THE OXIDATION STATE OF SULFUR IN MARTIAN APATITE- IMPLICATIONS FOR REDOX OF SURFICIAL PROCESSES. P. Chowdhury, M. Broune, J. W. Boyce, F. M Mc Cubbin, 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 /O2 values of ΔIW = -1 to +6.5 [1, 2]. This relatively large range in /O2 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 (~ΔIW = -1 [e.g., 1]). Trace element compositions reveal that those Martian meteorites that are light Rare Earth Elements (LREE) enriched record higher /O2 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 S2- in magmatic sulfides to S6+ in sedimentary sulfate deposits and alteration products like jarosite [4, 5]. Apatite (Ca3(PO4)3(F,Cl,OH)) is found in many of the Martian meteorites as a late stage crystallizing mineral. It can incorporate both S2- [6] or S6+ [7] or mixtures of both [7, 8] in its crystal structure, and it has been hypothesized that the relative proportions of S2- and S6+ in apatite will depend on the prevailing /O2 in which it formed (along with P, T, and major element composition).

We seek to constrain whether relative proportions of S2- and S6+ in apatite records the same /O2 recorded by the major, early-forming igneous minerals, a different /O2 that reflects the changes the magma has experienced as a result of crustal assimilation or other differentiation processes, or record an /O2 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 /O2 recorded in Martian meteorites will illuminate the large range of /O2 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 /O2, followed by Shergotty, and NWA 7034 records the highest /O2 (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 shergotite 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 /O2 during crystallization of QUE 94201 range from ~ΔIW = -1 to +1, determined by the partitioning of V and Eu in pyroxenes [12, 13]. At these /O2 values, sulfur is expected to be in its reduced form (S2-) 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 /O2 of NWA 7034 range from ~ΔIW = +4.5 to +6.5 determined by the Fe-Ti oxide oxybarometer [17] where sulfur is expected to be in its oxidized form (S6+) 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 /O2 during crystallization of ALH 84001 range from ~ΔIW = 0 to +1.3 determined by the spinel-olivine-orthopyroxene oxybarometer [19] where sulfur is expected to be in its reduced form (S2-) in the melt.

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 S2- and S6+. 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 S6+. Apatite grains in ALH 84001 have peaks at 2472, 2477 and 2482 eV, consistent with the presence of S2- and S6+.

The S6+/∑S ratios were estimated from peak area integration of merged, non-smoothed and normalized spectra. The range of S6+/∑S in QUE 94201 apatite is from 0.06-0.91, which corresponds to a /O2 of ~ΔIW +2.4 to ΔIW +6.4 calculated from experimental calibration of S6+/∑S
with $fO_2$ [8]. In contrast, ALH 84001 apatite hosts a range of $S^{6+}/S$ from 0.07-0.39, which corresponds to $fO_2$ of $\pm$150 to $\pm$600 $\DeltaIW$. NWA 7034 apatite has $S^{6+}/S$ of 1 which corresponds to $fO_2$ greater than $\pm$600 $\DeltaIW$.

**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 $S^{6+}/S$ 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 replacement, 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 $\Delta D_{SMOW}$ 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 $\Delta D_{SMOW}$ 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 $S^{6+}/S$ 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 $S^{6+}/S$ =0.07 to 0.39 and $\Delta D_{SMOW}$ 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 $\pm$300 $\DeltaIW$ = +4.5 to +6.5 $\DeltaIW$ [17], so it is possible that the presence of $S^{6+}$-only apatite is a record of the oxidized conditions during crystallization. However, the $\Delta D_{SMOW}$ 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 $S^{6+}$ (2482eV) are marked in vertical black lines.](image)