

THE OXIDATION STATE OF SULFUR IN MARTIAN APATITE- IMPLICATIONS FOR REDOX OF SURFICIAL PROCESSES. P. Chowdhury¹, M. Brounce¹, J. W. Boyce², F. M McCubbin², ¹Department of Earth and Planetary Sciences, University of California, Riverside, CA ²Astromaterials Research and Exploration Science Division, NASA Johnson Space Center, Houston, TX

Introduction: Meteorites from Mars record fO_2 values of $\Delta IW = -1$ to $+6.5$ [1, 2]. This relatively large range in fO_2 has been attributed to igneous processes like differentiation and assimilation, or sometimes to alteration [2, 3], modifying the range inherited from the Martian mantle, which is thought to be closer to the values recorded by lunar basalts ($\sim \Delta IW -1$ [e.g., 1]). Trace element compositions reveal that those Martian meteorites that are light Rare Earth Elements (LREE) enriched record higher fO_2 values than those that are LREE-depleted [2]. Sulfur (S) has been used to track redox and alteration processes on Mars because it can be present in multiple redox states varying from S^{2-} in magmatic sulfides to S^{6+} in sedimentary sulfate deposits and alteration products like jarosite [4, 5]. Apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) is found in many of the Martian meteorites as a late stage crystallizing mineral. It can incorporate both S^{2-} [6] or S^{6+} [7] or mixtures of both [7, 8] in its crystal structure, and it has been hypothesized that the relative proportions of S^{2-} and S^{6+} in apatite will depend on the prevailing fO_2 in which it formed (along with P, T, and major element composition).

We seek to constrain whether relative proportions of S^{2-} and S^{6+} in apatite records the same fO_2 recorded by the major, early-forming igneous minerals, a different fO_2 that reflects the changes the magma has experienced as a result of crustal assimilation or other differentiation processes, or record an fO_2 that reflects the extent to which the rocks have been altered after emplacement on the Martian surface or upon arrival to the relatively hydrous, warm, and oxidized conditions of Earth's atmosphere. Discriminating between these possibilities and quantifying the effect of any on the fO_2 recorded in Martian meteorites will illuminate the large range of fO_2 recorded by these rocks. To test between these possibilities, we present new S-XANES measurements of apatite grains and other associated phases from Martian meteorites QUE 94201, NWA 7034 and ALH 84001, which are known to have interacted with Martian crustal fluids [9]. These meteorites, plus recent analyses of Shergotty [10] vary in several ways that will provide specific tests of the possibilities listed above: amongst the shergottites, QUE 94201 is LREE depleted, while Shergotty is enriched. QUE 94201 and ALH 84001 records low fO_2 , followed by Shergotty, and NWA 7034 records the highest fO_2 (see Samples below). Shergotty is a fall, while the rest are finds – two finds were collected from the Antarctic ice shelf (QUE 94201, ALH 84001), and one from the Sahara Desert (NWA 7034).

Samples: QUE 94201 is a 321 Ma basaltic shergottite consisting predominantly of clinopyroxenes (augite and pigeonite), with variable amounts of maskelynite, Fe-Ti oxides and accessory merrillite and apatite [11]. QUE 94201 has alteration features on its fusion crust crosscut by jarosite

veins. Estimates for the fO_2 during crystallization of QUE 94201 range from $\sim \Delta IW = -1$ to $+1$, determined by the partitioning of V and Eu in pyroxenes [12, 13]. At these fO_2 values, sulfur is expected to be in its reduced form (S^{2-}) in the melt [14]. NWA 7034 is a regolith breccia with a basaltic bulk composition lithified at 1.5 Ga [15]. The igneous clasts of NWA 7034 include basalt, basaltic andesite, trachyandesite and a Fe-Ti and P rich (FTP) lithology [16]. It contains maskelynite, low-Ca pyroxene, clinopyroxene, Fe-Ti oxides, and apatite. Estimates for the fO_2 of NWA 7034 range from $\sim \Delta IW = +4.5$ to $+6.5$ determined by the Fe-Ti oxide oxybarometer [17] where sulfur is expected to be in its oxidized form (S^{6+}) in the melt. ALH 84001 is a ~ 4.5 to 4 Ga orthopyroxenite, which is thought to have crystallized in the Martian crust and later experienced hydrothermal alteration with crustal fluids at 3.9 Ga [18]. The constituent minerals of ALH 84001 are orthopyroxene, maskelynite and phosphates (merrillite and apatite). Estimates for the fO_2 during crystallization of ALH 84001 range from $\sim \Delta IW = 0$ to $+1.3$ determined by the spinel-olivine-orthopyroxene oxybarometer [19] where sulfur is expected to be in its reduced form (S^{2-}) in the melt.

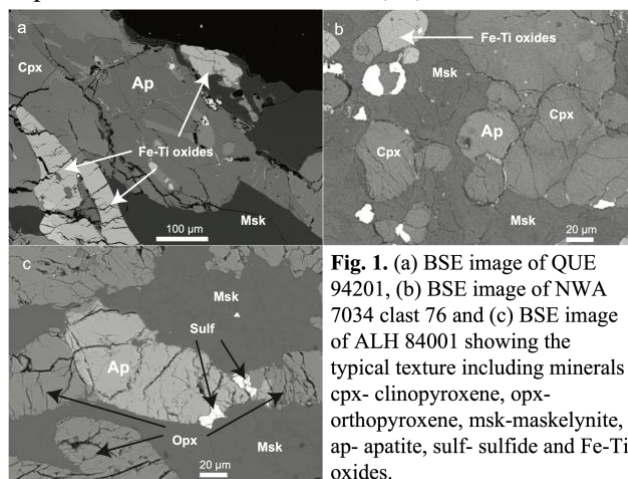


Fig. 1. (a) BSE image of QUE 94201, (b) BSE image of NWA 7034 clast 76 and (c) BSE image of ALH 84001 showing the typical texture including minerals cpx- clinopyroxene, opx- orthopyroxene, msk-maskelynite, ap- apatite, sulf- sulfide and Fe-Ti oxides.

Results: The oxidation state of sulfur in apatite and associated phases were measured using S-XANES at beamline 13-IDE at the Advanced Photon Source, Argonne National Laboratory. Apatite grains in QUE 94201 have peaks at 2470, 2477 and 2482 eV (Fig. 2), consistent with the presence of S^{2-} and S^{6+} . Apatite grains in NWA 7034 have a peak at 2482 eV, and no peaks at 2470 or 2477 eV, consistent with the presence of only S^{6+} . Apatite grains in ALH 84001 have peaks at 2472, 2477 and 2482 eV, consistent with the presence of S^{2-} and S^{6+} .

The $S^{6+}/\Sigma S$ ratios were estimated from peak area integration of merged, non-smoothed and normalized spectra. The range of $S^{6+}/\Sigma S$ in QUE 94201 apatite is from 0.06-0.91, which corresponds to a fO_2 of $\sim \Delta IW +2.4$ to $\Delta IW +6.4$ calculated from experimental calibration of $S^{6+}/\Sigma S$

with fO_2 [8]. In contrast, ALH 84001 apatite hosts a range of $S^{6+}/\Sigma S$ from 0.07-0.39, which corresponds to fO_2 of $\sim\Delta IW + 2.4$ to $\Delta IW + 3.7$. NWA 7034 apatite has $S^{6+}/\Sigma S$ of 1 which corresponds to fO_2 greater than $\sim\Delta IW + 6.5$.

Discussion: Recent analyses of apatite grains in Shergotty (enriched shergottite, a fall) show the occurrence of sulfide-only apatite [10], which is consistent with the low fO_2 during the crystallization of the Shergotty parent rock as inferred from Eu partitioning in clinopyroxene [13]. QUE 94201 is inferred to have been formed at lower fO_2 than Shergotty (according to Eu and V partitioning in clinopyroxene [12, 13]), however apatite grains in QUE94201 have $S^{6+}/\Sigma S$ between 0.06 and 0.91. This suggests that the measured apatite in QUE 94201 do not record the same fO_2 of the major igneous phase assemblage, rather it records the fO_2 at some later stage, which has imposed a substantially higher fO_2 during crystallization of the apatite. This process could be igneous – perhaps the magma underwent substantial differentiation that led to a very oxidized late-stage magma that contained some S^{6+} and from which the measured apatite crystallized. It is also possible that the primary apatite grains were crystallized from a reduced, S^{2-} -bearing melt, but after emplacement, an oxidized hydrothermal fluid led to the reprecipitation of apatite containing S^{6+} [8]. It is difficult to ascertain from texture because QUE94201 is a meteorite with a complex alteration history that obscures the igneous textures of the accessory apatite grains. A previous study of the hydrogen isotopic composition of apatite [20] and jarosite [21] from the same meteorite (not the same apatite grains measured here) reveal δD_{SMOW} values of apatite of 1700-3500‰, which are distinct from terrestrial values (-480 to +130 ‰ [21]) but overlaps with Martian crustal values (750 to 2750 ‰ [9]) and are thought to have been formed by mixing of the shergottite source with oxidized crustal fluid [9]. Measurements of jarosite reveal δD_{SMOW} values \sim -300 to 400‰, indistinguishable from Antarctic water [21]. If the apatite grains that we measured in QUE94201 were precipitated or modified by a hydrothermal fluid, as in the case of the apatite grains targeted in the hydrogen isotope study, then the $S^{6+}/\Sigma S$ of these apatite indicate that this hydrothermal fluid was oxidized enough to carry substantial proportions of S^{6+} .

Similarly, in ALH 84001, sulfide is the only S species expected in the melt at the oxygen fugacity conditions measured from other igneous proxies [19] but apatite have $S^{6+}/\Sigma S = 0.07$ to 0.39 and δD_{SMOW} from 800 to 1600‰ [9]. This indicates that they may have also undergone a similar alteration history as the apatite in QUE 94201 [22]. The occurrence of oxidized sulfur in both rocks suggest that oxidized fluid alteration may be somewhat pervasive in the Martian crust.

The igneous clasts of NWA 7034 were crystallized at $\sim\Delta IW = +4.5$ to $+6.5$ [17], so it is possible that the presence of S^{6+} -only apatite is a record of the oxidized conditions during crystallization. However, the δD_{SMOW} compositions

of apatite in NWA 7034 range from 1000 to 2000‰ [9], and the breccia is thought to have been lithified through thermal annealing in the presence of crustal fluids [15]. Therefore, the presence of S^{6+} -only apatite in NWA 7034 thus place a constraint on the fO_2 of that late-stage hydrothermal fluid.

Implications: Taken together, apatite in QUE94201, ALH84001, and NWA 7034 point to pervasive oxidized fluids percolating through the Martian crust, and this oxidized fluid leads to oxidation of the hydrothermal-sensitive minerals (e.g., apatite) in these rocks. Whether a fall or find, and whether found on the Antarctic ice sheet or Sahara Desert, this apatite preserves a record of Martian alteration and provides a record of the near-surface environment at some time in the past.

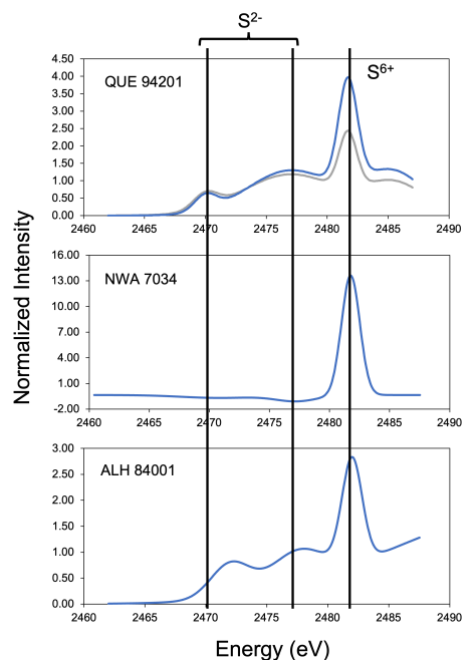


Fig. 2. Representative S-XANES spectra of QUE 94201, NWA 7034 and ALH 84001. The positions of absorption peaks are assigned to S^{2-} (2470 and 2477 eV) and to S^{6+} (2482 eV) are marked in vertical black lines.

References: [1] Wadhwa M. (2008) *RiMG*, 68, 493-510. [2] Herd C. D. K. et al. (2002) *GCA*, 66, 2025-2036. [3] Franz H. B (2014) *Nature*, 508, 364-368. [4] Gendrin A. et al. (2005) *Science*, 307, 1587-1591 [5] Madden M.E.E et al. (2004), *Nature*, 431,821-823. [6] Brounce M. et al. (2019) *Am. Min.*, 104, 307-312. [7] Konecke B.A. et al. (2019) *GCA*, 265, 242-258. [8] Sadove G. et al. (2019) *Ore Geol. Rev.*, 107, 1084-1096. [9] Barnes J. J et al. (2020), *Nat. Geosc.*, 13, 260-264. [10] Chowdhury P. et al. (2021) *LPSC 52nd*, Abstract# 1584 [11] Harvey R. P. et al. (1996) *LPSC 27th*, 497-498. [12] Karner J.M. et al. (2007) *Am. Min.*, 92, 2002-2005. [13] Wadhwa M. (2001) *Science*, 291, 1528-1530. [14] Jugo P. J. et al. (2005) *J. Petrol.*, 46, 783-798. [15] Agee C.B. et al. (2013) *Science*, 339, 780-785. [16] Santos A. R. et al. (2015), *GCA*, 157, 56-85. [17] Agee C.B. et al. (2013) *LPSC 44th*, Abstract# 2695. [18] Lapen T. J. et al. (2010) *Science*, 328, 347-351. [19] Righter, K. et al. (2008) *Meteor. Plan. Sci.*, 43, 1709-1723. [20] Lehsin L. A. (2000) *Geophys. Res. Lett.*, 27, 321-333. [21] Ross D. K. et al. (2010) *LPSC 41st*, Abstract# 1154 [22] Greenwood J. P. et al. (2000) *GCA*, 184, 23-35.