

# Ion-microprobe analyses of trace elements in anorthoclase, hedenbergite, aenigmatite, quartz, apatite, and glass in pantellerite: Evidence for high water contents in pantellerite melt

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## ABSTRACT

Ion-microprobe analyses of matrix glass and glass inclusions in anorthoclase and quartz phenocrysts in pantellerite show no major differences in chemistry except for H<sub>2</sub>O ( $4.3 \pm 0.2$  vs.  $0.5 \pm 0.1$  wt%) and Cl (1.3 vs. 0.9 wt%), which degassed from the matrix during the process of eruption. This high measured water content contrasts with current assumptions that pantellerites are relatively dry magmas. Comparison of secondary-ion intensities from glass and phenocrysts of anorthoclase, hedenbergite, aenigmatite, quartz, and apatite gives partition coefficients (with errors of a factor of two) that are  $\leq 1$  for B, P, Rb, Zr, Nb, Sn, and Cs for all silicate phenocrysts. Even if individual phase partition coefficients are  $> 1$  (Sr, Y, Ce in hedenbergite; Li in aenigmatite; Ba in anorthoclase; REE in apatite), the resulting *bulk* crystal/liquid partition coefficients are still  $< 1$  so that fractional crystallization of pantelleritic liquids could generate peralkaline rare-metal granites and pegmatites.

## INTRODUCTION

Pantellerite is an extremely peralkaline volcanic rock with high contents of many trace elements. To date, the available data have suggested that these rocks are nearly anhydrous (Bailey and Macdonald, 1987). Currently, the majority of petrologists and geochemists relate the major- and trace-element chemistry to fractionation of basic parental magmas (e.g., *Bulletin Volcanologique*, 1974). There is evidence that under hypabyssal conditions, extended fractionation of pantellerite magma will produce compositions similar to rare-metal granites and pegmatites (Kovalenko, 1977; Kovalenko et al., 1985). Such peralkaline rare-metal granites may be economically important because of their high concentrations of lithophile elements (Miller, 1985). To constrain the hypotheses concerning the origin of pantellerite and possible daughter magmas it could generate, it is important to know the pre-eruption volatile content (H, F, Cl) and the partitioning behavior of major and trace elements between the somewhat unusual phenocrysts and the coexisting pantellerite melt. Unfortunately, there are few data on partition coefficients for these compositions; most work has concentrated on tholeiites and less alkaline granitic compositions (Irving, 1978; Antipin et al., 1984; Nash and

Crecraft, 1985). The purpose of this study was to measure directly the volatile contents of trapped melt inclusions in phenocrysts with the ion microprobe. Trace-element abundances were collected at the same time on trapped melt inclusions and matrix and on coexisting phenocrysts to determine (1) the effect of outgassing on the chemistry of matrix glass and (2) the partitioning of trace elements between crystals and melt.

The magmatic rocks of the Island of Pantelleria in the Strait of Sicily have been studied by geologists for nearly 100 years. The most recent investigations have provided key information in the form of detailed maps that help define the evolution of this volcanic island (Cornette et al., 1983; Civetta et al., 1984; Villari, 1974; Mahood and Hildreth, 1986).

Magmatic activity has been dated from as early as 220 000 yr BP up to less than 9000 yr BP (Civetta et al., 1984). The surficial rocks comprise a bimodal distribution of basaltic (hawaiite) and trachyte-peralkaline rhyolite flows. The sample studied in this work was from the west shore of the island, Contrada Sencecci. This pantellerite lava erupted after caldera collapse and the emplacement of the Green Tuff. The thin section consists of 5–10% phenocrysts in an unaltered glassy matrix. The major crystals consist of anorthoclase, subordinate quartz,

hedenbergite and aenigmatite. We observed trace amounts of apatite in the matrix glass and as trapped inclusions in other phenocrysts. Rare microlites of Na-rich clinopyroxene were found in the matrix. This mineralogy is typical for pantellerite. The sample was chosen for microanalysis because of its unaltered nature and because the anorthoclase and quartz phenocrysts contained abundant inclusions of glass. Because of the microbeam technique we used, we were able to examine those inclusions that have preserved the volatile contents that were lost from the matrix glass upon eruption. It was thus possible to determine whether other trace elements were lost during this outgassing.

### ANALYTICAL TECHNIQUE

#### Sample preparation

A rectangular polished thin section of pantellerite was sized to a 1-in.-diameter (2.54-cm) circle with a diamond coring drill to fit the sample holder of the Cameca IMS 3f ion microscope. After polishing with 0.05- $\mu\text{m}$   $\text{Al}_2\text{O}_3$ , photomicrographs were taken of selected phenocrysts, and the sample was coated with 100- $\text{\AA}$  Au-Pd and placed in the ion microprobe. After pumping down overnight, analyses were taken on the phenocrysts, matrix glass, and one glass inclusion. Because of restrictions on sample size, we could not place glass standards in the ion microprobe with the polished thin section. After collecting data for several elements and attempting to relate the measured intensities to calibration curves obtained on an earlier analysis session, we drilled out two  $\frac{3}{16}$ -in.-diameter cores from the thin section so that rhyolite standards could be analyzed at the same time as the pantellerite. Although matrix glass was abundant and analyzed in each analysis session, only one 18- $\mu\text{m}$ -diameter glass inclusion in anorthoclase and one 100- $\mu\text{m}$ -diameter inclusion in quartz were found during remounting. Analysis of these inclusions gave secondary-ion count rates similar to analyses on the 1-in. thin section. Data for more elements were obtained during these latter sessions.

#### Analytical conditions

During all sessions, the analysis conditions were constant: mass-filtered  $^{16}\text{O}^-$  primary beam at 17-keV impact energy, 10-nA primary current focused to a 30- $\mu\text{m}$  spot. Secondary ions were accelerated into the mass spectrometer at +4500 eV, and secondary-ion intensities were measured by an electron multiplier in pulse-counting mode and normalized to the count rate for  $\text{Si}^{2+}$  at  $m/e$  (mass/charge) = 14. A combination of electrostatic lenses and physical apertures was used to restrict the analyzed portion of the secondary-ion beam to a 20- $\mu\text{m}$ -diameter circular area in the center of the crater.

#### Data reduction

Molecular interferences are very troublesome in ion-microprobe analysis; we discriminated against interferences, such as  $^{27}\text{Al}^{29}\text{Si}^{16}\text{O}_2^+$  with  $^{88}\text{Sr}^+$  using energy filtering (e.g., Shimizu et al., 1978).  $\text{Al}^{3+}$  was resolved from Be at  $m/e = 9$  at routine operating conditions by its mass difference. The interference of rare-earth oxides with middle and heavy rare-earth elements is a more serious problem. When analyzed, interferences were stripped by the method of Zinner and Crozaz (1986a). For apatite, secondary-ion intensities for rare-earth elements were converted to concentrations by correcting for differences in ion yield (Zinner and Crozaz, 1986b) and calibrating by comparison with an electron microprobe analysis for Ce on the same grain. Secondary-ion

intensity ratios on the pantellerite glass were related to those for other rhyolitic glasses for which bulk analyses were available and converted to concentrations, except for Sn for which we had no suitable standards and Zr, which gave 0.39 wt%  $\text{ZrO}_2$  by electron microprobe (Table 1). On the basis of the reproducibility of analyses on homogeneous glass standards, errors were estimated at  $\pm 15\%$  for each element except the middle to heavy REEs (Eu-Lu) for which we assumed  $\pm 50\%$  error because of the low count rates and the deconvolution routine we used. Absolute errors for the analysis of  $\text{H}_2\text{O}$  depend on the quality of the standards, which have maximum errors of  $\pm 0.1$  wt%. Precision of the hydrogen measurements was estimated by averaging the analyses on each inclusion and calculating the standard deviation. For comparison with the matrix glass, trace-element concentrations measured in the inclusions were normalized to an anhydrous basis.

Water contents were determined by comparison with a calibration curve obtained on experimentally hydrated rhyolites during the same analytical session. These standards were characterized by thermogravimetric analysis or Karl-Fisher titration. Techniques described in Hervig et al. (1987) kept backgrounds low so that analyses of anhydrous minerals gave "apparent" water contents of  $< 0.1$  wt%  $\text{H}_2\text{O}$ .

#### Matrix effects

The glass standards could not be used to quantify precisely the measured ion signals on the phenocrysts. Ray and Hart (1982) found that for the same matrix and trace-element abundance, the secondary-ion signal from pyroxene crystals was as much as *twice* that from glasses. Later studies (Zinner and Crozaz, 1986b; Muir et al., 1987) found much smaller matrix effects for REEs from silicate glasses compared to crystals (usually less than 10%). Ray and Hart (1982) found the largest effect for alkali metals, and our experience has been that atoms occupying sites with low coordination number (high bond strength) show the smallest glass-crystal discrimination (e.g., Hervig, 1985). However, even for H, calibration curves for basalt vs. rhyolite vs. amphibole are within 30% (Hervig and Williams, 1988). Havette (1985) called upon charge-driven diffusion to explain the results of Ray and Hart (1982), and this phenomenon should be investigated further.

We tested for the significance of the matrix effect by comparing the secondary-ion signals on bulk-analyzed anorthoclase,  $\text{An}_{67}$ ,  $\text{An}_{86}$ , borosilicate glass from Corning (57%  $\text{SiO}_2$ ), and NBS 610 glass (70%  $\text{SiO}_2$ ). Every element we examined—including Li, Na, K, Rb, and Sr in crystals and glass and Cs, Ba, La, and Ce in the two glasses—gave ion yields within a factor of two. We also compared the above standards with a pegmatitic quartz bulk analyzed by inductively coupled plasma spectrophotometry. The trace elements Mg, Al, and Fe gave ion yields within a factor of two of the other standards. Li and Na appear to have low ion yields from quartz compared to glass and feldspars (Li 10 times lower; Na 2.6), whereas B and K have high yields (B 7 times higher; K 11). The low ion yields for Li and Na may be related to charge-driven diffusion effects (Havette, 1985). This causes a problem when we simply relate the observed ion intensity ratios on quartz and matrix glass (corrected for differences in Si content) to determine partition coefficients (e.g., Yurimoto and Sueno, 1984), because results for alkali elements and B could be off by a factor of 10, whereas other elements should be within a factor of two. This measurement of the matrix effect should be considered to be a worst case because of the dissimilar nature of the chemistry of quartz to pantellerite melt. For the other minerals studied, count rates on crystals are not obviously enhanced compared to glass, so that any systematic errors in the calculated

TABLE 1. Analyses of trace elements in glass, apatite, and quartz from pantellerite

	1	2		1	2	3		4
Li	45	33	La	400	250	9800	Li	9
Be	17	—	Ce	740	390	19800	B	<1
B	28	—	Pr	75	—	2090	Na	11
F*	0.5	—	Nd	230	140	8690	Mg	<0.5
P	90	110	Sm	46	30	1230	Al	30
Rb	320	176	Eu	3	4.2	120	Fe	5
Sr	6	3	Gd	55	29	760		
Y	260	172	Tb	8	5	—		
Nb	540	410	Dy	59	—	450		
Cs	14	2.3	Ho	11	—	100		
Ba	68	70	Er	38	—	200		
Hf	80	45	Tm	5	—	35		
Pb	50	—	Yb	39	17	110		
Th	65	38	Lu	4	2	12		
U	20	11	H <sub>2</sub> O*	4.3**	0.5†	—		

Note: Values in ppm except where noted. Samples are (1) matrix glass (except for H<sub>2</sub>O), this study; (2) average of four pantellerite analyses from Civetta et al. (1984) with some data from Villari (1974); (3) apatite included in anorthoclase; and (4) quartz phenocryst.

\* Wt%.

\*\* Trapped melt inclusion.

† Matrix glass (this study).

partition coefficients are small compared to the factor-of-two error from the matrix effect. We have presented partition coefficients for F in Table 2, but these may have much larger errors. Preliminary data on several F-bearing crystals and glasses show large matrix effects (Hervig et al., unpub. data). Except for F, we feel confident that a factor-of-two error should apply to all the partition coefficients given in Table 2.

Separate from the problem of matrix effect is the error resulting from the assumption that our analysis of a phenocryst is not biased by chemical zoning. Nicholls and Carmichael (1969) found negligible zoning in anorthoclase and aenigmatite but noted that pyroxenes could have acmite-rich rims. Our analyses of hedenbergite were in the center of grains and should reflect the lower Na content therein. We did not determine if trace elements were zoned in these phenocrysts.

## EXPERIMENTAL RESULTS

### Pre-eruption volatile content of pantellerite

Three melt inclusions, two in anorthoclase and one in quartz, gave measured water contents of  $4.5 \pm 0.5$ ,  $4.3 \pm 0.4$ , and  $4.2 \pm 0.4$  wt% H<sub>2</sub>O, respectively (mean =  $4.3 \pm 0.2$  wt%). Analyses of matrix glass gave  $0.5 \pm 0.1$  wt% H<sub>2</sub>O. F was  $0.5 \pm 0.1$  wt% in both inclusions and matrix. Cl in the matrix was measured by electron microprobe at  $0.89 \pm 0.1$  wt% whereas the secondary-ion signal for Cl in the inclusion was 1.5 times greater than that measured in the matrix, giving 1.3 wt% Cl. Electron-microprobe analyses of inclusions and matrix in the Soviet laboratory

TABLE 2. Partition coefficients for phases in pantellerite

	1	2	3	4		5		6
Li	0.8	0.14	0.56	1.2	Li	0.2	La	24.5
Be	0.8	0.23	0.02	0.17	B	≤0.04	Ce	26.8
B	0.9	0.06	0.26	0.19	Na	$2.2 \times 10^{-3}$	Pr	27.9
F	1.0	$2.7 \times 10^{-3}$	0.08	0.27	Mg	$1.3 \times 10^{-3}$	Nd	37.8
P	1.0	0.06	0.45	0.63	Al	$7.1 \times 10^{-4}$	Sm	26.7
Rb	0.8	0.30	0.09	0.04	K	$3.7 \times 10^{-5}$	Eu	40.0
Sr	0.9	0.59	3.4	0.79	Fe	$8.1 \times 10^{-5}$	Gd	13.8
Y	0.9	$2.0 \times 10^{-4}$	1.2	0.02			Tb	—
Zr	0.9	$5.1 \times 10^{-5}$	0.71	0.10			Dy	7.6
Nb	0.9	$8.5 \times 10^{-5}$	0.03	0.79			Ho	9.1
Sn	0.9	$6.4 \times 10^{-3}$	0.49	0.57			Er	5.3
Cs	0.4	0.44	1.3	1.0			Tm	7.0
Ba	0.9	1.2	0.22	0.01			Yb	2.8
La	0.9	$1.2 \times 10^{-4}$	—	$6.4 \times 10^{-3}$			Lu	3.0
Ce	0.9	$2.4 \times 10^{-4}$	1.7	0.01				
Pr	0.9							
Nd	0.8							
Sm	0.9							
Eu	1.2	0.25	2.4	0.02				
Gd	1.0							
Tb	0.8							
Dy	0.8							
Ho	0.8							
Er	0.9							
Tm	0.9							

Note: Columns are (1) inclusion/matrix, (2) anorthoclase/matrix, (3) hedenbergite/matrix, (4) aenigmatite/matrix, (5) quartz/matrix, (6) apatite/matrix.

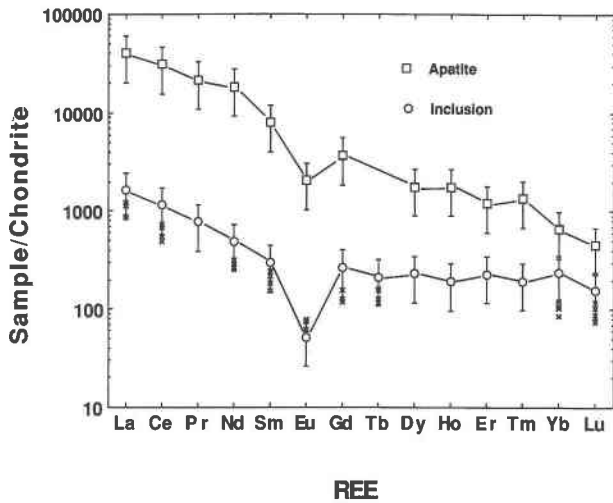


Fig. 1. Rare-earth-element abundance pattern in apatite inclusion in anorthoclase, melt inclusion in anorthoclase, and bulk samples from pantellerite. Apatite and melt inclusion from this study, bulk data from Civetta et al. (1984).

(Kovalenko, unpub. data) show similar variations in Cl between inclusions and matrix.

Table 1 compares analyses for glass from this study with average pantellerite analyses from Civetta et al. (1984) and Villari (1974). Our new analysis is similar except that Rb, Y, Cs, and REEs (except Eu) are enriched and Sr is depleted with respect to these mean compositions. The REE pattern is similar to earlier bulk analyses and is compared with them and the apatite pattern in Figure 1.

The question of homogeneity was addressed by making three separate analyses of the 100- $\mu\text{m}$  inclusion in quartz. Reproducibility was better than 10% for Li, B, Al, F, Na, P, Rb, Sr, Ba, Y, Zr, Nb, Hf, and H, but Cs and Pb varied over 50%. Matrix-glass analyses showed comparable homogeneity.

**Partition coefficients in the pantellerite**

**Inclusion glass vs. matrix glass.** Most elements are depleted in the inclusion relative to the matrix, even when normalized to an anhydrous basis. These partition coefficients, calculated as inclusion/matrix, are presented in Table 2 for the large (100- $\mu\text{m}$ ) inclusion in quartz and are displayed in Figs. 2a–2c. Ignoring F, Cl, and H, the mean depletion (inclusion/matrix) is  $0.86 (\pm 0.13 \sigma)$ . The very low secondary-ion signals for Cs and Pb in the inclusion are puzzling. However, inhomogeneous Pb has been noted in ion-microprobe analyses of glassy experimental run products of the peraluminous Macusani rhyolite (London et al., 1988). Give the  $\pm 15\%$  error for most analyses of trace elements, the depletion is approximately constant. Notably enriched elements in the inclusion (besides H) are Cl and Na.

**Anorthoclase.** In anorthoclase, partition coefficients are less than unity for all trace elements except Ba. However,

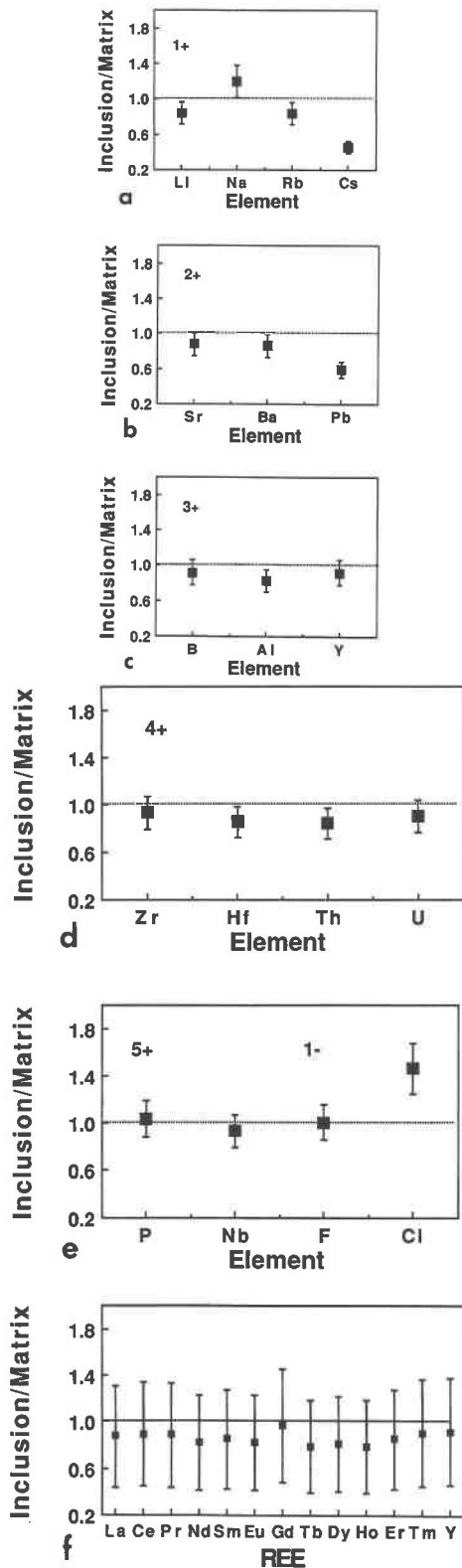


Fig. 2. Inclusion/matrix ratios for trace and major elements from a large (100- $\mu\text{m}$ ) inclusion in quartz compared to nearby matrix glass. Inclusion chemistry recalculated on an anhydrous basis for comparison with matrix. Errors for most trace elements are  $\pm 15\%$  relative on the basis of reproducibility of multiple analyses. Errors for rare-earth elements  $\leq 50\%$ .

Rb, Sr, and Cs are within about a factor of 3 of unity. The lowest values are for La, Ce, Y, Zr, and Nb at  $\sim 10^{-4}$ . Partition coefficients for Sr, Zr, Ba, La, Ce, and Eu are much less than for rhyolites (Leeman and Phelps, 1981; Nash and Crecraft, 1985). These elements and Y, Nb, Sn, and Cs are also less than measured in one peralkaline sample (Larsen, 1979). Li partitioning is similar to values determined for peralkaline rhyolite pumice from the far eastern USSR and for K-feldspar in ongonite (Antipin et al., 1984). Partitioning of Be, Sr, Cs, and Ba determined for peralkaline rocks and ongonites of Mongolia is similar to the values in Table 2, but B and Sn have much lower coefficients in the pantellerite. Mahood (1987) studied samples from the island of Pantelleria ranging from trachyte to pantellerite. Partition coefficients for Eu were shown to be extremely composition dependent, dropping from 2.5 to 0.02 as K increased in the anorthoclases. A similar trend was found by Drexler et al. (1983) as a function of peralkalinity. Our value of 0.25 is within this range. Mahood also measured Rb partition coefficients, which varied from 0.15 to 0.25 for the same sequence of samples, similar to our measurements and that of Larsen (1979). Mahood (1987) found that Cs was the most incompatible element in peralkaline suites, but our Cs and Rb values are similar.

**Clinopyroxene.** Many trace elements in the hedenbergitic clinopyroxene have partition coefficients  $\geq 1$  (Cs, Sr, Ce, Eu, Y). High values were not reported in Irving's (1978) review, but similar values for Ce and Eu were given in Nash and Crecraft (1985) for rhyolites. Slightly lower partition coefficients were given by Larsen (1979) for peralkaline samples. Although Nash and Crecraft (1985) did not measure Cs in clinopyroxene, they found significant levels in orthopyroxene, yielding partition coefficients for Cs of 0.8 and 0.4, not far from the value of 1.3 we measured for clinopyroxene. Cs partition coefficients measured by Larsen (1979) were  $< 0.05$ . Mahood (1987) measured REEs in coexisting clinopyroxene and glass from pantellerite, finding a maximum value of 2 for Sm, like our value of 1.7 for Ce.

Elements with  $D < 1$  but still within a factor of 3 of unity include P, Li, Zr, and Sn. Lowest values for clinopyroxene are for Be, Rb, and Nb between 0.01 and 0.1. Larsen (1979) gave values close to these, and Mahood (1987) found the partition coefficient for Zr in clinopyroxene at  $\sim 0.4$ , within 50% of our value of 0.7. Irving's summary also shows similar values for Zr as well as Nb and Ba. The compilation of Antipin et al. (1984) shows consistent values for Li, B, Rb, and Sn and low Sr, Cs, and Ba.

**Aenigmatite.** Partition coefficients for trace elements in aenigmatite that are within a factor of two of unity include Cs, Sr, Sn, Li, Nb, P. Several trace elements cluster between 0.1 and 0.01 (Rb, K, Ba, Eu, La, Ce, Y, Zr). Mahood (1987) has provided the only literature data for aenigmatite, finding that partition coefficients for all REEs were similar at  $\sim 0.1$ , somewhat higher than our 0.01 for La and Ce.

**Quartz.** Partition coefficients for quartz are presented only for elements included in the bulk analysis of our pegmatite quartz standard, as matrix effects appear to be very large for this mineral. All values are less than 1 (except for Si). Most are  $\leq 10^{-4}$ , but B and Li are  $\geq 10^{-2}$ . Except for Li, which is similar, our values are two orders of magnitude lower than the tabulated values in Antipin et al. (1984) and Nash and Crecraft (1985).

**Apatite.** We only present partition coefficients for REEs in apatite in Table 2. Values range from 3 to 40, with apatite favoring the lighter REEs. These values are in broad agreement with the experimental data of Watson and Green (1981) on a hydrous granite. In consonance with this agreement, Mahood (1987) found little effect of peralkalinity on REE partition coefficients in apatite.

## DISCUSSION

### Pre-eruption volatile content of pantellerite magmas

Ion-microprobe analyses provide direct evidence of high water contents in trapped melt inclusions. Analyses of trapped melt inclusions can be misleading for the same reasons that analyses of fluid inclusions can be suspect. Subsequent to entrapment, inward crystallization of the anhydrous host phenocryst can drive up the water content of residual melt. We have seen evidence of this phenomenon in analyses of "elongated" inclusions in pyroxenes and amphiboles from the Taupo rhyolite (N. Dunbar et al., unpub. data); thus we have restricted analyses to those inclusions that show a regular outline (negative crystal) and are isolated from other trapped phases. If some crystallization of quartz or anorthoclase did encroach on the inclusions we analyzed, then we would expect that the trace-element concentration in the residual glass would be higher than that in the matrix. The slight depletion (on average) of trace elements in the inclusions compared to the matrix glass is one argument for believing that the trapped melt is pristine. Indirect evidence for high pre-eruption water content in pantellerite comes from electron-microprobe analyses of inclusions showing low totals ( $\sim 97$  wt%; Kovalenko, unpub. data) compared to matrix glass. Bubbles are observed in the glass inclusions. These either formed during shrinkage of the melt upon cooling, or represent exsolved gas (no fluid can be seen). When inclusion-bearing phenocrysts are heated until melt and bubbles homogenize, very high water contents (from 7.7 to 12.4 wt%) are calculated (Naumov et al., 1987). In contrast, most of the literature on pantellerites refers to these magmas as relatively dry because of the following observations (e.g., Bailey and Macdonald, 1987): (1) Bulk analyses give low water contents ( $< 0.7$  wt% and usually  $\sim 0.1$  wt%  $H_2O$ ). (2) No hydrous phases are observed (barring late arfvedsonite). (3) Eruptions generally are not explosive. (4) The halogen content is quite high; if  $H_2O$  was lost during outgassing, why not the halogens? (5) Petrographic textures observed in natural samples suggest a crystallization sequence that matches well with experiments on dry pantellerite but not with  $H_2O$ -saturated compositions.

There are, however, alternative explanations for these observations that allow for higher water contents in pantellerite: (1) Low water contents in bulk analyses may simply mean that  $H_2O$  has outgassed during eruption. (2) The stability of hydrous phases can be significantly reduced if  $a_{H_2O} < 1$ , even though abundant water is present in the melt. (3) Earlier ion-microprobe analyses of trapped melt inclusions in phenocrysts from the catastrophic Taupo Ultraplinian eruption and the relatively mild Obsidian Dome eruption (Hervig et al., 1987) give nearly identical results, suggesting that high water contents are not sufficient to produce violent eruptions. (4) As shown in Table 2, Cl, as well as  $H_2O$  has been lost from the melt during outgassing; the amount of loss is minor and testifies to the high solubility of halogens in peralkaline melts. (5) Experiments have been conducted only on the water-saturated system. It is necessary to determine the phase relationships at  $a_{H_2O} < 1$  before concluding that the crystallization sequence represents a "dry" composition.

Further discussion of this last point is necessary because the solubility of water in peralkaline compositions is poorly understood. Dingwell et al. (1984) found that a slightly peralkaline melt showed slightly higher water solubility compared to haplogranite. They also found the same to be true for slightly peraluminous compositions. London et al. (1987) studied the strongly peraluminous Macusani glass, finding a water solubility of 11.2 wt%  $H_2O$  at 2 kbar, nearly twice that of metaluminous compositions. Ion-microprobe analyses for H agree well with the Burnham model (Burnham, 1981) when metaluminous rhyolites are studied (Webster et al., 1987) but confirm the high water solubility in Macusani peraluminous melts. In the absence of a detailed study, the available data suggest that the water solubility of pantellerite will be much greater than in metaluminous systems, and the 4.3 wt%  $H_2O$  that we have measured may represent the saturation level at pressures considerably less than 1000 bars.

Actually, it is required that saturation was not reached until the melt was about to erupt, as evolution of vapor at depth would have led to crystallization (Bailey and Macdonald, 1987). Thus, a model involving degassing during exsolution of water in the vent (Taylor et al., 1983) is attractive. However, Bailey and Macdonald (1987) have pointed out that pantellerite crystallizes much faster than the rhyolites studied by Taylor et al. (1983) and would require a much faster quenching period than suggested by Taylor et al. (1983) for rhyolites. Clearly, there is a need for measurements of the physical properties of peralkaline melts as well as their melting characteristics.

We cannot say that all pantellerites have these high water contents. The smooth variation of trace-element chemistry with stratigraphic horizon (e.g., Civetta et al., 1984; Mahood and Hildreth, 1986) may be explained as the progressive tapping of a zoned magma chamber (Mahood and Hildreth, 1986). In this case, volatiles may also be strongly zoned. As a follow-up study, we are pursuing an investigation to determine the variation of  $H_2O$  con-

centration in melt inclusions from a continuous erupted sequence.

#### Implication of low partition coefficients in pantellerite

It is desirable to use a microbeam technique to measure partition coefficients because of the problem of contamination of mineral separates by small amounts of trace-element-enriched phases. For example, for the pantellerite in the present study, only 0.01% contamination of an anorthoclase separate by apatite would raise the partition coefficient for Ce by one order of magnitude (from  $2 \times 10^{-4}$  to  $2 \times 10^{-3}$ ). Approximately 0.05% contamination by matrix glass would raise the Zr partition coefficient for anorthoclase from  $5 \times 10^{-5}$  to  $5 \times 10^{-4}$ . Despite careful mineral-separation techniques, Drexler et al. (1983) had to correct measured coefficients for 3–6% contamination of their anorthoclase by matrix glass, and Mahood (1987) had to correct olivine REE coefficients for the presence of apatite. One possible example of contaminated samples in the literature involves the partition coefficients for Rb and Zr in alkali feldspar from peralkaline samples (Bailey and Macdonald, 1987) where the values  $D_{Rb} = 0.3$  and  $D_{Zr} = 0.046$  were given. Using the analyses presented in this study, only 5% contamination by matrix glass could cause the high  $D_{Zr}$  values while this contamination would only change  $D_{Rb}$  by  $\frac{1}{6}$ . The use of the ion microprobe obviates such potential problems because the operator avoids inclusions and alteration in crystals and matrix glass. Other techniques, such as proton-induced X-ray emission (PIXE) and small-spot X-ray fluorescence have potential although all have technical problems, such as large (or deep) analyzed area. The major problem for the ion microprobe is the calibration of the secondary-ion signal, restricting our accuracy to roughly a factor of two until more trace-element standards become available.

**Daughter magmas of pantellerite.** Despite our large errors, we can still make predictions concerning the magmas that could evolve from fractionation of peralkaline melts. Details depend on the relative proportion of anorthoclase to quartz to hedenbergite to aenigmatite to apatite and on how the modes and the individual coefficients change with increasing fractionation. In general, feldspar is the dominant phase in pantellerite with quartz <5% and the other silicates and apatite <1% (Carmichael, 1962). With such proportions, it is clear that anorthoclase dominates the bulk partition coefficient, which will be less than unity for Li, Be, B, P, Rb, Sr, Y, Zr, Nb, Sn, Cs, La, Ce, and Eu within the factor-of-two error in the coefficients (only Ba may possibly be depleted in the melt). Thus, continued fractional crystallization of pantellerite could generate the trace-element enrichment associated with rare-metal alkaline granites and pegmatites (Kovalenko, 1977; Kovalenko et al., 1985).

**Rb and Cs.** Rb and Cs appear to have peculiar partition coefficients (Table 2) in hedenbergite and aenigmatite when compared with K. Mineral separates analyzed by Carmichael (1962) give  $D_K \approx 0.02$  for hedenbergite and

aenigmatite. Any contamination of the separates by matrix glass would make these values artificially high. Strangely, partition coefficients for Rb in Table 2 are a factor of 2 to 4 larger than these, and Cs coefficients are >50 times larger than K. In anorthoclase, a strong crystal chemical-control gives high values for  $D_K$  ( $\approx 1.3$ ; Carmichael, 1962), but  $D_{Cs}$  is still surprisingly large compared to  $D_{Rb}$  (0.4 vs. 0.3, respectively). Disequilibrium between quickly growing crystals and slowly diffusing alkali metals is one explanation (Albarede and Bottinga, 1972; Hart and Brooks, 1974). A corresponding enhancement of Ba partition coefficients relative to Sr for the mafic phases is difficult to detect because of the strong crystal-chemical control on Sr uptake by pyroxene and aenigmatite. Because Cs is twice as high in the matrix as the glass inclusions studied, changing the reference would drop the calculated partition coefficients by a factor of two. Although the changed reference would make  $D_{Cs}$  less than  $D_{Rb}$  in anorthoclase, partition coefficients for Cs in the mafic minerals would still be anomalously high. Because other workers note that Cs is extremely incompatible in peralkaline rocks (Larsen, 1979; Mahood, 1987), further study of the partitioning of Cs (perhaps as a function of cooling rate) is warranted.

An alternative explanation for our high measured Cs partition coefficients requires differential matrix effects between crystal and glass. Although we determined that there was a negligible effect for Rb among anorthoclase,  $An_{86}$ , and two standard glasses, we did not have a crystal with known Cs contents to compare with these glass standards. However, to get Cs partition coefficients less than or equal to Rb in the present data set would imply that Cs ions are generated 10 to 50 times more efficiently than Rb ions during the sputtering of crystals but not of glasses. We are investigating this and the possibility of a Cs background signal in the ion microprobe.

**Summary of partition coefficients.** We wish to emphasize the difference in silicate/liquid partition coefficients presented on Table 2 compared to the larger values determined for high-silica rhyolites (Mahood and Hildreth, 1983). Most of the coefficients in the present study are 2 to 10 times smaller than in high-silica rhyolites and testify to the extreme composition-dependence of trace-element partition coefficients (Watson, 1979).

### CONCLUSIONS

Ion-microprobe analyses of three melt inclusions trapped in anorthoclase and quartz phenocrysts in pantellerite show  $4.3 \pm 0.2$  wt%  $H_2O$ , whereas matrix glass has 0.5 wt%  $H_2O$ . Considerable degassing must have occurred during eruption, but the nature of this event is unclear given the state of knowledge of the physical properties of pantellerite melt (see Bailey and Macdonald, 1987). When this degassing occurred, lithophile elements remained in the melt, with only Na and Cl (but not F) showing small depletions in the matrix glass.

When secondary-ion count rates for trace elements from anorthoclase phenocrysts are compared with those from

matrix glass, the calculated partition coefficients (crystal/glass) are generally <1 and generally much lower than previous measurements on less peralkaline compositions. Although some partition coefficients are >1 in other phases, the very low modal abundance of crystals other than anorthoclase keeps bulk partition coefficients less than unity. Thus, during fractional crystallization of pantellerite, trace elements could be enriched to the point of generating peralkaline rare-metal granites and pegmatites.

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