TARGETING MANGANESE MINERALS ON MARS AS POTENTIAL BIOSIGNATURES. N. L. Lanza[1], W.W. Fischer[2], C. Yeager[1], U. Lingappa[2], A. M. Ollila[1], P. J. Gasda[1], S. N. Lamm[3], M. Salvatore[3], S. M. Clegg[1], and R. C. Wiens[1], [1]Los Alamos National Laboratory, Los Alamos, NM, U.S.A. (nlanza@lanl.gov), [2]California Institute of Technology, Pasadena, CA, U.S.A., [3]Northern Arizona University, Flagstaff, AZ, U.S.A.

Introduction: High concentrations of manganese have recently been discovered on Mars at two rover landing sites [1-3] and in martian meteorites [4-5]. Its presence indicates that Mars has been host to past episodes of strongly oxidizing conditions within an aqueous environment [1-2]. Given that the two landing sites are 1000s of km apart and that the meteorites are from a third (unknown) location, these observations as a whole suggest that aqueous, oxidizing conditions were likely widespread on Mars. On Earth, environments with such simultaneous conditions are almost always inhabited by microbes [6]. The close relationship between Mn and life on Earth makes Mn-bearing rocks and sediments a high priority target for the Mars 2020 mission, which has the goals of finding materials containing potential biosignatures to sample and cache for future return to Earth.

Manganese as redox indicator: Manganese minerals provide unique indicators of water-rich environments and their redox states. Whereas Fe and S are readily oxidized by a wide range of oxidants to high valence states under mildly oxidizing conditions (ca. -100 to 100 mV), manganese is uniquely sensitive to high potential oxidants (>> 500 mV) [7]. Iron-oxides can precipitate at a range of pE values at circumneutral pH, but Mn-oxides are only stable in strongly oxidizing, high pH (>8) environments. Without microbial mediation, Mn is less likely to oxidize than Fe in many natural environments. As a result, an environment may be "oxidizing" for Fe but not for Mn.

Manganese as biosignature: Because of manganese's unique sensitivity to redox conditions, Mn-rich rocks on Earth closely track the rise of atmospheric oxygen [9]. Concentrated Mn deposits do not appear in the terrestrial geologic record until after the flux of O_2 to Earth surface environments. This transition marks a major change in Earth's environment that was enabled by the rise of photosynthetic life.

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 [10-11], which are ubiquitous in the terrestrial environment [10]. Microbial catalysis greatly increases the rate of Mn oxidation at circumneutral and low pH compared to abiotic processes [13], allowing Mn-oxides to precipitate in environments in which they would otherwise be unstable [14].

Observable signatures of potentially microbial Mn with rover payload instruments: The Mars 2020 rover will carry with it a number of analytical instruments that can assess chemistry (SuperCam, PIXL), mineralogy (SuperCam, SHERLOC), and organic content (SuperCam, SHERLOC, PIXL) of martian surface materials, all of which can be used to identify Mn-related biosignatures. Typical products of microbial oxidation of Mn(II) are poorly crystalline layer-type Mn-oxides [10]. Although such materials can be a challenge to assess, some species may be discerned using Raman and luminescence [15]. Microbes also cycle between Mn^{3+} and Mn^{4+} in at least some contexts, making Mn redox state an important indicator of microbial origin [16-18]. Although the oxidation state of Mn is not directly measureable by the Mars 2020 payload, recent results show that trace elements in Mn minerals may be used to infer the redox state of Mn, thus identifying samples that are more likely to have a biogenic origin [16]. Manganese oxides are also well known to scavenge trace metals from water [19], which has been observed in several high Mn martian targets [2]. Manganese oxides may also trap and preserve organic carbon, including fatty acids and protein- and lipopolysaccharide-like carbon [20], which should be readily discernible in Raman and luminescence data.

References: [1] Lanza, N.L et al. (2014). GRL 41, 5755-5763. [2] Lanza, N.L. et al. (2016). GRL 43, 7398-7407. [3] Arvidson, R.E. et al. (2016). Am. Min. 101, 1389-1405. [4] Liu, Y. et al. (2017). 48th LPSC, Houston, TX, no. 1345. [5] Cao, F. et al. (2018). Goldschmidt2018 330. [6] Crerar, D.A. et al. (1980). Geol. & Geochem. of Mn vo1. 1, pp.293-334. [7] Stumm, W. & Morgan, J.J. (1996). Aq. Chem.: Chemical Equilibria & Rates in Natural Waters, 3rd edition, John Wiley & Sons, Inc.: New York, 1022p. [9] Maynard, J.B. (2010). Econ. Geol. 105, 535-552. [10] Tebo, B.M. et al. (2004) Ann. Rev. Earth & Planet. Sci. 32, 287-328. [11] Bargar, J.R. et al. (2005). Am. Min. 90, 143-154. [13] Morgan, J. J. (2005). Geochim. et Cosmochim. Acta 69 (1), 35–48. [14] Robins, E.I. & Corley, T.L. (2005). Hydrobiologia 534, 165-180. [15] Ollila, A. M. et al. (2018). 49th LPSC, Houston, TX, No. 2786. [16] Lanza, N.L. et al. (2017). 48th LPSC, Houston, TX, no. 2913. [17] Magyar, J. et al. (2018). Goldschmidt2018 1651. [18] Lingappa, U. et al. (2018). Goldschmidt2018 1541. [19] Sorem, R.K. (1989) Marine Mining 8(2), 185-200. [20] Estes, E.E. et al. (2017). Geobiology 15, 158-172.