

**THE CHLORINE ISOTOPE COMPOSITION OF MARS.** Z. D. Sharp<sup>1</sup>, C. K. Shearer, Jr.<sup>2</sup>, C. B. Agee<sup>1,2</sup> and K. D. McKeegan<sup>3</sup>, <sup>1</sup>Dept. Earth & Planet. Sci, 200 Yale Blvd, Univ. of New Mexico, Albuquerque, NM 87131, zsharp@unm.edu, <sup>2</sup>Institute of Meteoritics, Univ. of New Mexico, Albuquerque, NM, 87131; <sup>3</sup>Dept. of Earth and Space Science, U.C.L.A., Los Angeles, CA, 90095.

**Introduction:** The uncertainties of abundance and distribution of some volatile elements in Mars exceed an order of magnitude. Taylor *et al.* [1] suggested that the K/Cl ratio of Mars is close to the chondritic value of 1.3, in contrast to earlier estimates of 0.08 [2]. Similarly, estimates for the water content of Mars vary widely. Some researchers have argued that water content of the martian mantle is similar to that of Earth [3, 4]; others have suggested that a majority of water was lost to space [5-7]. In addition, the mechanism of volatile delivery to Mars and Earth may have been very different. On the basis of dynamical models, Lunine *et al.* [8] proposed that water was delivered to Mars from asteroids and comets sourced from beyond 2.5 AU. Carr *et al.* [9] hypothesized that the difference in water contents of the Earth and martian mantle is related to differences in size and position. The Earth, larger and closer to the Sun, would have had a steam atmosphere that partially dissolved into the planet's interior. In contrast, the surface of Mars may have never melted, preventing the incorporation of water into the mantle. Stable isotope ratios have been used as evidence for massive loss of martian volatiles [e.g., 10]. Near-chondritic abundances of halogens coupled with H<sub>2</sub>O contents far below chondritic have important implications for the formation temperatures of Mars. In this work we use the chlorine isotope composition of martian meteorites in order to shed further light on the distribution of volatile elements of Mars. If martian volatiles were sourced farther out in the asteroid belt, and/or had different degrees of devolatilization, then they should have distinct  $\delta^{37}\text{Cl}$  values from those of Earth. If the Cl isotope values of martian samples show a great deal of scatter, as is seen on the Moon, a distinct degassing history would be indicated.

**Background information:** Chlorine isotope data are reported in the standard delta notation, where  $\delta^{37}\text{Cl} = (R_{\text{sa}}/R_{\text{std}} - 1) 1000$ ,  $R = {}^{37}\text{Cl}/{}^{35}\text{Cl}$  ratio of sample (*sa*) and standard (*std*). Samples are normalized to SMOC (Standard Mean Ocean Chloride) with a defined value of 0.0‰. It is now generally recognized that the major terrestrial reservoirs and carbonaceous chondrites span a narrow  $\delta^{37}\text{Cl}$  range of -1.0 to +0.5‰ [11]. Sodalite from Allende CAIs [11] and halite from Zag H3-6 breccia [12] fall at slightly lower values of -2 to -0.5‰ (Fig. 1).

Recently, we measured the chlorine isotope compositions of lunar materials [13]. In contrast to the

narrow range of the major Earth reservoirs and chondrites, the lunar values vary by over 24‰ (Fig. 1). We interpret these variations as a manifestation of an anhydrous lunar mantle. Volatilization of metal chlorides during degassing cause an enrichment of  ${}^{37}\text{Cl}$  in the residual rock. Indeed, the  $\delta^{37}\text{Cl}$  values of lunar materials are always higher than the typical range of terrestrial materials. On Earth, the volatile Cl species is always HCl, and because the bond strength of HCl is greater than for metal-chloride bonds, HCl preferentially incorporates  ${}^{37}\text{Cl}$  relative to  ${}^{35}\text{Cl}$ . This effect is offset by fractionation associated with simple volatilization in which the light isotope is preferentially incorporated in the vapor phase. Together, these two effects tend to cancel each other, so that fractionation during volatilization in a hydrous magma on Earth is minimal.

In this work, we use the same analytical approach we took for lunar materials. The  $\delta^{37}\text{Cl}$  values of leachate and residue are measured from bulk samples using conventional magnetic sector mass spectrometry at the University of New Mexico [14]. *In situ* ion microprobe analyses are made on the large radius UCLA Cameca 1270 ion microprobe using a Cs<sup>+</sup> primary beam. Ion beams for mass 35 and 37 are measured simultaneously on Faraday cups with equivalent count rates of 2 to  $5 \times 10^7$  cps for  ${}^{35}\text{Cl}$ . Two apatite standards have been developed for calibration: Durango apatite with a Cl concentration of 0.37 wt% Cl and a synthetic Cl-apatite from the University of Heidelberg with a concentration of 5.5 wt%. Precision of individual spot analyses ranged from 0.4‰ to 1.2‰.

**Results:** Our preliminary martian data show both similarities and differences from terrestrial  $\delta^{37}\text{Cl}$  data (Table 1). The bulk analyses average -0.4‰, indistinguishable from the major terrestrial reservoirs, primitive carbonaceous chondrites, and the lowest (primary) value for the Moon. This result suggests that the solar nebula reservoir for the inner planets had a homogeneous  $\delta^{37}\text{Cl}$  value and that volatile fractionation during planetary formation was minimal. The *in situ* apatite data have a larger range and correlate strongly with Cl content (note: standards do not correlate with Cl content). LAR 06319 is oxidized relative to depleted shergottites and is enriched in incompatible trace elements [15], which may indicate incorporation of martian crust. ALH84001 is the only sample with a positive  $\delta^{37}\text{Cl}$  value. It is also the oldest sample and may be recording the martian mantle prior to any late-en-

richment of volatiles during late bombardment. The 5‰ range for three apatite grains is greater than nearly all terrestrial mafic materials and unlike the Moon in that  $\delta^{37}\text{Cl}$  values significantly less than 0‰ are found. On Earth, mafic samples with anomalously low or high  $\delta^{37}\text{Cl}$  values are thought to represent contamination of crustal material, which may be similar to LAR 06319.

**References:** [1] J. G. Taylor, W. V. Boynton, S. M. McLennan, L. M. V. Martel, *Geophys. Res. Lett.*, 37 (2010). [2] H. Wänke, G. Dreibus, I. P. Wright, *Phil. Trans. R. Soc. Lond. A* 349, 285-293 (1994). [3] M. C. Johnson, M. J. Rutherford, P. C. Hess, *Geochim. Cosmochim. Acta* 55, 349-366 (1991). [4] H. Y. J. McSween *et al.*, *Nature* 409, 487-490 (2001). [5] B. M. Jakosky, *Rev. Geophys.* 35, 1-16 (1997). [6] G. Dreibus, H. Wänke, *Icarus* 71, 225-240 (1987). [7] H.

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**Table 1:**  $\delta^{37}\text{Cl}$  values for martian meteorites. *rk* = rock; *lch* = leachate.

Sample	Classification	$\delta^{37}\text{Cl}$ value in apatite using ion probe (SMOC)	wt% Cl in apatite
ALH84001	orthopyroxenite	+1.4±0.5, n=3	3.0
LAR 06319	shergottite, olivine basalt	-3.2±0.8, n=5	0.7
Chassigny	nakhlite, dunnite	+0.3±0.1, n=4; <i>ap</i>	2.1
		$\delta^{37}\text{Cl}$ value of bulk rock (SMOC)	ppm Cl
Los Angeles	shergottite, basalt	-0.3 <i>rk</i> ; -0.5 <i>lch</i>	115 <i>rk</i> ; 10 <i>lch</i>
Zagami	shergottite, basalt	-0.9 <i>rk</i> ; -0.4 <i>lch</i>	49 <i>rk</i> ; 28 <i>lch</i>
NWA 2975	shergottite, basalt	-0.1 <i>rk</i> ; -2.6* <i>lch</i>	24 <i>rk</i> ; 6 <i>lch</i>

\*Very small sample. Value has low precision.

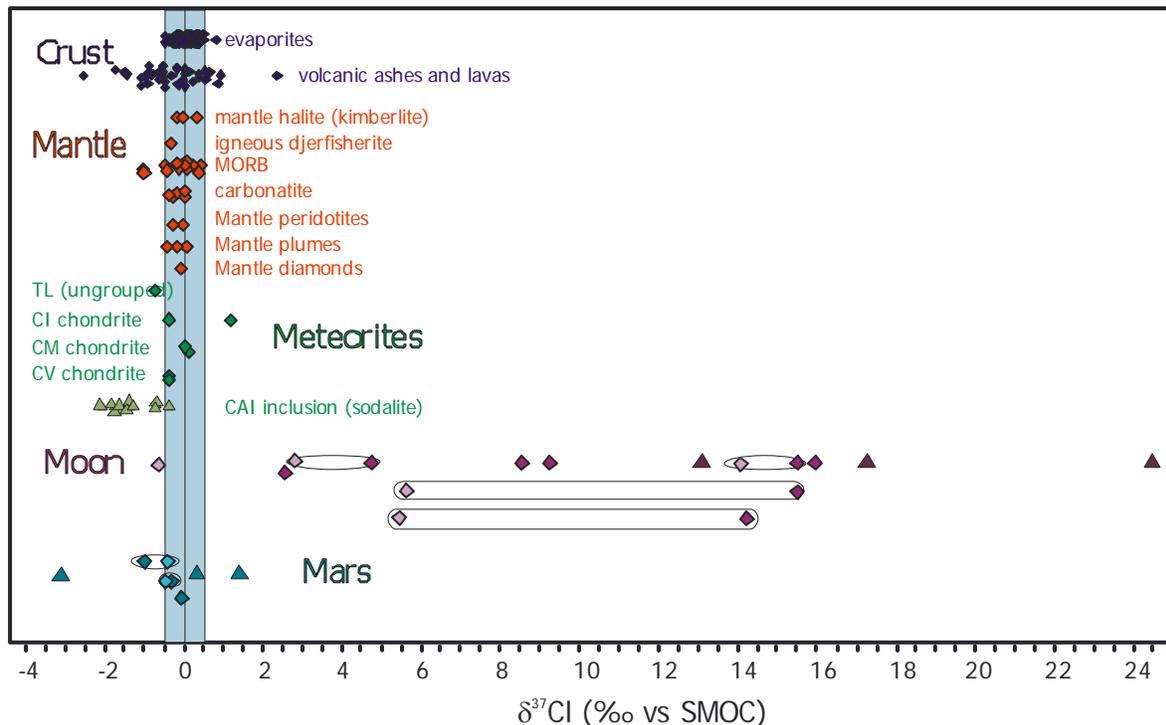


Fig. 1.  $\delta^{37}\text{Cl}$  values for selected Earth, Moon, chondrite and Mars samples. Data from [13] and this study. Diamonds – bulk analyses (light – leachate, dark – rock); triangles – apatites by ion probe.