

SULFUR SPECIATION IN LUNAR AND TERRESTRIAL APATITE. J. W. Boyce^{1,2}, C. Ma¹, J. M. Eiler¹, M. B. Baker¹, Y. Liu³, E. M. Stolper¹, L. A. Taylor³. ¹Division of Geological & Planetary Sciences, Caltech, 1200 E. California Blvd, Pasadena, CA 91125 *jwboyce@alum.mit.edu; ²Department of Earth & Space Sciences, UCLA; ³Department of Earth & Planetary Sciences, University of Tennessee, Knoxville, TN 37996.

Introduction: Apatites from some lunar basalts have hundreds of ppm of sulfur, comparable to terrestrial igneous apatites [1]. This is unexpected because apatite is commonly thought to incorporate sulfur only as S^{6+} substituting for P^{5+} [2]. Lunar magmas are generally thought to be too reducing to contain significant dissolved S^{6+} ; either this is not true of lunar melts that precipitate apatite, or S^{6+} is so strongly stabilized in apatite that melts in which S is dominantly present as S^{2-} can still precipitate S^{6+} -bearing apatite, or apatite has an additional substitution mechanism never previously observed in nature, such as S^{2-} ions occupying the halogen site [3].

To understand further the high-S contents of lunar apatites, we have performed measurements of the $K\alpha$ X-ray wavelength of sulfur in apatite using the Caltech JEOL 8200 electron microprobe. The $K\alpha$ X-ray wavelength is sensitive to the oxidation state of sulfur, so measurements of the sulfur peak position relative to S^{6+} and S^{2-} standards can be used to distinguish the relative proportions of the two species [4,5].

Materials: We analyzed apatite crystals from three sections of two paired samples: 14072,16, 14053,61, and 14053,241. These samples both have evidence for strong, late-stage reduction (e.g., production of Fe metal) [6-8], perhaps through reaction with solar wind implanted protons. We also analyzed: apatite from three lavas from Disko Island, Greenland, which contain metallic Fe [9,10]; synthetic apatite grown equilibrated with RGM-1 rhyolite melt + FeS in an Fe capsule at 1100°C and 1 GPa for ~48 hours; apatite from Durango, Mexico; and anhydrite and pyrite or troilite standards. We lack apatites with independently measured S speciation and so we cannot verify the accuracy of the $K\alpha$ method for measuring S^{6+}/S^{2-} ratios when applied to apatite. However, the relative abundances of S^{6+} and S^{2-} in the terrestrial samples analyzed to date matches expectations; i.e., Durango apatite is dominated by S^{6+} and the lunar and Disko Island apatites—although displaying a range—typically have higher ratios of reduced to oxidized sulfur (Fig. 2). Thus, it seems likely the method at least provides relative information about the S^{6+}/S^{2-} in apatite.

Analytical Methods: Given the 300–450 ppm S previously observed in lunar apatites, a 15 kV, 300nA beam was employed, at 2–60 s/step (with shorter count times for high-sulfur standards). The beam was defocused to 2–15 μ m (depending on grain size), and X-

rays were measured simultaneously using 3 or 4 PET crystals, including one large crystal and one in a high-yield position. Same-spot replicate analyses indicate that any electron-induced reduction of S^{6+} to S^{2-} due to prolonged exposure to the electron beam is less than a few percent on an absolute scale from 0–100% S^{2-} .

While every effort was made to avoid potential non-apatite sources of S, e.g., by avoiding cracks or grain boundaries, as well as neighboring sulfide minerals present in some samples, it is nevertheless possible that contamination from these or other sources affects some or all of our analyses. However, our results are consistent with previous ion-probe analyses of S abundance in these samples, and differences in oxidation state of S between samples seem to be reproducible).

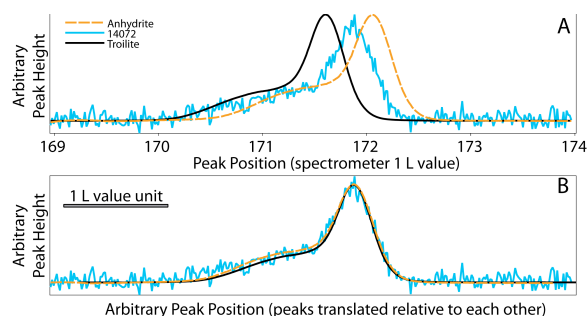


Figure 1. Sample $K\alpha$ spectra for anhydrite, troilite, and lunar apatite from 14072,16. Vertical scale is arbitrary intensity. (A). Peak position for lunar apatite relative to standards is distinctly intermediate (48% S^{2-}). (B). Peaks translated in L position such to facilitate comparison of shape. Slight change observed in height of minor peak relative to main peak does not affect peak-position fitting algorithms.

Data reduction: All raw spectra were corrected for non-linear background contributions. Comparisons of peak positions for spectra before and after background correction indicate that the correction does not significantly alter the peak position, even for low-S peaks.

Peak positions. Peak position was determined relative to anhydrite and troilite/pyrite in two ways: First, a “fractional peak height” position was determined by averaging the spectral positions of the two points with 50% of the intensity of the highest value in the main peak. This method regularly fails for low-S samples, in which low-intensity peaks where side-walls are do not increase or decrease steeply and monotonically. In the second method, the sulfur spectrum of the unknown was translated relative to a standard until the misfit of the overlapping sections of the unknown and standard

curves was minimized. This “best-fit” shift is the value of the peak shift between the standard and the unknown. Repeating the exercise with the two standards (one with 100% S^{6+} and one with 100% S^{2-}) allows speciations to be determined. The two peak-fitting methods agree well, with comparisons yielding $r^2 > 0.98$ for all four spectrometers.

Peak shifts relative to anhydrite and troilite were converted to speciation on a linearly proportional scale from 0–100% S^{2-} following previous workers [4,5]. Reproducibilities vary considerably; anhydrite and troilite are reproducible to 1–10% 2σ within a single session. Lower sulfur contents of apatites result in poorer reproducibility, ranging from 3–85% (2σ).

Sulfur concentrations. We used the background-corrected peak heights relative to peak heights of Durango apatite to determine S concentrations for each analysis, assuming 1480 ppm S in Durango apatite [2].

Results: Each spectrometer (3 or 4 per spot) yielded an independent estimate of both speciation and concentration. Obviously spurious measurements were discarded if they strongly disagreed with the others; i.e., if the 2σ of the range decreased by 50% or more after culling.

Sulfur concentrations. Lunar apatites measured in this study have sulfur concentrations ranging from 180–2000 ppm S (N=15), with all but one in the 180–720 ppm S range (Fig. 2). Eleven analyses of apatites from Disko Island lavas yielded a bimodal distribution of apparent S concentrations—from 50 to 2700 ppm (N=5) and from 5 to above 50 wt. % (N=6). The population with S contents ≥ 5 wt. % is interpreted to result from overlap of the electron beam with neighboring sulfide material. This interpretation is supported by the sulfur speciation of those analyses, which are within error of 100% S^{2-} . It is still possible, however, that the lower concentration analyses could also be affected by contamination.

The synthetic apatites are $<10 \mu\text{m}$ in diameter and difficult to analyze without encountering neighboring FeS or sulfide-bearing melt. However, one analysis apparently unaffected by external sulfide contamination yielded a concentration of 125 ppm S, comparable to the lower range of concentrations observed in Disko Island and lunar apatites.

Sulfur speciation. As lunar, synthetic, and Disko Island apatites generally have low sulfur concentrations, their peak positions are difficult to determine precisely, and they have poor reproducibility.

As mentioned above, Disko Island apatites may be variably contaminated by signal from nearby sulfides. Only two of the analyses with low S (the points with ~ 440 and ~ 560 ppm S in Fig. 2) yield a reasonably

well-constrained determination of speciation ($76 \pm 7\%$ and $105 \pm 33 S^{2-}$).

Sulfur speciation in lunar apatites is consistent with the presence of both S^{2-} and S^{6+} in most of the lunar samples. Taken at face value, these results confirm the speculation of Boyce et al. [1] that there is sulfide-bearing apatite component in apatite from highly reducing environments, most likely as S^{2-} substituting in the halogen site. Although not previously observed in nature, $\text{Ca}_{10}(\text{PO}_4)_6\text{S}$ apatite has been synthesized [3].

We also note a weak negative correlation ($r^2 =$

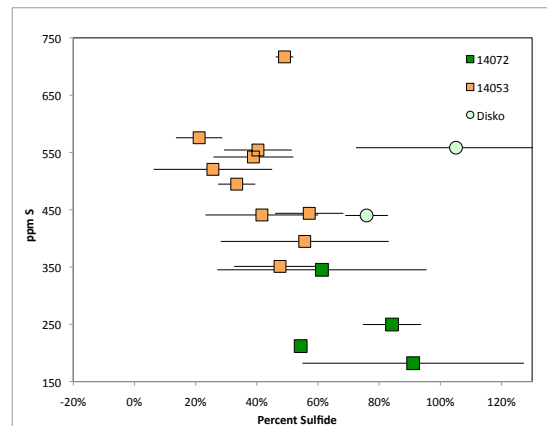


Figure 2. Sulfur concentration versus speciation for the lunar apatites that show the least evidence for extraneous signal due to neighboring sulfides. Each spot represents the mean of measurements of the same spot by multiple spectrometers, with error bars representing 2σ reproducibility.

0.53) between % S^{2-} and total S concentration for the lunar apatites, consistent with apatite-melt partition coefficients for S^{6+} being larger than for S^{2-} . The apparent presence of lunar apatite with S^{6+} as the dominant S-bearing species (i.e., those at the upper left of Fig. 2) could be evidence that, despite the generally reduced conditions of lunar petrogenesis, either there are late-stage residues of fractional crystallization in the mesostasis of lunar basalts or other processes (e.g., shock, deuteric alteration) that can lead to locally oxidized conditions.

References: [1] Boyce, J.W., et al., (2010) *Nature*, 466, 466-469. [2] Peng, G. et al., (1997) *Am Min*, 82, 1210-1224. [3] Henning, P. et al., (2000) *Z. Krist*, 215, 226-230. [4] Carroll, M.R. and Rutherford M.C., (1988) *Am Min*, 73, 845-849. [5] Rowe, M. et al., (2007) *Chem Geo*, 236, 303-322. [6] El Goresy, A. et al. (1971) *EPSL*, 13, 121-129. [7] El Goresy, A. et al. (1972) *LPSC III*, 1, 333-349. [8] Taylor, L. A. et al. (2004), *Am Min*, 89, 1617-1624. [9] Goodrich, C.A., (1984) *LPSC XV*, 15, 312. [10] Melson, W. and Switzer G., (1966) *Am Min*, 51, 664-676.