

The Nature of Barium Partitioning Between Immiscible Melts: A Comparison of Experimental and Natural Systems with Reference to Lunar Granite Petrogenesis

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In order to evaluate lunar granite petrogenesis, we have undertaken a study of elemental partitioning between immiscible melts. Experimental liquid-liquid Kd's have been combined with those determined by analysis of immiscible glasses in basalt mesostases. New probe data are presented of immiscible mesostasis glasses from basalt 15434,188. In general, the naturally and experimentally determined liquid-liquid Kd's agree, except for Ba. All experimental data indicate that Ba is partitioned into the basic immiscible melt ($D_{b/a} > 1$), whereas probe analyses of immiscible glasses suggest Ba is partitioned into the granitic immiscible melt ($D_{b/a} < 1$). The partitioning of Ba is dependent upon the "alkali" (molar $K_2O+Na_2O+CaO+BaO$) and Al_2O_3 (moles) contents of the granitic melt. If the "alkali"/ Al_2O_3 ratio is less than approximately 1, then Ba is preferentially partitioned into the granitic melt in order to charge balance tetrahedrally coordinated Al. If the "alkali"/ Al_2O_3 ratio is >1 , then tetrahedral Al is charge balanced by other alkalis, so Ba is partitioned into the basic melt. By calculating the "alkali"/alumina ratio of lunar granites, the $D_{b/a}$ for Ba can be estimated. The ratios of U/La and Th/La in granite are inconsistent with petrogenesis involving silicate liquid immiscibility (SLI). Although it is possible that these high ratios could be a result of the difference in magnitude between the respective liquid-liquid Kd's, they could also be the result of whitlockite fractionation. Whether this is pre- or post-SLI is unclear. Modeling of an average lunar granite and granitic glass from 15434,188 by SLI produces a pre-SLI melt composition compatible with extreme Fenner Trend fractionation. This composition is not the 15405 QMD suggested as a parent to lunar granite by Shih et al. (1985). The occurrence of VHK basalts, formed by granite assimilation, argues for discrete granite bodies within the Moon. In order to allow separation of immiscible liquids, cooling rates must be relatively slow. Therefore we conclude that lunar granite of significant size can only occur in a plutonic or deep hypabyssal environment. This may account for the lack of returned granite samples, as meteorite impact may not have sufficiently sampled the depths at which abundant granite is present.

INTRODUCTION

The occurrence of granite in generally mafic-to-ultramafic domains has been documented both on Earth, in ophiolite sequences (e.g., Dixon and Rutherford, 1979), and on the Moon (e.g., Blanchard et al., 1977; Warren et al., 1983a). The presence of granite in generally mafic settings is perplexing because of the lack of any intermediate rock types. These would be expected if normal magma fractionation generated such SiO_2 -rich rocks. The importance of lunar granite has increased markedly since the discovery of very high potassium (VHK) basalts (Sbervais et al., 1985a). These VHK basalts are considered to be the product of granite assimilation by an ordinary low-Ti, aluminous basalt (Sbervais et al., 1985a; Neal et al., 1988a).

Theories pertaining to the petrogenesis of lunar granite fall into two categories: (1) fractional crystallization alone (e.g., Lovering and Wark, 1975; Ryder, 1976); and (2) fractional crystallization of a basaltic magma followed by silicate liquid immiscibility (SLI) (e.g., Rutherford et al., 1974; Hess et al., 1975; Quick et al., 1977; Hess et al., 1978; Taylor et al., 1980). Previous authors have advocated a primitive mare basalt parental magma (e.g., Rutherford et al., 1974, 1976; Hess et al., 1975; Dickenson and Hess, 1983), or a KREEP basalt parent (e.g., Meyer, 1972; Ryder et al., 1975; Ryder, 1976; Crawford and Hollister, 1977).

This paper is concerned with the process of silicate liquid immiscibility, which has the potential to generate granitic compositions without any intermediate rock types. We apply this process to lunar granite petrogenesis and attempt to relate observed compositions of lunar granite and granitic immiscible glasses to experimental data. This allows granite petrogenesis to be constrained within the context of a lunar regime and the process of SLI.

Reported lunar granite compositions that are utilized in this paper are: two from Apollo 12 (12013 and 12033,517); five from Apollo 14 (14303,204; 14305,441; 14305,443B; 14321,1027; and 14321,1198); and two from Apollo 17 (73215c and 73255c). Granite compositions are taken from: Quick et al. (1977)—12013; Warren et al. (1987)—12033,517; Blanchard et al. (1977)—73215c; Blanchard and Budahn (1979)—73255c; and Warren et al. (1983a)—14303,204 and 14321,1027. The remaining granite compositions have been briefly reported by Sbervais and Taylor (1983) and Salpas et al. (1985).

GEOCHEMICAL CLASSIFICATION OF LUNAR GRANITE

The term "lunar granite" encompasses both felsites (Blanchard et al. 1977; Quick et al., 1977; Blanchard and Budahn, 1979; Warren et al., 1987) and granites proper (Sbervais and Taylor, 1983; Salpas et al., 1985; Warren et al.,

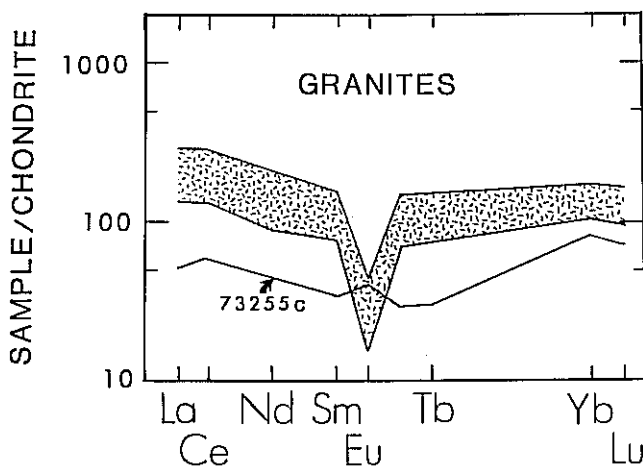


Fig. 1. Chondrite-normalized plot of all lunar granite REE profiles. Data from Blanchard *et al.* (1977), Quick *et al.* (1977), Blanchard and Budahn (1979), Shervais and Taylor (1983), Warren *et al.* (1983a), Salpas *et al.* (1985), and Warren *et al.* (1987).

1983a). Generally, lunar granites comprise myrmikitic intergrowths of quartz and K-feldspar (e.g., Blanchard and Budahn, 1979; Shervais and Taylor, 1983; Warren *et al.*, 1983a), with accessory phosphate, ilmenite, zircon, plagioclase, and K-rich glass. Fayalite and Ca- and Fe-rich pyroxene are also present. All reported lunar granites contain elevated K_2O (3.0–9.4 wt.%) and BaO (2100–5860 ppm) abundances, higher than in any other lunar rock type. The compatible elements (Cr, Sc, Co, and V) are less abundant in granites than in other lunar lithologies. The REE abundances are lower than in KREEP but overlap the more evolved high-Al (HA) mare basalt compositions. Generally the REE profile is “concave upward” with a strong negative Eu anomaly (Fig. 1). The felsite 73255c (Blanchard and Budahn, 1979) contains rare earth and high field strength (HFS) element abundances, which are much lower relative to other reported lunar granites (Fig. 1). Although 73255c does exhibit a concave upward REE profile, it contains a slight positive Eu anomaly. However, this sample may still be classified as a lunar granite because of estimated high SiO_2 content, the high Ba (5470 ppm) and K_2O (7.55 wt.%) contents, and low-compatible element abundances (e.g., Cr = 70 ppm; Sc = 2.3 ppm).

Chemical Variations within Lunar Granites

Lunar granite compositions exhibit a range of elemental abundances (Figs. 1 and 2), and no correlation is seen between granite composition and Apollo site. The small sample size (<5 mm clasts) reported for most granite samples (e.g., Warren *et al.*, 1983a) can produce apparent chemical heterogeneities due to modal variations (Lindstrom and Haskin, 1978; Haskin and Korotev, 1977). However, with the granites, modal variations do not disguise the distinctive concave upward REE profile or the REE abundances, which are greater than in primitive high-Al (HA) basalts, but less than

in KREEP. Also, although elemental abundances of lunar granites are variable, trace element patterns are generally consistent between samples. Thus, for some elements at least, the problem of sample size is not major. We conclude that while differences in modal proportions could cause chemical heterogeneities within an otherwise homogeneous body, they do not mask the overall granitic signature.

EVIDENCE FOR SILICATE LIQUID IMMISCIBILITY IN LUNAR GRANITE PETROGENESIS

Interelement ratios of such elements as K, U, Th, Rb, Ba, P, REE, and Zr are relatively unaffected by normal fractional crystallization of the major silicate minerals from basaltic magmas. As such, these ratios can usually be taken as representative of the source region (e.g., Duncan *et al.*, 1973). However, both silicate liquid immiscibility and late-stage fractionation of zircon, whitlockite, apatite, and K-feldspar can dramatically alter such ratios as K/P, K/La, and K/Zr.

Immiscible granitic glasses in basalt mesostasis have similar compositions to actual lunar granites (except for lower CaO

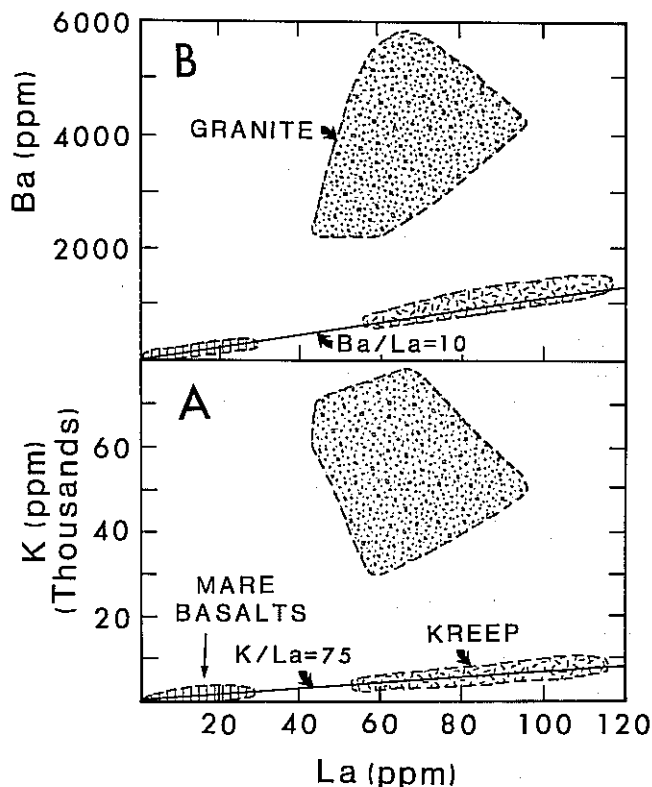


Fig. 2. Lanthanum plotted against K and Ba, demonstrating the possible effects of SLI in lunar granite petrogenesis. Basalt data from Dickinson *et al.* (1985), Shervais *et al.* (1985b), and Neal *et al.* (1988b). KREEP data from Warren *et al.* (1983b). Granite data from Blanchard *et al.* (1977), Quick *et al.* (1977), Blanchard and Budahn (1979), Shervais and Taylor (1983), Warren *et al.* (1983a), Salpas *et al.* (1985), and Warren *et al.* (1987).

TABLE 1. Liquid-liquid partition coefficients calculated from immiscible glasses in basaltic mesostases and experimental results.

	1	2	3	3	4	5	5	5	5	6
SiO ₂	0.50	—	0.55	0.58	0.59	0.72	0.70	0.58	0.59	0.52
TiO ₂	6.86	8.10	6.18	7.17	5.42	2.33	2.86	7.75	2.16	4.43
Al ₂ O ₃	0.38	—	0.47	0.26	0.42	0.79	0.74	0.60	0.54	0.62
Cr ₂ O ₃	—	—	—	—	—	—	—	—	—	—
FeO	16.5	—	11.0	12.5	10.2	2.42	3.07	5.00	5.34	4.82
MnO	21.9	—	—	—	—	—	—	—	—	6.80
MgO	59.4	—	11.3	7.60	—	1.50	—	—	3.00	10.2
CaO	11.1	—	6.69	6.05	7.84	2.07	2.54	3.00	4.46	5.44
BaO	0.49	0.61	—	—	—	—	—	—	—	—
Na ₂ O	0.30	—	—	0.31	—	0.67	0.33	0.25	—	0.41
K ₂ O	0.12	0.37	0.06	0.04	0.03	0.46	0.32	0.18	0.19	0.14
P ₂ O ₅	35.6	6.38	3.80	—	—	—	—	—	—	21.6
Zr	3.77	1.17	—	—	—	—	—	—	—	—
La	—	—	—	—	—	—	—	—	—	—

TABLE 1. (continued)

	6	6	6	7	7	7	7	7	7	7
SiO ₂	0.66	0.65	0.51	0.64	0.71	0.73	0.68	0.74	0.81	0.58
TiO ₂	2.75	2.59	9.00	2.38	2.79	2.28	2.62	2.54	2.01	4.13
Al ₂ O ₃	0.70	0.81	0.38	0.59	0.58	0.62	0.59	0.65	0.73	0.64
Cr ₂ O ₃	1.50	4.00	2.67	—	—	—	—	—	—	—
FeO	3.19	3.20	45.5	3.02	2.57	2.77	2.76	2.52	1.73	5.92
MnO	2.71	2.75	—	3.34	2.32	2.30	2.93	1.91	1.60	6.80
MgO	2.33	2.36	80.0	2.58	2.13	3.04	2.60	2.67	1.00	9.00
CaO	2.50	2.36	20.9	2.58	2.13	1.98	2.47	2.14	1.67	6.71
BaO	—	—	—	—	—	—	—	—	1.47	—
Na ₂ O	0.51	0.54	0.23	0.61	0.47	0.46	0.43	0.53	0.54	0.46
K ₂ O	0.20	0.36	0.01	0.26	0.31	0.32	0.27	0.35	0.49	0.18
P ₂ O ₅	12.4	4.60	42.9	—	—	—	—	—	—	33.2
Zr	—	—	—	—	—	—	—	—	—	—
La	—	—	—	4.42	4.58	3.92	—	—	—	13.8
Sm	—	—	—	—	—	—	—	—	—	—
Yb	—	—	—	—	—	—	4.18	3.60	—	16.6

TABLE 1. (continued)

	7	8	Average Kd
SiO ₂	0.59	0.75	0.64
TiO ₂	3.11	3.08	4.21
Al ₂ O ₃	0.77	0.64	0.59
Cr ₂ O ₃	—	3.76	3.99
FeO	4.43	2.18	7.17
MnO	8.29	2.93	5.12
MgO	4.25	2.15	4.77
CaO	4.39	2.35	4.83
BaO	1.34	1.50	0.49
Na ₂ O	0.44	—	0.44
K ₂ O	0.21	0.45	0.45
P ₂ O ₅	13.3	10.8	10.8
Zr	—	2.37	2.44
La	—	3.91	5.29
Sm	—	4.42	4.42
Yb	—	—	4.18
Lu	—	5.66	5.66
Th	—	4.31	4.31
Cs	—	0.30	0.30

References: 1 = 15434,188 this study; 2 = Ryder, unpublished data; 3 = Roedder and Weiblen (1971); 4 = Weiblen and Roedder (1973); 5 = Rutherford et al. (1974); 6 = Hess et al. (1975); 7 = Ryerson and Hess (1980); 8 = Watson (1976).

Kd's calculated by dividing amount of element in basic melt by the amount in acid melt.

contents), suggesting a similar petrogenesis. Experimental results from high- and low-Ti mare basalts (Rutherford et al., 1973; Hess et al., 1975) demonstrate the relative ease with which lunar basalts, under low fO₂ conditions and slow cooling, can eventually undergo silicate liquid immiscibility. Finally, the lack of any intermediate rock types between basalt and granite on the Moon negates any fractional crystallization scheme that does not follow the "Fenner Trend." Magmas that undergo this type of fractionation produce a ferrobasaltic residual, ideal for the production of immiscible melts (Hess et al., 1975). The experimental results, coupled with the immiscible glass analyses from lunar basalts (Roedder and Weiblen, 1970, 1971, 1972; Weiblen and Roedder, 1973), indicate that SLI is a feasible process in the lunar environment and for the generation of lunar granite. For example, Roedder and Weiblen (1972) have shown that K/P ratios in lunar basalts are close to 1 but are increased up to 100 in high-SiO₂ immiscible melts. However, although evidence suggests that SLI is likely for the petrogenesis of lunar granites, it cannot be unequivocally proven.

In order to ascertain the role of SLI in the production of lunar granite, comparison of K/La and Ba/La ratios between granite, Apollo 14 basalts, and KREEP have been made (Fig. 2). The granite compositions are compared with Apollo 14 HA

mare basalts (*Dickinson et al.*, 1975; *Shervais et al.*, 1985b; *Neal et al.*, 1988b) and KREEP compositions (*Warren et al.*, 1983b). The K/La and Ba/La ratios are similar for both the basalts and KREEP (≈ 75 and 10, respectively). The granites exhibit K/La ratio of up to 1000. Therefore, if the parent of granite were either a KREEP or mare basalt, it is unlikely that granite was produced by fractional crystallization alone, unless much phosphate/zircon fractionation occurred during the late stages. *Neal and Taylor* (1988) demonstrated that the trace element abundances in granite could not be generated from a mare basalt by fractional crystallization alone, even with phosphate on the liquidus. Silicate liquid immiscibility can also fractionate La from K, thus elevating the K/La ratio in granite. The Ba/La ratios exhibit similar increases (up to 70) over HA basalts and KREEP. However, controversy exists as to whether Ba partitions into the high- or low-SiO₂ immiscible melt.

THE PROCESS OF SILICATE LIQUID IMMISCIBILITY

The occurrence of immiscibility at geologically feasible temperatures was discovered by *Roedder* (1951), where two immiscible liquids form between 1000-1200°C in the system SiO₂-K₂O-FeO-Al₂O₃. The size of the immiscibility field has been demonstrated to increase with increasing fO₂ (*Nashund*, 1976) and with the addition of oxides, such as TiO₂ and P₂O₅ (*Watson*, 1976; *Ryerson and Hess*, 1980). *Hess and Rutherford* (1974) observed immiscibility at 300 bars (equivalent to a depth of 6 km on the Moon), and *Watson and Nashund* (1977) demonstrated that this field was expanded dramatically by CO₂-free total pressures of 1-5Kb. However, *Nakamura* (1974) showed that the immiscibility field was reduced or eliminated at 15 kb.

The experiments of *Rutherford et al.* (1974, 1976),

TABLE 2. Granitic and ferrobasic immiscible glasses in mesostasis of 15434,188.

	Granitic Melt							Average
	78.1	75.1	76.5	76.8	74.9	76.5	78.2	76.6
SiO ₂	78.1	75.1	76.5	76.8	74.9	76.5	78.2	76.6
TiO ₂	0.65	0.71	0.53	0.67	0.60	0.60	0.60	0.62
Al ₂ O ₃	11.8	11.4	11.4	11.9	11.1	10.6	11.4	11.4
Cr ₂ O ₃	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	0.02	—
FeO	1.06	2.55	2.29	1.54	1.98	2.79	1.28	1.93
MnO	0.02	0.03	0.03	<0.01	<0.01	0.04	<0.01	0.02
MgO	0.02	0.12	0.03	<0.01	0.03	0.06	<0.01	0.04
CaO	0.75	1.20	1.07	0.91	0.75	1.00	0.78	0.92
BaO	0.46	0.48	0.91	0.50	1.39	0.31	0.47	0.65
Na ₂ O	0.83	0.78	0.77	0.80	0.49	0.81	0.73	0.74
K ₂ O	6.13	5.75	6.47	6.31	7.01	6.96	6.09	6.39
P ₂ O ₅	0.13	0.21	0.12	0.09	0.27	0.04	0.13	0.14
ZrO ₂	0.25	0.14	0.20	0.35	0.27	0.40	0.26	0.27
La ₂ O ₃	0.04	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	—
F	<0.02	<0.02	0.06	<0.02	<0.02	<0.02	0.10	—
Cl	<0.02	<0.02	0.03	<0.02	0.04	<0.02	0.03	—
Total	100.29	98.55	100.41	99.96	98.89	100.18	100.13	99.72

TABLE 2. (continued)

	Basic Melt							Average
	43.9	41.9	37.3	37.1	31.8	33.9	41.4	38.2
SiO ₂	43.9	41.9	37.3	37.1	31.8	33.9	41.4	38.2
TiO ₂	2.57	2.00	2.28	4.32	7.04	7.78	3.90	4.27
Al ₂ O ₃	2.62	5.28	4.84	2.24	1.82	5.39	7.62	4.26
Cr ₂ O ₃	0.05	<0.02	<0.02	0.06	0.14	0.06	<0.02	0.05
FeO	34.9	26.5	28.1	33.0	34.6	35.6	30.2	31.8
MnO	0.59	0.31	0.47	0.42	0.46	0.43	0.38	0.44
MgO	4.49	1.89	2.32	2.74	3.44	0.91	0.83	2.37
CaO	9.02	11.2	12.5	11.5	11.6	7.85	7.80	10.2
Na ₂ O	0.07	0.32	0.28	0.10	0.04	0.29	0.46	0.22
K ₂ O	0.05	1.44	0.69	0.15	0.08	0.81	2.00	0.75
P ₂ O ₅	0.95	8.09	8.05	5.33	6.29	3.38	3.16	5.04
ZrO ₂	0.57	0.89	0.94	0.96	0.81	1.55	1.33	1.01
La ₂ O ₃	0.05	0.09	0.17	<0.02	<0.02	0.04	0.10	0.07
F	<0.02	0.18	0.09	0.30	0.49	0.17	0.18	0.20
Cl	<0.02	0.03	0.05	0.09	0.17	0.12	0.07	0.08
Total	100.09	99.56	98.69	98.56	99.07	98.69	100.02	99.28

Analyses were conducted on a Cameca SX-50 electron microprobe using an accelerating voltage of 15kV, with a filament current of 100μA. Beam current was 20nA. Extended count times of 60 seconds were used on all minor elements. All phases were corrected using the ZAF procedure.

Rutherford and Hess (1975), and Hess *et al.* (1975), and the observations of Roedder and Weiblen (1970, 1971, 1972) and Weiblen and Roedder (1973), suggest that SLI can only occur after extreme (90-98%) crystallization of mare basalt, but perhaps after 80-90% crystallization of a KREEP basalt. Hess *et al.* (1975) concluded that the fractionation path required for ultimate immiscibility of the residual is similar to the Fenner Trend (i.e., FeO rather than SiO₂ enrichment, with a dramatic decrease in MgO). These authors also suggested that under conditions of low oxygen fugacity (such as in a lunar environment), there is a "thermal valley" that leads residual magmas toward a ferrobasic composition. This type of fractionation does not produce intermediate rock types between basalt and granite, because silica enrichment is suppressed.

Partitioning Between Immiscible Melts

When a fractionated magma encounters the immiscibility field, high-silica (acidic) and low-silica (basic) melts are produced. Partitioning of elements between these melts is a function of melt structure (Ryerson and Hess, 1975, 1978, 1980; Watson, 1976). In Table 1 we have presented liquid-liquid Kd's determined by experimentation and from immiscible glasses in basaltic mesostasis. These Kd's are presented as

$$D_{b/a}^* = \frac{\text{conc. of element in basic melt}}{\text{conc. of element in acid melt}}$$

(* $D_{b/a}$ = liquid-liquid Kd)

and are produced for both major and trace elements. Therefore a liquid-liquid Kd of >1 indicates that the element is preferentially partitioned into the basic melt. The elements Si, Al, Na, K, Rb, and Cs are concentrated in the acid or granitic melt (i.e., Kd < 1), whereas Ti, Cr, Fe, Mn, Mg, Ca, P, Zr, U, Th, the REE, F, Cl, Sr, and Ta are concentrated in the basic or ferrobasic melt (i.e., Kd > 1; Hess and Rutherford, 1974; Hess *et al.*, 1975; Watson, 1976). Generally, there is good agreement between the liquid-liquid Kd's produced experimentally and those determined by direct measurement, although the magnitudes vary (Table 1). The liquid-liquid Kd's have been shown to increase with decreasing temperature and the addition of phosphorus to the system (Ryerson and Hess, 1978, 1980). Variable P₂O₅ contents coupled with temperature variations probably account for a large part of the range in Kd values presented in Table 1. However, other compositional variables, such as the alkali/alumina ratio, cannot be ignored.

The Barium Problem

Roedder and Weiblen (1970, 1971, 1972) and Weiblen and Roedder (1973) reported the occurrence of residual mesostasis glass in lunar basalts that had undergone SLI. Their results indicated that the granitic melt contained ≈0.6 wt.% BaO, whereas the basic melt contained <0.1 wt.% BaO (i.e., $D_{b/a} < 1$). This conclusion was reiterated by Hess and

Rutherford (1974) and Hess *et al.* (1975). We have analyzed immiscible mesostasis glasses from Apollo 15 basalt 15434,188 (Table 2). In order to increase the precision of the minor element analyses, extended count times of 60 sec were used. Liquid-liquid Kd's were calculated from adjacent glasses. The results obtained also demonstrate that barium is partitioned into the granitic melt ($D_{b/a} = 0.49$). Furthermore, G. Ryder (personal communication, 1988) recently analyzed immiscible glasses from Apollo 15 KREEP basalts (Table 1). His results conform with the experimental data, except for Ba, which has a $D_{b/a}$ of 0.61.

However, the experimental results of Watson (1976) demonstrated that Ba was concentrated in the ferrobasic or basic immiscible melt ($D_{b/a} = 1.5$). Ryerson and Hess (1978) predicted that cations of intermediate charge density, such as Ba and Sr, have partition coefficients close to unity; but after conducting experiments in which SLI occurred, Ryerson and Hess (1980) concluded that Ba does indeed partition preferentially into the basic melt ($D_{b/a} = 1.4$).

In order to explain the apparent dichotomy of the Ba two-liquid Kd in experimental and natural systems, the structure of the immiscible melts must be considered. Charge balance is maintained throughout the melt by each cation occupying a site associated with an anionic complex (Ryerson and Hess, 1980). It has been suggested that Al can assume the role of either a network-forming or network-modifying cation in silicate melts (Kushiro, 1975; Wood and Hess, 1980; Hess and Wood, 1982). However, in order to substitute for Si, Al must be charge balanced by a monovalent or divalent cation. Wood and Hess (1980) and Hess and Wood (1982) have demon-

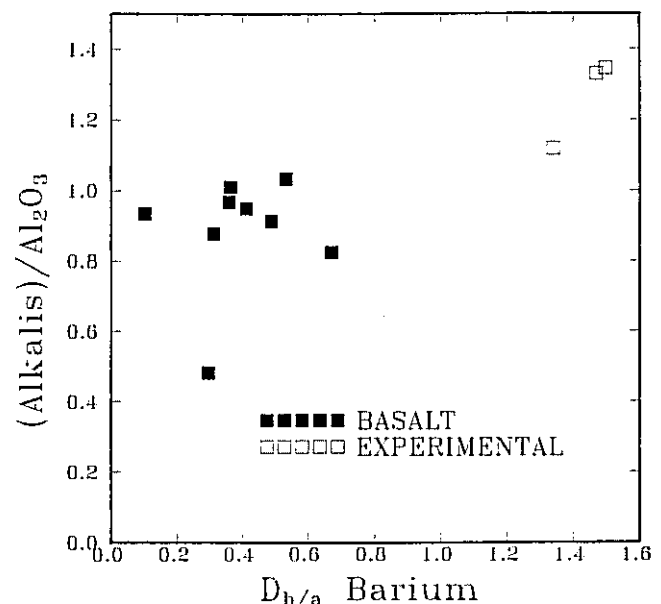


Fig. 3. Molar (K₂O+Na₂O+CaO+BaO)/Al₂O₃ vs. $D_{b/a}$ Ba for both experimentally determined and analyzed basaltic immiscible glasses. Data from Watson (1976), Ryerson and Hess (1980), and this study.

TABLE 3. Calculation of "alkalis"/Al₂O₃ for lunar granites.

	Lunar Granites							
	14305 441	14305 443B	14321 1198	14303 204	14321 1027	12013 Light	73255c	12033 517
Al ₂ O ₃	12.2	13.7	11.9	18.5	12.5	11.9	12.3	12.9
CaO	3.10	1.26	5.71	8.80	1.25	1.40	0.50	4.90
Na ₂ O	0.72	0.68	0.46	1.25	0.52	1.40	0.53	1.47
K ₂ O	6.71	9.41	5.97	3.60	8.60	6.80	7.55	3.00
BaO	0.62	0.68	0.46	0.23	0.24	0.65	0.61	0.51
A	1.189	1.025	1.504	1.195	1.009	1.063	0.844	1.156
B	0.727	0.858	0.633	0.331	0.827	0.850	0.770	0.466

A = (K₂O+Na₂O+BaO+CaO)/Al₂O₃; B = (K₂O+Na₂O+BaO)/Al₂O₃.

Moles of the oxides are used. Data from Warren *et al.* (1983a, 1987), Sbervais and Taylor (1983), Salpas *et al.* (1985), and unpublished data.

strated that in a K- and Na-free system, which undergoes SLI, Al is preferentially partitioned into the low-SiO₂ melt as a CaAl₂O₄ complex (Ca is also strongly partitioned into the basic melt). However, with increasing alkali content, Al is preferentially partitioned into the high-SiO₂ melt. Potassium (or Na) displaces Ca as the charge balancing cation for the network-forming AlO₄ tetrahedra. The (Na,K)AlO₂ species favor the more polymerized silicate melt structure. Ryerson and Hess (1980) concluded that the behavior of K⁺, Na⁺, and Ba²⁺ is explained by their strong affinity for sites associated with tetrahedral Al. Calcium and the REE's display the opposite effect as a result of their greater affinity for the phosphate complexes in the basic melt.

Hess and Wood (1982) and Roy and Navrotsky (1984) proposed a list of cations with which tetrahedrally coordinated Al would complex. These are, in order of preference: K > Na > Li > Ba > Pb > Sr > Ca > Fe²⁺ > Mg. Hess and Wood (1982) concluded that AlO₄ species formed with cations at the beginning of this series preferentially enter the most polymerized silicate units (i.e., the high-SiO₂ melt); those formed with cations at the end favor the least polymerized melt structures (i.e., the basic melt). Ryerson and Hess (1978) suggested that the liquid-liquid Kd for Ba and Sr is ≈1, and Wood and Hess (1982) indicate that the transition between the two states occurs at Ba. This is entirely consistent with the observed D_{h/a}'s for Ba presented in Table 1.

TABLE 4. Calculation of the pre-SLI melt for average granite and the average granitic glass from 15434,188.

	Db/a	Lunar Granite			Pre-SLI Melt
		1	2	3	
SiO ₂	0.61	69.2	70.8	43.3	48.5
TiO ₂	4.20	0.68	0.69	2.91	2.42
Al ₂ O ₃	0.60	13.2	13.5	8.06	9.15
FeO	6.70	3.68	3.75	25.2	20.9
MgO	4.72	0.20	0.20	0.96	0.80
CaO	4.55	3.37	3.45	15.7	13.1
Na ₂ O	0.44	0.88	0.90	0.40	0.50
K ₂ O	0.24	6.46	6.61	1.58	3.10
P ₂ O ₅ *	18.5	0.10	0.10	1.89	1.53
Total		97.77	100.00	100.00	100.00
Cr	3.99	410		1634	1389
Mn	5.12	114		582	488
Rb	0.24†	152		36.6	59.7
Sr	1.54	153		235	219
Cs	0.30	4.21		1.28	1.86
Ba	0.49	4450		2194	2645
La	5.29	61.2		324	271
Sm	4.42	19.7		87.2	73.7
Yb	4.18	27.5		115	97.5
Lu	5.66	4.00		22.6	18.9
Hf	2.44†	18.1		44.2	39.0
Ta	4.13	5.45		22.5	19.1
Th	2.44†	42.9		105	92.5
U	2.44†	12.5		30.5	25.1
Zr	2.44	1000		2435	2148

TABLE 4. (continued)

	Db/a	15434,188 Immiscible Glasses				Pre-SLI Melt
		4	5	6	7	
SiO ₂	0.51	76.6	77.6	39.6	39.3	47.2
TiO ₂	6.86	0.62	0.63	4.30	4.40	3.56
Al ₂ O ₃	0.38	11.4	11.5	4.33	4.37	5.79
FeO	16.5	1.93	1.95	32.3	32.8	26.2
MgO	59.4	0.04	0.04	2.40	2.44	1.93
CaO	11.1	0.92	0.93	10.3	10.5	8.42
Na ₂ O	0.30	0.74	0.75	0.22	0.23	0.33
K ₂ O	0.12	6.39	6.44	0.78	0.77	1.92
P ₂ O ₅ *	35.6	0.16	0.16	5.77	5.19	4.65
Total		98.80	100.00	100.00	100.00	100.00
Cr	8.00	68.4		547	342	287
Ba	0.49	5822		2870	2877	3466
La	9.60	62.2		600	597	490
Zr	3.77	1999		7536	7477	6381

* Maximum P₂O₅ wt.% in granite calculated from modal % apatite/whitlockite.

† Estimated Db/a.

1 = average lunar granite; 2 = average lunar granite normalized to 100; 3 = calculated basic immiscible melt which compliments lunar granite; 4 = average granitic glass; 5 = average granitic glass normalized to 100; 6 = calculated basic melt; 7 = analyzed average basic melt normalized to 100. The pre-SLI melt composition is calculated from 20% granitic and 80% basic melt.

In order to understand the partitioning behavior of Ba in immiscible systems, our immiscible glass analyses are combined with the experimental results of *Watson* (1976) and *Ryerson and Hess* (1980). The $D_{b/a}$ for barium is plotted against the "alkali"/alumina ratio ("alkali" = $K_2O+Na_2O+CaO+BaO$) in the granitic melt (Fig. 3). Moles of the oxides have been used in these calculations. The partitioning of Ba into the acidic melt depends upon the ratio of the moles of "alkalis" to alumina. A $D_{b/a}$ barium of 1 corresponds to a molar "alkali"/alumina ratio of approximately 1 in the granitic melt. Therefore, if Ba is to be partitioned into the granitic immiscible melt, the amount of K, Na, and Ca present in the granitic melt must be less than required to charge balance Al. Note that although Ca is strongly partitioned into the basic melt (Table 1), small quantities of Ca will be present in the granitic portion.

A value for $D_{b/a}$ for barium in lunar granites cannot be directly determined, assuming formation involving SLI. However, all lunar granites contain molar "alkali"/ Al_2O_3 values slightly greater than 1 (Table 3), except for 73255c (0.844) and 14321,1198 (1.504). These values straddle the range corresponding to a $D_{b/a}$ for barium of 1. It is clear, however, that even if $D_{b/a}$ barium is never less than unity, the Ba/La ratio can change by a factor of 5 during SLI (Table 1). This is because La is strongly partitioned into the basic liquid, and even this degree of fractionation is sufficient to change the Ba/La ratio of either a mare or KREEP basalt to that of granite.

Uranium and Thorium Considerations

Lunar granites contain high abundances of Zr, U, and Th (HFS elements). Average lunar granite (Table 4) contains 43 ppm Th, 12.5 ppm U, and 1000 ppm Zr. This has been cited as a problem in granite petrogenesis by SLI (e.g., *Warren et al.*, 1983a; *Salpas et al.*, 1985). The experimental results and measurements of natural immiscible glasses both indicate that the high field strength (HFS) elements are preferentially partitioned into the basic melt (Table 1; *Hess and Rutherford*, 1974; *Watson*, 1976). These elements cannot complex with tetrahedrally coordinated aluminum, so a scenario similar to that for Ba cannot be used to explain lunar granite HFS element abundances. If the magnitude of $D_{b/a}$'s for Zr (1.2-3.8) is the same for other HFS elements, then the relative difference between them and La (3.9-13.8) could cause a change in the HFS/La ratio after immiscibility. However, the average $D_{b/a}$ for La and Zr are similar, and such an explanation cannot be considered absolute.

Another possible explanation for the high U and Th abundances in lunar granites is whitlockite fractionation. The crystal/liquid Kd for La is about ten times greater than that for Zr and Hf (*Fujimaki and Tatsumoto*, 1984). *Murrell et al.* (1984) and J. Jones (personal communication, 1988) also show the Kd for La to be greater than that for U and Th in whitlockite. Therefore whitlockite fractionation could serve to increase the U/La and Th/La ratios. Whether whitlockite fractionation occurs before or after immiscibility is unclear. Regardless, extensive whitlockite fractionation could generate the high K/P, U/La, and Th/La ratios with or without SLI. It

is important to note that zircon (the main sink for the HFS elements) does not crystallize until after SLI (*Dickenson and Hess*, 1982a,b), as only then are both the immiscible melts saturated in Zr. This will not elevate the K/La ratio because of the low zircon/liquid Kd for both La and K, but supports the enrichment of the HFS elements in the pre-SLI melt. A further important consideration of the U and Th contents of lunar granites is that of sample size. One small crystal of zircon might totally skew the U and Th data. In any event, the high U and Th contents of lunar granites remain a problem if either a fractional crystallization or a SLI model is favored for their petrogenesis.

Modeling of Silicate Liquid Immiscibility in Lunar Granite

Shib et al. (1985) conducted an isotopic study of granite clast 14321,1062 (14321,1027 of *Warren et al.*, 1983a). They concluded that granites and Mg-gabbronorites could have crystallized ≈ 4.1 Ga from similar Mg-rich parent magmas intruded into the highland crust. Magnesian-gabbronorites were the early cumulates and granites the final differentiates. Note that this age does not negate a basaltic parent for granites, as basalts >4.2 Ga have been reported (*Taylor et al.*, 1983; *Dasch et al.*, 1987). However, *Shib et al.* (1985) noted that Rb/Sr ratios were highly enriched and, along with K/La ratios, could only have been generated by silicate liquid immiscibility, once the magma was emplaced into the crust. Modeling of SLI was attempted by these authors, using the mass balance equation

$$C_1 = C_a[F_a + (1-F_a)D_{b/a}]$$

where C_1 = trace element concentration in a parental liquid; C_a = trace element concentration in the acidic liquid formed by SLI; F_a = mass fraction of acidic liquid; and, $D_{b/a}$ = elemental distribution coefficient between basic and acidic liquid. *Shib et al.* (1985) have used the liquid-liquid partition coefficients of *Watson* (1976) ($D_{b/a}$ for: the REE ≈ 4 ; Eu and Sr ≈ 2 ; K and Rb ≈ 0.3) in their semiquantitative modeling of SLI. These authors conclude that lunar granite 14321,1062 formed from an evolved parent (i.e., 15405 QMD), which underwent $\approx 3\%$ fractional crystallization of phosphate phases followed by SLI.

The modeling undertaken here differs from that of *Shib et al.* (1985) in that we define, rather than infer, a "pre-SLI" magma composition. This composition is critical for determining whether granite is a SLI product that has resulted from Fenner Trend fractional crystallization. Therefore, lunar granite should have been produced from a magma low in silica and high in Fe. We have utilized the same equation as in *Shib et al.* (1985), in order to generate a pre-SLI magma composition. Two basic assumptions are made: (1) lunar granite is a product of SLI after extreme Fenner Trend fractionation; (2) the pre-SLI melt is ferrobasaltic, as indicated by experimentation (e.g., *Rutherford et al.*, 1974, 1976; *Hess et al.*, 1975).

In order to calculate the proportions of acid to basic immiscible melt produced by SLI, we examined the experi-

mental results of *Rutherford et al.* (1974) and *Hess et al.* (1975). These authors describe experimental SLI results from actual lunar basalt compositions (i.e., 75055, 70017, and 12038). The composition of the magma just prior to SLI, as well as the immiscible melt products, are reported. As such, an approximation of the proportions of immiscible melts can be calculated. The basic:acid proportions is nearly always in the range of 85:15 to 75:25 for these lunar rocks. Consequently, the proportion of basic to acid immiscible melt for the purposes of our model was taken as 80:20. Although the proportions of acid:basic would change if the pre-SLI melt were more silicic, we are assuming a ferrobasaltic residual (see above).

An average lunar granite composition has been calculated from the nine reported compositions (see introduction) and the granitic immiscible glass from 15434,188 are used in our modeling (Table 4). Initially, we took the averaged $D_{b/a}$ values from all reported liquid-liquid Kd 's (Table 1) and applied them to granite. Similarly, the averaged $D_{b/a}$ values, calculated from the immiscible glasses, were used in the 15434,188 modeling. Both major element compositions have been normalized to 100. If the Kd 's are correct, then calculation of the basic melt composition (performed by multiplying the wt.% oxide in the granitic melt by the $D_{b/a}$) should also sum to 100. In order to achieve this, the Kd 's needed a small adjustment. As a cross-check, we calculated the basic immiscible melt in 15434,188 and compared it with the averaged analyzed composition. The calculated melt is very similar to the measured average basic melt composition (Table 4). The $D_{b/a}$ values used for the modeling of lunar granite (Table 4) are within ranges for all reported liquid-liquid Kd 's. Similarly, the $D_{b/a}$'s used in the modeling of 15434,188 are within the range of analyzed immiscible glass pairs from this basalt. As a cross-check, we calculated the basic immiscible melt in 15434,188 and compared it with the averaged analyzed composition. The calculated melt is very similar to the measured average basic melt composition (Table 4). The Ba value used in both models is 0.49, the value calculated from 15434,188. Trace element values are from *Watson* (1976) and *Ryerson and Hess* (1980). In the granite modeling, we assumed that the Rb $D_{b/a}$ is similar to that for K, and the values for U and Th are similar to Zr.

The basic companion to the average granite is typical of the composition of basic immiscible glasses from basaltic mesostasis (*Roedder and Weiblen*, 1970, 1971, 1972; *Weiblen and Roedder*, 1973; and this study: Table 4). It is low in SiO_2 and Al_2O_3 and greatly reduced in MgO (0.97 wt.%), but is enriched in FeO (25.2 wt.%), CaO, and P_2O_5 (Table 4). Consequently, the pre-SLI melt is intermediate to this basic end member and granite. However, because of the proportions required (20% granite, 80% basic melt), the pre-SLI composition resembles the calculated basic immiscible melt, being ferrobasaltic in character. A similar result is obtained with the modeling of a pre-SLI melt composition from the immiscible glasses from 15434,188.

The pre-SLI compositions for both the average granite and 15434,188 granitic glass are compatible with a melt produced by Fenner Trend fractional crystallization (high FeO, very low

MgO). The compositions also compare well with the experimentally produced pre-SLI melt compositions from lunar basalts (Table 4) reported in *Rutherford et al.* (1974) and *Hess et al.* (1975). This type of calculation suggests that a composition similar to the 15405 QMD is probably not a likely parent to lunar granites, as suggested by *Sibb et al.* (1985). The major elements are too evolved in the QMD relative to the calculated pre-SLI melt composition. Furthermore, the REE of the pre-SLI melt have a concave upward REE profile (Fig. 4). As discussed earlier, this suggests that pre-SLI whitlockite fractionation may have occurred during the Fenner Trend evolution in order to produce this REE profile.

Origin of Lunar Granite

The presence of micron-sized late-stage high- and low- SiO_2 immiscible glass (modally comprising 1% in lunar basalts: *Roedder and Weiblen*, 1970, 1971), demonstrates the localized nature of SLI. In these rapidly cooled rocks, the two liquids are retained as immiscible globules in the mesostasis (*Roedder and Weiblen*, 1971). However, under conditions of slower cooling, it is possible that significant gravity separation of immiscible liquids may occur, as the density difference between them can be up to 0.8 g/cm^3 (*Philpotts*, 1972). *Hess et al.* (1975) reported that Stokes' law calculations indicate that granitic liquid would rise in the iron-rich melt at the rate of meters per day (densities and viscosities calculated by the methods of *Bottinga and Weill*, 1970, 1972). Furthermore, the development of immiscibility in the residual magma is dependent on both the cooling rate (slow) and the final temperature ($\approx 1000^\circ\text{C}$) in the cooling cycle (*Rutherford et al.*, 1974). It follows that efficient separation of melts and

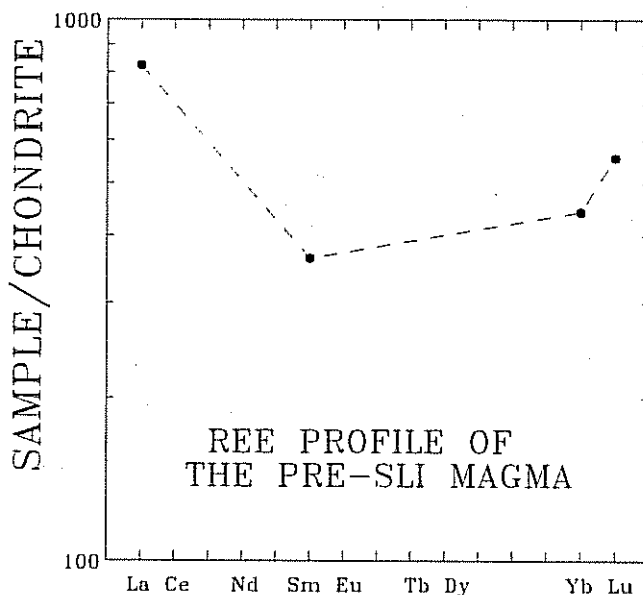


Fig. 4. Calculated pre-SLI magma REE profile for average lunar granite. Only La, Sm, Yb, and Lu $D_{b/a}$ values are known, but a concave upward profile is apparent.

generation of significant granite bodies may only be produced in a hypabyssal or plutonic environment, where cooling rates are sufficiently slow. We envisage that such an environment would be within the upper lunar crust. Silicate liquid immiscibility can still occur at a depth of 6 km (Hess and Rutherford, 1974). Such density and pressure considerations allow the formation of granite "pods" within the crystallate to be a feasible process. The hypabyssal-plutonic origin suggested for lunar granite could also account for the paucity of returned granite samples. It is possible that meteorite impact has not sampled from sufficient depths in order to expose a large, representative granite sample at the lunar surface.

SUMMARY AND CONCLUSIONS

The petrogenesis of VHK basalts argues for discrete granite bodies within the lunar crust (Sbervais et al., 1985a; Neal et al., 1988a). Neal and Taylor (1987) demonstrated that fractional crystallization of a basaltic parent demonstrates the applicability of SLI to lunar granite petrogenesis, by examining the partitioning of elements between immiscible melts and relating the results to observed granite compositions. Specific conclusions are outlined below.

1. It is feasible to generate lunar granite by Fenner Trend fractional crystallization of a basaltic magma, followed by silicate liquid immiscibility (SLI) as the terminal process.

2. Barium can be preferentially partitioned into the acid or basic immiscible melt. The critical factor is the "alkali"/Al₂O₃ ratio of the granitic melt. If this is greater than ≈1, Ba preferentially partitions into the basic melt, as there is sufficient K+Na to charge balance the tetrahedrally coordinated Al in the granitic melt. If the "alkali"/Al₂O₃ ratio is <1, Ba is required to charge balance Al and preferentially partitions into the granitic melt.

3. A calculated pre-SLI composition suggests that whitlockite fractionation could have occurred prior to SLI because of the calculated "concave upwards" REE pattern. This will enhance the high K/La ratios observed in lunar granite.

4. The scarcity of lunar granite may be due to thermal considerations, i.e., the immiscible melts should have sufficient time to effectively separate: a function of cooling rate and gravity. Therefore this would restrict significant lunar granite formation to a hypabyssal or plutonic environment, within the upper lunar crust (i.e., within the upper 6 km, where SLI can still occur).

5. Granite may be far more abundant in the lunar crust than the paucity of collected samples would seem to indicate. Meteorite impact may not have penetrated to sufficient depth in order to sample the lower crust, where abundant granite pods may reside.

Acknowledgments. This study has greatly benefited from useful discussions with A. Patchen and P. Hess. This paper has also benefited from the thoughtful reviews of P. Hess, O. James, J. Jones, D. Mittlefehldt, and an anonymous reviewer. The Cameca SX-50 electron microprobe was purchased with funds from NASA and NSF through grants to L. A. Taylor. The research presented in this paper was supported by NASA grant NAG 9-62 to L.A.T.

REFERENCES

- Blanchard D. P. and Budahn J. R. (1979) Remnants from the ancient lunar crust: clasts from consortium breccia 73255. *Proc. Lunar Planet. Sci. Conf. 10th*, pp. 803-816.
- Blanchard D. P., Jacobs J. W., and Brannon J. C. (1977) Chemistry of ANT-suite and felsite clasts from consortium breccia 73215 and of gabbroic anorthosite 79215. *Proc. Lunar Sci. Conf. 8th*, pp. 2507-2524.
- Bottinga Y. and Weill D. F. (1970) Densities of liquid silicate systems calculated from partial molar volumes of oxide components. *Am. J. Sci.*, 269, 169-182.
- Bottinga Y. and Weill D. F. (1972) The viscosity of magmatic silicate liquids: A model for calculation. *Am. J. Sci.*, 271, 438-475.
- Crawford M. L. and Hollister L. S. (1977) Evolution of KREEP: Further petrologic evidence. *Proc. Lunar Sci. Conf. 8th*, pp. 2403-2417.
- Dasch E. J., Shih C.-Y., Bansal B. M., Wiesmann H., and Nyquist L. E. (1987) Isotopic analysis of basaltic fragments from lunar breccia 14321: Chronology and petrogenesis of pre-Imbrium mare volcanism. *Geochim. Cosmochim. Acta*, 51, 3241-3254.
- Dickenson J. E. and Hess P. C. (1982a) Zircon saturation in lunar basalts and granites. *Earth Planet. Sci. Lett.*, 57, 336-344.
- Dickenson J. E. and Hess P. C. (1982b) Whitlockite saturation in lunar basalts (abstract). In *Lunar and Planetary Science XIII*, pp. 172-173. Lunar and Planetary Institute, Houston.
- Dickenson J. E. and Hess P. C. (1983) Role of Whitlockite and Apatite in lunar felsite (abstract). In *Lunar and Planetary Science XIV*, pp. 158-159. Lunar and Planetary Institute, Houston.
- Dickinson T., Taylor G. J., Keil K., Schmitt R. A., Hughes S. S., and Smith M. R. (1985) Apollo 14 aluminous Mare Basalts and their possible relationship to KREEP. *Proc. Lunar Planet. Sci. Conf. 15th*, in *J. Geophys. Res.*, 90, C365-C374.
- Dixon S. and Rutherford M. J. (1979) Plagiogranites as late-stage immiscible liquids in ophiolite and mid-ocean ridge suites: An experimental study. *Earth Planet. Sci. Lett.*, 45, 45-60.
- Duncan A. R., Erlank A. J., Willis J. P., and Ahrens L. H. (1973) Composition and inter-relationships of some Apollo 16 samples. *Proc. Lunar Sci. Conf. 4th*, pp. 1097-1114.
- Fujimaki H. and Tatsumoto M. (1984) Partition coefficients of Hf, Zr, and REE between zircon, apatite, and liquid and their inferences to lunar granite petrogenesis (abstract). In *Lunar and Planetary Science XV*, pp. 280-281. Lunar and Planetary Institute, Houston.
- Haskin L. A. and Korotev R. L. (1977) Test of a model for trace element partitioning during closed-system solidification of a silicate liquid. *Geochim. Cosmochim. Acta*, 41, 921-939.
- Hess P. C. and Rutherford M. J. (1974) Element fractionation between immiscible melts (abstract). In *Lunar Science V*, pp. 328-330. The Lunar Science Institute, Houston.
- Hess P. C. and Wood M. I. (1982) Aluminum coordination on metaluminous and peralkaline silicate melts. *Contrib. Mineral. Petrol.*, 81, 103-112.
- Hess P. C., Rutherford M. J., Guillemette R. N., Ryersen E. J., and Tuchfeld H. A. (1975) Residual products of fractional crystallization of lunar magmas: An experimental study. *Proc. Lunar Sci. Conf. 6th*, pp. 895-909.
- Hess P. C., Rutherford M. J., and Campbell H. W. (1978) Ilmenite crystallization in non-mare basalt: Genesis of KREEP and high-Ti mare basalt. *Proc. Lunar Planet. Sci. Conf. 9th*, pp. 705-724.
- Kushiro I. (1975) On the nature of silicate melt and its significance in magma genesis: Regularities in the shift of the liquidus boundaries involving olivine, pyroxene, and silicate minerals. *Am. J. Sci.*, 275, 411-431.

- Lindstrom M. M. and Haskin L. A. (1978) Causes of compositional variations within mare basalt suites. *Proc. Lunar Planet. Sci. Conf. 9th*, pp. 465-486.
- Lovering J. F. and Wark D. A. (1975) The lunar crust—chemically defined rock groups and their potassium-uranium fractionation. *Proc. Lunar Sci. Conf. 6th*, pp. 1203-1217.
- Meyer C. (1972) Mineral assemblages and the origin of non-mare lunar rock types (abstract). In *Lunar Science III*, pp. 542-544. The Lunar Science Institute, Houston.
- Murrell M. T., Brandriss M., Woolum D. S., and Burnett D. S. (1984) Pu-REE-Y partitioning between apatite and whitlockite (abstract). In *Lunar and Planetary Science XV*, pp. 579-580. Lunar and Planetary Institute, Houston.
- Nakamura Y. (1974) The system $\text{Fe}_2\text{SiO}_4\text{-KAlSi}_2\text{O}_6\text{-SiO}_2$ at 15 kbar. *Carnegie Inst. Wash. Yearb.*, 73, 352-354.
- Naslund H.R. (1976) Liquid immiscibility in the system $\text{KAlSi}_3\text{O}_8\text{-NaAlSi}_3\text{O}_8\text{-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ and its application to natural magma systems. *Carnegie Inst. Wash. Yearb.*, 75, 592-597.
- Neal C. R. and Taylor L. A. (1987) Lunar granite: An enigma with a new perspective (abstract). In *Lunar and Planetary Science XVIII*, pp. 704-705. Lunar and Planetary Institute, Houston.
- Neal C. R. and Taylor L. A. (1988) "K-Frac + REEP-Frac": A new understanding of KREEP in terms of granite and phosphate petrogenesis (abstract). In *Lunar and Planetary Science XIX*, pp. 831-832. Lunar and Planetary Institute, Houston.
- Neal C. R., Taylor L. A., and Lindstrom M. M. (1988a) The importance of lunar granite and KREEP in Very High Potassium (VHK) basalt petrogenesis. *Proc. Lunar Planet. Sci. Conf. 18th*, pp. 121-137.
- Neal C. R., Taylor L. A., and Lindstrom M. M. (1988b) Apollo 14 mare basalt petrogenesis: Assimilation of KREEP-like components by a fractionating magma. *Proc. Lunar Planet. Sci. Conf. 18th*, pp. 139-153.
- Philpotts J. A. (1972) Density, surface tension, and viscosity of the immiscible phase in a basic, alkaline magma. *Lithos*, 5, 1-18.
- Quick J. E., Albee A. L., Ma M. -S., Murali A. V., and Schmitt R. A. (1977) Chemical compositions and possible immiscibility of two silicate melts in 12013. *Proc. Lunar Sci. Conf. 8th*, pp. 2153-2189.
- Roedder E. (1951) The system $\text{K}_2\text{O-MgO-SiO}_2$. *Am. J. Sci.*, 249, 81-130.
- Roedder E. and Weiblen P. W. (1970) Lunar petrology of silicate melt inclusions, Apollo 11 rocks. *Proc. Apollo 11 Lunar Sci. Conf.*, pp. 801-837.
- Roedder E. and Weiblen P. W. (1971) Petrology of silicate melt inclusions, Apollo 11 and Apollo 12 and terrestrial equivalents. *Proc. Lunar Sci. Conf. 2nd*, pp. 507-528.
- Roedder E. and Weiblen P. W. (1972) Silicate melt inclusions and glasses in lunar soil fragments from the Luna 16 core sample. *Earth Planet. Sci. Lett.*, 13, 272-285.
- Roy B. N. and Navrotsky A. (1984) Thermochemistry of charge-coupled substitutions in silicate glasses: The systems $\text{M}_{1/n}\text{AlO}_2\text{-SiO}_2$ (M = Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Pb). *J. Am. Ceramic Soc.*, 67, 606-610.
- Rutherford M. J., Hess P. C., and Daniel G. H. (1974) Experimental liquid line of descent and liquid immiscibility for basalt 70017. *Proc. Lunar Sci. Conf. 5th*, pp. 569-583.
- Rutherford M. J. and Hess P. C. (1975) Origin of lunar granites as immiscible liquids (abstract). In *Lunar Science VI*, pp. 696-698. The Lunar Science Institute, Houston.
- Rutherford M. J., Hess P. C., Ryerson F. J., Campbell H. W., and Dick P. A. (1976) The chemistry, origin, and petrogenetic implications of lunar granite and monzonite. *Proc. Lunar Sci. Conf. 7th*, pp. 1723-1740.
- Ryder G. (1976) Lunar sample 15405: Remnant of a KREEP-Granite differentiated pluton. *Earth Planet. Sci. Lett.*, 29, 255-268.
- Ryder G., Stoesser D. B., Marvin U. B., and Bower J. F. (1975) Lunar granites with unique ternary feldspars. *Proc. Lunar Sci. Conf. 6th*, pp. 435-449.
- Ryerson F. J. and Hess P. C. (1975) The partitioning of trace elements between immiscible silicate melts (abstract). *Eos Trans. AGU*, 56, 470.
- Ryerson F. J. and Hess P. C. (1978) Implications of liquid-liquid distribution coefficients to mineral-liquid partitioning. *Geochim. Cosmochim. Acta*, 42, 921-932.
- Ryerson F. J. and Hess P. C. (1980) The role of P_2O_5 in silicate melts. *Geochim. Cosmochim. Acta*, 44, 611-624.
- Salpas P. A., Shervais J. W., Knapp S. A., and Taylor L. A. (1985) Petrogenesis of lunar granites: The result of apatite fractionation (abstract). In *Lunar and Planetary Science XVI*, pp. 726-727. Lunar and Planetary Institute, Houston.
- Shervais J. W. and Taylor L. A. (1983) Micrographic granite: more from Apollo 14 (abstract). In *Lunar and Planetary Science XIV*, pp. 696-697. Lunar and Planetary Institute, Houston.
- Shervais J. W., Taylor L. A., Lau J. C., Shih C. -Y., and Nyquist L. E. (1985a) Very High Potassium (VHK) basalt: Complications in mare basalt petrogenesis. *Proc. Lunar Planet. Sci. Conf. 16th*, in *J. Geophys. Res.*, 90, D3-D18.
- Shervais J. W., Taylor L. A., and Lindstrom M. M. (1985b) Apollo 14 mare basalts: Petrology and geochemistry of clasts from consortium breccia 14321. *Proc. Lunar Planet. Sci. Conf. 15th*, in *J. Geophys. Res.* 90, C375-C395.
- Shih C. -Y., Nyquist L. E., Bogard D. D., Wooden J. L., Bansal B. M., and Weismann H. (1985) Chronology and petrogenesis of a 1.8g lunar granite clast: 14321,1062. *Geochim. Cosmochim. Acta*, 49, 411-426.
- Taylor G. J., Warner R. E., Keil K., Ma M. -S., and Schmitt R. A. (1980) Silicate liquid immiscibility, evolved lunar rocks and the formation of KREEP. *Proc. Conf. Lunar Highlands Crust* (J. J. Papike and R. B. Merrill, eds.), pp. 339-352. Pergamon, New York.
- Taylor L. A., Shervais J. W., Hunter R. H., Shih C. -Y., Nyquist L. E., Bansal B. M., Wooden J., and Lau J. C. (1983) Pre-4.2 AE mare basalt volcanism in the lunar highlands. *Earth Planet. Sci. Lett.*, 66, 33-47.
- Warren P. H., Taylor G. J., Keil K., Shirley D. N., and Wasson J. T. (1983a) Petrology and chemistry of two "large" granite clasts from the Moon. *Earth Planet. Sci. Lett.*, 64, 175-185.
- Warren P. H., Taylor G. J., Keil K., Kallemeyn G. W., Shirley D. N., and Wasson J. T. (1983b) Seventh foray: Whitlockite-rich lithologies, a diopside-bearing troctolitic anorthosite, ferroan anorthosites and KREEP. *Proc. Lunar Planet. Sci. Conf. 14th*, in *J. Geophys. Res.*, 88, B151-B164.
- Warren P. H., Jerde E. A., and Kallemeyn G. W. (1987) Pristine moon rocks: A "large" felsite and a metal-rich ferroan anorthosite. *Proc. Lunar Planet. Sci. Conf. 17th*, in *J. Geophys. Res.*, 92, E303-E313.
- Watson E. B. (1976) Two-liquid partition coefficients: Experimental data and geochemical implications. *Contrib. Mineral. Petrol.*, 56, 119-134.
- Watson E. B. and Naslund H. R. (1977) The effect of pressure on liquid immiscibility in the system $\text{K}_2\text{O-FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2$. *Carnegie Inst. Wash. Yearb.*, 76, 410-414.
- Weiblen P. W. and Roedder E. (1973) Petrology of melt inclusions in Apollo samples 15598 and 62295, and of clasts in 67915 and several lunar soils. *Proc. Lunar Sci. Conf. 4th*, pp. 681-703.
- Wood M. I. and Hess P. C. (1980) The structural role of Al_2O_3 and TiO_2 in immiscible silicate liquids in the system $\text{SiO}_2\text{-MgO-CaO-FeO-TiO}_2\text{-Al}_2\text{O}_3$. *Contrib. Mineral. Petrol.*, 72, 319-328.