

MANGANESE ON MARS AS AN INDICATOR OF HABITABLE ENVIRONMENTS AND A BIOSIGNATURE. N. L. Lanza¹, W. W. Fischer², S. N. Lamm³, P. J. Gasda¹, P.-Y. Meslin⁴, A. M. Ollila¹, J. Frydenvang⁵, S. M. Clegg¹, A. Cousin⁶, D. DeLapp¹, O. Forni⁶, A. Reyes-Newell¹, M. Salvatore³, and R. C. Wiens¹, ¹Los Alamos National Laboratory (nlanza@lanl.gov), ²California Institute of Technology, ³Northern Arizona University, ⁴Universite Paul Sabatier, France, ⁵University of Copenhagen, ⁶IRAP-CNRS, France.

Introduction: The recently discovered high concentrations of manganese (as high as 40 wt% MnOT) in Gale crater on Mars point to past episodes of strongly oxidizing conditions within an aqueous environment [1-2]. On Earth, such simultaneous conditions are almost always both habitable and inhabited by microbes [3]. Present day oxidation of terrestrial Mn(II) is catalyzed primarily by Mn-oxidizing microbes [e.g., 4-5]. In addition, manganese is closely associated with the influx of O₂ into the terrestrial atmosphere and subsequent global shift in redox conditions to the oxidizing environments observed today. Given its close association with life and habitable environments on Earth, manganese has long been considered a principal biosignature for Mars [e.g., 6]. Here we provide an overview of manganese as a redox indicator and describe how specific characteristics of Mn-bearing materials may be used to identify potential biosignatures.

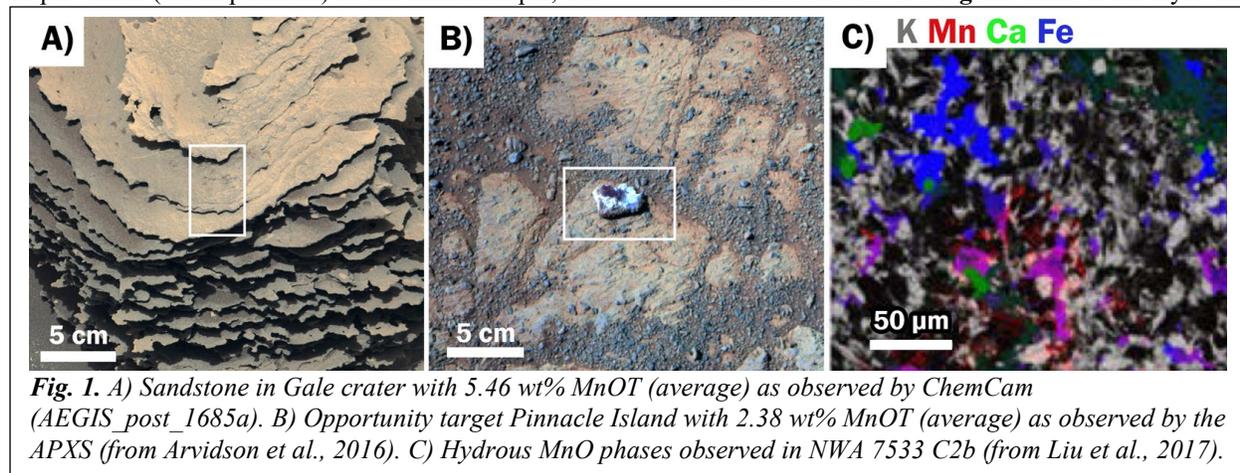
Manganese as redox indicator: Manganese minerals provide unique indicators of water-rich environments and their redox states. Significant oxygen fugacities and readily available water are required to drive Mn²⁺ oxidation and cycling. No igneous phases in which Mn is the dominant cation have been observed in any terrestrial system; thus high Mn minerals are always secondary in nature. Once Mn(II) is released from rocks and dissolved in fluids, high-potential oxidants are required to oxidize and precipitate Mn. Whereas Fe and S are readily oxidized by a wide range of oxidants to high valence states under mildly oxidizing conditions (-100-100 mV), manganese is uniquely sensitive to high potential oxidants (>> 500 mV) [7]. Iron oxides can precipitate at a range of pE values (redox potential) at circumneutral pH, but

Mn-oxides are only stable in strongly oxidizing, high pH (>8) aqueous environments. As a result, an environment may be “oxidizing” for Fe but not when viewed in the context of Mn. Without microbial mediation, Mn is less likely to oxidize than Fe in many natural environments.

Because of the unique sensitivity of Mn to redox conditions, Mn-rich rocks on Earth closely track the rise of atmospheric oxygen [8-11]. Prior to the Great Oxygenation Event ~2.35 Ga, the early anaerobic Earth was characterized by redox cycles of Fe and S, but not Mn [12-15]. Concentrated Mn deposits do not occur until after the flux of O₂ reached a critical threshold in Earth’s atmosphere (~1% present terrestrial atmospheric levels of O₂). This transition marks a major change in Earth’s environment in which the diversity of minerals produced by redox processes was greatly increased [8, 16-17].

Manganese as biosignature: In addition to its indirect association with photosynthesis in the past, Mn is also directly associated with microbial action in the present day. On present-day Earth, oxidation of Mn(II) is catalyzed primarily by Mn-oxidizing microbes [e.g., 4-5], which are ubiquitous in the terrestrial environment [4]. Microbial catalysis greatly increases the rate of Mn oxidation at circumneutral and low pH compared to abiotic processes [18], allowing Mn-oxides to precipitate in thermodynamically unstable conditions [19-20]. Microbes can catalyze Mn(II) oxidation by modifying pE-pH conditions in the local aqueous environment, or by releasing metabolites that chemically oxidize Mn(II) [21-22]. When Mn-oxides precipitate in disequilibrium conditions, they are a strong indicator for the presence of catalyzing microbial communities.

Characteristics of biogenic Mn: Both layer and



tunnel mineral structures have been observed in terrestrial biogenic Mn-oxides [e.g., 23], but typical products of microbial oxidation of Mn(II) are layer-type Mn-oxides whose mineral structures are poorly crystalline and contain mostly Mn(IV) and little Mn(III) [4]. Preliminary work suggests that the presence and abundance of specific trace elements also provides evidence for a biogenic origin in Mn-bearing materials [24]. Manganese oxides are well known to scavenge trace metals from water [25-26] because of their surface charge properties, which exhibit a strong dependence on the pH of the waters with which they are in contact [27]. Such scavenging has been observed even in acidic stream environments where biogenic Mn-oxides uptake Co, Ni, Zn, and other metals and thus metals are found in higher abundance in these Mn-oxides [e.g., 28]. In these environments, Mn-oxide precipitation must be biogenic in nature. Recent experimental results suggest that the scavenging pattern observed in Mn-rich fracture fills in Gale are consistent with deposits of MnO₂ [29].

Observations of manganese on Mars and in martian meteorites: High concentrations of manganese have been observed in a wide range of martian materials, including in situ and within martian meteorites.

Gale crater: High manganese has been observed in a variety of geologic settings in Gale including as a surface coating [1], fracture fills [2], and embedded in fine to coarse grained sediments [30-31]. Some instances are clearly diagenetic [e.g., 2] while others may be either authigenic or diagenetic [30-31] (Fig 1A). In terrestrial lakes, Mn is typically deposited in shallow water environments due to the increased abundance of dissolved oxygen [e.g., 32-33]. The water column within the Gale lake may have been redox stratified, leading to more oxidizing conditions in shallow water and less oxidizing conditions in deeper waters, as evidenced by the deposition of different redox sensitive mineral species [34].

Endeavor crater: Manganese oxides were observed by the Opportunity rover at the rim of Endeavor crater in Meridiani Planum [35] (Fig 1B). High-Mn materials were observed in a low-Mn host rock, pointing to the presence of strongly oxidizing groundwaters.

Martian meteorites: Primary manganese minerals have been observed in multiple pairings of the “Black Beauty” meteorite group (Fig 1C), which represents a martian regolith breccia. Hydrous Mn(IV)-oxides were observed in NWA 7034 and NWA 7533 within unaltered mineral grains, suggesting that they formed while on Mars and not as the result of terrestrial alteration [36]. Mn-oxide was also observed in NWA 8171 and determined not to be terrestrial alteration [37].

Discussion: Manganese-bearing materials represent an important new class of analysis targets for in situ and

orbital Mars missions. Observations of Mn-bearing materials in at least three locations on Mars (Gale, Endeavor, and the Black Beauty source location) suggests that manganese minerals are likely more widespread than was previously recognized, and that the conditions required to concentrate and deposit Mn minerals were present on Mars at a broad scale. The presence of high abundances of Mn (>1 wt% MnOT) point to the existence of strongly oxidizing conditions well beyond those required to oxidize Fe, which opens up the range of potentially habitable environments that may have existed on Mars. In addition, the close relationship between Mn minerals and microbial communities on Earth makes Mn-bearing materials a key target for biosignatures. In some environments (e.g., acidic waters), the mere presence of Mn minerals may itself be a biosignature. Given the broad distribution of Mn-bearing materials within the Gale lake sediments [38], it is highly plausible that Mn will be similarly abundant in the apparently lacustrine environment in Jezero crater, the landing site of the upcoming Mars 2020 rover. A main goal of the Mars 2020 mission is to identify materials with high biosignature potential for sample caching and future return. Should a high Mn sample be identified, it would provide key information about redox conditions and could give critical insight into the formation mechanism of Mn minerals on Mars.

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