Deposit Items 1: Treiman et al. AM-14-1011

Item 1a: Chemical and Compositions of Rocks and KREEP.

The data in Figure 2 of the main text comes from many sources, not all of which may be consistent and intercalibrated.

KREEP.

Elemental abundances of KREEP are taken as those of 'high-KREEP impact melt breccias," column 12 of Table 2 of Jolliff (1999), except for Cl and F which Jolliff did not report.

The abundance of F in KREEP is calculated to be ~660 ppm, or ~11 x CI from the average of two independent measures: the F/P ratios in several samples (Reed and Jovanovic 1973a), and the abundances of F, Be, and Li in KREEPy soil 14136 (Rose et al. 1972; Wänke et al. 1972, 1973; Dreibus et al. 1977; Meyer 2012). Both measures are consistent with a mass ratio F/La = ~1.0×10^{-2} x CI, or that KREEP (Jolliff 1999; La at 1270 x CI) contains ~660 ppm F.

The abundance of Cl in KREEP is calculated to be ~ 150 ppm from the ratio of abundances of non-leachable Cl (Cl*) and P in KREEPy samples (Reed et al. 1972; Reed and Jovanovic 1981). These data imply that KREEP has a mass ratio Cl*/P = 0.018; for KREEP with 8850 ppm of P (Jolliff 1999), Cl* is ~150 ppm. This value gives Cl*/La = ~2×10^{-3} x CI, which is approximately an order of magnitude smaller than F/La[CI] calculated above.

78155.

Elemental abundances in 78155 are the average of analyses compiled in the Lunar Sample Compendium (Meyer 2012), with F and Cl from Wänke et al. (1976).

What proportions of apatite and merrillite should KREEP contain?

Knowing the abundances of P, Cl, and F in KREEP, one can calculate the relative proportions of apatite and merrillite in KREEP-rich rocks and thus constrain the proportion of P that would remain in a source rock after it lost a metasomatic vapor like that invoked for 79215. The calculations above imply that KREEP had a molar ratio F/Cl of ~ 7.5, which is consistent with estimates of ~9 from bulk samples (Reed and Jovanovic 1973b), and ~6 from analyses apatite in KREEPy rocks (McCubbin et al. 2011)

The relative abundance of apatite and merrillite in KREEP can be derived from the assumptions that KREEP contains little H (McCubbin et al. 2011, 2012; Robinson et al. 2013), and that all of the F and Cl in KREEP is accommodated by apatite. The molar ratio [(Cl+F)/P] is derived from the mass ratio Cl/P = 0.018 in KREEP [Reed et al. 1972], which implies a molar ratio [Cl/P] = 0.016. From the above calculation the mass ratio F/P = 1100 ppm / 8850 ppm (using KREEP F as calculated above, and P from Jolliff 1999) implying a molar ratio [F/P] = 0.20. These values give a molar ratio [(F+Cl)/P] = 0.22. The stoichiometric formula for apatite is $Ca_5(PO_4)_3(F,Cl,OH)$, so each mole of F+Cl+OH is associated with 3 moles of P. Thus [(F+Cl)/P] = 0.22 implies that ~66% of the P (molar) in KREEP could be associated with F and Cl to make apatite, with the remaining 34% (molar) to make merrilllite (assuming no other phases that contain F or Cl, like amphibole, biotite, or scapolite).

Item 1b: Element Partition Coefficients.

If the phosphorus in 79215 was originally from a KREEP component in some source material, then it is crucial to understand how that P could become concentrated by an order of magnitude compared to other KREEP element (Fig. 2) This fractionation is especially problematic in that phosphate minerals will contain most of a rock's load of those elements (Treiman 1996). Thus, an understanding of the P enrichment in 79215 requires recognition of a process involving melts or fluids that can deposit apatite and significantly fractionate P from other KREEP elements.

It seems inevitable that a crystalline phase must be involved in fractionation of P from the other KREEP elements, as fluids lack the crystal chemical specificity required for such strong fractionations (Veksler et al. 2012). The fractionations seen in 79215 most likely involved merrillite and apatite, the two most common phosphate minerals in lunar rocks (Jolliff et al. 1993).

Chemical fractionations among merrillite, apatite, and melt appear to be consistent with the relative abundances the REE, U, and Th in 79215. Merrillite and apatite contain nearly the same proportion of P_2O_5, ~ 45% wt., but partition other KREEP elements differently. Jolliff et al. (1993) showed that the REE are strongly partitioned into merrillite over apatite, with a significant dependence on REE abundances. For instance, $^{Nd}D_{Merrillite/Apatite}$ ~70 for REE-poor merrillite, but only ~10 for REE-rich merrillite (Fig. 6 of Jolliff et al. 1993). Also, at merrillite-apatite equilibrium, merrillite is relatively enriched in the light REE (LREE) compared to apatite, e.g. $La/Yb_{merrillite/melt} > La/Yb_{apatite/melt}$, see Table EA2 (Jolliff et al. 1993).

Table EA 2. Trace Element Partition Coefficients

El or Ratio	$^{El}D_{Merrillite/Melt}$	$^{El}D_{Apatite/Melt}$	$^{El}D_{Merrillite/Apatite}$	Comment
Nd (≈Sm)	24 [1]	0.3 [1] 2 [2]	70 [1]	[1] Low REE
Yb, Lu	7 [1]	0.2 [1] 0.7 [2]	50 [1]	[1] Low REE
Nd (≈Sm)	9 [1]	0.75 [1]	12 [1]	[1] High REE
Yb, Lu	2.5 [1]	0.25 [1]	9 [1]	[1] High REE
Nd/Yb, Nd/Lu	3.5 [1]	3 [1]	1.3	[1] High REE
U	0.6 [4]	0.5 [2]	1 [2,4] 0.04 [3]	
Th	1.3 [4]	1 [2]	1.4 [2,4] 0.3 [3]	
Th/U	2.2 [4]	2 [2]	1.25 [2,4] 10 [3]	
U/Sm (≈2xU/Pu)	0.4 [4]	1 [1,2]	5 [1,4]	High REE

[1] Jolliff et al. (1993); from Figs. 6, 10, Tab. 8. [2] Prowatke and Klemme (2006), melt 71A (closest to a normal basalt). [3] Crozaz (1979). [4]Benjamin et al. (1980, 1983); Pu^{3+} behaves like a light rare earth element, with $^{Pu/Sm}D_{merrillite/melt} \approx 2$, Jones and Burnett (1987).

Table EA2 also lists the sparse (and not necessarily consistent) partition coefficients for U and Th among merrillite, apatite, and melt. Under metamorphic conditions, $^{U}D_{Merrillite/Apatite} \approx$ 0.04-0.09, $^{Th}D_{Merrillite/Apatite} \approx$ 0.3-0.8 and $^{Th/U}D_{Merrillite/Apatite} \approx 10$ (Crozaz 1979; Goreva and Burnett 2001; Terada et al. 2003). Benjamin et al. (1980, 1983) found $^{U}D_{Merrillite/Melt}$ ~ 0.6, and $^{Th}D_{Merrillite/Melt}$ ~ 1.3. However, Prowatke and Klemme (2006) found that actinide partitioning between apatite and melt depended strongly on melt composition, with $^{U}D_{Apatite\ /Melt}$ from 0.08 to 1.4, $^{Th}D_{Apatite/Melt}$ from 0.3 to 1.0, and $^{Th/U}D_{Apatite/Melt}$ from 0.9 to 12. These values are not consistent with the solid phase merrillite/apatite partitioning, again suggesting a strong control by silicate melt composition.

With these data, simple scenarios of merrillite fractionation appear consistent with the relative abundances of the REEs, U, Th, and P in 79215 (compared to KREEP). Consider a fluid or partial melt in source rock containing merrillite and apatite. The fluid or melt will contain more apatite component than merrillite, because apatites melt at lower T than merrillite (Tacker and Stormer 1993), and the presence of additional cations (like REE) stabilize merrillite. If all of the original apatite is dissolved into the fluid or melt, it will bear the geochemical signature of equilibration with merrillite in terms of $^{El}D_{Melt/Merrillite}$ or $^{El}D_{Fluid/Merrillite}$. When this fluid is removed from its source rock and enters a target rock (i.e., 79215), it will carry the geochemical signature of merrillite fractionation, i.e. overall low REE, HREE > LREE, and low Th/U.

These predictions are realized in 79215, if the source rock contained REE, Th, and U in the proportions of normal KREEP (Warren and Wasson 1979; Jolliff 1999). As seen in Figure 2b of the main text, 79215 has: low REE compared to P, Cl, and F; LREE/HREE less than in KREEP; and U/LREE and Th/LREE (i.e., La) greater than in KREEP; and U/Th greater than in KREEP. Thus, it is entirely reasonable that the relative abundances of P, REE, U, and Th in 79215 reflect merrillite fractionation.

Annex References

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