* **68**, 101-124.
- ARCULUS R.J. (1976) Geology and geochemistry of the alkali basalt-andesite association of Grenada, Lesser Antilles island arc. *Geol. Soc. American Bull.* **87**, 612-624.
- ARTH J.G. (1974) REE in the basalt-andesite-dacite-rhyolite suites of Talasea and Rabaul, New Britain. *Abs. Geol. Soc. America* **6**, 638.
- ARTH J.G. (1976) Behavior of trace elements during magmatic processes - a summary of theoretical models and their applications. *Jour. Research U.S. Geol. Survey* **4**, 41-47.
- BAKER P.E. (1968) Petrology of Mt. Misery volcano, St. Kitts, West Indies. *Lithos* **1**, 124-150.
- BAKER P.E. (in press) The South Sandwich Islands: II. Petrology and geochemistry. *Brit. Antarct. Surv. Sci. Rept.*
- BALDRIDGE W.S., MCGETCHIN T.R., and FREY F.A. (1973) Magmatic evolution of Hekla, Iceland. *Contr. Mineral. and Petrol.* **42**, 245-258.

- BESWICK A.E. (1973) An experimental study of alkali metal distribution in feldspars and micas. *Geochim. Cosmochim. Acta* **37**, 183-208.
- BLAKE D.H. and EWART A. (1974) Petrography and geochemistry of the Cape Hoskins volcanoes, New Britain, Papua New Guinea. *J. Geol. Soc. Australia* **21**, 319-332.
- BROWN G.M., HOLLAND J.G., SIGURDSSON H., TOMBLIN J.F., and ARCULUS R.J. (1977) Geochemistry of the Lesser Antilles volcanic island arc. *Geochim. Cosmochim. Acta* **41**, 785-801.
- BUDDINGTON A.F. and LINDSLEY D.H. (1964) Iron-titanium oxide minerals and synthetic equivalents. *J. Petrol.* **5**, 310-357.
- CARMICHAEL I.S.E. (1967a) The iron-titanium oxides of salic volcanic rocks and their associated ferromagnesian silicates. *Contr. Mineral. and Petrol.* **14**, 36-64.
- CARMICHAEL, I.S.E. (1967b) The mineralogy of Thingmuli, A Tertiary volcano in eastern Iceland. *Am. Mineral.* **52**, 1815-1841.
- CAWTHORNE R.G. and O'HARA M.J. (1976) Amphibole fractionation in calcalkaline magma genesis. *Am. J. Sci.* **276**, 309-329.
- CHURCH, S.E. and TILTON G.R. (1973) Lead and strontium isotopic studies in the Cascade mountains: bearing on andesite genesis. *Geol. Soc. America Bull.* **84**, 431-454.
- COLE J.W. (in press) Andesites in the Tongariro volcanic centre, North Island, New Zealand. *J. Volcanol. Geotherm. Res.*
- CONDIE K.C. and SWENSON D.H. (1973) Compositional variations in three Cascade stratovolcanoes: Jefferson, Rainier, and Shasta. *Bull. Volcanol.* **37**, 205-230.
- DAVIS K.E. and HART S.R. (1977) Partitioning of nickel between olivine and silicate liquid. In: Papers presented to the International Conference on Experimental Trace Element Geochemistry, p. 16-17.
- DELONG S.E. (1974) Distribution of Rb, Sr, and Ni in igneous rocks, Central and Western Aleutian Islands, Alaska. *Geochim. Cosmochim. Acta* **38**, 245-266.
- DOSTAL J., ZENTILLI M., CAELLES J.C., and CLARK A.H. (1977) Geochemistry and origin of volcanic rocks of the Andes (26-28°S). *Contr. Mineral. and Petrol.* **63**, 113-128.
- DRAKE M.J. and HOLLOWAY J.R. (1977) Partitioning of Sm between plagioclase, clinopyroxene, amphibole, and hydrous silicate liquid at high pressures: preliminary results. In: Papers presented to the International Conference of Trace Element Geochemistry.
- DRAKE M.J. and WEILL D.F. (1975) Partition of Sr, Ba, Ca, Y, Eu^{2+} , Eu^{3+} and other REE between plagioclase feldspar and magmatic liquid: an experimental study. *Geochim. Cosmochim. Acta* **39**, 689-712.
- DUNCAN A.R. and TAYLOR S.R. (1969) Trace element analyses of magnetites from andesitic and dacitic lavas from Bay of Plenty, New Zealand. *Contr. Mineral. and Petrol.* **20**, 30-33.
- DUPUY C. and LEFEVRE C. (1974) Fractionnement des éléments en trace Li, Rb, Ba, Sr dans les séries andésitiques et shoshonitiques de Pérou. Comparaison avec d'autres zones orogéniques. *Contr. Mineral. and Petrol.* **46**, 147-157.
- EGGLER D.H. (1972) Water-saturated and undersaturated melting relations in a Particutin andesite and an estimate of water content in the natural magma. *Contr. Mineral. and Petrol.* **34**, 261-271.
- EICHELBERGER J.C. (1975) Origin of andesite and dacite: evidence of mixing at Glass Mountain in California and at other circum-Pacific volcanoes. *Geol. Soc. America Bull.* **86**, 1381-1391.
- ENGDAHL E.R. (1973) Relocation of intermediate depth earthquakes in the Central Aleutians by seismic ray tracing. *Nature Phys. Sci.* **245**, 23-25.
- EWART A. (1976a) Mineralogy and chemistry of modern orogenic lavas - some statistics and implications. *Earth Planet. Sci. Letters* **31**, 417-432.
- EWART A. (1976b) A petrological study of the younger Tongan andesites and dacites, and the olivine tholeiites of Niua Fo'ou Island, S.W. Pacific. *Contr. Mineral. and Petrol.* **58**, 1-21.
- EWART A., BRYAN W., and GILL J. (1973) Mineralogy and geochemistry of the younger volcanic islands of Tonga, S.W. Pacific. *J. Petrology* **14**, 429-465.
- EWART A. and STIPP J.J. (1968) Petrogenesis of the volcanic rocks of the Central North Island, New Zealand, as indicated by a study of Sr 87/86 ratios, and Sr, Rb, K, U, and Th abundances. *Geochim. Cosmochim. Acta* **32**, 699-736.
- EWART A. and TAYLOR S.R. (1969) Trace element geochemistry of the rhyolitic volcanic rocks, Central North Island, New Zealand. Phenocryst data. *Contr. Mineral. and Petrol.* **22**, 127-146.
- FUDALI R.F. *Geochim*
- FUJIMAKI H. and nor
- GILL J.B. (19) calc-all
- GILL J.B. (19) implicat
- GREEN T.H. (19) high-pre
- GUNN B. (1971) Hawaiiar
- HEDGE C.E. (19) 35, 522-
- HEMING R.F. a the Raba
- IRVING A.J. (19) garnet a
- IRVING A.J. a national
- IRVING A.J. a garnet n
- IWASAKI I., K the volc
- JAKES P. and tholeiit
- JAMES D.E., B magma ge
- KATSUI Y., AN Mashu vo
- KAY R.W. (in Pacific
- KELLER J. (19) southern
- KUNO H. (1968) Bull. Vo
- KUSHIRO I. (19) high pres
- KUSHIRO I., Y andesite
- LAMBERT R. ST of a suit
- LEEMAN W.P. ar and Mn be
- LOPEZ-ESCOBAR south Ch
- LOPEZ-ESCOBAR on "Andea
- LOWDER G.G. ar Talasa,
- MACKENZIE D.E. western F
- Johnson),

- FUDALI R.F. (1965) Oxygen fugacities of basaltic and andesitic magmas. *Geochim. Cosmochim. Acta* **29**, 1063-1075.
- FUJIMAKI H. (1975) Rare earth elements in volcanic rocks from Hakone volcano and northern Izu Peninsula, Japan. *Jour. Fac. Sci. Univ. Tokyo, Sec. II*, **19**, 81-93.
- GILL J.B. (1974) Role of underthrust oceanic crust in the genesis of a Fijian calc-alkaline suite. *Contr. Mineral. and Petrol.* **43**, 29-45.
- GILL J.B. (1976) Composition and age of Lau Basin and Ridge volcanic rocks: implications for evolution of an interarc basin and remnant arc. *Geol. Soc. America Bull.* **87**, 1384-1395.
- GREEN T.H. (1972) Crystallization of calc-alkaline andesite under controlled high-pressure hydrous conditions. *Contr. Mineral. and Petrol.* **34**, 150-166.
- GUNN B. (1971) Trace element partitioning during olivine fractionation of Hawaiian basalts. *Chem. Geol.* **8**, 1-13.
- HEDGE C.E. (1971) Nickel in high-alumina basalts. *Geochim. Cosmochim. Acta* **35**, 522-524.
- HEMING R.F. and CARMICHAEL I.S.E. (1973) High-temperature pumice flows from the Rabaul caldera, Papua New Guinea. *Contr. Mineral. and Petrol.* **38**, 1-20.
- IRVING A.J. (1977) Experimental partitioning of trace elements between garnet and hydrous acidic melt. In: Papers presented to the International Conference on Experimental Trace Element Geochemistry, p. 59-61.
- IRVING A.J. and FREY F.A. (1977) Distribution of trace elements between garnet megacrysts and host volcanic liquids of kimberlitic to rhyolitic compositions. In: Papers presented to the International Conference on Experimental Trace Element Geochemistry, p. 56-58.
- IKASAKI I., KATSURA T., and YOSHIDA M. (1962) Geochemical investigations of the volcanoes in Japan. LI. Titanomagnetites in volcanic rocks of Nekodake, Aso volcano. *Bull. Chem. Soc. Japan* **35**, 448.
- JAKES P. and GILL J.B. (1970) Rare earth elements and the island arc tholeiitic series. *Earth Planet. Sci. Letters* v. **9**, p. 17-28.
- JAKES P. and WHITE A.J.R. (1970) K/Rb ratios of rocks from island arcs. *Geochim. Cosmochim. Acta* **34**, 849-856.
- JAMES D.E., BROOKS C., and CUYUBAMBA A. (1976) Andean Cenozoic volcanism: magma genesis in the light of strontium isotopic composition and trace element geochemistry. *Geol. Soc. America Bull.* **87**, 592-600.
- KATSUI Y., ANDO S., and INABA K. (1975) Formation and magmatic evolution of Mashu volcano, East Hokkaido, Japan. *J. Fac. Sci. Hokkaido Univ., Ser. IV*, **16**, 533-552.
- KAY R.W. (in press) Aleutian magnesian andesites: melts from subducted Pacific Ocean crust. *J. Volc. Geotherm. Res.*
- KELLER J. (1974) Petrology of some volcanic rock series of the Aeolian arc, southern Tyrrhenian Sea: calc-alkaline and shoshonitic associations. *Contr. Mineral. and Petrol.* **46**, 29-47.
- KUNO H. (1968) Origin of andesite and its bearing on the island arc structure. *Bull. Volcanol.* **32**, 141-176.
- KUSHIRO I. (1972) Effect of water on the compositions of magmas formed at high pressures. *J. Petrology* **13**, 311-334.
- KUSHIRO I., YODER H.S., JR., and MYSEN B.O. (1976) Viscosities of basalt and andesite melts at high pressures. *J. Geophys. Res.* **81**, 6351-6356.
- LAMBERT R. ST. JOHN, HOLLAND J.G., and OWEN P.F. (1974) Chemical petrology of a suite of calc-alkaline lavas from Mount Ararat, Turkey. *J. Geol.* **82**, 419-438.
- LEEMAN W.P. and LINDSTROM D.J. (1977) Partitioning of Mg, Fe²⁺, Ni, Co, and Mn between olivine and basaltic liquid: an experimental study. In: Papers presented to the International Conference on Experimental Trace Element Geochemistry, p. 73-74.
- LOPEZ-ESCOBAR L., FREY F.A. and VERGARA M. (1976) Andesites from central-south Chile: trace element abundances and petrogenesis. In: Proc. Symp. on "Andean and Antarctic Volcanology Problems", IAVCEI, Naples, p. 725-761.
- LOPEZ-ESCOBAR L., FREY F.A., and VERGARA M. (1977) Andesites and high-alumina basalts from the central-south Chile High Andes: geochemical evidence bearing on their petrogenesis. *Contr. Mineral. and Petrol.*
- LOWDER G.G. and CARMICHAEL I.S.E. (1970) The volcanoes and caldera at Talasea, New Britain. *Geol. Soc. America Bull.* **81**, 17-38.
- MACKENZIE D.E. (1976) Nature and origin of Late Cenozoic volcanoes in western Papua New Guinea. In: *Volcanism in Australasia* (ed. R.W. Johnson), Elsevier Sci. Pub. Co., p. 221-238.

- MASUDA Y., NISHIMURA S., IKEDA T., and KATSUI Y. (1975) Rare-earth and trace elements in the Quaternary volcanic rocks of Hokkaido, Japan. *Chem. Geol.* 15, 251-271.
- MATUMOTO T. (1971) Seismic body waves observed in the vicinity of Mount Katmai, Alaska, and evidence for the existence of molten chambers. *Geol. Soc. America Bull.* 82, 2905-2920.
- MIYASHIRO A. and SHIDO F. (1976) Behavior of nickel in volcanic rocks. In: *Volcanoes and Tectosphere* (ed. H. Aoki), Tokyo, Tokai Univ. Press, p. 115-121.
- MYSEN B.O., ARCULUS R.J., and EGGLEER D.H. (1975) Solubility of carbon dioxide in melts of andesite, tholeiite, and olivine nephelinite composition at 30 kbar pressure. *Contr. Mineral. and Petrol.* 53, 227-239.
- PHILPOTTS J.A. and SCHNETZLER C.C. (1970) Phenocryst-matrix partition coefficients for K, Rb, Sr, and Ba, with applications to anorthosite and basalt genesis. *Geochim. Cosmochim. Acta* 36, 1131-1166.
- PUSHKAR P., STEUBER A.M., TOMBLIN J.F., and JULIAN G.M. (1973) Strontium isotopic ratios in volcanic rocks from St. Vincent and St. Lucia, Lesser Antilles. *J. Geophys. Res.* 78, 1279-1287.
- ROOBOL M.J., RIDLEY W.I., RHODES M.J., WALKER G.P.L., FRANCIS P.W., and COBBLEY T. (1976) Physico-chemical characters of the Andean volcanic chain between latitudes 21° and 22°S. In: *Proc. Symp. Andean Antarctic Volcanology Problems*,
- ROSE W.I., JR. (1973) Pattern and mechanism of volcanic activity at the Santiaguillo volcanic dome, Guatemala. *Bull. Volcanol.* 37, 73-94.
- ROSE W.I., JR., ANDERSON A.T., JR., BONIS S. and WOODRUFF L.G. (in press) The October 1974 basaltic tephra from Fuego volcano Guatemala: description and history of the magma body.
- ROSE W.I., JR., GRANT N.K., HAHN G.A., LANGE I.M., POWELL J.L., EASTER J., and DE GRAFF J.M. (1977) The evolution of Santa Maria Volcano, Guatemala. *J. Geol.* 85, 63-88.
- SCHNETZLER C.C. and PHILPOTTS J.A. (1970) Partition coefficients of rare-earth elements between igneous matrix material and rock-forming mineral phenocrysts-II. *Geochim. Cosmochim. Acta* 34, 331-340.
- SHAW D.M. (1968) A review of K-Rb fractionation trends by covariance analysis. *Geochim. Cosmochim. Acta* 32, 573-601.
- SUN C., WILLIAMS R.J., and SUN S. (1974) Distribution coefficients of Eu and Sr for plagioclase-liquid and clinopyroxene-liquid equilibria in ocean ridge basalt: an experimental study. *Geochim. Cosmochim. Acta* 38, 1415-1433.
- TAYLOR S.R. (1969) Trace element chemistry of andesites and associated calc-alkaline rocks. In: *Proc. Andesite Conf.* (ed. A.R. McBirney), Dept. Geol. Min. Res. Oregon Bull. 65, 43-64.
- THORARINSSON S. and SIGVALDASON G.E. (1973) The Hekla eruption of 1970. *Bull. Volcanol.* 36, 269-288.
- THORPE R.S., POTTS P.J., and FRANCIS P.W. (1976) Rare earth data and petrogenesis of andesite from the North Chilean Andes. *Contr. Mineral. and Petrol.* 54, 65-78.
- WELL D.F. and DRAKE M.J. (1973) Europium anomaly in plagioclase feldspar: experimental results and semi-quantitative model. *Science* 180, 1059-1060.
- WHITFORD D.J. (1975) Strontium isotopic studies of the volcanic rocks of the Sunda arc, Indonesia, and their petrogenetic implications. *Geochim. Cosmochim. Acta* 39, 1287-1302.
- WILCOX R.E. (1956) Petrology of Parícutin Volcano, Mexico. *U.S. Geol. Survey Bull.* 965-C.
- YAJIMA T., HIGUCHI H., and NAGASAWA H. (1972) Variation of rare earth concentrations in pigeonitic and hypersthene rock series from Izu-Hakone region, Japan. *Contr. Mineral. and Petrol.* 35, 235-244.
- ZIELINSKI R.A. and LIPMAN P.W. (1976) Trace element variations at Summer Coon volcano, San Juan Mountains, Colorado, and the origin of continental-interior andesite. *Geol. Soc. America Bull.* 87, 1477-1485

Major
model
ments
ometry
partic
traceCalcul
ple of
missib
the pa
which
the me
rocks
ject t
differ
melts
derive
olivine
be res
sure,
smalleIn pet
ally b
sively
so valThe di
the dis
those v
sidered
recogni
melt ph
of abun
describ
stalliz
1970; eThe dis
has bee
distrib
fractio
diagram
(1976)
and dea
efficie
with si
showed