DIVERSE FLUID ACTIVITIES ON MARS: ZINC-BEARING SILICATE AND OXIDE IN THE MARTIAN BRECCIA METEORITE NORTHWEST AFRICA (NWA) 7533.

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Introduction: Fluid-mobile elements, such as Zn, are excellent tracers of fluid activities in near-surface environments. On Mars, surface soils and sedimentary rocks often display enrichments in non-sulfide Zn that are correlated with enrichments in other fluid-mobile elements like Mn, Ge, and Cl (e.g., [1-5]). However, these mission findings reflect bulk analyses so that the identity of the specific Zn-bearing phases generating these enhanced concentrations, their petrographic context, and their connections to enrichments in other elements are currently unavailable. Here, *we report the first findings of non-sulfide Zn-bearing phases* in NWA 7533, a member of the Black Beauty clan, enabling ground-truth study of fluid activities on Mars. We also demonstrate that tracers of fluid activities in a petrological context can be easily recognized by PIXL, a Mars 2020 rover instrument.

Methods: Zinc-rich phases were recognized during synchrotron X-ray fluorescence (SXRF) mapping of NWA 7533 section C2b, using the Beam Line 2-3 at Stanford Synchrotron Radiation Lightsource. Subsequently, we scanned eight sections of NWA 7034 and 7533 with an ARTAX µXRF spectrometer, operated at 28 kV and 0.6 mA with an X-ray beam of ~0.125 mm diameter, integration time of 10s and a step size of 0.2 mm. This mimics the operational conditions of PIXL, a Mars 2020 rover instrument. Regions of elevated Zn were then examined using a Zeiss 1550VP field-emission scanning electron microscope (FE SEM). Preliminary compositions of mineral phases in NWA 7533 C2b were determined using an Oxford X-Max SDD energy-dispersive X-ray spectrometer (EDS) attached to the SEM, with the XPP matrix correction procedure calibrated with internal standards. EPMA analysis will be completed before conference, but these results are expected to differ only slightly from the SEM-EDS data (on the order of 100s ppm).

Results: We recognized two types of Zn-rich phases in the SXRF map of NWA 7533 C2b (Fig. 1):

- Zn-rich nanocrystalline pyroxene in spherules (Sph, Figs. 1-3)
- Zn-bearing chromite (Chr, Fig. 1).

Zinc-rich phases are not correlated with the presence of the hydrous Mn^{4+}-dominant oxides, (Fig. 1), described in Liu et al. (2017 [6]). The µXRF maps of eight sections show that only two sections, NWA 7533 C2 and C2b, contain Zn-rich spherules, although all sections contain Zn-rich chromites.

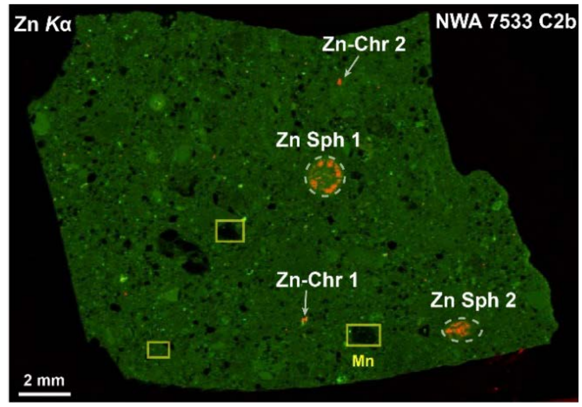

Fig. 1. SXRF Zn *K*α map of NWA 7533 C2b, showing Zn enrichment in spherules (Sph, Figs. 2 and 3) and in chromite (Chr). Yellow rectangles show the location of hydrous Mn-oxides described by Liu et al. (2017) [6].

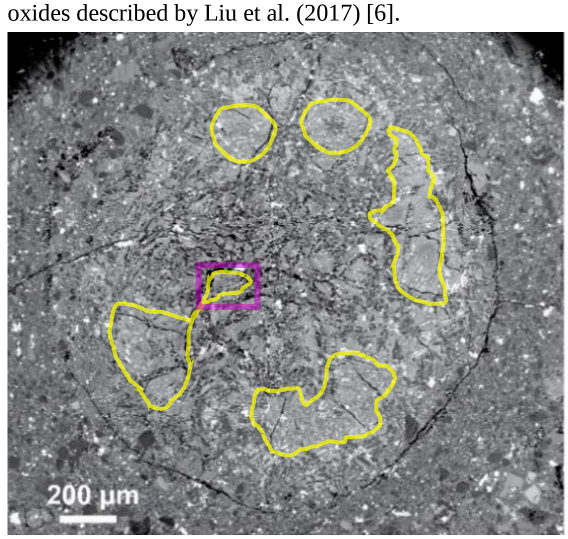

Fig. 2. Back-scattered electron (BSE) image of Zn Sph1 in Fig. 1. Yellow curves demarcate Zn-rich regions. Pink box outlines the area shown in the inset in Fig. 3.

The Zn-rich spherules are >1 mm in the smallest diameter (Figs. 1 and 2). The interiors of the spherules consist of <1 µm augite (~$En_{42-59}Wo_{16-25}$), plagioclase (~$Ab_{\sim55}An_{\sim42}$) laden with magnetite, partially altered pyrite, and phosphate. A texturally-distinct rim (~200 µm in width) consists mainly of pyroxene, feldspar, magnetite, phosphate, and ilmenite. The Zn-rich regions are about 100 µm inward from the edge, and consist of clots with <1 µm augite and ilmenite (Fig. 3). SEM EDS analysis indicates Zn is mainly associated with the augite. These regions contain ≤1.6 wt% ZnO with ≤0.9

wt% P_2O_5, ~0.1 wt% Cl, and no detectable S (<0.04 wt%).

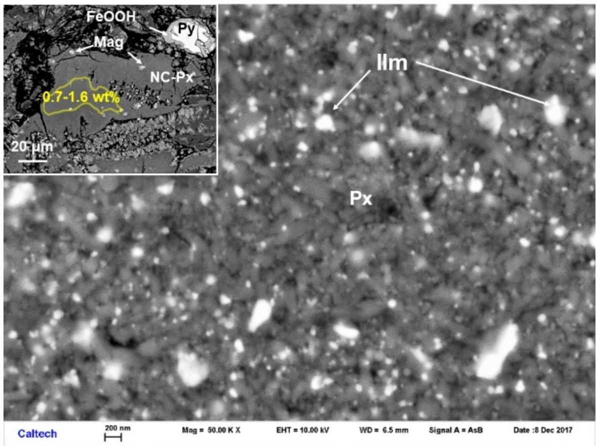

Fig. 3. High magnification image of one Zn-rich region in Sph 1 (inset and purple box in Fig. 2). Bright grains are ilmenite, and gray laths are pyroxenes (Px). Inset shows the region with ZnO contents (in yellow) from SEM-EDS measurements. NC-Px: nanocrystalline pyroxene; Mag: magnetite; Py: pyrite. Scale bar is 200 nm.

All chromite-magnetite grains in NWA 7533 zoned from chromite to Cr-magnetite [7]. The Zn-enrichment occurs within the chromite portions in NWA 7533 C2b, and those with $Cr_2O_3 \geq$ ~50 wt% contain ~0.5 to ~0.9 wt% ZnO (SEM-EDS). These values are similar to EPMA analysis of polycrystalline chromite and detrital chromite grains in NWA 7533 C1 [7].

Discussion:

Zinc in chromite from Martian igneous rocks has rarely been analyzed, available data of chromites in shergottite Sau 005 and EETA 79001 lithology A show significantly lower ZnO contents (<0.15 wt%, [8]). Terrestrial chromite grains with ZnO contents >0.5 wt% are considered to be exceptional [9] and are often linked to high-T hydrothermal fluids (e.g., [10]). Thus, by analogy, some of the Zn-rich chromite grains in NWA 7533 may indicate a hydrothermal origin. Hydrothermal chromite would represent a new form of hydrothermal processes on Mars.

The small size of Zn-rich pyroxene grains (<200 nm wide and <400 nm long, Fig. 3) could contribute to the high Zn sedimentary rocks in the Murray formation at Gale crater, which also contain pyroxenes as determined by CheMin analyses [5, 11].

Enrichment of Zn in terrestrial fluids is typically achieved through high-T alteration of crustal rocks and Zn remains mobile/soluble in fluid as long as pH < 7. Deposition of Zn occurs by precipitating oxide or carbonate if pH becomes more basic. The presence of two apparently unrelated forms of Zn-rich phases in NWA 7533 indicate fluids of different T, pH, and Eh in Martian crusts.

Our finding adds to a long list of observations supporting crustal fluid-rock interactions, recognized in the Martian regolith breccia meteorites (NWA 7034, 7533, 7475). Surface weathering under an exceptionally oxidizing environment is recorded by hydrous Mn^{4+}-dominant-oxides in these meteorites [6]. Higher temperature fluids are indicated by: smectite along grain boundaries [12], Ni-rich pyrite [13], Fe-oxide veins [14], monazite inclusions in F-rich regions in chlorapatite [15], and irregular eskolaite encased by polycrystalline chromite-magnetite [7]. The Zn-rich phases in NWA 7533 are not related to the above alteration features in the sections, suggesting that Zn-enrichment and deposition occurred before their inclusion in NWA 7533.

All of the above features are observable using PIXL (Fig. 4 and [6]). Martian meteorites provide the only advanced opportunity for PIXL to determine and examine real Martian petrologic features. Among them, the Black Beauty meteorites are most similar to the types of sedimentary rocks that the Mars 2020 rover would likely explore in search of habitable environments. Therefore, detailed analysis of fluid-related features in NWA 7034 and 7533 is important for Mars 2020 and its search for habitable environments and biosignatures.

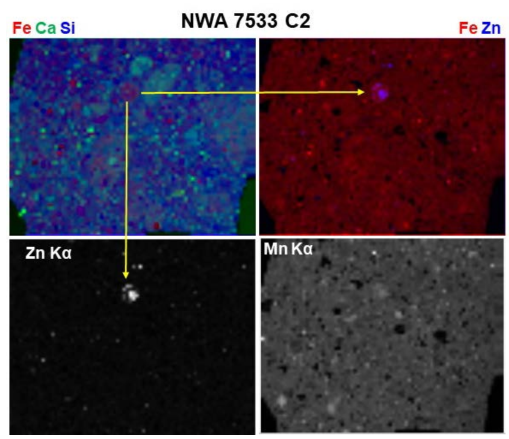

Fig. 4. PIXL-like µXRF map of NWA 7533 C2, showing the ability to detect the Zn, Mn rich phases. F.O.V. 15 mm.

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