

**VOLATILES IN HIGHLY EVOLVED LUNAR ROCKS: CONNECTING WATER AND CHLORINE.** K. L. Robinson<sup>1\*</sup>, J.J. Barnes<sup>1</sup>, M. Anand<sup>1,2</sup>, G.J. Taylor<sup>3</sup>, and I.A. Franchi<sup>1</sup>. <sup>1</sup>Dept. of Physical Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA UK. <sup>2</sup>Department of Earth Sciences, Natural History Museum, London, SW7 5BD, UK, <sup>3</sup>Hawaii Institute of Geophysics and Planetology, The University of Hawaii at Manoa, 96822 USA. \*katie.robinson@open.ac.uk

**Introduction:** As the only lunar mineral thus found to incorporate volatiles such as water and Cl, apatite [ $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$ ] is invaluable for investigating the volatile content of the Moon. Water in apatite has now been measured in most major lunar rock types [1-9]. Water (here used as shorthand for OH, H, and  $\text{H}_2\text{O}$ ) in the lunar interior seems to vary both by abundance (e.g. “wet” and “dry” reservoirs) and by H isotopic composition [6,10].

Chlorine is also an important lunar volatile. The range of ratios of  $^{37}\text{Cl}$  to  $^{35}\text{Cl}$  (usually expressed as  $\delta^{37}\text{Cl}$  relative to standard mean ocean chloride, SMOC) in the Moon has been found to be much larger than that of Earth ( $\sim -4$  to  $> +30$  ‰ versus  $\sim 0$  to  $+1$  ‰ in Earth’s mantle, [9,12-16]). The isotopic variation of Cl in lunar apatites has been used to argue for an anhydrous lunar mantle [12], but could also be related to the amount of KREEP component in lunar rocks rather than the presence (or absence) of water [16].

The quartz monzodiorites (QMDs) are highly evolved lunar rocks thought to have been formed intrusively through extensive fractional crystallization of a KREEP basaltic magma [10,17-18]. This intrusive origin makes them attractive for  $\text{H}_2\text{O}$  and H isotope studies as intrusive rocks, formed at depth and pressure, may have undergone less magmatic degassing (which fractionates H isotopes) than eruptive rocks such as the mare basalts [e.g. 4-5,7-8]. Previous work by Robinson et al. [10-11] on a set of QMDs from Apollo 15 showed that their apatites have extremely low (D-depleted) D/H ratios, which may represent a primitive H component in the lunar interior. Here, we present new data for the isotopic composition of Cl in apatite in these same samples, which may help clarify the sources and history of lunar volatiles.

**Samples and Methods:** We studied apatite in three QMD thin sections: 15404, 51 and -,55, and 15403, 71. Two apatite grains in 15404, 55 and one apatite in 15404, 51 had been previously measured for  $\text{H}_2\text{O}$  content and H-isotopic composition at the Open University (OU) and Univ. of Hawaii [10-11]. Two additional apatite crystals in 15404, 55 were measured for Cl in this study, one previously measured for OH content by McCubbin et al. [1]. Thin section 15403, 71 contains one large ( $< 400\mu\text{m}$ ) apatite grain that has also been previously measured for  $\text{H}_2\text{O}$  content and H-

isotopic composition at the Univ. of Hawaii. All of these apatite grains have extremely low  $\delta\text{D}$  values ( $\sim -440$  to  $-750$  ‰) [10-11].

Cl isotopes were measured using the OU Cameca NanoSIMS 50L following a similar protocol to those described in Tartèse et al. [9], and Barnes et al. [15]. A  $10 \times 10 \mu\text{m}$  area was pre-sputtered using a rastered  $\sim 30$  pA  $\text{Cs}^+$  beam. The beam was subsequently set to 15 pA and the raster to  $5 \times 5 \mu\text{m}$  for 9 minutes of analysis. Real time isotope imaging was used to ensure the area was free of cracks ( $\text{OH}^-$  hotspots) or other contamination prior to analysis. If a clean area of  $5 \times 5 \mu\text{m}$  could not be located, then the raster size was reduced to  $4 \times 4 \mu\text{m}$ . During the analysis,  $^{16}\text{O}^1\text{H}$ ,  $^{18}\text{O}$ ,  $^{35}\text{Cl}$ ,  $^{37}\text{Cl}$ , and  $^{40}\text{Ca}^{19}\text{F}$  were collected simultaneously on electron multipliers. Beam blanking was not used. We do not report  $\text{H}_2\text{O}$  data from these measurements, as apatite in all sections have been previously measured [10-11] and found to contain  $< 300$  ppm  $\text{H}_2\text{O}$ .

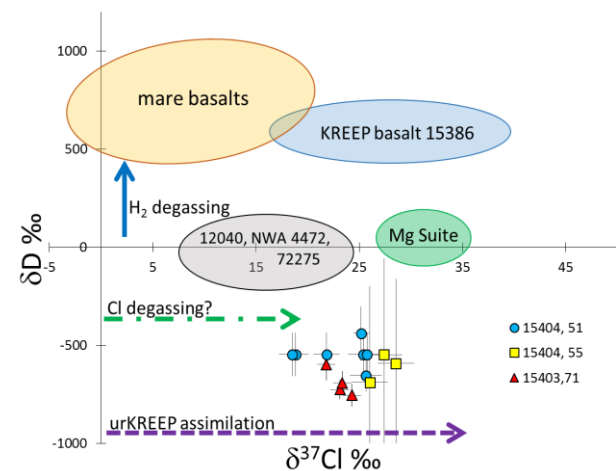


Fig. 1.  $\delta\text{D}$  value vs  $\delta^{37}\text{Cl}$  value of lunar apatites. The new data from this study are shown as points. If a  $\delta\text{D}$  value for a given apatite was not available, the average of all other apatite  $\delta\text{D}$  analyses in the same section was used. Literature data are represented by fields [4-5,7-9,12,15-16], and arrows indicate the effects of various processes that could have caused the observed H and Cl isotopic variations [4-5,7-8,15-16,19].

**Results:** Apatite grains in the QMDs studied here are very enriched in  $^{37}\text{Cl}$  with respect to Earth’s mantle,

which has a  $\delta^{37}\text{Cl}$  value of  $\sim 0$  ‰ [13] (Fig. 1). With respect to the Moon, they are enriched in the heavy  $^{37}\text{Cl}$  isotope and exhibit a relatively narrow range in  $\delta^{37}\text{Cl}$  values, from  $\sim +19$  to  $\sim +29$  ‰ (Fig. 1.). The uncertainties on these measurements was normally better than 2 ‰. There do not appear to be any systematic variations (such as zoning) within the grains studied here.

**Discussion:** Lunar samples have been shown to exhibit a large range in  $\delta^{37}\text{Cl}$  values [9,12,14-16], and an astonishing range in  $\delta\text{D}$  values (-750 to +1200 ‰) [2,4-11]. We compare the  $\delta\text{D}$  and  $\delta^{37}\text{Cl}$  values of lunar apatites in Fig. 1. Apatite in the mare basalts have elevated  $\delta\text{D}$  values [2,4,5] and display a large spread in  $\delta^{37}\text{Cl}$  values ( $\sim -4$  to  $+18$  ‰) [15-16], while KREEP basalt 15386 contains apatite with moderately elevated  $\delta\text{D}$  values [8] and a large spread in  $\delta^{37}\text{Cl}$  values [15]. Apatite, in mare basalt 12040, KREEP basalt 72275, and in KREEP basalt clasts from meteorite NWA 4472 have low  $\delta\text{D}$  values but moderately elevated  $\delta^{37}\text{Cl}$  values [8-9,12,16]. In addition, rocks from the magnesian suite have apatite characterized by low  $\delta\text{D}$  values and elevated  $\delta^{37}\text{Cl}$  values [7,15].

A number of processes may have affected the isotopic composition of H and Cl in mare magmas (Fig. 1). High  $\delta\text{D}$  values recorded by apatite in lunar basalts have been attributed to magmatic degassing of  $\text{H}_2$ , which likely enriched the residual melt in D [4-5,7-8]. Degassing of Cl in the form of metal chlorides may also have enriched basaltic melts in the heavier  $^{37}\text{Cl}$  isotope, causing isotopic fractionations of up to 20 ‰ [19].

On a wider scale, Cl degassing from the lunar magma ocean has been suggested to have caused the apparently elevated ( $\sim +30$  ‰)  $\delta^{37}\text{Cl}$  composition of urKREEP [15-16]. This argument is supported by the positive correlation between Cl isotopic composition and KREEP component (defined by incompatible trace element ratios) in lunar samples [15-16, 20, this meeting].

If the elevated  $\delta^{37}\text{Cl}$  values of apatite correspond to a greater amounts of KREEP component in the samples, then the Apollo 15 QMDs discussed here are interesting. The Cl isotopic composition of apatite in the QMDs (Fig. 1) are consistent with the compositions of apatite from other KREEP-rich samples [9,12,15]. This similarity in Cl isotopic composition makes it more difficult to reconcile the ultralow  $\delta\text{D}$  values of apatite in the QMDs [10-11], which are highly anomalous among lunar rocks. It appears that in the KREEPy parental melts to the QMDs, water and Cl were decoupled, and our results indicate that perhaps Cl and water were derived from different sources within the Moon.

**Conclusions:** The distribution in the lunar interior of both water and Cl is heterogeneous. Cl appears to be decoupled from water and related instead to urKREEP content, as proposed by [14]. The Apollo 15 QMDs contain very dry apatite ( $< 300$  ppm  $\text{H}_2\text{O}$ , [10-11]) and are high in KREEP content. They have correspondingly high  $\delta^{37}\text{Cl}$  values (Fig. 1). However, their anomalously low  $\delta\text{D}$  values (as low as  $-750$  ‰ [11]) cannot be explained by any of the processes (degassing, etc.) discussed so far and therefore, may indicate a unique source of H in the lunar interior.

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