# Trace-element partitioning between immiscible lunar melts: An example from naturally occurring lunar melt inclusions

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# ABSTRACT

Evidence for liquid immiscibility on the Moon has been documented in melt inclusions in minerals that crystallized from mare basalts, within mesostasis in mare basalts and in at least one sample of a lunar plutonic rock. This study focuses on trace-element partitioning between immiscible melt pairs occurring as inclusions in plagioclase. These inclusions are blade-like in shape and range in length from 2 to 150  $\mu$ m. They consist of two coexisting glasses separated by a sharp meniscus. The colorless, low-index glass (felsite) is spherical and immersed in a dark-brown, high-index glass (high-Fe basalt). The Fe-rich basaltic component of the inclusion is quartz + hypersthene normative with low Mg/(Mg + Fe) and variable SiO<sub>2</sub> content (between 34 and 45 wt%). The felsic component has a SiO<sub>2</sub> content between 72 and 82 wt% and variable K<sub>2</sub>O (4.4 to 8.5 wt%)

In most cases, the partitioning behavior of the trace elements agrees with behavior either predicted or measured in experimental and natural systems. The high charge density elements preferentially partition into the basaltic component. High  $P_2O_5$  and a wider solvus increase the *D*<sup>basalt/felsite</sup> for these elements. In contrast to many experimental studies and in agreement with studies of natural silicate liquid immiscibility, the *D*<sup>basalt/felsite</sup> for Ba indicates a preference for the felsic component. This difference in Ba behavior between experimental and natural samples has been attributed to differences in melt polymerization and compensation for charge unbalance within the polymerized melt structure. The apparent differences in *D*<sup>basalt/felsite</sup> for Sr and divalent Eu between the Apollo 11 high-Ti basalts and Apollo 12 low-Ti basalts may be a result of either subtle differences in bulk composition or the extent of plagioclase plating on inclusion walls. Based on our partitioning data from melt inclusions and the chemical characteristics of lunar felsites, the latter cannot be a product of simple fractional crystallization. Silicate liquid immiscibility can account for fractionation of Ba/ La, K/U, and Ba/U in the lunar felsites or the fractionation in Zr/La. However, it cannot account for the REE pattern of the lunar felsites or the fractionation of U/La. These characteristics must be attributed to whitlockite crystallization prior to the onset of liquid immiscibility.

# INTRODUCTION

Zirkel (1873) and Rosenbush (1887) proposed that silicate liquid immiscibility is an important mechanism to account for spatially associated rocks with divergent compositions. Numerous experimental and field studies during the first half of the twentieth century (e.g., Greig 1927; Bowen 1928) demonstrated that the role that silicate liquid immiscibility plays in igneous processes is significantly smaller than the earlier studies had envisioned. During the second half of the twentieth century, silicate liquid immiscibility has been advocated as a potential process for producing specific rock types [e.g., lunar felsites (fine-grained granite)] and appears to be the end-product of extensive low-pressure fractional crystallization of most lunar and dry terrestrial basalts (Hess et al. 1975; Philpotts 1982; Roedder 1984). Experimental studies demonstrate that silicate immiscibility also occurs at petrologically relevant compositions (Rutherford et al. 1974; Hess et al. 1975; Longhi 1990; Roedder 1984).

Distinguishing between evolved magmas produced by fractional crystallization and those produced by silicate liquid immiscibility is difficult. However, experimental studies of trace element partitioning between immiscible basaltic and felsic liquids indicate that silicate liquid immiscibility produces trace element distributions that are distinct from fractional crystallization (Watson 1976; Ryerson and Hess 1978). Whereas fractional crystallization of a basalt produces a more-evolved

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magma enriched in incompatible elements such as REE and rare alkalis (Rb, Cs), immiscibility results in a basalt enriched in REE and a contemporaneous felsite enriched in the alkali and alkaline earth elements. The experimental study of Ryerson and Hess (1978) demonstrated that a number of variables affect the partitioning behavior of trace elements between basalt and felsic melts. Because high-field-strength elements (P, Ti, REE, Zr, Hf ) act to depolymerize melts, their concentration levels affect the two-liquid field in differentiating magmas and the extent of trace-element partitioning. For example, Ryerson and Hess (1978) showed that the REE distribution coefficients for basalt-felsite are approximately four times higher in P-bearing experiments than in P-absent experiments. Longhi (1990) also showed that increasing P increases the two-liquid separation, whereas increasing Mg/(Mg + Fe) and increasing olivine and plagioclase content tended to decrease it. Neal and Taylor (1989) argued that the alkali content of the felsic component may influence the partitioning behavior of cations with intermediate charge densities (i.e., Ba). Because of this dependency of partitioning behavior on melt composition and the lack of  $D^{\text{basalt/felsite}}$  for numerous elements for natural bulk compositions, application of basalt-felsite distribution coefficients as fingerprints of natural petrologic systems are somewhat compromised and the results may be qualitative to semiquantitative at best.

As an extension of these experimental studies, we have conducted a study of partitioning for a wide range of trace elements between naturally occurring immiscible melts preserved within melt inclusions in plagioclase in lunar basalts. This investigation differs from other studies of trace-element partitioning between immiscible melts in natural lunar rocks (Neal and Taylor 1989; Snyder et al. 1993; Jolliff 1991, 1998), because for the melt inclusions there is less textural ambiguity for coexisting immiscible melts.

# LIQUID IMMISCIBILITY ON THE MOON

Evidence for liquid immiscibility on the Moon has been documented in melt inclusions in minerals that crystallized from mare basalts (see summary by Roedder 1984), within mesostasis in mare basalts, and in at least one sample of a lunar plutonic rock that crystallized in a shallow crustal environment (Jolliff 1991, 1998). In his initial search for liquid H<sub>2</sub>O and CO<sub>2</sub> inclusions in the newly returned Apollo 11 samples, Roedder (1984) first identified inclusions containing both high-Si felsic and Fe-rich basaltic glasses. As summarized by Roedder (1984), these inclusions occurred in a wide range of minerals and with a range of textural relationships. Inclusions that trapped and preserved both high-Si felsic and Fe-rich basaltic melts occur primarily in plagioclase and ilmenite. These inclusions are commonly blade-like and consist of a spherical high-Si felsite globule immersed in a basaltic matrix. The contact between the two melts is defined by a sharp meniscus. Roedder (1984) and Longhi (1990) concluded that the immiscibility represents stable, not metastable, equilibrium. Depending on cooling history, the inclusions range from having a very feathery texture to exhibiting complete crystallization textures. The ilmenite component of the Fe-rich basaltic melt crystallized at the interface between host ilmenite and the inclusion.

Other inclusions occur as tooth-shaped rows of silicate melt

along the rims of host grains of plagioclase, pyroxene, and pyroxferroite. These inclusions trapped only the high-Si melt and now consist of glass plus a vapor bubble. Roedder (1984) suggested two mechanisms for the absence of the Fe-rich basaltic melt in some of the inclusions. In one model, the high-Si melt was trapped on the crystal growth surfaces, whereas the coexisting Fe-rich basaltic melt was remixed into the surrounding melt. Evidence of this mechanism was observed in immiscibility experiments which showed that upon entering the miscibility gap during crystallization caused by slow cooling, granitic melt spherules were nucleated preferentially on plagioclase crystals adjacent to melt pools (Rutherford et al. 1974). Alternatively, Roedder (1984) suggested that in the pyroxenehost, the pyroxene-rich basaltic melt crystallized at the hostinclusion interface and thereby eliminated evidence of its presence.

In addition to small-scale textural evidence for liquid immiscibility, it has been proposed that silicate liquid immiscibility occurred on a much larger scale and was important during the last stages of lunar magma-ocean (LMO) crystallization (Neal and Taylor 1989) and for producing post-LMO felsites (Hess et al. 1975; Taylor et al. 1980; Neal and Taylor 1989; Longhi 1990; Snyder et al. 1993; Jolliff 1991). Neal and Taylor (1989) proposed that the precursor to the lunar felsites was a late-stage product of magma-ocean crystallization (urKREEP) that experienced silicate liquid immiscibility essentially fractionating K from REE and P. However, Longhi (1990) concluded from his experimental study that little evidence for silicate liquid immiscibility exists at the K<sub>2</sub>O/P<sub>2</sub>O<sub>5</sub> ratios predicted for urKREEP. He suggested that extensive fractionation of post-magma ocean magmas equivalent to KREEP basalts and Mg-suite parental magmas produced evolved melts that experienced silicate liquid immiscibility. It is this type of process that has been proposed to produce the lunar felsites. Unfortunately, lunar rocks that are demonstrably formed from immiscible pairs of residual basalt-felsite are rare. However, the unambiguous fingerprint of trace-element behavior during lunar liquid immiscibility is retained by the melt inclusions and may be used to better understand the origin of lunar felsites.

#### **ANALYTICAL APPROACH**

Of all the immiscible melt inclusions described by Roedder (1984), we elected to analyze only those inclusions trapped within plagioclase. We limited our work to this type of inclusion because: (1) they contain both high-Si felsic and Fe-rich basaltic phases whose interface is defined by a sharp meniscus; (2) there is less obvious crystallization at the inclusionplagioclase boundary than observed in inclusions that are hosted by pyroxene and ilmenite (Roedder 1984); and (3) these inclusions present less of an analytical problem because they are generally larger. Compared to the study of element partitioning between immiscible melts in mesostasis and in glass fragments (Neal and Taylor 1989; Snyder et al. 1993), melt inclusions provide a less ambiguous textural relationship between the two melts and between the melts and associated mineral phases. We analyzed inclusions in mare basalts collected from the Apollo 11 and 12 sites: 10050,31; 10071,28; 12035,24; 12057,28. The Apollo 11 samples are high-Ti mare basalts, whereas the Apollo 12 samples are low-Ti mare basalts.

Using optical microscopy, we identified melt inclusions of appropriate size for ion microprobe analysis (>40  $\mu$ m) that were at the surface of the thin section. Coexisting high-Si felsite and Fe-rich basalt phases from each inclusion were imaged and analyzed using a JEOL 733 Superprobe. Initial electron microprobe analyses of several glasses from the Apollo 12 mare basalts gave anomalously high values for SiO<sub>2</sub> for the felsic component and high values for FeO for the basaltic component. This was the result of the coarser grain size for the Apollo 12 inclusions. This analytical problem was remedied by increasing the diameter of the electron beam.

Trace elements were analyzed in the inclusions using the Cameca ims 4f ion microprobe that is jointly operated by the University of New Mexico and Sandia National Laboratory. Analyses were performed using an O- primary beam, accelerated through a nominal potential of 10 kV and focused into a 15 µm diameter area. Prior to analysis, each component of the melt inclusion was ion-imaged to identify the target and to assure that the proper phase was analyzed. When necessary, smaller secondary apertures were used to minimize secondary ion contributions from phases adjacent to the analytical target. Positive secondary ions (REE, Zr, Ba, Sr, U) were counted and normalized to <sup>30</sup>Si intensity and SiO<sub>2</sub> wt%. A suite of basaltic and rhyolitic glass standards were used to establish calibration curves for each element and each bulk composition. A more detailed description of this analytical process is presented in Shearer et al. (1990, 1996).

## LUNAR MELT INCLUSIONS

## **Petrographic description**

Examples of immiscible melt inclusions in plagioclase are illustrated in Figure 1. These inclusions are blade-like in shape and range in length from 2-150 µm. They commonly occur as swarms parallel to plagioclase growth surfaces. Inclusions analyzed in this study consisted of two coexisting "glasses" separated by a sharp meniscus. The colorless, low-index glass (high-Si felsite) is spherical and immersed in a dark brown, high-index "glass" (ferrobasalt). The colorless spheres have radii ranging from <1 µm to ~30 µm. The high-Si felsite exhibits three textures: a glassy, one in which acicular daughter crystals may be present, and one with intergrowths of minute K-feldspar and silica crystals. The ferrobasalt rarely occurs as a glass and more commonly consists of fine, feathery crystals of pyroxene and minor ilmenite. Unlike similar inclusions in pyroxene and ilmenite, the ferrobasalt component in plagioclase appears to be more homogeneous and lacks extensive crystallization of ilmenite or pyroxene at the host-inclusion boundary (Fig. 2).

# Major and minor element chemistry

Electorn microprobe analysis of the two coexisting, immiscible melts were given in the numerous studies of Roedder and Weiblen (data and references summarized by Roedder 1984). Our electron microprobe analyses of the immiscible melts overlap with the analyses from these previous studies. As docu-



FIGURE 1. Photomicrographs of immiscible melt inclusions in plagioclase from lunar mare basalts. (a) Cluster of lath-shaped melt inclusions in plagioclase from a mare basalt (scale bar =  $150 \mu m$ ). (b) Close-up image of several melt inclusions from the cluster in a. Felsic component forms spherical body immersed in the dark basaltic matrix (scale bar =  $75 \mu m$ ). (c) Large single inclusion illustrating the feathery texture of the basaltic component (scale bar = 75 mm).

mented in this and previous studies, the melt inclusion chemistries show considerable variation among samples (Table 1 and Fig. 3). The Fe-rich basaltic component of the inclusion is quartz and hypersthene normative with variable Mg/(Mg + Fe) (0.05 to 0.14), FeO between 28 and 39 wt%, and SiO<sub>2</sub> between 34 and 45 wt%. The Si-rich felsic component is barely corundum normative (0 to 1.2%) and exhibits a range of compositions with FeO between 1.0 and 4.1 wt%, K<sub>2</sub>O between 4.4 and 8.5 wt%, and SiO<sub>2</sub> between 72 and 82 wt% (Fig. 3). Some of this compositional variability is attributed to the inhomogeneity of some of the melt inclusions on a scale greater than the electron beam diameter. The basaltic component making up the inclusions in the Apollo 11 high-Ti basalts is generally higher in MgO and P<sub>2</sub>O<sub>5</sub> than the basaltic component in the inclusions from the Apollo 12 low-Ti basalts. The basaltic components also differ in (Ca + Na + K)/Al, Mg/(Mg + Fe), and polymerization index [(normative SiO<sub>2</sub> + feldspar)/(normative pyroxene + SiO<sub>2</sub> + feldspar)] (Table 1).

The variability in the composition of the basaltic component from other sites is even greater. Roedder and Weiblen (1972) documented basaltic components with as much as 14% normative olivine from sample 14310. An interesting similarity between melt inclusions from the Apollo 11 and 12 sites is the TiO<sub>2</sub> content of the basaltic components. Even though the bulk mare basalts differ substantially in TiO<sub>2</sub> (~11.5% compared to ~2%), the TiO<sub>2</sub> concentrations of the basaltic components for all the melt inclusions show limited variation. Our TiO<sub>2</sub> values for the Apollo 11 and Apollo 12 basaltic components are approximately 4.68 and 4.00 wt%, respectively. The



average values from Roedder and Weiblen (1971) and Roedder (1984) are 3.8 and 4.2 wt%, respectively. These similarities may be attributed to the crystallization of ilmenite in the high-Ti mare basalts prior to trapping by plagioclase.

The compositional variation in the felsic component among samples is smaller than that among the basaltic component (Roedder and Weiblen 1971). In the samples from this study, the felsic component in the Apollo 11 samples tend to have higher FeO, Na<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub> and lower Al<sub>2</sub>O<sub>3</sub>, CaO, and K<sub>2</sub>O than the felsic component in inclusions from Apollo 12.

The basalt-felsite pairs are plotted on a pseudoternary Grieg



FIGURE 3. Plot of SiO<sub>2</sub> vs. FeO for selected immiscible melt pairs.



**FIGURE 2.** Backscattered-electron image (BEI) and X-ray maps (Si, Ca, K, P, Ti) of a single melt inclusion in plagioclase. The X-ray maps of this inclusion illustrate the chemical distribution of major and minor elements between the high-Si felsite and high-Fe basalt and the relative homogeneity (on the micrometer scale) of the inclusions selected for more detailed study (scale bar =  $10 \mu m$ ).

**FIGURE 4.** Pseudoternary Greig diagram showing fields of lowtemperature (SLI 1) and high-temperature (SLI 2) immiscibility in the system leucite-fayalite-SiO<sub>2</sub>. Tie lines for the various immiscible melt pairs analyzed in this study (filled circles) are plotted. Also plotted are average immiscible melt pairs for Apollo 11 (open circles, n = 42) and Apollo 12 (open squares, n = 20) from Roedder and Weiblen (1971) and Roedder (1984).

	1	1		2		3		4 (Apollo 11)		5 (Apollo 12)		6	
	Low Si	High Si	Low Si	High Si	Low Si	High Si	Low Si	High Si	Low Si	High Si	Low Si	High Si	
SiO <sub>2</sub>	50.5	68.3	47.7	69.0	38.4	74.3	41.94	77.76	44.14	78.00	38.2	76.6	
TiO <sub>2</sub>	_	_	3.7	1.1	3.1	0.7	4.68	0.68	4.00	0.67	4.27	0.62	
Al <sub>2</sub> O <sub>3</sub>	3.6	5.6	6.0	10.9	6.7	11.1	2.53	10.44	5.00	10.9	4.26	11.4	
Cr <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	-	0.05	0.00	0.20	0.02	0.05	-	
FeO	43.4	20.3	32.2	9.9	33.1	6.9	33.99	2.86	32.5	2.00	31.8	1.93	
MnO	-	-	0.6	0.2	0.7	0.1	0.46	0.04	0.32	0.05	0.44	0.02	
MgO	-	-	0.7	0.1	0.5	0.1	2.95	0.07	1.00	0.15	2.37	0.04	
CaO	-	-	8.0	2.8	11.3	2.1	9.84	0.79	10.83	1.38	10.2	0.92	
Na₂O	-	-	0.3	0.7	0.2	0.4	0.03	0.45	0.10	0.14	0.22	0.74	
K₂O	2.6	5.8	1.3	4.8	0.6	4.2	0.15	5.94	0.32	7.10	0.75	6.39	
$P_2O_5$	-	-	-	-	4.8	0.2	1.55	0.05	0.50	0.00	5.04	0.14	
SO <sub>2</sub>	-	-	-	-	-	-	1.00	0.00	0.20	0.013	-	-	
CI	-	-	-	-	-	-	0.00	0.017	0.015	0.014	0.08	-	
Total	100.1	100.0	100.5	99.5	99.4	100.1	98.8	99.1	99.1	100.4	98.2	98.8	
(Ca + Na + K)/Al	0.78	1.37	2.74	1.05	3.21	0.81	7.15	0.83	4.04	0.95	4.63	0.86	
Mg/(Mg + Fe)	0.0	0.0	0.04	0.02	0.03	0.03	0.14	0.04	0.05	0.04	0.12	0.04	
Polymerization in	dex†0.20	0.66	0.28	0.82	0.26	0.84	0.09	0.92	0.21	0.97	0.16	0.94	
Basaltic/Felsic D	istribution	Coefficients											
Z/r	Z/r 1		2		3		4		5		6		
P 29	13.33-	13.33-8.43		-		24		10–30		>19		17.4–36	
K 0.7	0.5	0.5		0.27		0.14		0.04-0.4		0.05-0.1		0.12-0.35	
Ti 6.6	2.87-	2.87-3.32		3.4		4.4		6–10		10		18.3	
Cr 4.9	3. 22–	3. 22-4.29		-		-		> 5		10.0		4.9	
Mn 2.4	2.86-	2.86-3.09		3.0		7.0		6–11		6.4		3.1-22	
Sr 1.7	1.33–	1.33–1.84		-		-		1.3		0.5		-	
Zr 5.6	2.28-	2.28-2.54		2.5-4		20		2.5-3.5		10		1.17-3.77	
Nb 5.8		-		-		-		3–4		40		-	
Ba 1.4	1.5	1.5		1.4		1.4		0.3		0.3		0.49-0.61	
La 2.8	3.70-	3.70-4.31		<sup>a</sup> 4		≈ 16		9–15		12		20.8	
Yb 3.5	-		<sup>a</sup> 4		16.8		18–30		15		8.0		
U 4	4 –		-		-		10		15		1.1-8.4*		
Mater Malt mains		line and MA		(O) O = = = = 0	D		4070) 4				L a a d Taud		

TABLE 1. Comparison of experimental and lunar immiscible melt pairs

Note: Melt-pair column headings: 1 = Watson (1976), 2 and 3 = Ryerson and Hess (1978), 4 and 5 = data from this study, 6 = Neal and Taylor (1989). \* Lovering and Wark (1975) data from the analysis of mesostasis in mare basalts and Snyder et al (1993) from glass in sample 14001,7003. † Polymerization Index = (normative SiO<sub>2</sub> + feldspar)/(normative SiO<sub>2</sub> + feldspar + pyroxene).

diagram in Figure 4. The diagram contains two immiscibility fields. Field SLI 1 is a field of low-temperature immiscibility, which is relatively high in alkalis and alumina. The high-temperature immiscibility field (SLI 2) occurs along the (CaO + MgO + FeO + TiO<sub>2</sub> + P<sub>2</sub>O<sub>5</sub>)-SiO<sub>2</sub> join. Within the ternary system leucite-fayalite-SiO<sub>2</sub>, a plane in the system K<sub>2</sub>O-FeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, the SLI 1 field corresponds to a temperature of ~1155 °C, whereas SLI 2 corresponds to a temperature greater than 1690 °C (Roedder 1951). The felsite-basalt pairs from these four samples plot very close to the position of the low-temperature immiscibility field (SLI 1 in Fig. 4) and overlap the larger data set of Roedder and Weiblen (1971) and Roedder (1984).

#### **Trace element chemistry**

Substantial trace element differences exist between coexisting pairs and among immiscible melt inclusions. Differences in REE between felsite-basalt pairs and between inclusions from different mare basalts (Apollo 11 high-Ti mare basalts and Apollo 12 low-Ti mare basalts) are illustrated in Figure 5. The basalts are more enriched in REE than the coexisting felsite component. The slopes of the REE patterns for the basalt-felsite pairs are generally flat and approximately parallel. The basaltic component has a negative Eu anomaly, whereas the felsite has only a slightly positive (positive or negative) inflection at Eu. This difference in Eu behavior reflects the similarity of divalent Eu to Sr rather than to the other trivalent REE. The inclusions from the Apollo 12 low-Ti basalts contain lower concentrations of REE and other incompatible elements (Figs. 5 and 6). The differences in REE concentrations between Apollo 11 and Apollo 12 melt inclusions tend to correspond to the REE concentrations in the bulk mare basalt. For example, the two Apollo 11 high-Ti mare basalts have chondrite-normalized Ce abundances of 61 and 138, whereas sample 12035 has  $Ce_N = 20$  (Lofgren and Lofgren 1981). Only limited trace element data exist for the mare basalt represented by 12057.

In addition to the REE, elements with high charge densities (charge/ionic radius) such as Nb, Zr, Cr, S, and U are enriched in the basaltic component relative to the coexisting felsite component (Fig. 6 and Table 1). Barium and K are more enriched in the felsite component, whereas the relative enrichment of Sr is variable. Strontium is enriched in the basaltic component in the Apollo 11 inclusions, but it is somewhat depleted in the basaltic component in the Apollo 12 inclusions.

#### DISCUSSION

# Comparison with other immiscible melt partitioning studies

Differences exist between experimental studies (Watson 1976; Ryerson and Hess 1978) and our observations of coexisting immiscible melts in lunar melt inclusions. Most of these discrepancies in partitioning behavior appear to be the result of major and minor element bulk-compositional differences that influence both the polymerization of melts and the width of the solvus. These influences have been documented by Ryerson and Hess (1978) and Longhi (1990).

Compared with the bulk compositions used by Watson



**FIGURE 5.** Examples of CI chondrite-normalized REE patterns for basaltic–felsic pairs from melt inclusions in plagioclase from the Apollo 11 high-Ti basalts and the Apollo 12 low-Ti basalts. CI chondrite normalization values are from Anders and Ebihara (1982).

(1976) and the  $P_2O_5$ -absent compositions used by Ryerson and Hess (1978), the natural compositions of the basalts encountered in this study have higher Mg/(Mg + Fe) and (Ca + Na + K)/Al (Table 1). In addition, differences in (Ca + Na + K)/Al and normative mineralogy between coexisting basalt-felsite pairs is greater for the natural compositions. In particular, the ratio between normative framework silicates to normative pyroxene [(normative SiO<sub>2</sub> + feldspar)/(normative SiO<sub>2</sub> + feldspar + pyroxene)] indicates that the solvus is wider for the natural lunar compositions, and the extent of polymerization between the melt pairs is substantially different between experimental and natural lunar compositions. Compared to the P2O5-bearing experiments of Ryerson and Hess (1978), the high-Si felsite phases (compositions 3 and 4 in Table 1) have similar Mg/(Mg + Fe) and (Ca + Na + K)/Al. Again, the differences between coexisting pairs in (Ca + Na + K)/Al and (normative  $SiO_2$  + feldspar)/(normative  $SiO_2$  + feldspar + pyroxene) is much greater in the natural pairs. The differences in Mg/(Mg + Fe), (Ca + Na + K)/Al, and (normative SiO<sub>2</sub> + feldspar)/(normative  $SiO_2$  + feldspar + pyroxene) may reflect differences in the width of the miscibility gap and contrasts in melt structure that would affect partitioning behavior.

Elements analyzed in this and other studies show three different types of partitioning behavior between the coexisting melts: cations with high charge densities (Z/r = 2.4 to 29) are strongly partitioned into the basalt component (P, Ti, Zr, Nb, trivalent REE, U); cations with low charge densities (Z/r = 0. 55 to 0.7) are strongly partitioned into the felsic component (K, Rb, Cs); and cations of intermediate charge densities (Z/r = 1.4 to 1.7; Ba, Sr, divalent Eu) are partitioned moderately into either the basalt or felsite. These observations generally agree with the theoretical model proposed by Hess and Rutherford (1974) and predicted by Ryerson and Hess (1978).

Our results for the small radii, highly charged cations agree with the observations and predictions made by Ryerson and Hess (1978): these cations become more enriched in the basaltic component of the immiscible pair with the addition of P to



**FIGURE 6.** Concentration of selected major, minor, and trace elements (ppm) in coexisting basalt and felsite pairs from melt inclusions in plagioclase from mare basalts. Superimposed on the diagram are lines that represent *D*<sup>basalt/felsite</sup> values of 0.01, 1.0, and 100.

the system and/or with a widening of the two-liquid solvus. As shown in Table 1, the measured D values are substantially higher than those measured in fairly simple systems (Watson 1976; Ryerson and Hess 1978) and equivalent to or slightly higher than the P-bearing systems (Ryerson and Hess 1978). Ryerson and Hess (1978) attributed this perturbation in the partitioning behavior to complexing of highly charged cations with PO<sub>4</sub>-3 anion groups. It is clear from the "polymerization index" of the various melts, that the difference between basaltic and felsic melts is greater in the natural samples. The partitioning behavior of U was not studied by either Watson (1976) or Ryerson and Hess (1978). As would be predicted by Ryerson and Hess (1978) and illustrated in a natural lunar sample by Lovering and Wark (1975), U is partitioned into the basalt phase. Our results indicate that U has a slightly higher D than measured by Lovering and Wark (1975).

Of the large radii, monovalent cations (K, Rb, Cs), we measured only K. As expected, K is strongly partitioned into the felsic component and this behavior is similar to findings in both experimental and natural samples. Preferential partitioning of cations with low charge densities into the felsic melt is a result of both the high polymerization of the felsic melt and the local charge imbalance resulting from the local substitution of Al for tetrahedral Si. This charge imbalance in a highly structured melt is alleviated by a coupled substitution of alkalis. Although it would appear that the structure and composition of the coexisting immiscible melts would substantially affect the partitioning behavior of the alkali elements, our study does not document this behavior.

Ryerson and Hess (1978) predicted that the partitioning behavior of divalent cations with intermediate charge densities (Ba, Sr, Eu) between melt pairs should not significantly fluctuate with changing melt composition or polymerization. Our results clearly indicate that Ba (Z/r = 1.4) prefers the felsic component in the melt inclusions ( $D^{\text{basalt/felsite}} \approx 0.3$ ) (Table 1). This contrasts with experimental studies ( $D^{\text{basalt/felsite}} \approx 1.4$  to 1.5), but is in agreement with the observations made by Neal and Taylor (1989) for immiscible melt components in mare basalt mesostasis ( $D^{\text{basalt/felsite}} \approx 0.49$  to 0.61). To explain the discrepancy between experimental and natural determinations of  $D^{\text{basalt/felsite}}$  for Ba, Neal and Taylor (1989) postulated that the change in  $D^{\text{basalt/felsite}}$  from >1 for experimental studies to <1 for natural samples is dependent upon the relative abundance of "alkali" elements (Ca, Na, K) and Al content of the felsic component. They concluded that if the highly polymerized felsic melt was deficient in "alkali elements" relative to Al [i.e., (Ca + Na + K)/Al < 1], Ba would be favorably partitioned into the felsic melt to charge-balance the tetrahedrally coordinated Al  $(Ba + 2Al \Leftrightarrow 2Si)$ . On the other hand, if the felsic melt had excessive alkali elements relative to Al [(Ca + Na + K)/Al > 1], Ba would be favorably partitioned into the basaltic component. Although the substitution mechanism may be correct, the (Ca + Na + K)/Al for the felsic melt is not the only important variable. [Coincidentally, the (Ca + Na + K)/Al for the felsite from the  $P_2O_5$ -bearing experiments of Ryerson and Hess (1978) is similar to that of our natural occurring felsites (Table 1).] We suggest that, as the miscibility gap becomes wider and the difference in the degree of polymerization becomes greater between the melt pairs, the  $D^{\text{basalt/felsite}}$  changes from >1 to <1.

Unlike the elements discussed thus far, which are incompatible  $(D^{\text{plagioclase/basalt}} < 1)$  in the plagioclase host for the inclusions, the observed behavior of Sr and Eu is more complicated because of their compatible behavior  $(D^{\text{plagioclase/basalt}} > 1)$  in plagioclase. The observed partitioning behavior of Sr (Z/r  $\approx 1.7$ ) and Eu (Z/r  $\approx$  1.7 for divalent Eu and 3.2 for trivalent Eu) between the melt pairs exhibits some ambiguous results. The D<sup>basalt/</sup> felsite for Sr appears to be the same for experimental compositions (~1.3–1.8) and the melt pairs in the Apollo 11 high-Ti basalts (composition 4 in Table 1). However, Sr appears to prefer the felsic component in melt pairs from the Apollo 12 low-Ti basalts (composition 5 in Table 1). Europium shows a similar behavior, although the data is somewhat equivocal because of the multiple valance states of Eu in lunar magmas. Our results clearly indicate D<sup>basalt/felsite</sup> for Eu is greater than 1. However, as illustrated in Figure 6, D<sup>basalt/felsite</sup> decreases from the Apollo 11 basalt-felsite pairs to the Apollo 12 basalt-felsite pairs. One interpretation of this observation is that subtle compositional differences between the melt pairs result in the divalent Eu and Sr preferring the felsic component in the Apollo 12 inclusions, but the basalt component in the Apollo 11 inclusions. Alternatively, plagioclase plating on the walls of the inclusion could decrease the abundance of Sr and Eu in the basaltic component of the Apollo 12 melt inclusions. For example, if we assume a spherical melt inclusion with a diameter of 50 micrometers,  $D^{\text{plagioclase/basalt}}$  for Eu and Sr of 1.5, and that a simple Rayleigh fractionation approximates plagioclase crystallization on the melt inclusion wall, plating of 2 micrometers of plagioclase at the inclusion wall will reduce the Sr and divalent Eu in the basalt by 12%. Therefore, based on this simple calculation, differential plating of plagioclase on a small scale (1-3 micrometers) can account for the apparent difference in partitioning behavior between the Apollo 11 ( $D^{\text{basalt/felsite}} = 1.3$ ) and Apollo  $12 (D^{\text{basalt/felsite}} = 0.5)$  inclusions. However, using scanning electron microscopy, we have not been able to identify plagioclase plating on inclusion walls in order to document this effect. Although the Eu anomaly in the basalt component does not appear to be unusually depressed in the Apollo 12 inclusions (Fig. 5), it may not be obvious with only 12% plagioclase crystallization. Therefore, observations for the true partitioning behavior of Sr and Eu between melt pairs are potentially compromised by these inclusions being present in plagioclase hosts.

# **Relevance to Lunar felsites**

Two petrologic models have been suggested for the origin of lunar felsites: (1) extensive fractional crystallization of basaltic magmas (Lovering and Wark 1975; Ryder 1976); and (2) extensive fractional crystallization of select basaltic magma compositions (i.e. KREEP basalts) followed by silicate liquid immiscibility (Rutherford et al. 1974; Hess et al. 1975; Quick et al. 1977; Hess et al. 1978; Taylor et al. 1980; Neal and Taylor 1989; Longhi 1990; Jolliff 1991, 1998). Both processes have been shown to occur under lunar magmatic conditions in both experiments and natural samples. In lunar samples, fractional crystallization has been documented to occur on a planetary scale, whereas silicate liquid immiscibility has been documented unequivocally on a microscopic scale in melt inclusions, in mare basalt mesostasis, and in only a limited number of other lunar lithologies. Nevertheless, the role of both fractionation and immiscibility in producing lunar felsites may be evaluated, to a first approximation, by using the observations made in this melt inclusion study.

As illustrated in our partitioning behavior in melt inclusions, several key trace element ratios may be used to distinguish between fractional crystallization and silicate liquid immiscibility. For example, during fractionation of a basalt, it would be expected that incompatible elements such as P, K, Ti, REE, Zr, Nb, Ba, U, and K should be enriched in the residual melt and therefore ratios such as K/La, Ba/U, Ba/La, Zr/La, and U/ La should not be changed dramatically. However, the stability of accessory phases such as phosphates (apatite, whitlockite) and zircon during late stages of crystallization will perturb these ratios in the residual melt. Whitlockite should fractionate K/ La, Ba/La, and perhaps U/La, apatite should fractionate K/La, Ba/U, and Ba/La, and zircon should fractionate Zr/La and U/ La. Based on our immiscible melt data for lunar compositions, silicate liquid immiscibility should fractionate K/La, Ba/U, and Ba/La, whereas U/La and perhaps Zr/La should not be fractionated.

In the lunar felsites, many of these ratios are fractionated from crystallization trajectories defined by mare and KREEP basalts (Jolliff 1991). These differences are illustrated in Figure 7. Differences in these incompatible element ratios between the lunar felsites and basalts may be the result of: (1) silicate liquid immiscibility after substantial crystallization of KREEP basaltic magma; (2) crystallization and removal of accessory phases; (3) the felsites being unrelated to the KREEP basalts by either process; or (4) unrepresentative sampling of the lunar felsites. The latter two possibilities appear less likely. Although our sampling of the Moon is limited, there is no indication that lunar basalts exist with incompatible element ratios similar to the lunar felsites. Samples of the lunar felsites are indeed com-



**FIGURE 7.** Comparison of trace element characteristics of mare and KREEP basalts (filled circles) and lunar felsites (filled squares). Data from summary tables in Papike et al. (1998).

promised to varying degrees because of size. This is one reason behind the scatter in the felsite data set. However, the sample size is not thought to be the only reason for displacement of the felsites away from the trajectories defined by the lunar basalts (Neal and Taylor 1989).

From the analyses of lunar felsites and basalts (tabulated in Papike et al. 1998), the increase in Ba/La (Fig. 7a), K/U (Fig. 7c), and Ba/U (Fig. 7d) ratios and limited variation in Zr/La (Fig. 7e) in the felsites relative to the basalt trajectory agree with our liquid immiscibility partitioning data. Silicate liquid immiscibility should result in Ba and K being enriched in the felsite relative to La and U. Zirconium and La should exhibit limited enrichment in the felsite and the Zr/La ratio should not be fractionated. However, on its own, silicate liquid immiscibility cannot account for the fractionation of U from La (Fig. 7b). Likewise, the concave up REE pattern typical of the lunar felsites (Neal and Taylor 1989) is dissimilar to the rather flat REE patterns that occur in the felsite component in the melt inclusions (Fig. 5). Because of some of these inconsistencies, precipitation of an accessory phase(s) must also accompany silicate liquid immiscibility during the formation of lunar felsites. Although whitlockite crystallization should not significantly fractionate K/U and Ba/U, it should fractionate the Ba/ La and U/La as observed. In addition, whitlockite potentially could be responsible for the REE pattern observed in the lunar felsites (Jolliff 1991 1998; Jolliff et al. 1993). It is therefore



most likely that lunar felsites are a product of extensive fractionation followed by whitlockite fractionation and silicate liquid immiscibility. Similar conclusions were reached by Neal and Taylor (1989) and Jolliff (1991, 1998).

#### IMPLICATIONS

Evidence for small-scale liquid immiscibility processes are preserved in lunar mare basalts as melt inclusions in numerous minerals. Here, we studied the melt inclusions within plagioclase. In these melt inclusions, "glass" compositions generally agree with determined fields of liquid immiscibility in simplified experimental systems. Compositions of the immiscible melt pairs are similar to immiscible melts also observed in mesostasis in mare basalts, but the textural relationships between melt pairs is much less ambiguous in the trapped melts. Minor elements such as S, P, Ti, and Mn are partitioned into the high-Fe basalt component, whereas K and Na are partitioned into the felsic component. The trace elements Nb, Zr, REE, and U are partitioned into the high-Fe basalt component, whereas Ba is partitioned into the felsite component. The partitioning behavior of Sr and perhaps divalent Eu appear to change with differing bulk compostions of immiscible melt pairs. These elements appear to favor the basalt component in the inclusions from the Apollo 11 high-Ti basalts, but they favor the felsic component in the Apollo 12 low-Ti basalts. This partitioning behavior may be an effect of differences in melt composition, but slight differences in the degree of plagioclase plating on the inclusion wall may also result in this apparent behavior.

In most cases, partitioning behavior of the trace elements agrees with behavior either predicted or measured in experimental and natural systems. High  $P_2O_5$  and a wider solvus increases the  $D^{basalt/felsite}$  for high charge density elements that prefer the basalt component. In contrast to experimental studies and in agreement with studies of naturally occurring silicate liquid immiscibility, the  $D^{basalt/felsite}$  for Ba indicates a preference for the felsic component. This difference in Ba behavior between experimental and natural samples is a result of melt polymerization and compensation for charge unbalance within the polymerized melt structure. Naturally occurring melt inclusions represent melt pairs on a wider solvus [(quartz + feldspar/quartz + feldspar + pyroxene)], a greater difference in the degree of polymerization, and a different alkali/Al ratio.

Based on our partitioning data from melt inclusions, the chemical characteristics of lunar felsites cannot be exclusively a product of simple fractional crystallization. Silicate liquid immiscibility can account for fractionation of Ba/La, K/U, and Ba/U in the lunar felsites and the limited variation in Zr/La. However, it cannot account for the REE pattern of the lunar felsites or the fractionation of U/La. These characteristics must be attributed to whitlockite crystallization as previously documented by Jolliff (1991, 1998).

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