

NON-CHONDRITIC VOLATILE SIGNATURES IN A UREILITE TRACHYANDESITE. J. J. Barnes^{1,2}, C. Goodrich³, F. M. McCubbin¹, A. Bischoff⁴, S. Decker⁵, and J. W. Boyce¹. ¹NASA Johnson Space Center, 2101 E NASA Pkwy, Houston, TX 77058, U.S.A, ²Lunar and Planetary Laboratory, University of Arizona, 1629 E University Blvd, Tucson, AZ 85721, U.S.A (jjbarnes@lpl.arizona.edu), ³Lunar and Planetary Institute, USRA, 3600 Bay Area Blvd, Houston, TX 77058, U.S.A, ⁴Institut für Planetologie, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany, and ⁵Decker Meteorite-Museum, Oberstraße 10a, 55430 Oberwesel, Germany.

Introduction: Chlorine is incompatible, moderately volatile, and hydrophilic making it an important tracer of hydrous activity and evaporation processes. Chlorine isotopes are relatively unfractionated among terrestrial rocks and most chondritic materials [1-2], although some negative values in chondrites may represent trapped Cl from the solar nebula [3-4] (Fig. 1). (Note: $\delta^{37}\text{Cl} = ((^{37}\text{Cl}/^{35}\text{Cl})_{\text{sample}}/^{37}\text{Cl}/^{35}\text{Cl}_{\text{SMOC}}) - 1) \times 1000$, where SMOC = standard mean ocean chloride). In the case of the Moon, degassing of Cl in the form of metal chlorides from the lunar magma ocean and subsequent mixing of Cl-rich (and high $\delta^{37}\text{Cl}$) and Cl-poor (and low $\delta^{37}\text{Cl}$) reservoirs is thought to have produced the range in Cl isotopes (Fig. 1) observed in lunar rocks [5-8]. Loss of metal chlorides from a magma ocean (MO) present on the howardite-eucrite-diogenite (HED) parent body may also have produced the range in Cl isotopes seen in the eucrites [9] (Fig. 1). Positively fractionated Cl isotope values may therefore be diagnostic of whether or not a planetary body, without plate tectonics, went through a MO phase. The ureilites are ultramafic rocks that likely represent mantle material, formed from the partial melting of a C-rich asteroid [10-12]. Importantly the ureilite parent body (UPB) never completely melted, and melts were likely extracted rapidly and fractionally in small veins and dikes [12-13] - i.e., the UPB never had a MO. In this study we investigated a lava derived from the UPB in order to test the Cl isotope fractionation model.

Sample & Methods: Asteroid 2008 TC₃ fell to Earth as the polymict ureilite Almahata Sitta (AhS) [14]. Among its clasts was a rock of trachyandesitic composition which is now referred to as ALM-A (e.g., [15]). This rock is mineralogically and chemically similar to the most abundant ureilitic melt lithology identified from feldspathic clasts in polymict ureilites [16-18], and is interpreted to represent the early, fractional melts of the UPB. We performed X-ray mapping of a thin section of the ALM-A lithology (MS-MU-035) using the JEOL 7600F scanning electron microscope at NASA's JSC in order to identify and characterize selected apatites. The JEOL 8530F electron microprobe at JSC was used to analyze the chemistry of the apatites, following the methods of [19].

Isotopic analyses were made using the CAMECA Nanoscale Secondary Ion Mass Spectrometer (Na-

noSIMS) 50L at JSC. The NanoSIMS was operated in multicollection mode, a Cs⁺ primary ion beam was used, and negative secondary ions were collected simultaneously in electron multipliers. Two protocols were used to analyze (1) H-isotopes and H₂O contents, and (2) Cl isotopes and Cl contents of ALM-A apatites (following the procedures of [6,20]). Well-characterized apatite reference materials were used to correct for instrumental mass fractionation of measured D/H and ³⁷Cl/³⁵Cl ratios, respectively, and for calibrating volatile abundances. In addition, the use of Cl-rich and Cl-poor reference materials allowed us to correct measured ³⁷Cl/³⁵Cl ratios for matrix-effects.

Results: The apatites in ALM-A are Cl-rich, and F- and OH-poor (Fig. 2). The apatites have $\delta^{37}\text{Cl}$ values averaging $\sim 4 \pm 1$ ‰ (2 SD) (Fig. 1). The apatites are H₂O-poor (containing <300 ppm H₂O) and have extremely fractionated δD values (where $\delta\text{D} = ((\text{D}/\text{H})_{\text{sample}}/(\text{D}/\text{H})_{\text{SMOW}}) - 1) \times 1000$, where SMOW = standard mean ocean water) of between 1500 and 2500 ‰.

Discussion: The chemical composition of the apatites in ALM-A are unusual. Notably the apatites contain less H₂O (as measured by NanoSIMS) than indicated from simply calculating the missing component of the X crystallographic site (i.e., $1 - \text{F} - \text{Cl} = \text{missing component}$). This could be due to structural changes associated with the high Cl contents that result in an oxy component in the apatite X-site or the presence of another X-site species like CO₃²⁻. The apatites in ALM-A have similar water contents to apatites in eucrites and ordinary chondrites (OCs), but they are more Cl-rich than those from other achondrites and less Cl-rich than apatites from most OCs (Fig. 2). We found that the apatites in ALM-A record notably non-chondritic Cl-isotope signatures being ~ 4 ‰ heavier than bulk analyses of most chondritic materials and unaltered terrestrial basalts (Fig. 1). Surprisingly, the $\delta^{37}\text{Cl}$ values for ALM-A lithology are in the range of values that have been measured in samples from the Moon, Mars, and eucrites (Fig. 1), even though the UPB never had a MO. The trachyandesite apatites also record highly fractionated H-isotopic compositions compared to terrestrial reservoirs (e.g., [21]) or apatites from eucrites [22-23]. These signatures are in the range of the bulk H-isotopic compositions of ordinary and Rumuruti chondrites (e.g., [24]).

The isotope systematics of volatiles in the ALM-A lithology are unique, especially for a sample derived from a parent body that did not pass through a MO phase. If the fractionated volatile signatures are not related to MO processing, then at what stage in the formation and evolution of the UPB were volatiles fractionated? The UPB is thought to have accreted ~0.5 to 0.6 Ma after calcium aluminum-rich inclusions (CAIs) (e.g., [25]). The trachyandesite ALM-A is dated to $\sim 5.3 \pm 3.4$ Ma after CAIs [26], and is therefore concurrent with formation of feldspathic clasts found in polymict ureilites, and pre-dates the catastrophic breakup of the UPB [12]. However, it remains unclear whether the age of feldspathic materials like ALM-A represent quenching age, due to the breakup, or a crystallization age. It is possible that the fractionated melt was generated earlier, and was extracted and emplaced in the crust where it sat perhaps for up to a couple of million years before being quenched during the disruption of the UPB [12-13]. The catastrophic breakup of the UPB has been implicated as fractionating the isotopes of Zn in the ureilites [27-28], but is not thought to be the cause of fractionated Zn isotopes in ALM-A [28]. Since ALM-A is lava, it is possible that the volatile features of this rock are related to magmatic processing during eruption and emplacement or secondary effects, rather than reflecting the isotopic signatures of the mantle source or the breakup of the UPB. Furthermore, H-isotopes systematics of ALM-A may be indicative of aqueous alteration on the UPB before partial melting of the ALM-A melt (e.g., [29]).

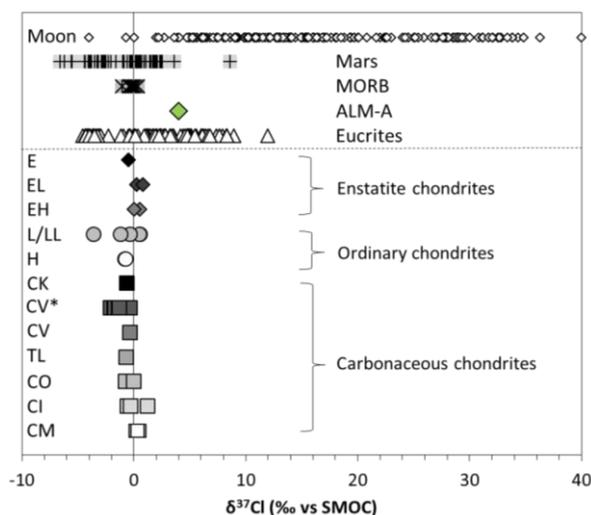


Figure 1. Chlorine isotopic compositions of meteorites, their components, and terrestrial mid-ocean ridge basalt (MORB) glasses. Data from this study for ALM-A and for other samples from [1-7,9,30-35].

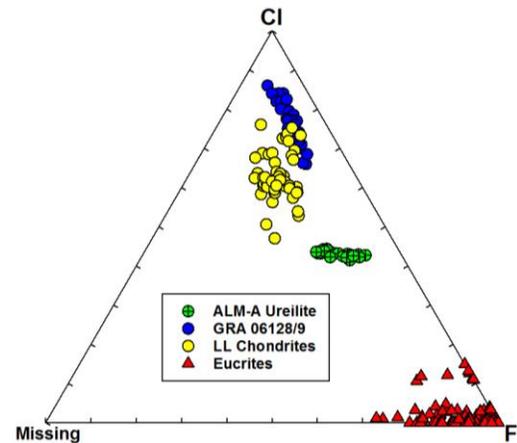


Figure 2. Apatite ternary diagram showing the compositions of apatites in ALM-A compared with apatites from chondrites and achondrites (after [36]).

Acknowledgements: J.J.B thanks NASA's post-doctoral program for a fellowship during which this research was conducted.

References: [1] Sharp Z. D. et al. (2007) *Nature*, 446, 1062-1065. [2] Sharp Z. D. et al. (2013) *GCA*, 107, 189-204. [3] Sharp Z. D. et al. (2016) *MaPS*, 51, 211-2126. [4] Williams J. T. et al. (2016) *MaPS*, 51, 2092-2110. [5] Boyce J. W. et al. (2015) *Sci. Adv.*, 1, e1500380. [6] Barnes J. J. et al. (2016) *EPSL*, 447, 84-94. [7] Boyce J. W. et al. (2018) *EPSL*, 500, 205-214. [8] Barnes J. J. et al. (2019) *GCA*, *In press*. [9] Sarafian A. R. et al. (2017) *EPSL*, 459, 311-319. [10] Goodrich C. A. (1992) *Meteoritics*, 27, 327-352. [11] Mittlefehldt D. W. et al. (1998) *RiM*, 36, 4-01-4-195. [12] Goodrich C. A. et al. (2015) *MaPS*, 50, 782-809. [13] Wilson L. et al. (2018) *GCA*, 72, 6154-6176. [14] Jenniskens P. et al. (2009) *Nature*, 458, 485-488. [15] Bischoff A. et al. (2014) *PNAS*, 111, 12689-12692. [16] Cohen B. et al. (2004) *GCA*, 68, 4249-4266. [17] Goodrich C. A. et al. (2004) *Chemie der Erde*, 64, 283-327. [18] Goodrich C. A. et al. (2017) *LPS* 48, #1196. [19] McCubbin F. M. et al. (2011) *GCA*, 75, 5073-5093. [20] Barnes J. J. et al. (2014) *EPSL*, 390, 244-252. [21] Lécuyer C. et al. (1998) *Chem. Geol.*, 145, 249-261. [22] Sarafian A. R. et al. (2014) *Science*, 346, 623-626. [23] Barrett T. J. et al. (2016) *MaPS*, 51, 1110-1124. [24] Alexander C. M. O'D. et al. (2012) *Science*, 337, 721-723. [25] Goodrich C. A. et al. (2010) *EPSL*, 295, 531-540. [26] Amelin Y. et al. (2015) *MetSoc* 78, #5344. [27] Moynier F. et al. (2010) *Chem. Geol.*, 276, 374-379. [28] Brugier Y-A. et al. (2019) *GCA*, 246, 450-460. [29] Sanders I. S. et al. (2017) *MaPS*, 52, 690-708. [30] Sharp Z. D. et al. (2010) *Science*, 1050-1053. [31] Tartèse R. et al. (2014) *MaPS*, 49, 2266-2289. [32] Treiman A. H. et al. (2014) *Am. Min.*, 99, 1860-1870. [33] Bellucci J. J. et al. (2017) *EPSL*, 458, 192-202. [34] Shearer C. K. et al. (2018) *GCA*, 234, 24-36. [35] Potts N. J. et al. (2018) *GCA*, 230, 46-59. [36] McCubbin F. M. and Jones R. H. (2015) *Elements*, 11, 183-188.