

DETERMINATION OF SULFUR SPECIATION IN APATITES FROM MARTIAN METEORITE-SHERGOTTY USING μ -XANES

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Apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$] is one of the primary and ubiquitous phosphate minerals in different planetary bodies including the Martian meteorite, Shergotty. Terrestrial apatites have sulfur mostly as S^{6+} because of their formation in oxidized environments [1, 2]. Recently, S^{2-} -only bearing apatites have been documented in natural environments (lunar and terrestrial) and in experiments [1-3], however, the latter also reports simultaneous incorporation of both S^{6+} and S^{2-} at intermediate oxygen fugacities ($f\text{O}_2$) [2]. Thus, it is suggested that proportions of $\text{S}^{6+}/\text{S}^{2-}$ in apatite, together with major element compositions, T and P , may be a record of the $f\text{O}_2$ of formation of these apatites. Martian rocks record intermediate $f\text{O}_2$ between the Moon and Earth and thus may contain only S^{2-} bearing apatites that provide a record of $f\text{O}_2$ during apatite crystallization [4].

The Martian meteorite Shergotty has recorded $f\text{O}_2$ of $\sim\text{IW}+1.9 - \text{IW}+2.8$ [5, 6]. At these low $f\text{O}_2$ s, silicate liquids are expected to contain sulfur exclusively as S^{2-} [7] and thus apatites crystallized from these liquids and which preserve their igneous signatures are expected to contain only S^{2-} , like in the case of lunar apatites [1]. In order to examine the oxidation state of sulfur in apatites from Shergotty, we present S-XANES measurements of apatite grains and other associated phases (e.g., Fig. 1). These measurements were undertaken at beamline 13-IDE at the Advanced Photon Source, Argonne National Laboratory. Spectra were collected in fluorescence mode between 2447 eV and 2547 eV (at every 2.5 eV from 2447-2462 eV, every 0.1 eV from 2462-2487 eV and every 1.5 eV from 2487-2547 eV), with a dwell time of two seconds on each point.

The S-XANES spectra of Shergotty apatites contain 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 eV) and S^{6+} (2481 eV). This demonstrates that, like in the case of Apollo rocks 12039 and 10044, Shergotty apatites incorporate only S^{2-} into their mineral structures, consistent with independent mineralogical constraints on the $f\text{O}_2$ of crystallization for Shergotty meteorite (between $\text{IW}+1.9$ and $\text{IW}+2.8$; [5, 6]) and expectations of the oxidation state of sulfur in silicate liquids at those low $f\text{O}_2$ s [7]. Additionally, variability in the relative intensities of peaks at 2470 and 2477 eV (attributed to S^{2-}) suggests that there may be significant variability in the bonding environment of S^{2-} in these apatites. For example, the 2470 eV peak is commonly attributed to Fe^{2+} - S^{2-} interactions [8], and the variability in the intensity in this peak may arise as the result of significant variations in the FeO^* concentration of Shergotty apatites [e.g., 9].

The presence of S^{2-} only apatites in Shergotty, which is relatively oxidized amongst the shergottites [5], suggest that apatites in other shergottites also contain sulfur in its reduced form in the column anionic site with F^- , Cl^- and OH^- [10], calling for consideration of sulfur in studies using apatite to constrain volatile behavior and abundances on Mars.

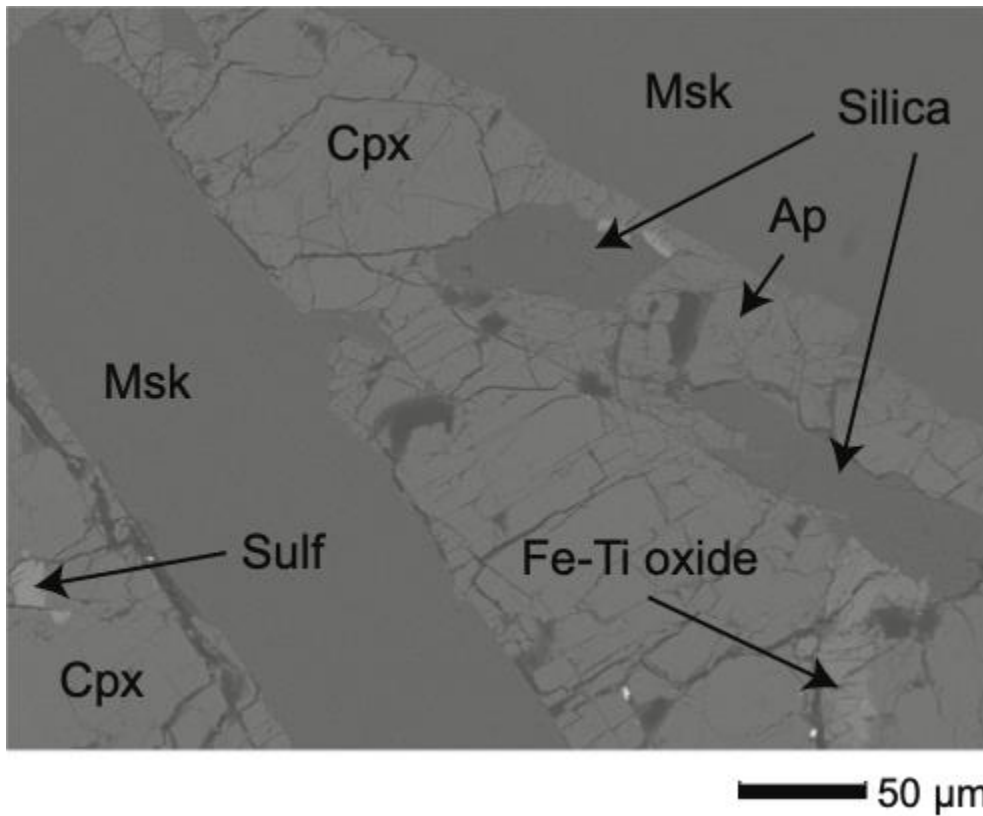


Figure 1. Figure 1- Back scattered electron (BSE) image of Shergotty showing the typical texture including minerals cpx- clinopyroxene, msk-maskelynite, ap- apatite, sulf- sulfide, silica and Fe-Ti oxide.

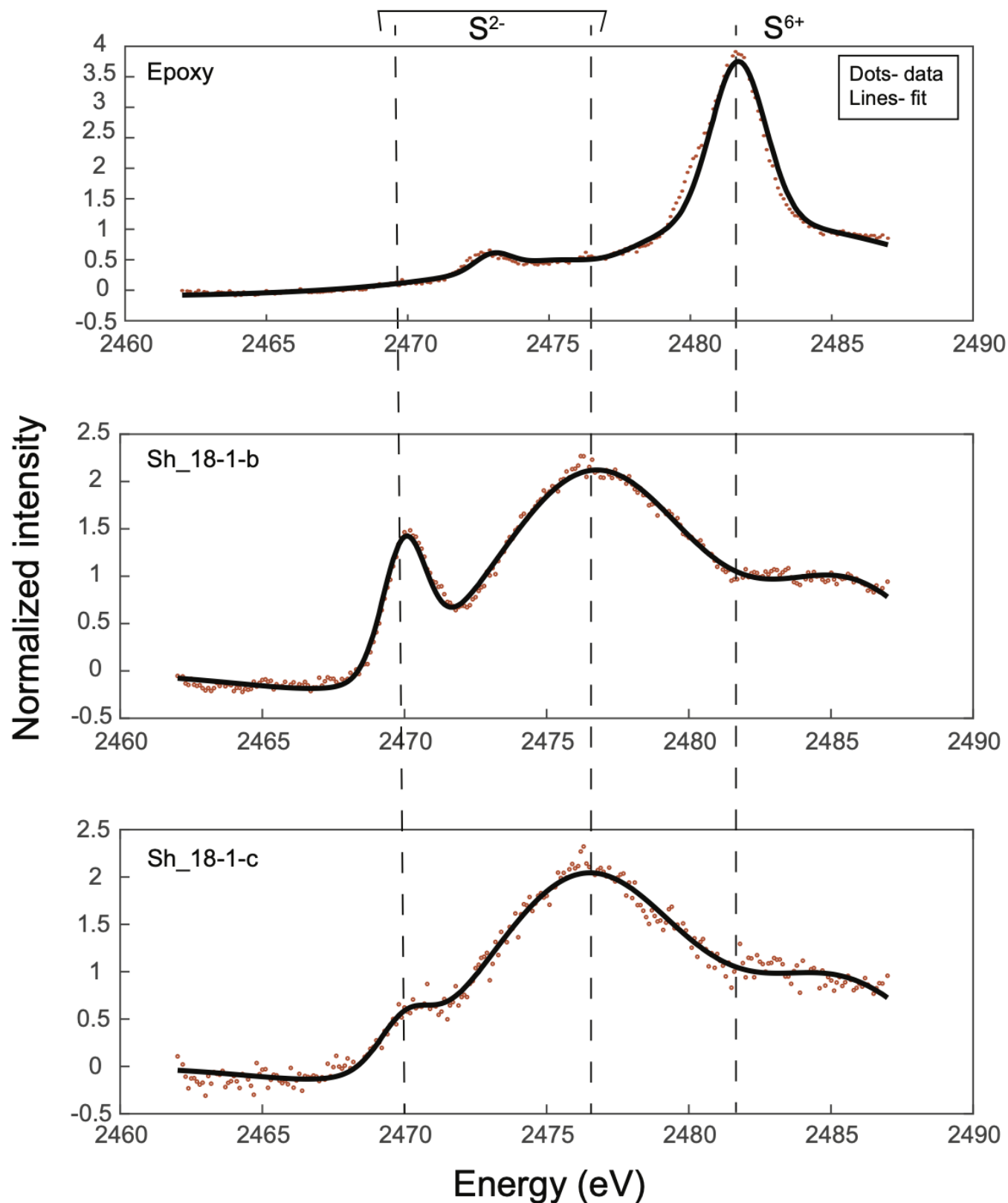


Figure 2. Figure 2- S- XANES spectra for analysis points on epoxy, apatite Sh_18-1-b and SH_18-1-c. The positions of absorption peaks are assigned to S²⁻ (2470 and 2477 eV) and to S⁶⁺ (2481.7 eV) are marked in

vertical dashed lines. The orange dots are data, and the black curves are fit spectra produced using Fityk software.

References

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