

**ABUNDANCES OF CL, F, H, AND S IN APATITES FROM MARTIAN METEORITES.** M. B. Channon, J. W. Boyce, E. M. Stolper, and J. M. Eiler, California Institute of Technology, Pasadena, California 91125, USA. E-mail: mchannon@gps.caltech.edu.

**Introduction:** Magmatic volatiles (e.g., H<sub>2</sub>O, CO<sub>2</sub>, S, F, Cl, etc.) strongly influence igneous phase equilibria, eruptive behavior, atmospheric composition and, indirectly, climate. Several lines of evidence suggest that Mars is rich in chlorine and sulfur relative to Earth [1-2]. However, magmatic volatile abundances and their effects on magmatic processes on Mars remain unclear [3-5]. We report measurements of Cl, F, H, and S from SNC apatites in an effort to constrain the volatile abundances of martian magmas.

**Methods:** We measured the abundances of Cl, F, H (reported as H<sub>2</sub>O), and S in 23 apatite grains from 3 basaltic shergottites (JaH 479, NWA 856, and NWA 2986), 1 lherzolitic shergottite (NWA 1950), and 1 nakhlite (NWA 998) by SIMS using the Cameca 7f at Caltech. We also measured these same elements in 3 apatite grains from the basaltic shergottite Shergotty and 3 grains in the chassignite NWA 2737 using Caltech's NanoSIMS. The NanoSIMS was also used to generate elemental images of 5 grains (some that have spot analyses, and some that do not) from 1 basaltic shergottite (JaH 479) and 1 olivine-phyric shergottite (NWA 6710) in order to determine the homogeneity of apatite grains. We used 4 independently analyzed natural apatites (provided by F. McCubbin and colleagues) and synthetic fluorapatite and chlorapatite as standards. Another natural apatite was used as an intralaboratory standard. All spot analyses were made after making secondary ion images of carbon (typically associated with contaminants) to identify and avoid cracks. Additionally, the cracks were analyzed and compared to nominally crack-free samples to better recognize sample measurements that accidentally included cryptic crack-associated contaminants. Finally, we rejected any analyses in which measured H, Cl, and F summed to significantly greater than 1 atom per formula unit (i.e., were greater than possible in stoichiometric apatite). Fifteen analyses were rejected for one or more of these reasons.

**Results:** An example of the NanoSIMS images is shown in Figure 1, and all spot analyses are displayed in Figures 2 and 3.

**H<sub>2</sub>O:** Our new measurements of H<sub>2</sub>O contents of SNC apatites are similar to previous data, but the increased amount of data now available sheds light on systematic variations in H<sub>2</sub>O abundance by rock type (Figure 2). Apatites from the 4 basaltic shergottites measured here have 3180-8960 ppm H<sub>2</sub>O (literature data are 1800-6400 ppm [6-7]). Apatites from the lherzolitic shergottite contain 750-2840 ppm H<sub>2</sub>O; the only

other measurement of H<sub>2</sub>O in apatite from a lherzolitic shergottite is 4300 ppm [8]. Apatites from the nakhlite included in our study have 690-1110 ppm H<sub>2</sub>O; we are not aware of any other measurements of H<sub>2</sub>O in apatite from nakhlites. Apatites from the chassignite contain 1220-2490 ppm H<sub>2</sub>O; a previous study reports 2130 ppm for apatite from Chassigny [9]. Apatites from ALH 84001 contain 800 ppm [7] and 2210 ppm [9].

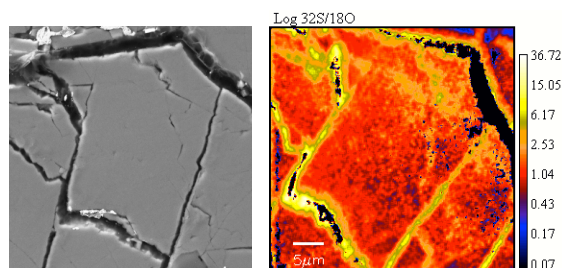


Figure 1. SEM image on the left and NanoSIMS image for S on the right of a region of an apatite from basaltic shergottite JaH 479. The spot analysis for this apatite was not performed on this region, but on a similar (yet larger), uncracked region nearby.

**Cl and F:** Cl and F measurements from this study agree with previous observations that SNC apatites have more Cl and less F than terrestrial igneous apatites (Figure 2).

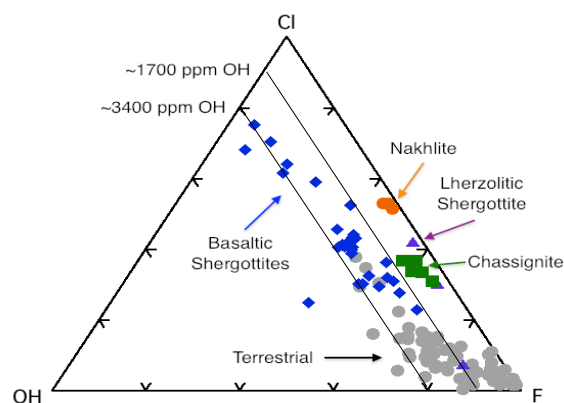


Figure 2. Apatite compositions from this study compared to terrestrial, igneous, mafic apatites. Data on terrestrial apatites come from GEOROC.

**S:** Sulfur in SNC apatites ranges from the detection limit (theoretically <10 ppm) to 2230 ppm; the few previous measurements range from 40 to 800 ppm [9-12]. As with H<sub>2</sub>O, S abundances are lower in apatites from the lherzolitic shergottite, nakhlite, and chassignite than in those from the basaltic shergottites (Figure 3). Figure

1 illustrates an example of the distribution of S in SNC apatite grains. It should be noted that the Cl, F, and H images do not illustrate any obvious zonation.

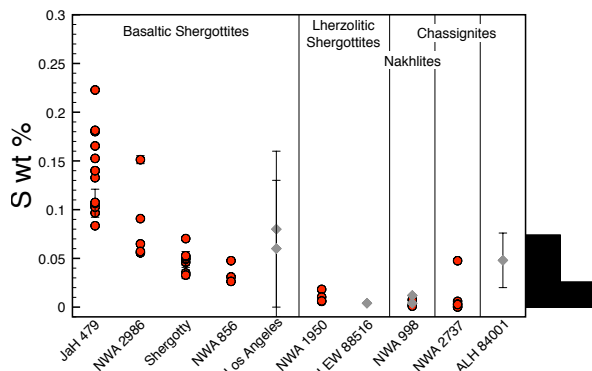


Figure 3. Data for sulfur in apatites from this study compared to published SNC data and terrestrial data. Red circles are from this study, grey triangles are previous SNC data, the histogram summarizes data for apatites from terrestrial mafic igneous rocks.

**Discussion:** Apatites in basaltic shergottites span a range of H<sub>2</sub>O contents similar to those from terrestrial mafic igneous rocks but are systematically enriched in H<sub>2</sub>O relative to those from other SNC lithologies, all of which are cumulates (Figure 2). The higher H<sub>2</sub>O contents of apatites from basaltic shergottites relative to other SNC rock types have several possible explanations, including higher water contents of their parent liquids; different extents of crystallization of the groundmass (or intercumulus melt) prior to apatite crystallization; or different degassing histories in extrusive or hypabyssal rocks compared to deeper intrusive rocks. Perhaps, slow cooling of deeper rocks permits redistribution of H<sub>2</sub>O (although it is important to note that low-H<sub>2</sub>O apatites in the SNC's are not accompanied by high F; a phenomenon observed in terrestrial apatites associated with loss of volatiles). If the H<sub>2</sub>O contents of apatites faithfully record the relative H<sub>2</sub>O contents of their parent magmas (but see [13] for possible complexities), the similarities between apatites in basaltic shergottites and terrestrial basalts could signify similar water contents in the sources of basalts on these two planets.

The high S contents in some of the basaltic shergottites are distinctive; these apatites are richer in S (by up to a factor of 3) than terrestrial basaltic apatites (Figure 3).

SNC apatites with the highest S contents are only found in basaltic shergottites, which could be a result of either higher oxygen fugacities (i.e., because high  $f_{O_2}$  supports high concentrations of sulfate, which is thought to be more compatible in apatite than reduced sulfur) or higher S abundances in their parent magmas. Of the basaltic shergottites from this study, we are only

aware of oxygen fugacities reported for Shergotty; -1.6 (using Eu anomalies in augite cores [14]), -1.17 (using Fe-Ti oxides [15]) and -0.92 (using the QUIF model [15])  $\Delta FMQ$ . An  $f_{O_2}$  of -1  $\Delta FMQ$  approaches the lower limit at which sulfate may be present in significant amounts. Because crystallization tends to increase  $f_{O_2}$  in the residual melt, and apatite is a late-stage crystallization phase, apatite may be crystallizing at a slightly higher  $f_{O_2}$  than determinations for the bulk rock. The other basaltic shergottites in this study are all enriched in incompatible elements, which, for the shergottites, is positively correlated with oxygen fugacity [16]. Thus, the other basaltic shergottites examined in this study were also plausibly high enough in  $f_{O_2}$  to support high dissolved sulfate contents.

**References:** [1] Clark B. C. and Baird A. K. (1979) *Journal of Geophysical Research*, 84, 8395-8403 [2] Dreibus G. and Wanke H. (1985) *Meteoritics*, 20, 367-381 [3] Gaillard F. and Scaillet B. (2009) *Earth and Planetary Science Letters*, 279, 34-43 [4] Righter K. et al. (2009) *Earth and Planetary Science Letters*, 288, 235-243 [5] King P. L. and McLennan S. M. (2010) *Elements*, 6, 107-112 [6] Leshin L. A. (2000) *Geophysical Research Letters*, 27, 2017-2020 [7] Greenwood J. P. et al. (2008) *Geophysical Research Letters*, 35, L05203 [8] Guan Y. et al. (2003) Abstract #1830 34<sup>th</sup> Lunar & Planetary Science Conference [9] Boctor N. Z. et al. (2003) *Geochimica et Cosmochimica Acta*, 67, 3971-3989 [9] Harvey R. P. et al. (1993) *Geochimica et Cosmochimica Acta*, 57, 4769-4783 [10] Xirouchakis D. et al. (2002) *Geochimica et Cosmochimica Acta*, 66, 1867-1880 [11] Greenwood J. P. et al. (2003) *Geochimica et Cosmochimica Acta*, 67, 2289-2298 [12] Treiman A. H. and Irving A. J. (2008) *Meteoritics & Planetary Science*, 43, 829-854 [13] Piccoli P. M. and Candela P. A. (2002) MSA, Reviews in Mineralogy, 48, p.255-287 [14] Wadhwa M. (2001) *Science* 291, 1527-1530 [15] Herd C. D. K. et al. (2001) *American Mineralogist*, 86, 1015-1024 [16] Herd C. D. K. (2003) *Meteoritics & Planetary Science*, 38, 1793-1805