

THE OXIDATION STATE OF SULFUR IN APATITES FROM MARTIAN METEORITE- SHERGOTTY.

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Introduction: Apatite $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$ is one of the primary phosphate minerals found in planetary materials including the Martian meteorite, Shergotty. Sulfur in terrestrial apatites formed in oxidized settings are predominantly present as S^{6+} (e.g., Durango apatite [1, 2]), where oxygen fugacities ($f\text{O}_2$) are high enough to produce S as S^{6+} . However, recently S^{2-} -only bearing apatites have been documented from low $f\text{O}_2$ environments, both in lunar and select terrestrial rocks [1, 3]. Additionally, experimentally grown apatites have been shown to simultaneously incorporate both oxidized and reduced sulfur at intermediate $f\text{O}_2$ s [3]. For these reasons, it has been suggested that the proportions of $\text{S}^{6+}/\text{S}^{2-}$ in the apatite (together with major element composition, temperature, and pressure) record the $f\text{O}_2$ at which these apatites were formed and that a well-calibrated oxybarometer could be applied to Martian rocks. Martian rocks have recorded $f\text{O}_2$ broadly intermediate between that of Earth and Moon, from IW-1 to IW+4.5 [4,5]. At these $f\text{O}_2$, sulfur is expected to be present as S^{2-} and both as S^{2-} and S^{6+} [6], such that apatites from Martian rocks are reasonably expected to contain only S^{2-} in some cases, and mixtures of both S^{2-} and S^{6+} in others [7].

In order to determine the oxidation state of sulfur in apatites from the Martian meteorite Shergotty, we present S-XANES measurements of apatite grains and other associated phases. Previous work suggests that Shergotty parent rocks crystallized at $f\text{O}_2$ s between $\sim\text{IW}+1.9$ and $\text{IW}+2.8$ [4,8] where sulfide is the dominant sulfur phase [9]. We show that, like apatites from Apollo lunar rocks 12039 and 10044, which crystallized at $f\text{O}_2$ s of $\sim\text{IW}-1$ [1], these apatites have sulfur only in its reduced form (S^{2-}). Variability in the intensity of 2470 and 2477 eV peaks suggests that these apatites vary in Fe^{2+} and Ca^{2+} composition sufficiently to generate differences in the S^{2-} bonding environments.

Samples: Shergotty is a 165 Ma basaltic shergottite [e.g. 8, 10-11] consisting predominantly of clinopyroxenes (augite and pigeonite), with variable amounts of maskelynite, titanomagnetite, ilmenite, pyrrhotite, merrillite and accessory apatite, silica, baddeleyite, fayalite and mesostasis. Apatites are euhedral to anhedral in shape and occurs both as mineral inclusions in clinopyroxene and as late-stage phases along with other minerals like silica, oxides and sulfides, which fill the interstitial spaces between earlier

crystallized assemblages [12]. Estimates for the $f\text{O}_2$ during crystallization of Shergotty range from $\sim\text{IW}+1.9$ to $\text{IW}+2.8$ determined using Fe-Ti oxide oxybarometer [8] and from partitioning of Eu in pyroxenes [4]. Sulfur is expected to be in its reduced form (S^{2-}) in the melt at these $f\text{O}_2$ s.

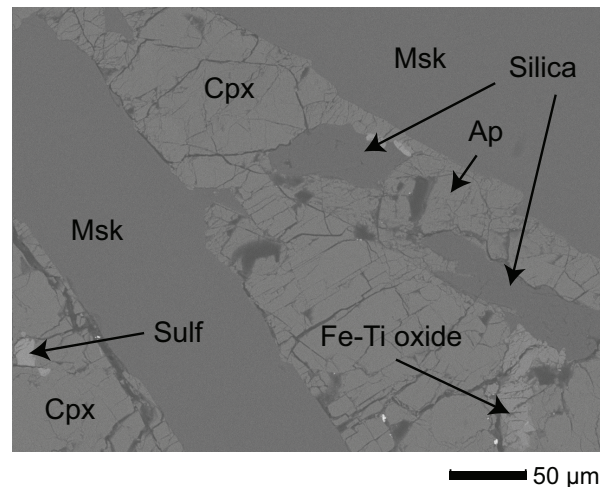


Fig. 1: Back scattered electron image and SEM element map of Shergotty showing the typical texture including minerals cpx- clinopyroxene, msk- maskelynite, ap- apatite, sulf- sulfide, silica and Fe-Ti oxide.

Results: The $\text{S}^{6+}/\Sigma\text{S}$ [(i.e. S^{6+} divided by the sum of S^{6+} and S^{2-}] ratios of apatites and associated phases were measured using S-XANES at beamline 13-IDE at the Advanced Photon Source, Argonne National Laboratory. Spectra were collected in fluorescence mode between 2447 eV and 2547 eV, with a dwell time of two seconds on each point.

The S-XANES spectra of Shergotty apatites feature peaks at 2470 and 2477 eV (Fig. 2), consistent with the presence of structural S^{2-} in apatite, and an absence of peaks commonly associated with oxidized forms of sulfur, S^{4+} (2473.3 eV) and S^{6+} (2481.7 eV). This indicates that Shergotty apatites incorporate only S^{2-} into their mineral structures, similar to lunar apatites [3].

S-XANES spectra of epoxy in thin section shows peak at 2473.3 eV and 2481.7 eV, which distinguishes them from apatite spectra (particularly the peak at 2473.3; Fig. 2).

After merging and normalizing the raw spectra using Athena [13], curve and peak fitting software Fityk [14] was used for peak area integration of merged, non-smoothed and corrected spectra. An exponentially modified Gaussian (EMG) function was used to fit the background and Gaussian function was used to separately fit S^{6+} and S^{2-} peaks.

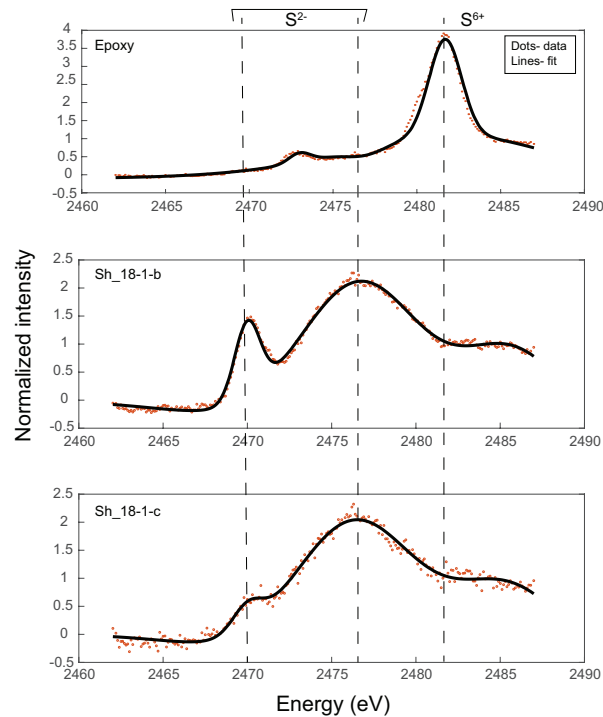


Fig. 2: S-XANES spectra for analysis points on epoxy, apatite Sh_18-1-b and Sh_18-1-c. The positions of absorption peaks are assigned to S^{2-} (2470 and 2477 eV) and to S^{6+} (2481.7 eV) are marked in vertical dashed lines. The orange dots are the data and the black curves are fit spectra produced using Fityk software. Clear absence of S^{6+} peak in the apatite spectra indicates lack of sulfate in the apatites. Epoxy, however, shows a clear sulfate peak.

Discussion: We have documented the occurrence of sulfide-only apatites from Mars. This observation is consistent with the presence of sulfide in apatites at low fO_2 s from lunar and terrestrial samples [1,3], and reinforces the hypothesis that the oxidation state of sulfur in apatite responds to the fO_2 during apatite crystallization. It also demonstrates that apatites crystallizing from low fO_2 environments on any planet should not be assumed to be sulfur-free.

Additionally, the S-XANES spectra of Shergotty apatites show significant variability in the intensity of the 2470 eV peak, a feature which has not been observed

in their lunar counterparts [1]. The 2470 eV peak is commonly attributed to the energy of the lowest unoccupied orbitals on S as the result of $Fe^{2+}-S^{2-}$ interactions, whereas the broad peak from 2475-2477 eV is attributed to the energy of the lowest unoccupied orbitals on S as the result of $Ca^{2+}-S^{2-}$ interactions [15]. It is possible that the observed variability in the intensity of the 2470 eV peak indicates variability in the FeO* content of Shergotty apatites, where measured apatites that have weak or absent peaks at 2470 eV have the lowest FeO contents. The persistent presence of ~2477 eV peak indicates that S^{2-} is mostly bonded with Ca^{2+} in apatites.

Implications: Shergotty is a relatively oxidized shergottite with fO_2 of IW +1.9 during crystallization [4] when compared to other shergottites like Zagami (IW +0.4), Los Angeles (IW +0.2), EETA 79001A (IW +0.3), EETA 79001B (IW -0.7), DaG 476 (IW -0.5) and QUE 94201 (IW -1). Shergotty on the other hand is more reduced than Nakhilites (IW +4) [5]. The presence of sulfide-only apatites in a relatively oxidized shergottite suggest that apatite grains in many other shergottites might have sulfur as sulfide as well, and because S^{2-} is thought to partition into the column anion site with F^- , Cl^- , and OH^- , should be considered in studies using apatite to constrain the abundance and behavior of these volatile elements on Mars.

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