AN ANCIENT KREEP-POOR, CHLORINE-37-RICH SOURCE WITHIN THE MOON. Katharine L. Robinson[*,1,2] Kazuhide Nagashima[3], Gary R. Huss[3], G. Jeffrey Taylor[3], and David A. Kring[1,2]. [1]CLSE, Lunar and Planetary Institute, USRA, 3600 Bay Area Blvd., Houston, TX 77058. [2]NASA SSERVI. [3]HIGP, University of Hawaii at Manoa, 1680 East-West Rd., Honolulu, HI 96822. *robinson@lpi.usra.edu

Introduction: Lunar meteorite Miller Range (MIL) 13317 was initially classified as an anorthositic breccia, but subsequent studies revealed numerous low Ti basaltic fragments [1-3]. Recent work has shown these basaltic fragments represent some of the oldest volcanism on the Moon [2,4]. MIL 13317's basalts formed at 4.332 Ga (only ~38 Ma after the model age for crystallization of the Lunar Magma Ocean [4]), making them ideal samples for assessing volatiles associated with the Moon's earliest volcanic processes. Here, we present new data from a preliminary study of H and Cl isotopes in apatite in MIL 13317's ancient basalt (**Fig. 1**).
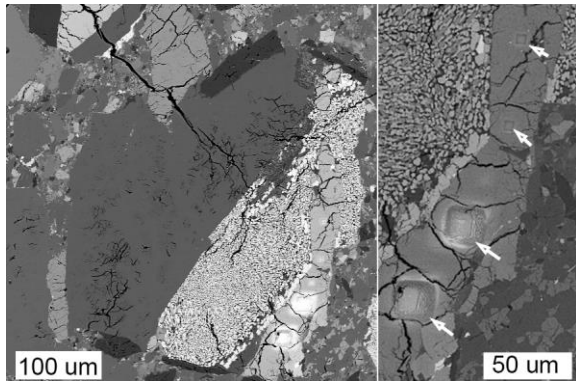

Fig. 1. Backscatter electron images of (left) Clast 2, a mesostasis region in MIL 13317,23, consisting of a large plagioclase bounded with symplectite, silica, and Cl-apatite, and (right) Apatite 2 with SIMS analysis pits indicated by arrows. The larger pits are from the H isotope measurements; smaller pits are from the Cl isotope measurements.

Methods: Apatite in MIL 13317,23 was identified via X-ray mapping with a FE-SEM at Johnson Space Center (JSC). Major-element data for apatite and surrounding silicate phases were then obtained with the JEOL 8530F electron microprobe at JSC. Apatite volatiles are not affected by electron-beam exposure under typical working conditions of 15 kV and 15 nA [5]. Silicates were measured with 20 nA beam current.

We developed two new protocols for the measurement of H and Cl `isotopes and abundances with the University of Hawaii Cameca ims-1280 ion microprobe. For H, a ~5 nA Cs^+ primary beam was rastered over a 25 μm square for presputtering and a 15 μm square for the measurement. Data collection was restricted with a field aperture to the inner ~4 μm of the 15 μm area. We measured H^-, D^-, and $^{18}O^-$, and constructed a $^1H/^{18}O$ vs. H_2O calibration curve using terrestrial apatite standards to determine the H_2O abundance of the apatite [6-7,22]. The same apatite stand-

ards were used to correct instrumental mass fractionation for D/H ratios. Our H_2O detection limit was ~3 ppm and the uncertainty on δD was ~±28 ‰ (2σ).

For Cl isotopes and abundance, a ~50 pA Cs^+ primary beam was rastered over a 8 μm square for presputtering and was reduced to a 5 μm square for the measurement. Using electronic gating, data collection was restricted to the inner ~3 μm of the 5 μm area. $^{35}Cl^-$ and $^{37}Cl^-$ were measured simultaneously on two electron multipliers. The mass resolving power was sufficent to resolve all molecular interference. Instrumental fractionation was corrected with terrestrial apatite standards [10,22]. Our Cl detection limit was < 1 ppm and uncertainties on δ37Cl ranged from < ±1 to ±3 ‰ (2σ).
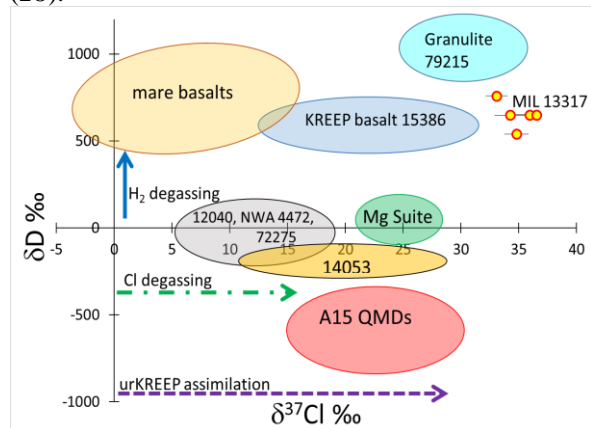

Fig.2. δD vs. δ37Cl of lunar apatite. Fields represent literature data [5-16], while the points represent the range of δD and δ37Cl found in MIL 13317,23 apatite. If there were more analyses of δ37Cl than δD, the average δD for all apatite in the sample was used.

Results and Discussion: Apatite in MIL 13317 Clast 2 is rich in H_2O (~2000 ppm) and elevated in δD (**Fig. 2**), which is consistent with existing data for lunar mare basalts (e.g., [5,6,12]). However, this same apatite grain contains over 8000 ppm Cl, with δ37Cl of +33 to +35 ‰ (**Fig. 2**). Additional Cl data for apatite grains in other areas of MIL 13317 too small to analyze for H have δ37Cl between +33 to +37 ‰. This is substantially elevated compared with δ37Cl in most mare basalt apatite, which contains < 4000 ppm Cl and has δ37Cl < 18 ‰ (**Fig. 2** [9,10]). Elevated δ37Cl values in lunar samples have been attributed to KREEP content [9,10,13], though vapor-phase metasomatism has been suggested as a way to cause extreme 37Cl enrichment observed in

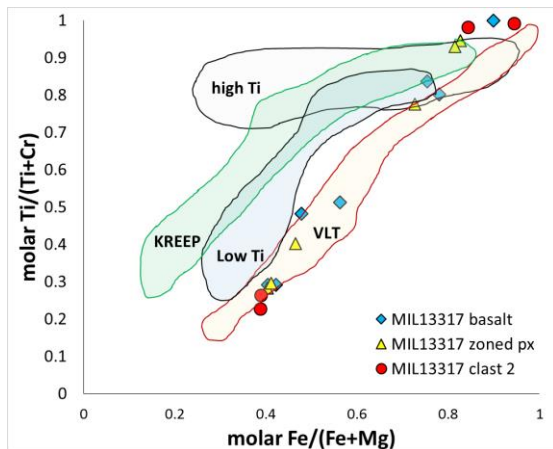apatite from granulite 79215 and a suite of Apollo 14 high-Al basalts [8,11].

Fig. 3. *Pyroxene molar Ti/Ti+Cr vs. molar Fe/Fe+Mg for classifying lunar basalt after [17], with KREEP basalt data from [18]. Pyroxene in MIL 13317,23 Clast 2 and other basaltic fragments is consistent with Apollo and Luna VLT basalt.*

We interpret Clast 2 as fragment of basalt too small to provide a representative sample of its bulk mineralogy (i.e., the clast is too rich in plagioclase and too poor in mafic minerals; **Fig.1**). The molar Ti/(Ti+Cr) versus molar Fe/(Fe+Mg) of pyroxene grains in Clast 2 suggests that the clast originated from a VLT basalt. Figure 3 compares the Ti# versus Fe# of MIL 13317 pyroxenes with Apollo mare and KREEP basalt data. The Fe# of pyroxene in Clast 2 is too high to be consistent with KREEP basalt. The range of Fe# and Ti# are consistent with pyroxene in texturally unambiguous, VLT basaltic fragments found in MIL 13317,23. The mineralogy of Clast 2 is consistent with mesostasis observed in basaltic fragments in multiple sections of MIL 13317 [1-4] (**Fig. 3**). Clast 2 may, therefore, represent a piece of mesostasis and plagioclase broken from a larger basaltic fragment during an impact event.

MIL 13317 seems to be KREEP-poor [1-4]. Typical KREEP-rich lithologies are rare in MIL 13317 [1-3]. Using $^{238}U/^{204}Pb$ ratios, Snape et al. [4] determined that while MIL 13317's source regolith may include some KREEP-bearing material, the mantle source of the ancient basalts was KREEP-poor. No evidence suggests the MIL 13317 basalts obtained their high $\delta^{37}Cl$ from KREEP.

Other potential mechanisms for enriching ^{37}Cl in MIL 13317 basalts include vapor-phase metasomatism [8,11] and magmatic degassing [11,19,20]. Vapor-phase metasomatism was hypothesized to explain elevated ^{37}Cl in granulite breccia 79215 [8] and five Apollo 14 high-Al basalts [11]. Granulite 79215 is unusual for its high abundance (~1%) of REE-poor apatite [8] and may not be a good comparison to MIL 13317 bas-

alts. The A14 high-Al basalts are a better petrologic comparison, but exhibit a much greater range of $\delta^{37}Cl$ (+15 to +40 ‰) than we have observed in MIL 13317 thus far. More measurements of apatite in MIL 13317 basalts are necessary to further assess any effect vapor-phase metasomatism may have had on their $\delta^{37}Cl$.

Magmatic degassing of metal chlorides from a melt can raise $\delta^{37}Cl$ significantly (**Fig. 2**) [19,20]. Degassing also greatly effects δD ratios as lighter H escapes and heavier D concentrates in the melt. The high δD values of mare basalt apatite are thought to reflect up to 95% degassing of H from their initial melts [12]. The high δD (>500 ‰) of apatite 2 in MIL 13317 and the basaltic nature of its source fragment indicates that degassing likely occurred, which could have increased $\delta^{37}Cl$ in the parental melt. However, degassing alone may not have caused the ^{37}Cl enrichment of MIL 13317 apatite. MIL 13317 apatite has $\delta^{37}Cl > ~30$ ‰, and degassing has been shown to increase $\delta^{37}Cl$ up to 20 ‰ after 95% Cl is lost [19,20]. In order to reach a $\delta^{37}Cl > 30$ ‰ through degassing, the parent melt to the MIL 13317 ancient basalts may have had an initial $\delta^{37}Cl$ greater than the estimated ~ 0 ‰ for Apollo mare basalts [20,21].

Conclusion: VLT basalts from MIL 13317 could represent an ancient, high ^{37}Cl reservoir in the lunar interior (possibly intermediate to Apollo mare basalt ($\delta^{37}Cl$ ~0 ‰) and urKREEP ($\delta^{37}Cl$ ~25 ‰) [21]), but further study is required to quantify the potentially confounding effects of vapor-phase metasomatism and/or magmatic degassing. If MIL 13317's elevated ^{37}Cl proves to be a primary signature, it may indicate we need to reassess the timing of Cl loss from the Lunar Magma Ocean, as well as the role of urKREEP in ^{37}Cl enrichment observed in lunar apatite [9,10,21].

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