

**HALOGEN ISOTOPE GEOCHEMISTRY OF LUNAR MATERIALS.** A. M. Gargano<sup>1</sup>, Z. D. Sharp<sup>1</sup>, and C.K. Shearer<sup>2</sup> <sup>1</sup>Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, 87131 ([agargano@unm.edu](mailto:agargano@unm.edu)), <sup>2</sup>Institute of Meteoritics, University of New Mexico, Albuquerque, 87131.

**Introduction:** The Moon is depleted in volatile elements relative to the Earth due in part from vaporization and volatile loss throughout the Lunar Magma Ocean (LMO)[1, 2]. Additionally, lunar materials exhibit large ranges in chlorine isotope compositions ( $\delta^{37}\text{Cl}$ ) that are not observed on Earth, thought to result from the preferential loss of light isotopes to space ( $^{35}\text{Cl}$ )[3-6]. It would be expected that high  $\delta^{37}\text{Cl}$  values would be measured in materials with the lowest Cl concentration. Enigmatically, however, apatite geochemistry suggests that the Cl-poor lithologies (typically mare basalts) have the lowest range of  $\delta^{37}\text{Cl}$  values, whereas the Cl-rich lithologies (typically KREEPy) have the highest range in  $\delta^{37}\text{Cl}$  values [4-7]. Although the Cl isotope compositions are achievable by degassing following Rayleigh fractionation and Graham's law diffusion, such that the fractionation factor ( $\alpha$ ) is proportional to the ratios of the isotopologues of interest (i.e.  $\text{Fe}^{35}\text{Cl}_2/\text{Fe}^{37}\text{Cl}^{35}\text{Cl}$ ) this does not account for why the most Cl-rich lithologies have the highest  $\delta^{37}\text{Cl}$  values. The underlying assumption that is made, however, when discussing the  $\delta^{37}\text{Cl}$  values of lunar materials relative to their Cl concentrations is that all materials had the same initial Cl content. A more appropriate comparison may be the loss of light volatile elements relative to heavy ones of similar geochemical affinity (i.e. Cl/Br and Cl/I). We intend to address why the most Cl-rich lunar lithologies tend to exhibit the largest ranges in  $\delta^{37}\text{Cl}$  values by measuring the halogen contents and Cl isotope compositions of lunar materials.

**Samples and Methods:** We will report bulk halogen contents (F, Cl, Br and I) and Cl isotope compositions on a suite of lunar lithologies of both water-soluble chloride, and structurally-bound chloride in the following samples: 71546, 74275, 70255, 70215, 14053, 12018, 12063, 12054, 15016, 10017, 10020, and 10044. Our methodology follows that of Sharp et al. (2010) for Cl isotope measurements, and will be performed by pyrohydrolysis and Gas Source Mass Spectrometry with a Delta<sup>PLUS</sup>XL at the Center for Stable Isotopes at the University of New Mexico (UNM). Halogen concentration measurements will be performed by pyrohydrolysis followed by High Performance Liquid Chromatography (HPLC) at the Analytical Chemistry Lab at UNM. Both measurements will be performed from aliquots gathered from

a single sample preparation to account for intra sample heterogeneities.

**Modeling and Expected Outcomes:** It is assumed to a first approximation that the geochemical affinities of Cl, Br and I are identical, such that the fractionation of I and Br from Cl should result from degassing following Graham's law diffusion and Rayleigh fractionation. The initial Br/Cl, I/Cl ratio and  $\delta^{37}\text{Cl}$  value is assumed to be comparable to the Bulk-Silicate Earth. In Figure 1A changes in the Br/Cl, and I/Cl ratio are shown to change as Cl is lost to space. In Figure 1B we model the relationship between the chlorine isotope composition and the preferential loss of Cl from Br and I. We expect that  $\delta^{37}\text{Cl}$  values should correlate most strongly with  $[\text{I}]/[\text{Cl}]$ , and strongly with  $[\text{Br}]/[\text{Cl}]$  as the relative mass difference decreases.

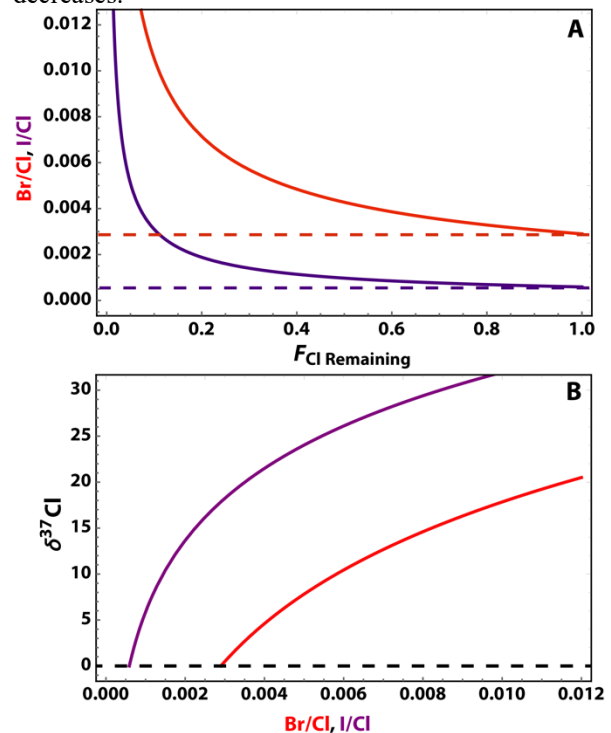


Figure 1: A) Br/Cl (red) and I/Cl (purple) modeled as a function of the fraction of Cl remaining assumed to follow Graham's law diffusion and Rayleigh fractionation. The initial ratios are shown as horizontal lines assumed to be comparable to BSE. B) A) The chlorine isotope composition is modeled as a function of changing Br/Cl and I/Cl assuming Graham's law diffusion and Rayleigh fractionation. The initial isotopic composition is shown as the black horizontal line.

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**References:** [1] Sossi A. and Fegley B. (2018) *Reviews in Mineralogy and Geochemistry* 84, 393-459. [2] Wood J.A. et al. (1970) *Geochimica et Cosmochimica Acta Supplement*, 1, 965. [3] Sharp Z.D. (2010) *Science* 329, 1050-1053. [4] Barnes J.J et al. (2016) *Earth and Planetary Science Letters*, 447, 84-94. [5] Boyce J.W. et al. (2015) *Science Advances* 1. [6] Tartèse R. et al. (2014) *Meteoritics & Planetary Science* 49, 2266-2289. [7] McCubbin F. et al. (2015) *American Mineralogist* 100, 1668-1707.