

K-FRAC AND REEP-FRAC IMMISCIBLE LIQUIDS AT APOLLO 14: A SIMS SEARCH FOR THE REAL urKREEP COMPOSITION

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An incompatible-element-enriched chemical signature, termed KREEP (elevated in K, REE, and P) [1] is pervasive in samples returned from the moon. Warren & Wasson [2] have postulated that this KREEP signature is actually the last 0.5% of residual liquid remaining after crystallization of the Lunar Magma Ocean (LMO); they called this late-stage liquid urKREEP. However, the exact chemical composition of this urKREEP component has remained elusive. Neal & Taylor have hypothesized that a magma this late in its fractionation sequence (>99.5% crystallized) would have undergone silicate liquid immiscibility (SLI) [3]. Although glasses representative of immiscible melts have been known since the early days of Apollo [4], the importance of the occurrence of SLI has only recently been realized. The magma precursor to SLI is an Fe-rich, late-stage basaltic melt which has undergone extreme Fenner-trend fractionation [5]. As outlined by Roedder, this magma then reaches the threshold of miscibility [6] and splits into granitic (elevated K and Si, or K-fraction) and ferrobasaltic (elevated Fe, Ti, P, and REE, or REEP-fraction) liquids. The K-fraction commonly crystallizes as granite, whereas the REEP-fraction is largely dissipated into the crust as a metasomatizing agent [3].

In an effort to calculate the chemical composition of urKREEP, Neal & Taylor [3] have back-calculated the pre-SLI magma composition from glasses which represent known immiscible liquids on the moon. They have also back-calculated urKREEP from lunar granites by utilizing published liquid-liquid partition coefficients. Compositions calculated from both methods agree. This study continues the search for the elusive urKREEP composition by re-analyzing immiscible glasses from Apollo 14.

IMMISCIBLE GLASSES IN 14001,7003: An elegant study by Morris et al. [7] of samples 14001,7003,28.3 and 14001,7003,28.4 has revealed glasses which represent possible immiscible liquids. They have also presented electron microprobe analyses of these glasses. These samples are 2-4 mm in size and are wholly composed of granite clasts and brown to tan glass. The glasses occur as ropy coatings on the granitic portion and as schlieren and veins interstitial to the granitic clasts. The granitic clasts contain quartz and feldspar (up to 1 mm, but generally <0.4 mm) set in a colorless glass matrix. Angular grains of zircon occur (.04 to 0.06 mm) in the colorless glass. We report here SIMS analyses of the brown, colorless, and intermediate tan glasses from these sections. Using these new trace element data and the major element data of Morris et al. [7], we have calculated the pre-SLI composition for these immiscible liquids.

SIMS DATA: Morris et al. [7] suggested that the REE patterns (concave downward) of the brown glasses, as analyzed on an electron microprobe, indicated the fractionation of apatite and zircon. SIMS analyses of spots in the same glasses, however, do not indicate a concave downward pattern (Figure 1), but a pattern which is *indistinguishable from KREEP, albeit an order of magnitude greater in abundance*. REE patterns from the intermediate tan glasses are similar to the brown glasses, but are lower by a factor of 4-5 in abundances than the brown glasses.

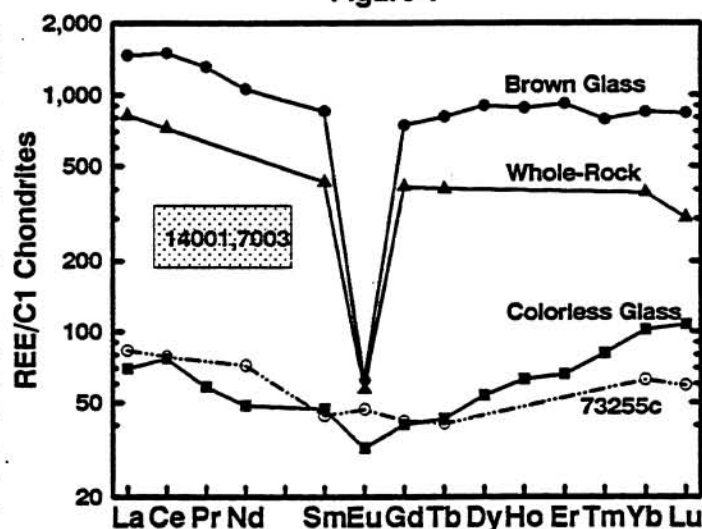
Analyses of the colorless glasses are equivocal. One sample has a pattern and abundances similar to the tan glasses; the other has much lower abundances of the REE ($La = 70\times$ chondrites), hints at a concave-upward pattern (particularly indicated in the very low $(Gd/Lu)_n$), and shows only a slight negative Eu anomaly. The REE pattern and abundances of this colorless glass are nearly indistinguishable from a lunar felsite, 73255c [8]. This

felsite has a major element composition which consists almost solely of SiO_2 , Al_2O_3 , and K_2O and has been interpreted as a product of silicate liquid immiscibility (SLI) by Blanchard & Budahn [8]. By analogy, our colorless glasses could be the K-frac produced by SLI as proposed by Neal & Taylor [6]. The brown glasses could represent the REEP-frac component of liquid immiscibility.

LIQUID-LIQUID ELEMENT PARTITIONING BEHAVIOR: Relative partitioning of elements indicates that these glasses may be explained by the K-frac/REEP-frac model of liquid immiscibility. Colorless glasses, which have the lowest Fe, Ti, P, Mg and the highest K, Na, and Si, also tend to have the lowest REE abundances. Brown glasses have the highest REE abundances by over an order of magnitude. Without exception, these partitionings are parallel to the experimental liquid-liquid data compiled by Neal & Taylor [9, and references therein].

Using the most evolved brown glass and the most primitive colorless glass (Figure 1), maximum liquid/liquid distribution coefficients can be calculated for this sample. These calculated distribution coefficients are given in Table 1, relative to those given in Neal and Taylor

Figure 1



K-FRAC & REEP-FRAC IMMISCIBLE LIQUIDS AT A-14: Snyder et al.

Table 1: Liquid-Liquid Partition Coefficients

	Dbg/cg ¹	Db/a ²	ave. ³
F	4.6		
Na	0.37	0.23-0.67	0.44
Mg	5.0	1.0-80.0	4.77
Si	0.74	0.50-0.81	0.64
P	5.8	3.8-35.6	10.8
K	0.30	0.01-0.46	0.45
Ca	3.1		
Sc	2.60		
Ti	4.1	2.01-9.00	4.21
V	5.48		
Cr	4.98	1.67-20.9	4.83
Mn	4.60	1.60-21.9	5.12
Fe	4.4	1.73-45.5	7.17
Co	4.89		
Ni	3.78		
Cu	19.45		
Zn	1.73		
Rb	0.56		
Sr	1.05		
Y	17.2		
Zr	2.83	1.17-3.77	2.44
Ba	0.54	0.49-1.50	0.49
Hf	1.99		
La	21.1	3.91-13.8	5.29
Sm	18.1	4.42	4.42
Eu	1.94		
Gd	18.4		
Yb	8.27	3.6-16.6	4.18
Lu	7.81	5.66	5.66

¹ A-14 brown glass/clear glass.² range in experimental D's.³ average of exp. D's.

[9]. Most of the liquid/liquid distribution coefficients fall within the ranges of partitioning data which were determined experimentally or taken from other natural lunar glass samples. However, sample 14001,7003 exhibits much higher basic/acidic glass partition coefficients for the REE than any other system from the literature [9](see Table 1, ranges).

BACK-CALCULATING PRE-SLI, urKREEP

MAGMA: Following the method outlined in Neal & Taylor [6], the composition of the pre-SLI magma which gave rise to the brown and colorless glasses may be calculated. This calculation assumes that the brown glasses (REEP-frac) and colorless glasses (K-frac) are produced in proportions of 80:20 during SLI of the parent magma [2]. The calculated pre-SLI magma has a composition similar to that calculated by Neal & Taylor from lunar granites [6] using two-liquid partition coefficients (Table 2). The pre-SLI melt calculated from Apollo 14 glasses has higher CaO, but both melts are roughly ferrobasaltic in composition. Trace elements for both calculated pre-SLI magmas are also distinctly similar. That pre-SLI magma compositions, calculated by different methods from vastly different samples, should achieve such similarity is telling. It would appear that we are converging on the true bulk composition of urKREEP.

CONCLUSIONS: The similarity in the conclusions of this study with other studies, in both the partitioning behavior of magmas which have undergone SLI and back-calculated pre-SLI (urKREEP?) magmas, indicates the uniformity and consistency of SLI in the differentiation of the upper mantle and crust of the moon. It is also evident that this process is pervasive in the upper portions of the moon. Most important is the understanding that REE-enrichment in lunar basalts and plutonic rocks is not necessarily accompanied by K-enrichment. In fact, the REE may be enhanced by orders of magnitude in a rock, without changing the bulk composition, by addition of a small proportion of the REEP-frac component of SLI.

Table 2: Back-Calculated Pre-SLI Magmas

	STC	N&T
SiO ₂	51.74	48.5
TiO ₂	2.55	2.42
Al ₂ O ₃	8.44	9.15
FeO	22.74	20.9
MgO	1.85	0.80
CaO	6.14	13.1
Na ₂ O	0.98	0.50
K ₂ O	1.92	3.10
P ₂ O ₅	1.50	1.53
Ba	1832	2645
La	290	271
Sm	106	74
Yb	115	98
Lu	18	19

REFERENCES: [1] Hubbard et al. (1971), *EPSL* 10, 341-350; [2] Warren & Wasson (1979), *Rev. Geophys. & Space Phys.* 17, 73-88; [3] Neal and Taylor (1989), *GCA* 53, 529-541; [4] Roedder & Weiblen (1970), *PLSC* 1, 801-837; [5] Hess et al. (1975), *PLSC* 6, 895-909; [6] Roedder (1978), *GCA* 42, 1597-1617; [7] Morris et al. (1990), *PLPSC* 20, 61-75; [8] Blanchard & Budahn (1979), *PLPSC* 10, 803-816; [9] Neal and Taylor (1989), *PLPSC* 19, 209-218.