

**ENIGMATIC MAJOR- AND TRACE-ELEMENT CHEMISTRY OF SOME KREEPY TO SUPER-KREEPY MG-RICH HIGHLAND ROCKS;** John G. CHAMBERS, Gregory A. SNYDER, Lawrence A. TAYLOR, Planetary Geosciences Inst., Dept. of Geol. Sci, Univ. of Tennessee, Knoxville, TN 37996; and Clive R. NEAL, Dept. of Earth Sciences, Univ. of Notre Dame, IN 46556

KREEPy (potassium-rare earth elements-phosphorous enriched) rocks are ubiquitous on the lunar near-side. This geochemical signature is understandable in highly evolved lithologies such as granite and quartz monzodiorites, but Mg-rich/KREEPy highland rocks provide a dichotomy with respect to primitive major- and evolved trace-element composition. The latter have been explained by metasomatism via a super-KREEPy melt or more likely a REEP-fraction liquid [a product of KREEP silicate-liquid-immiscibility (SLI)] [1]. Recent crystallization modelling by Jolliff et al. [2] has brought this hypothesis into question and favors equilibrium and/or step-wise equilibrium crystallization followed by autometasomatism. Our examination of this modelling demonstrates that several Mg-rich (MG# > 62) rocks were modeled using starting compositions that are 1-1.25 x high-K KREEP REE concentrations. Jolliff et al. [2] did not explain how a rock with MG# of 50-70 can contain such elevated REE abundances. It is plausible that metasomatism by, or assimilation of, a REE-enriched material is responsible for this relationship.

**Whitlockite Equilibrium Liquids (WEL)** - Whitlockite is a REE-bearing phosphate that is the major host for REE and P in KREEPy rocks. It contains 9-13 wt.% REE-oxides ( $10^4$ - $10^5$  x chondrites abundances). As such, whitlockites apparently crystallized from a melt rich in REE. Whitlockite REE mineral-melt partition coefficients ( $K_d$ 's) range from 5-20 and are a function of REE content and temperature [2-3]. Using  $K_d$ 's and whitlockite compositions, the REE concentration of whitlockite equilibrium liquids (WEL) were calculated by Neal and Taylor [3]. These liquids are 1-10 x richer in REE than the various proposed compositions of KREEP [4] and urKREEP [2]. Apparently melts more enriched in REE are required to produce the observed whitlockite compositions. However, Jolliff et al. [2] have brought this interpretation into question.

**SLI: Production of REEPy liquids** - The physical form of KREEP was likely a highly evolved Fe-rich/Si-poor residual melt formed by extreme fractional crystallization of the LMO. It is probable that some KREEPy liquids experienced SLI similar to that described by Roedder [5]. This phenomenon produces two liquids: one basic (Fe-rich/Si-poor) and the other acidic (K-rich/Si-rich) [5]. Evidence that SLI has occurred on the Moon is found as lunar granites (acidic portion) and ferrotroctolites (basic portion)[e.g., 1]. REE, P, and other high-field-strength elements partition strongly into the basic melt, and K preferentially enters the acidic melt. Therefore, the "KREEP" signature is effectively split into a "K-fraction" and a "REEP-fraction"[1]. The REEP-fraction is more REE-enriched than the original KREEPy liquid. In fact, proposed REEPy immiscible melts (i.e., REEP-frac) have REE abundances similar to WEL.

**Crystallization Models of Whitlockite** - Crystallization models have been used to counter the REEP-fraction metasomatism hypothesis [2]. These calculations attempted to produce the observed whitlockite compositions of various KREEPy highland lithologies by using the measured whole-rock chemistry, modal mineralogy, and REE partition coefficients as model parameters. While some of these rocks contain both evolved major- and trace-element compositions, others have relatively high MG# (>62) and evolved REE concentrations. Jolliff et al. [2] performed model calculations using REE concentrations 1-1.25 x high-K KREEP as the starting compositions of the Mg-rich samples. They did not address the issue of how a rock with MG# of 50-70 possesses REE concentrations 1-1.25 x high-K KREEP. Furthermore, REE concentrations 3-4 x high-K KREEP (i.e., super-KREEPy liquids) were used to model the evolved lithologies, thereby suggesting the necessity of super-KREEPy liquids to produce the REE content of the whitlockite grains in these rocks. It is likely that either metasomatism by, or assimilation of, a REE-enriched material is responsible for the primitive major- and evolved trace-element chemistry [4]. The composition of a metasomatic agent or assimilant, calculated from mass balance, would have super-KREEPy REE abundances. Apparently, liquids with REE contents higher than high-K KREEP are required to produce some of the observed lunar whitlockite compositions, and therefore, discarding the REEP-fraction metasomatism hypothesis may be unwarranted.

**Discussion of REEP-fraction Metasomatism** - In order to demonstrate the viability of a REEP-fraction metasomatic agent, a chondrite normalized REE plot (Figure 1) of the compositional field of WEL [3], high-K KREEP [4], urKREEP [1], and REEP-fraction liquids was constructed. The REEP-fraction REE content is

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governed by a liquid-liquid partition coefficient ( $D_{b/a} = C_b/C_a$ ), which is a strong function of phosphorous content of the original melt. As such, a range of REEP-fraction compositions is possible, and Figure 1 displays the low-P and high-P endmembers. For this calculation, we assumed that the average lunar granite composition represented the acidic or K-fraction elemental abundances (i.e.,  $C_a$ ). Various starting compositions of Jolliff et al. [2] are plotted for reference and

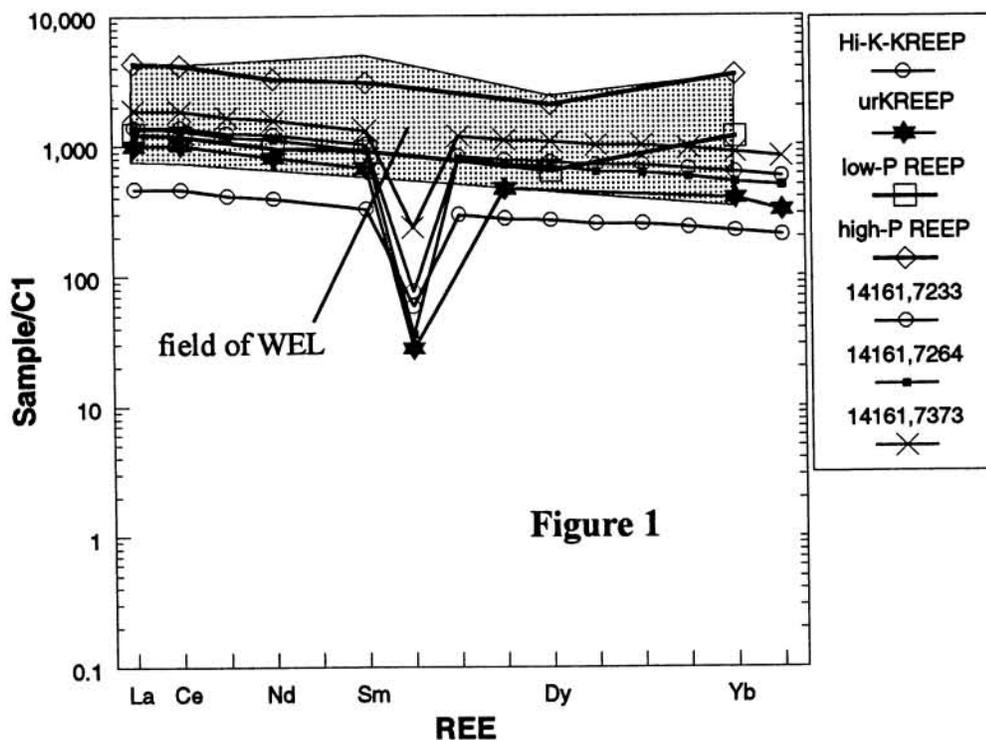


Figure 1

discussion. Several observations are important: 1) WEL are enriched in total REE as compared to the estimated composition of KREEP and urKREEP; 2) the calculated composition of low-P/high-P REEP-fraction liquids nearly encompass the range of WEL; and 3) some of the starting compositions of Jolliff et al. [2] plot within the field of WEL and therefore, within the range of the REEP-fraction liquids. This diagram illustrates that the REEP-fraction formed by KREEP immiscibility is a plausible parental liquid to the observed lunar whitlockite compositions. In addition to the evidence in Figure 1, Table 1 compares the abundances of other important elements such as Ti, K, Zr, and Hf calculated in the REEP-fraction with the various starting compositions of Jolliff et al. [2]. The composition of the REEP-fraction was calculated according to the method described above, with the average lunar granite [6] and estimated  $D_{b/a}$  values [7] provided in Table 1 as well. Note that the REEP-fraction concentrations of these elements are not unlike those of the whitlockite-bearing samples. The suggestion by Jolliff et al. [2] that super-KREEPY, or more likely "super-REEPY", melts are not required to produce many lunar whitlockites is questionable, as it is clear that some of the crystallization models have used super-KREEPY liquids as starting compositions (14161, 7233, 7264, 7373).

Table 1. Comparison of Ti, K, Zr, and Hf concentrations in calculated REEP-fractions and samples 14161, 7233, 7264, 7373<sup>§</sup>.

	Avg. granite <sup>†</sup>	$D_{b/a}$ <sup>‡</sup>	REEP	,7233	,7264	,7373
TiO <sub>2</sub>	0.78	4	3.1	4.52	2.49	1.8
K <sub>2</sub> O	4.44	0.55	1.5	3.4	1.08	0.64
ZrO <sub>2</sub>	0.17	2.4	0.41	0.55	0.28	0.97
Hf (ppm)	27	2	54	112	53	163

<sup>§</sup>from Jolliff et al. [2]; <sup>†</sup>Snyder et al. [6]; <sup>‡</sup>Snyder et al. [7].

abundances similar to the liquids in equilibrium with whitlockite. Therefore, we suggest that these postulated REEP-fractions are plausible parental liquids for lunar whitlockites.

**References** - [1] Neal and Taylor, 1989 *GCA*, v. 53, 529-41; [2] Jolliff et al., 1993 *GCA*, v. 57, 4069-94, [3] Neal and Taylor, 1989 *GCA*, v. 55 2695-80; [4] Warren, 1988 *LPITR*, 89-03, 149-53; [5] Roedder, 1978 *GCA*, v. 42, 1597-1617; [6] Snyder et al., 1995 *GCA*-in press; [7] Snyder et al., *GCA*, v. 57, 1143-1149.

**Conclusions** - Re-evaluation of various models attempting to explain the observed lunar whitlockite compositions supports the need for a super-KREEPY parental melt. Quantitative modelling of late-stage liquids is fraught with difficulty, including a paucity of reliable liquid-liquid  $K_d$ 's, a lack of experimental data on fractionation mechanisms and liquidus phases, and a lack of understanding of the physics of such extremely viscous liquids. However, using the limited partition-coefficient data set, we calculated elemental partitioning during KREEP silicate-liquid-immiscibility. This modelling indicates that the REEP-fraction has REE