

**EVIDENCE FOR O<sub>2</sub>-RICH ENVIRONMENTS ON MARS FROM HYDROUS Mn(IV)-OXIDES IN NORTHWEST AFRICA (NWA) 7034 AND 7533 METEORITES.** Yang Liu<sup>1,\*</sup>, Chi Ma<sup>2</sup>, Woodward W. Fischer<sup>2</sup>, Yunbin Guan<sup>2</sup>, Samuel M. Webb<sup>3</sup>, John R. Beckett<sup>2</sup>, Jinping Hu<sup>2</sup>, Carl B. Agee<sup>4</sup>. <sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology (Caltech), Pasadena, CA 91109. <sup>2</sup>Division of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125. <sup>3</sup>Stanford Synchrotron Radiation Lightsource, Stanford University, Menlo Park, CA 94025. <sup>4</sup>Institute of Meteoritics, University of New Mexico, Albuquerque, NM, 87131. \*yang.liu@jpl.nasa.gov.

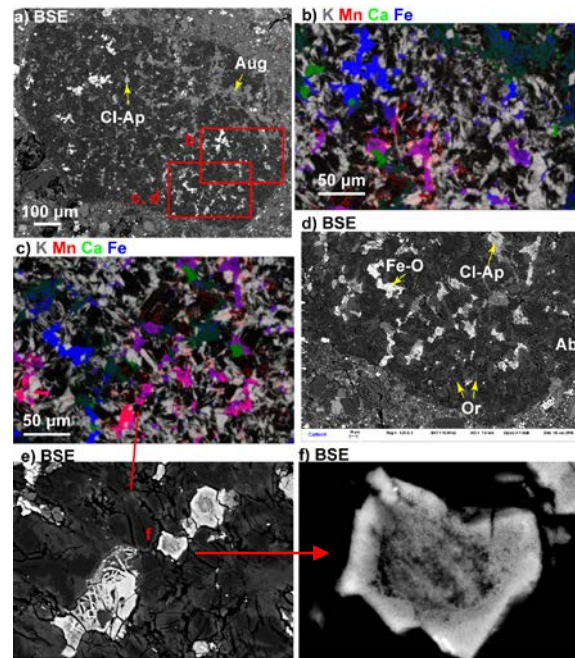
**Introduction:** Oxidants of exceptionally high redox potential (> 500 mV) are required to convert soluble Mn(II) to insoluble Mn(III) and Mn(IV) (hydr)oxides. Consequently, Mn(III) and Mn(IV) (hydr)oxides are used as proxies for dioxygen (O<sub>2</sub>) in the Earth surface system [1]. Although Mn-rich materials were observed at two locations on Mars by *in-situ* instruments [2-4], the redox states of manganese and the mineralogical identity of these phases remain unknown. And such material had not been observed in a martian meteorite. The unknown Mn speciation in [2-4] precludes a definitive connection to O<sub>2</sub> in current or ancient Martian surface environments. Here, we present the first report of hydrous Mn(IV)-dominant oxides in Martian breccia meteorites NWA 7034 and 7533—these phases contain Mn contents up to ~32 wt%. The textures, composition, and chemistry of hydrous Mn(IV)-oxides imply the petrogenesis of these phases occurred within the shallow regolith on Mars, implying O<sub>2</sub>-rich martian surface and crustal environment during their emplacement.

**Sample and Methods:** We studied four sections of NWA 7034 and four sections of NWA 7533, using optical microscopy, scanning electron microscopy (SEM), electron probe microanalyzer (EPMA), secondary ion mass spectroscopy (SIMS), and synchrotron microprobe X-ray absorption spectroscopy (XAS), and X-ray absorption near-edge spectroscopy (XANES) at the Mn K-edge.

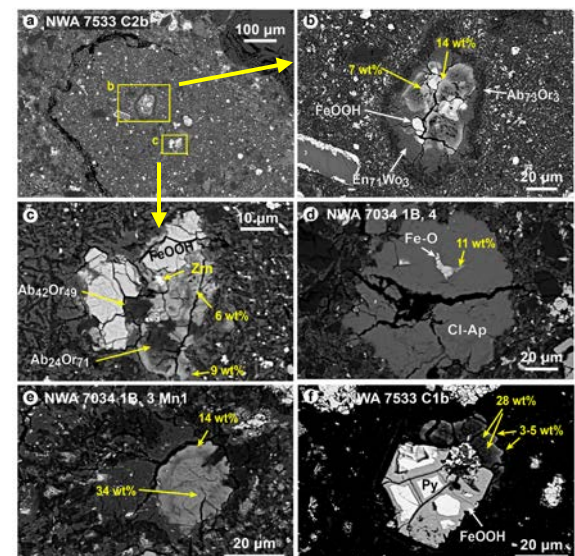
### Results:

**Occurrence.** The Mn-bearing material occurs as nanocrystalline aggregates in diverse petrography contexts in all eight sections (e.g., Figs. 1 and 2). The most common occurrence is in perthite-rich clasts (Fig. 1). The second main occurrence is in spherules (Fig. 2a-c, e). Only one case was found with altered Fe-Ti-oxides in the matrix (Fig. 2f), and one with an Fe-oxide (possible magnetite) in chlorapatite (Fig. 2d). The Mn-bearing material was not part of the matrix of the breccias. The occurrences do not correlate with the distance to the section edge.

**Elemental composition.** The EPMA analysis shows variable compositions, ranging in Mn from 32 wt% to 1.5%, Fe from ~18% to 31%, Si from ~1% to ~10%, Ba from 1.1% to <0.08, P from 1.2% to 0.3, S from 0.4 to 0.1%, Ni from 0.2% to <0.06% to, and Zn <0.1%. The EPMA totals are ~95 to 98 wt%, increasing with



**Fig. 1.** Example of hydrous Mn(IV)-oxides in a perthite-rich clast in NWA 7533 C2b. Aug: augite; Cl-Ap, chlorapatite; Ab: albite; Or: orthoclase; Fe-O: Fe oxides.



**Fig. 2.** Examples of other occurrences of hydrous Mn(IV)-oxides in NWA 7034 and 7533. Mn contents in wt% are from SEM EDS analysis. Py: pyrite. All are BSE images.

decreasing Mn contents. The Mn contents are negatively correlated with Fe, but are positively correlated with

Ba. The Mn-bearing material in perthite-rich clasts generally contains higher Mn and Ba than that in spherules.

Compared to the FeOOH alteration of the pyrite in the vicinity (Fig. 2b-c), the Mn-rich material contains higher Si (5-10% vs 2-3%), Al (2-2.7% vs <0.02), Mg (3-5% vs 0.3-0.8%), Na (0.3-0.5% vs ~0.1%), K (0.2 vs. ~0.02%) and P (0.3-1% vs ~0.1%), but comparable S (~0.2-0.4%).

**Hydrogen isotope compositions.** The NanoSIMS H and D analyses confirm the hydrous nature of the Mn-rich material. Based on a glass standard (47:1-5, 1.76% H<sub>2</sub>O, [5]) analyzed under the same conditions, H<sub>2</sub>O contents of two Mn-rich regions (with 10% and 32% Mn, NWA 7034 1B, 4) are ~3%, consistent with the low EPMA totals. Estimated using the glass standard, the  $\delta D$  values of the Mn-rich regions are about  $-380 \pm 100\text{‰}$ , much lower than those reported for FeOOH ( $+10 \pm 85\text{‰}$ , [6]).

**Mn valence.** Both XAS redox mapping and XANES Mn K-edge spectra generated using the Stanford Synchrotron light source indicate that the vast majority of Mn is IV+, with varying smaller amounts of III+. The XAS data confirm that these Mn-rich phases are predominantly Mn(IV)-oxides.

**Discussion:** Our results suggest the Mn(IV)-dominant material is either birnessite or vernadite, but a clear distinction between them is difficult because of their fine grain size and the aggregate nature. We refer to them collectively as *hydrous Mn(IV)-oxides*.

**Non-terrestrial origin of Mn(IV)-oxides.** Terrestrial alteration has been suggested for FeOOH (likely goethite) mantling pyrite in NWA 7034 and its pairs, based on terrestrial-like  $\delta D$  values [6-8]. The hydrous Mn(IV)-oxides were not formed by altering pyrite, because pyrite does not contain significant Mn, the FeOOH alteration of pyrite has different compositions, and the Mn(IV)-oxides are not directly in contact with pyrite or its alteration product.

There are not any Mn-rich igneous phases that can be readily altered to Mn(IV)-oxides. Mn substitutes exclusively as Mn(II) for Fe(II) in igneous minerals, and as a minor to trace component relative to Fe(II), e.g., martian olivine and pyroxene in ratios of 1:50 to 1:35, respectively [9]. Among primary minerals in NWA 7034 and 7533, the Fe-Ti oxides contain highest MnO (up to 3% [10]). None of these minerals are extensively altered. Therefore, Mn needs to be introduced and oxidized. However, terrestrial weathering of NWA 7034 and 7533 is present as Ca-carbonates in cracks with low Mn contents. The hydrous Mn(IV)-oxides are enclosed deep within the fully indurate parts of the meteorites (Fig. 1 and 2), unrelated to the carbonates.

Alternatively, a Mn-rich phase in NWA 7034 and 7533 could have been altered by O<sub>2</sub>-rich terrestrial water. Secondary Fe(II)-Mn(II)-Ca-Mg carbonates were observed in ALH 84001 and Nakhilites [11-12]. Mn contents are <4% except for ~15% Mn in some siderites in Nakhla [12]. Elemental fractionation during terrestrial weathering is not well constrained. Given the petrography of the hydrous Mn(IV)-oxides, the water/rock (or water/mineral) ratio is small, and the removal of Fe and Ca is possibly inefficient. Other Mn-rich phases have not been reported in Martian samples.

Considering the report of suspected birnessite on Mars [3-4], we regard the most likely explanation is that the Mn(IV)-oxides formed on Mars.

**Potential oxidants.** There is a limited set of reactants of sufficient redox potential to produce the Mn(IV)-oxides we observe, including: UV oxidation, O<sub>2</sub> or its derivatives (e.g., oxychloride compounds, nitrate). When a large amount of Fe is present, UV oxidation is inefficient in oxidizing Mn, because of the shielding effect of Fe [15]. Additionally, our petrographic observations preclude a mechanism requiring light. Oxychloride compounds detected at Gale crater [16-18] are very stable unless heated to >200 °C, at which they can generate O<sub>2</sub>. Alternatively, free O<sub>2</sub> may exist at one time (or still in isolated locations) on Mars as suggested by Lanza et al. [1].

Based on their diverse petrographic occurrences and compositions, hydrous Mn(IV)-oxides may have formed through recurring events from before the enclosure to after the lithification of NWA 7034 and 7533. Considering the evidence for a whole-rock scale thermal event at 500-800 °C and ~1.5 Ga that corresponds to the lithification of the whole sample [19], it is likely that some of the hydrous Mn(IV)-oxides formed after the whole rock formation.

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