**THE ABUNDANCE AND ISOTOPIC SIGNATURE OF CHLORINE IN urKREEP: IMPLICATIONS FOR THE EARLY DEGASSING OF THE MOON.** J.W. Boyce[1], S. Kanee[2], F.M. McCubbin[1], J.J. Barnes[1], H. Bricker[2] and A.H. Treiman[3], [1]NASA – Johnson Space Center, 2101 NASA Parkway, Houston, TX, 77058 (jwboyce@alum.mit.edu), [2] Department of Earth, Planetary, and Space Sciences, UCLA, 595 CE Young Drive East, Los Angeles, CA, 90095-1567, [3] Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston, TX, 77058.

**Introduction:** Initially, the elevated $\delta^{37}Cl$ values of lunar materials were attributed to volcanic degassing [1]. However, chlorine isotope ratios of apatite in lunar mare basalts appear to reflect mixing between two reservoirs. One component, with elevated $\delta^{37}Cl \geq +25‰$ [2] may represent the urKREEP—the final product of the crystallization of the lunar magma ocean. The second component, with $\delta^{37}Cl \sim 0‰$, is inferred to represent either a mare basalt reservoir or meteoritic materials. The idea that high $\delta^{37}Cl$ is related to urKREEP suggests a global enrichment that occurred earlier in lunar history [2,3]. Here we test this urKREEP-mixing hypothesis more rigorously, and report the observed limits of the model. We then use the results to calculate the Cl content of the urKREEP component and use those results to update estimates of the bulk Cl content of the Moon. This allows us to speculate on the mechanisms of loss of Cl from the lunar magma ocean.

**Mixing model.** Ideally, one would use hyperbolic mixing relationships to constrain the isotopic composition of the two end members (in this case $\delta^{37}Cl_{mare}$ and $\delta^{37}Cl_{urKREEP}$) in addition to the elemental abundances ($Cl_{mare}$ and $Cl_{urKREEP}$, with the former representing the KREEP-free abundance in mare basalts, and the latter representing the Cl content of the urKREEP). However, this analysis requires knowledge of the Cl content of the basalts studied. This is a problem because the "gold standard" for magmatic volatile studies—melt inclusions—are of limited use for most mare basalts. And unfortunately, both of the alternative methods for constraining the Cl content of basalts are limited in their utility. One can analyze a bulk basalt for Cl ($Cl_{basalt}$), but the degassing accompanying eruption would almost certainly cause this value to be far less than that of the pre-eruptive basalt. Given that the extent of degassing before, during, and after eruption can be different for different magmas, it is unlikely that we would learn much from the bulk Cl abundances of mare basalt samples. Alternatively, we can use the Cl content of apatite to determine the Cl content of the melt from which it crystallized [8]. However, using the composition of apatite to infer the magmatic abundance of Cl requires knowledge of the F (and or H) content of the magma, which is rarely known with sufficient precision and accuracy to permit quantitative modeling. In addition, Cl abundances in apatite can be increased by fractionation of F [9] and decreased by

degassing, making interpretation difficult.

**Proxy-based mixing models.** The enrichment of all incompatible elements in urKREEP provides an alternative to using Cl abundances in bulk rocks or apatites to constrain $Cl_{mare}$ and $Cl_{urKREEP}$. We can use other elements (for which more robust bulk estimates



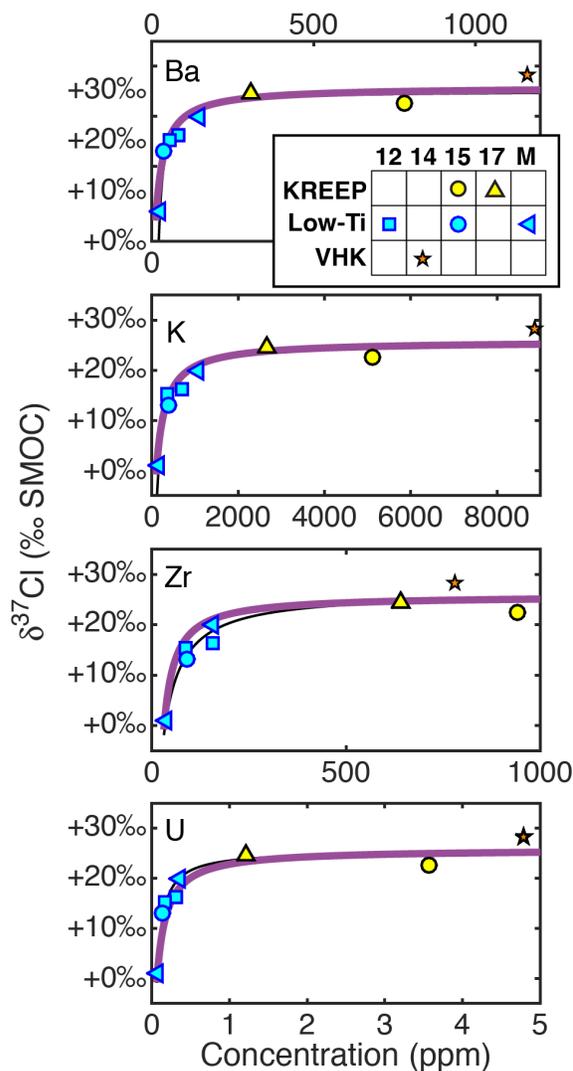**Figure 1 Relationship between $\delta^{37}Cl$ and trace elements of different geochemical affinities, for all low-Ti basalts, including those categorized as KREEP- or VHK-basalts [1-6]. Data are well-fit by mixing curves for individual elements (thin black curves) and for all element simultaneously (thick purple curves).**

are available) as proxies for Cl and build mixing models with those elements taking the place of Cl. Models constructed with proxies can constrain the isotopic composition of the two end members. However, because the ratios of the abundance of Cl to the abundances of various proxy elements (Cl/La, Cl/K, Cl/U, etc.) are not known *a priori* for any sample, we are limited to constraining the "enrichment factor", which is the ratio of the two end member Cl abundances ($Cl_{urKREEP}/Cl_{mare}$). With this simplification, the two-component mixing model requires only 3 variables: the isotopic compositions of the two end members ($\delta^{37}Cl_{mare}$ and $\delta^{37}Cl_{urKREEP}$), and the enrichment factor. The advantage of proxy-based models is that each proxy element provides an independent constraint on the 3 parameters, as well as serving as a test of the model's assumption that urKREEP is one of the end-members. As proxies for Cl, we use a geochemically diverse suite of elements: K, Ba, La, Lu, Th, U, Zr, and Hf that are all incompatible and enriched in urKREEP by factors of ~14 (K) to ~750 (Th and U) compared to their abundances in C.I. chondrites [5, 6].
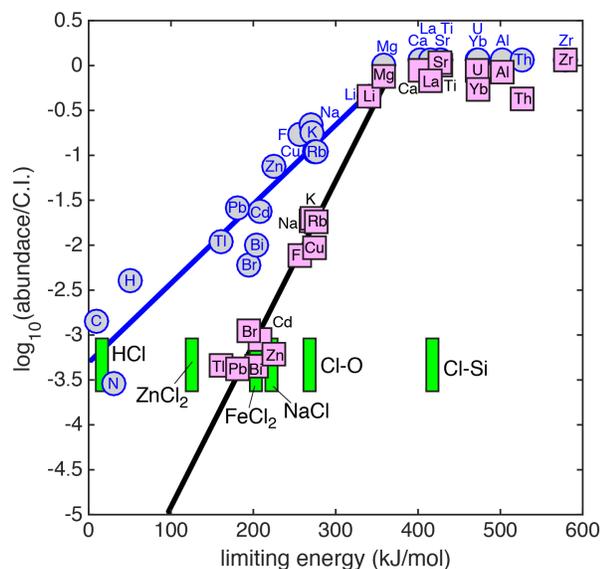


**Figure 2. Model abundances for the Earth (circles) and Moon (squares) normalized to C.I. chondrite, following [7], as a function of the energy that limits loss, which is either the bond energy of the element with a logical pair, or the heat of vaporization of a compound of the element. Green bars indicate the full range of values compatible with bulk Cl content for the Moon proposed here, for various species/bonds that might limit Cl loss. The trend for lunar depletion is consistent with loss being governed by mixtures of more volatile chlorides such as HCl and ZnCl₂ with more refractory species such as FeCl₂ and NaCl.**

**Results.** All of the proxy elements can be well-fit simultaneously for all low-Ti basalts (including VHK and KREEP-basalts), consistent with a single set of best fit parameters (purple curves, Fig. 1): $\delta^{37}Cl_{mare}$ = −0.8‰, $\delta^{37}Cl_{urKREEP}$ = +25.1‰, and $Cl_{urKREEP}/Cl_{mare}$ = 51. High-Ti basalts are not well fit by the model and are the focus of work in progress.

**Discussion.** This result confirms the hypothesis that elevated $\delta^{37}Cl$ in low-Ti basalts derives from the urKREEP reservoir, and also that there are two reservoirs of Cl involved in the generation of those basalts. The preservation of multiple, isotopically distinct reservoirs of Cl can be explained by: 1) development of both high-Cl, high-$\delta^{37}Cl$ and low-Cl, low-$\delta^{37}Cl$ reservoirs during the degassing and crystallization of the lunar magma ocean; 2) incomplete degassing pre- or syn-giant impact, with preservation of undegassed chondritic Cl and formation of an enriched and fractionated reservoir; 3) extensive degassing during early (pre- or syn-giant impact) accretion with extrinsic, low-$\delta^{37}Cl$ chlorine added to the Moon (e.g. late delivery of chondritic Cl.)

Chlorine is the least enriched highly incompatible element in the urKREEP—with Cl = 0.14 x C.I. This is ~5000 times less enriched than refractory incompatibles such as U and Th, and is consistent with extensive but incomplete loss of Cl taking place during or prior to the magma ocean phase. Robust minimum model bulk lunar Cl abundances of 0.7 ppm and 0.2 ppm—with and without Cl in the lunar mantle [10]—allows us to place Cl in the context of the rest of the elements of the periodic table, and suggests that Cl behaves as only a cosmochemically moderately volatile element during degassing. Abundance and isotopic constraints are consistent with Cl loss by vaporization of mixtures of HCl, ZnCl₂, FeCl₂, and NaCl (Fig. 2).

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