

VOLATILES IN EVOLVED LUNAR ROCKS: CONNECTING WATER AND CHLORINE. K. L. Robinson^{1*}, J.J. Barnes¹, M. Anand^{1,2}, G.J. Taylor³, and I.A. Franchi¹. ¹DPS, The Open University, Walton Hall, Milton Keynes MK7 6AA UK. ²Dept. of Earth Sciences, Natural History Museum, London, SW7 5BD, UK, ³HIGP, The University of Hawaii at Manoa, 96822 USA. *katie.robinson@open.ac.uk

Introduction: Apatite [Ca₅(PO₄)₃(OH,F,Cl)] is a useful tracer for investigating the history of volatiles in the Moon. Hydrogen (typically reported in terms of equivalent H₂O or OH and referred to as ‘water’) in apatite has been measured in most major lunar rock types [1-9], and seems to vary both in terms of abundance (e.g. “wet” and “dry” reservoirs) and isotopic composition [6,10] in the lunar interior. Chlorine is also an important lunar volatile. The range of ratios of ³⁷Cl to ³⁵Cl (expressed as δ³⁷Cl relative to standard mean ocean chloride) in the Moon (~-4 to > +36 ‰) is much larger than that of Earth’s mantle (~0 to +1 ‰, [9,12-16]). Previous work by Robinson et al. [10-11] on a set of quartz monzodiorites (QMDs) from Apollo 15 showed that their apatites have extremely low D/H ratios, which may represent a primitive H component in the lunar interior. We present δ³⁷Cl data for 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. Apatite in these sections had been previously measured for H₂O content and δD at the Open University and Univ. of Hawaii [10-11]. All of these apatite grains have extremely low δD values (~ -440 to -750 ‰) and < 300 ppm H₂O [10-11]. Two additional apatite crystals in 15404, 55 were measured for Cl isotopes using the OU Cameca NanoSIMS 50L following an established protocol [9, 15].

Results and Discussion: Apatite grains in the QMDs studied here are very enriched in ³⁷Cl with respect to Earth’s mantle. They exhibit a relatively narrow range in δ³⁷Cl values, from ~ +19 to ~ +29 ‰. The uncertainties on these measurements was usually better than 2 ‰.

Lunar apatites exhibit a large range in δ³⁷Cl values (-4 to +36 ‰) [9,12,14-16], and an astonishing range in δD values (-750 to +1200 ‰) [2,4-11]. A number of processes may have affected the isotopic composition of H and Cl. High δD values recorded by apatite in lunar basalts have been attributed to magmatic degassing of H₂, 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 ³⁷Cl 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 (~+30 ‰) δ³⁷Cl 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].

The Cl isotopic composition of apatite in the QMDs studied here are consistent with the compositions of apatite from other KREEP-rich samples [9,12,15]. However, this similarity in Cl isotopic composition makes it more difficult to reconcile the ultralow δD 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 [10-11] and are high in KREEP content. They have correspondingly high δ³⁷Cl values. However, their anomalously low δD values (as low as -750 ‰ [11]) cannot be explained by any of the processes discussed so far and therefore, may indicate a unique source of H in the lunar interior.

References: [1] McCubbin, F. M. et al. (2010) *PNAS*, 107, 11223-11228. [2] Greenwood, J. P. et al. (2011) *Nat. Geosci.*, 4, 79-82. [3] Boyce J. W. et al. (2010) *Nature*, 466, 466-469. [4] Barnes J. J. et al. (2013) *Chem. Geol.*, 337-338, 48-55. [5] Tartèse R. et al. (2013) *GCA*, 122, 58-74. [6] Robinson K. L. and Taylor G. J. (2014) *Nat. Geosci.*, 7, 401-408. [7] Barnes J. J. et al. (2014) *EPSL*, 390, 244-252. [8] Tartèse R. et al. (2014) *Geology*, 42, 363-366. [9] Tartèse R. et al. (2014) *MaPS*, 49, 2266-2289. [10] Robinson K. L. et al. In review, *GCA* [11] Robinson K. L. et al. (2014) *LPS XLV*, Abstract #1607. [12] Sharp Z. D et al. (2010) *Science*, 329, 1050-1053. [13] Sharp Z. D. et al. (2013) *GCA*, 107, 189-204. [14] Treiman A. H. et al. (2014) *Am. Min.*, 99, 1860-1870. [15] Barnes J. J. et al. In revision, *EPSL*. [16] Boyce J. W. et al. (2015) *Sci. Adv.*, 1 (8), 1-8. [17] Ryder G. (1976) *EPSL*, 29, 255-268. [18] Ryder G. & Martinez R. R. (1991) *LPS XXI*, 127-150. [19] Ustunisik G. et al. (2015) *Am. Min.*, 100, 1717-1727. [20] Barnes J. J. et al. (2016) *LPS XLVII*, Abstract #1439.