ELECTRON BEAM DAMAGE IN APATITE: LIMITATIONS FOR SKα MEASUREMENTS OF $S^{6+}/\sum S$.

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Introduction: In magmatic systems, the availability of excess oxygen that can react with multivalent elements such as Fe and S to change their charge (oxidation of Fe^{2+} to Fe^{3+} or reduction of S^{6+} to S^{2-}) is characterized by a parameter called the oxygen fugacity (fO_2). The fO_2 controls the availability of these ions and consequently the minerals—and the chemistry of those minerals—that crystallize from a melt. Mineral mode and chemistry control how magmas evolve, and given that fO_2 varies by many orders of magnitude on different planets [2], understanding the fO_2 of a magma is critical to relating observations about a magma to the body on which it forms.

The mineral apatite was long thought to only incorporate S^{6+} in a coupled substitution for P^{5+}, but recently natural apatites with S^{2-} were identified in lunar mare basalts that crystallized at low fO_2 [3]. This suggests that apatite can be used as a monitor of fO_2 assuming that one can 1) measure $S^{6+}/\sum S$ (S^{6+} over total sulfur), and 2) determine some partitioning relationship between apatite and melt for S^{6+} and S^{2-}.

The most common method for measuring $S^{6+}/\sum S$ is X-ray Absorption Near-Edge Spectroscopy (XANES), but given the limited access to synchrotron facilities, it is wise to explore the potential of other methods for measuring $S^{6+}/\sum S$. One such possible method relies upon the shift in energy of the sulfur K-α peak on the electron microprobe. However, apatite is subject to well-documented beam damage [4, 5], so it is necessary to evaluate under what conditions can reliable $S^{6+}/\sum S$ be determined using this method.

Methodology: We performed a series of measurements of $S^{6+}/\sum S$ on natural and synthetic apatites at the NASA Johnson Space Center.

Methodology. The JEOL 8530F field emission electron probe at NASA-Johnson Space Center was used to acquire WDS scans over the S peak centroid in various apatite grains and standards, in order to attempt to constrain the S speciation in apatite. The S peak centroid shifts by ~ 1.5 eV between sulfate (here measured on celestite – $SrSO_4$) and sulfide (measured on troilite - FeS). This shift is readily determined on PET crystals in the electron probe. This method has been used by [6] to determine sulfur speciation in natural basaltic glasses at abundance levels of 650 to 2450 ppm. We experimented with a variety of beam currents, from 20 nA to 150 nA, with the beam defocused to 20 microns in diameter, to assess the extent of beam damage and the effects of damage on the apparent S speciation. Higher currents are desirable to improve the count rate, but often result in significant beam damage. The peak centroid was determined by scanning over a limited range of spectrometer motion, only in the near-centroid region, which enabled the detection of the peak position, but also allowed for efficient measurements, without prolonging the time of exposure of samples to electron beam. We routinely re-measured celestite and troilite during these runs, in order to show that peak positions in these sulfur-rich standards were not shifting due to drift in the lab environment. Peak centroids were determined after subtracting backgrounds.

Materials. We analyzed four different apatites as “unknowns”: two synthetic and two natural. The two synthetics are an S^{2-}-rich (AP25) and S^{6+}-rich (AP26) apatite, grown with salt-flux methods modeled on the work of Prener [7]. The natural apatites are two from Cerro de Mercado, Durango, Mexico, dominated by S^{6+} [8]. One is a commercial electron probe standard provided by Geller, Inc, while the other is an internal standard purchased on the internet.

Results: Average apparent speciation values for two spectrometers are shown in Figure 1. Peak positions of troilite and anhydrite are reproducible within 10% S^{6+}/TS, though we did not make observations at higher current, so this is a minimum uncertainty.

Synthetic apatites. Synthetic S^{6+}-rich apatite peak positions show a general trend towards lower S^{6+}/TS with increasing current (Figure 1), consistent with a simple model of reduction of S^{6+} due to the addition of electrons. Below 50nA the trend is no longer obvious, possibly because the signal/noise ratio is too small at low currents. Synthetic S^{2-}-rich apatites do plot with lower S^{6+}/TS, but not nearly as low as expected for an apatite dominated by S^{2-} (S^{6+}/TS ~ 0). As beam currents increase, S^{6+}/TS is observed to increase slightly, nearly converging with the S^{6+}-rich synthetic apatite.

Natural apatites. The S^{6+}-rich JSC Durango apatite behaves much like the synthetic S^{6+}-rich apatite. We observe slightly decreasing S^{6+}/TS (from ~80% to ~70 S^{6+}/TS) with increasing current, a trend that is linear over the entire range of currents explored in this study (20-150nA). The apatite purchased from Geller behaves quite differently despite supposedly being from

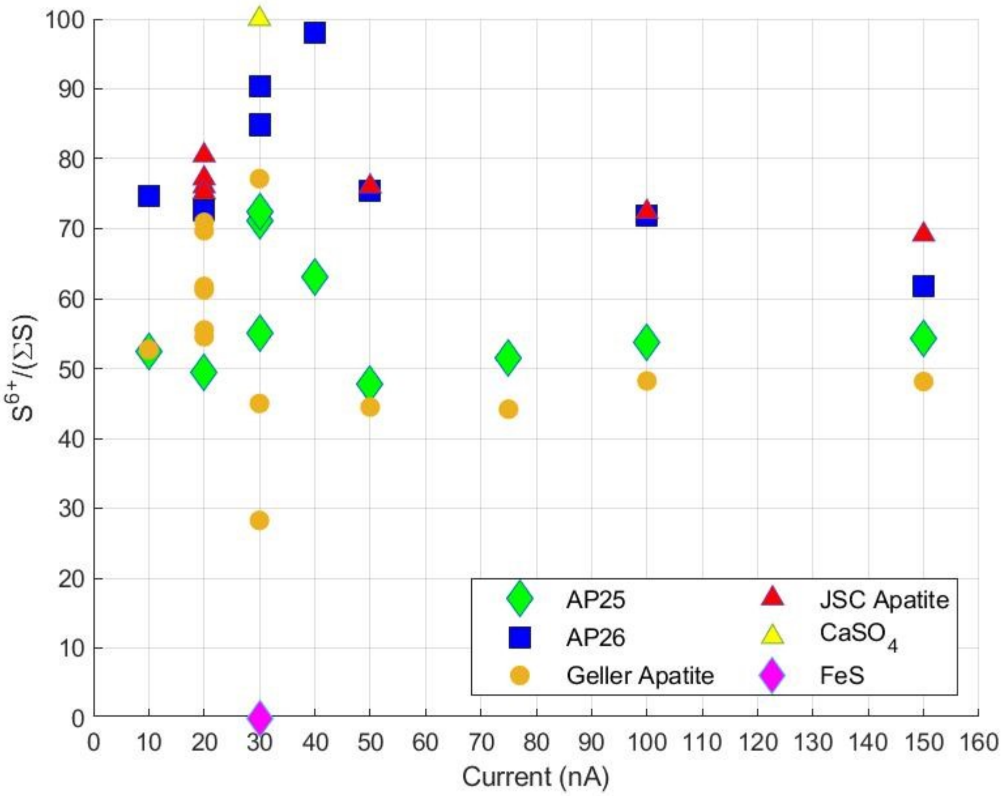

Figure 1. Apparent S^{6+}/TS for apatite as a function of beam current. Few of the measurements are consistent with the known speciation of the apatite being studied.

the same deposit: The Geller Durango shows low apparent S^{6+}/TS—at or below the S^{2-}-rich synthetic apatites—at all beam currents. This suggests that either the Geller apatite is not from Durango, or it is more susceptible to beam damage than the other Durango (and synthetic) apatites. S^{6+}/TS in Geller apatite is also observed to increase slightly with increasing current, though like with all the observed trends, the variation is small relative to the reproducibility. All the apatites converge slightly towards intermediate S^{6+}/TS with increasing current, an unexplained phenomenon.

Implications: We were unable to discover any conditions for electron probe S^{6+}/TS analysis that yielded precise and accurate data for natural or synthetic apatite: At low beam current, measurements are probably dominated by noise (low precision), whereas at higher beam currents, measurements are dominated by beam damage (low accuracy). Use of the electron probe for S^{6+}/TS in apatite is discouraged.

The S^{6+}/TS measurements of [1] in lunar apatite from 14053 and 14072 utilized even higher beam currents than described here (300nA). We would have predicted that all values converged towards intermediate speciation, however [1] observed a wide range of S^{6+}/TS from <20% to >75%. It is possible that lunar apatite is more resistant to beam damage than terrestrial or synthetic apatite. However, a less speculative hypothesis is that the measurements were contaminated by at a minimum some sulfate that is not hosted by apatite, and therefore is more stable under the electron beam. A mixture of sulfide-bearing apatite and sulfate in other minerals can explain the range observed here. Although S^{2-} has been confirmed in lunar apatite by XANES, the evidence for S^{6+} is limited to regions with fractures and is still unexplained.

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