OXIDATION OF MANGANESE AT KIMBERLEY, GALE CRATER: MORE FREE OXYGEN IN MARS' PAST?

N.L. Lanza (nlanza@lanl.gov)[1], R.C. Wiens[1], R. E. Arvidson[2], B.C. Clark[3], W.W. Fischer[4], R. Gellert[5], J.P. Grotzinger[4], J.A. Hurowitz[6], S.M. McLennan[6], R.V. Morris[7], M. S. Rice[8], J.F. Bell III[9], J.A. Berger[10], D.L. Blaney[11], N.T. Bridges[12], F. Calef III[11], J.L. Campbell[5], S.M. Clegg[1], A.Cousin[1], K.S. Edgett[13], C. Fabre[14], M.R. Fisk[15], O. Forni[16], J. Frydenvang[17], K.R. Hardy[18], C. Hardgrove[9], J.R. Johnson[12], J. Lasue[16], S. Le Mouélic[19], M.C. Malin[13], N. Mangold[19], J. Martìn-Torres[20, 21], S. Maurice[16], M.J. McBride[13], D.W. Ming[7], H.E. Newsom[22], S. Schröder[16], L.M. Thompson[23], A.H. Treiman[24], S. VanBommel[5], D.T. Vaniman[25], and M.-P. Zorzano[26]. [1]Los Alamos National Laboratory, Los Alamos, NM, U.S.A. [2]Washington University, St. Louis, MO, U.S.A. [3]Space Science Institute, Boulder, CO, U.S.A. [4]California Institute of Technology, Pasadena, CA, U.S.A. [5]University of Guelph, Guelph, Ontario, N1G 2W1, Canada. [6]Stony Brook University, Stony Brook, NY, U.S.A. [7]NASA Johnson Space Center, Houston, TX, U.S.A. [8]Western Washington University, Bellingham, WA, U.S.A. [9]Arizona State University, Tempe, AZ. [10]University of Western Ontario, London, Ontario, N6A 5B7, Canada. [11]Jet Propulsion Laboratory, Pasadena, CA, U.S.A. [12]APL, Johns Hopkins University, Laurel, MD, U.S.A. [13]Malin Space Science Systems, San Diego, CA, U.S.A. [14]Université de Lorraine, Nancy, France. [15]Oregon State University, Corvallis, OR, U.S.A. [16]Institut de Recherche en Astrophysique et Planétologie (IRAP), Toulouse, France. [17]Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark. [18]U.S. Naval Academy, Annapolis, MD, U.S.A. [19] LPGNantes, CNRS UMR 6112, Université de Nantes, Nantes, France. [20]Instituto Andaluz de Ciencias de la Tierra, Granada, Spain. [21]Luleå University of Technology, Kiruna, Sweden. [22]University of New Mexico, Albuquerque, NM, U.S.A. [23]Univeristy of New Brunswick, New Brunswick, Canada. [24]Lunar and Planetary Institute, Houston, TX, U.S.A. [25]Planetary Science Institute, Tucson, AZ, U.S.A. [26]Instituto Nacional de Técnica Aeroespacial, Madrid, Spain.

Introduction: High Mn concentrations provide unique indicators of water-rich environments and their redox state. Very high-potential oxidants are required to oxidize Mn to insoluble, high-valence oxides that can precipitate and concentrate Mn in rocks and sediments; these redox potentials are much higher than those needed to oxidize Fe or S. Consequently, Mn-rich rocks on Earth closely track the rise of atmospheric oxygen [1-4]. Given the association between Mn-rich rocks and the redox state of surface environments, observations of anomalous Mn enrichments on Mars raise similar questions about redox history, solubility and aqueous transport, and availability as a metabolic substrate. Our observations suggest that at least some of the high Mn present in Gale crater occurs in the form of Mn-oxides filling veins that crosscut sandstones, requiring post-depositional precipitation as highly oxidizing fluids moved through the fractured strata after their deposition and lithification.

High manganese observations: Three rock targets in the Dillinger member of the Kimberley waypoint were found to have Mn concentrations highly elevated above those of average martian crust and other rocks of the same member: Stephen (sols 611, 619, 630), Neil (sol 619), and Mondooma (sol 625) (Fig. 1) [5]. All of these targets sample resistant fracture fills that crosscut this member. ChemCam manganese abundances at Stephen, Neil, and Mondooma show average MnO abundances of 5.2 wt% (Stephen), 5.3 wt% (Neil), and 6.7 wt% (Mondooma). Alpha Particle Xray Spectrometer (APXS) measurements on Stephen show an average MnO abundance of 3.7 wt%, the highest Mn abundance observed by this instrument in Gale crater to date. The average Mn values from both instruments are well above typical martian igneous values of ~0.4 wt% MnO [6].
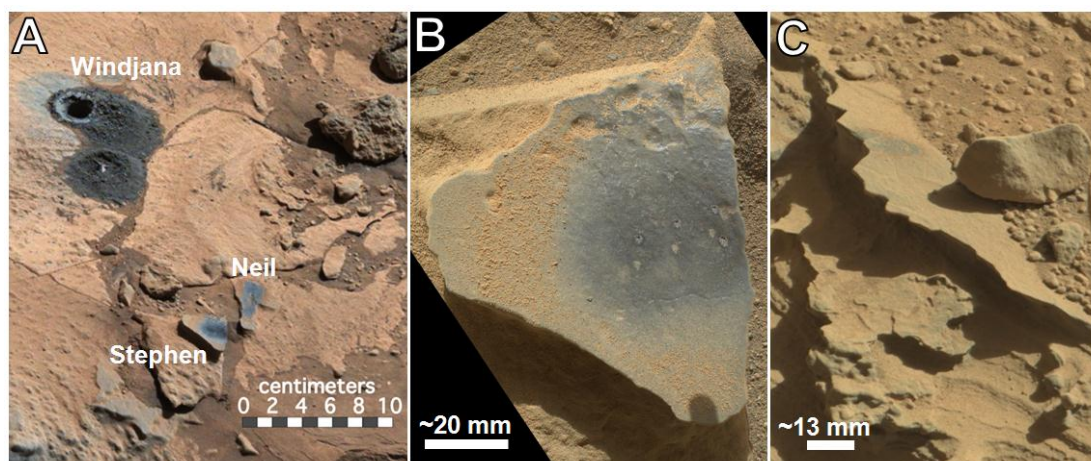

Fig. 1. Targets at Kimberley containing elevated Mn. **(A)** Overview of the Windjana drill site showing targets Stephen and Neil (MCAM 0626ML0026760010302385E01). **(B)** Closeup of Stephen showing a dark material beneath the surface dust layer; this target was analyzed by both ChemCam and APXS. Note that the ChemCam analysis locations are visible as small, rounded pits in the rock surface (MAHLI 0627MH0004070000203592R00). **(C)** The Mondooma target is a fin-like, more resistant feature that is eroding out from the surrounding outcrop; the highest Mn location at Kimberley was found in this target (~35 wt% MnO) (MCAM 0626MR0026790000401609E01).
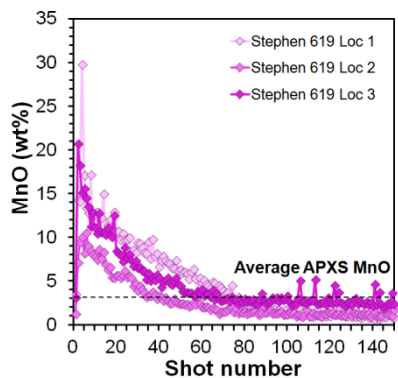
Fig. 2. Mn abundance decreases with depth (shot) in ChemCam data obtained on the target Stephen (619).

Trends with depth: Mn abundance in ChemCam sampling locations was greatest in the first post-dust shots of the series and systematically decreased with succeeding shots (i.e. depth) (Fig. 2), with a maximum of ~35 wt% MnO on Mondooma location 1, shot 4. These results are consistent with a thin layer containing elevated Mn that was deposited adjacent to the Windjana outcrop material.

Geochemical trends: In ChemCam data, Si and Ca are inversely correlated with Mn, suggesting that the high Mn phase is not a silicate and does not contain abundant Ca. ChemCam did not detect any Cl or S in the three high Mn targets; this along with the absence of C above atmospheric levels also suggest that the Mn is not present as a sulfate, chloride, or carbonate phase. The APXS composition of Stephen is generally similar to the Windjana bedrock except for elevated abundances in Mg, Cl, Ni, Cu, Co, and Zn in addition to elevated Mn; however, of the elements showing enrichment, only Ni and Cu show a strong correlation with Mn. These trends suggest the presence of Mn-oxides, which are well known to scavenge trace metals from water [7,8].

Implications for the martian environment: The presence of likely Mn-oxides has important implications for the past redox conditions of Gale groundwater and the martian atmosphere. Very high potential redox reactions are needed to oxidize Mn^{2+} at circumneutral pH ($\gg$500 mV), which requires either O_2 or species derived from O_2 (e.g. reactive oxygen species). The subsurface geological setting of the fractures rules out photooxidation as a mechanism for oxidation. Oxychlorine species have been detected by the Sample Analysis at Mars (SAM) instrument in solid samples throughout the rover's traverse [9-11], some of which can have high enough redox potentials to oxidize Mn(II) [12]. However, none of these oxychlorine detections were associated with Mn enrichments, despite thorough analysis by the CheMin, APXS, and Chem-Cam instruments [13-16]. Accordingly, we hypothesize that O_2 (or species derived thereby) provides the

most reasonable pathway to Mn oxidation and enrichment.

On Earth, O_2 is present in groundwaters due to interaction and equilibrium with the atmosphere. Due to the extremely slow kinetics of Mn oxidation, either concentrations of martian atmospheric O_2 were much higher in the past than observed today or the timescale for water flowing through these fractures were remarkably long (Fig. 3). Oxidation in a long timescale, low O_2 aqueous environment is a less favorable model because chemical weathering in this environment is expected to remove O_2 from fluids, making them more reducing rather than more oxidizing over time. Our results suggest that the fluids moving along Kimberley fractures were in at least partial contact with the atmosphere and that the atmosphere contained sufficient amounts of O_2 to oxidize Mn. Additionally, the discovery of Mn-oxides at the rim of Endeavor crater [17] suggests that the conditions required to concentrate and deposit Mn were present well beyond Gale crater.
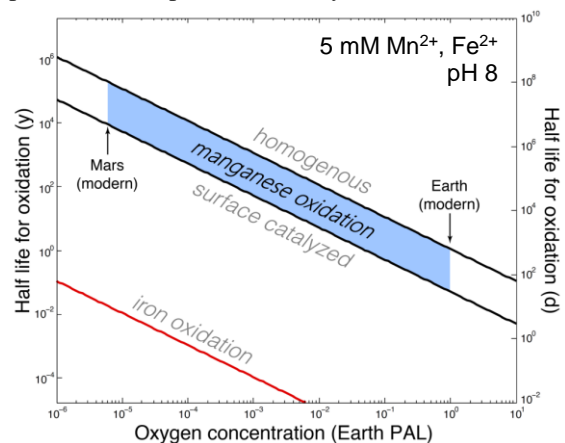

Fig. 3 . Characteristic half-lives for the kinetics of Mn oxidation by O_2 in terms of terrestrial present-day O_2 levels (PAL) for both homogenous oxidation from solution (upper black line) and typical surface-catalyzed oxidation by metal oxides (lower black line), with Fe oxidation by O_2 for comparison (red line).

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