

IRON-MANGANESE REDOX REACTIONS IN ENDEAVOUR CRATER RIM APRON ROCKS. D. W. Ming¹, D. W. Mittlefehldt¹, R. Gellert², T. Peretyazhko³, B. C. Clark⁴, R. V. Morris¹, A. S. Yen⁵, R. E. Arvidson⁶, L. S. Crumpler⁷, W. H. Farrand⁴, J. A. Grant III⁸, B. L. Jolliff⁶, T. J. Parker⁵, C. Schröder⁹, and the Athena Science Team, ¹NASA Johnson Space Center, Houston, TX, USA, 77058, USA, douglas.w.ming@nasa.gov, ²University of Guelph, Guelph, ON, Canada, ³Jacobs Technology, NASA Johnson Space Center, Houston, TX, USA, ⁴Space Science Institute, Boulder, CO, USA, ⁵NASA Jet Propulsion Laboratory, Pasadena, CA, USA, ⁶Washington University in St. Louis, St. Louis, MO, USA, ⁷New Mexico Museum Natural History & Science, Albuquerque, NM, USA, ⁸Smithsonian National Air & Space Museum, Center for Earth & Planetary Studies, Washington, DC, USA, ⁹University of Stirling, Stirling, Scotland, UK.

Introduction: The Mars Exploration Rover *Opportunity* has been exploring Noachian age rocks and outcrops on the rim of the 22 km diameter Endeavour crater since August 2011. The Cape York area is a low-lying rim of Endeavour that contains 3 distinct lithologies: 1) the stratigraphically lowest Matijevec fm of pre-impact lithology, 2) Shoemaker fm of impact breccias, and 3) the stratigraphically highest rim lithology Grasberg fm of post-impact sediments that drape the lower slopes of the rim [1-2]. The sulfate-rich sediment of the Burns fm lies unconformably over the Grasberg fm. Ca-sulfate veins were discovered in Grasberg fm sediments; the sulfates precipitated from aqueous fluids flowing upward through these materials [3]. *Opportunity* investigated the chemistry and morphology of outcrops in the Matijevec fm that have Fe³⁺-rich smectite detected by orbital signatures returned by CRISM on MRO [1]. Matijevec fm also contains “boxwork” fractures with chemistry consistent with an Al-rich smectite and veins that appear to be rich in Ca-sulfate [1]. More recently on Cape Tribulation, *Opportunity* has characterized two S-, Mg- and Mn-rich rocks overturned and fractured by the rover’s wheels on Cook Haven [4]. Those rocks have been dubbed “Pinnacle Island” and “Stuart Island” and will be referred to as the “Island” rocks.

The objectives of this study are to characterize the Fe and Mn contents in the Cape York materials, including the two Island rocks, and to provide a model for Mn mobilization and precipitation. Detailed geochemistry of Endeavour rim rocks is presented in a companion paper [5]. Geochemical trends and elemental associations were obtained from data returned by the Alpha Particle X-ray Spectrometer (APXS) on *Opportunity*.

Fe/Mn, Ni, and S: Elemental Fe/Mn of “high” S-bearing materials on Endeavour rim deviate substantial from the expected ratio of 45-55 for unaltered martian basalts (Fig. 1). Mn in Grasberg fm sediments is leached as indicated by low Mn contents resulting in high Fe/Mn; whereas, Mn is precipitated in S-rich materials in the Matijevec fm veins and Island rocks as indicated by low Fe/Mn (Figs. 1-2) and high Mn con-

tent (Fig. 3). Grasberg fm materials have the lowest Mn measured by *Opportunity* at Meridiani Planum, with the exception of the Ca-sulfate veins (Homestake and Ootsark) in Grasberg fm and purported phyllosilicate-rich boxworks in Matijevec fm (Figs. 1,3). Grasberg fm Ca-sulfate veins and boxwork fractures however have Fe/Mn expected for basaltic materials suggesting redox conditions have not fractionated Mn from Fe. A strong correlation exists between S and Fe/Mn suggesting Mn precipitation/oxidation with S in the Matijevec fm veins and Island rocks (Fig. 2). This correlation suggests that the same fluid or fluids from the same source region precipitated in Matijevec fm veins and Island rocks. Ni has a correlation with Fe/Mn in these rocks suggesting Ni was transported by the S-rich fluids (Fig. 1b).

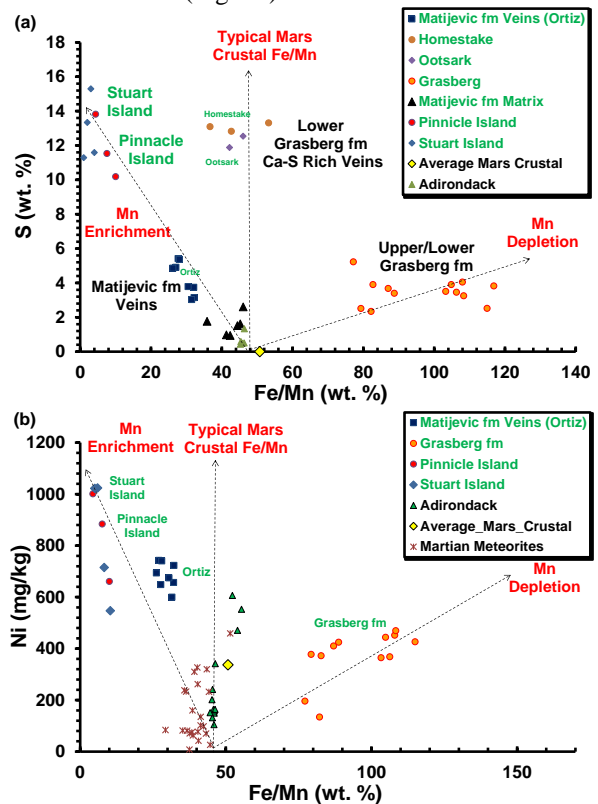


Figure 1. Elemental S (a) and Ni (b) vs Fe/Mn in Endeavour crater rim rocks with high S.

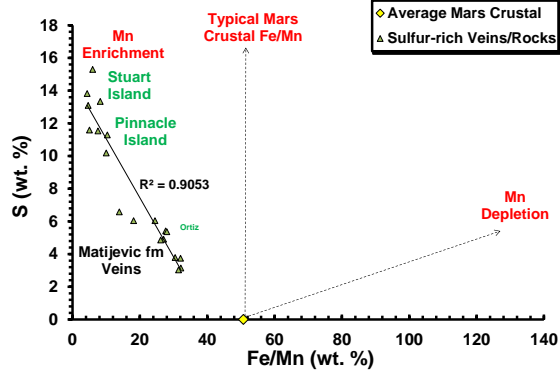


Figure 2. Trend line for elemental S vs Fe/Mn in Endeavour crater rim rocks with high S.

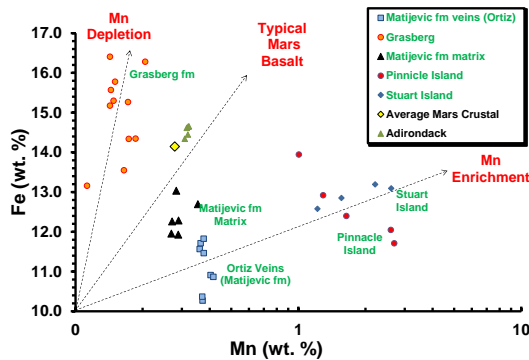
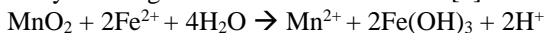


Figure 3. Elemental Fe vs Mn for Endeavour rim apron rocks and veins.

Model for Mn Mobilization: High Fe/Mn in Grasberg fm sediments suggests leaching of Mn in these materials. Fractionation of Mn from Fe is indication of redox and/or pH reactions in Grasberg fm. Alkaline and alkaline earth cations do not vary substantially for Grasberg, Matijevec, and Shoemaker fm rocks [5] suggesting that redox reactions, not pH, mobilized Mn. Higher Fe in Grasberg fm materials compared with Matijevec fm matrix materials suggests Fe precipitation in Grasberg fm (Fig. 3). It is likely that highly oxidized solutions from the overlying Burns fm interacted with Grasberg fm sediments leading to the oxidation of Fe and Mn. We hypothesize that oxidized Mn was mobilized (Mn reduced) in Grasberg sediments by late stage fluxes of Fe²⁺-rich fluids [6]:



This reaction also produces excess acidity. Others have suggested that the Burns fm acid-sulfate deposits were formed by subsurface waters of near-neutral pH and rich in Fe²⁺ that were rapidly oxidized to Fe³⁺ producing excess acidity [7]. The Grasberg formation materials have likely been extensively altered to high Fe³⁺/Fe_T, but unfortunately, the source of the Mössbauer spectrometer on *Opportunity* was too weak to acquire Fe oxidation states at this stage of the mission.

Model for Mn Precipitation in Endeavour Rim Materials. Mn²⁺, Ni²⁺, and possibly other ions were transported with S-rich fluids through the Endeavour crater rim materials (Fig. 4). Regional groundwater upwelling, possibly with recharge from the southern highlands, is one model for the movement of water up through Meridiani Planum and the Endeavour crater rim deposits [8]. Endeavour crater's rim may have been degraded up to 200 meters [9]; hence, there may have been hydraulic head to move fluids during the alteration of the Burns fm into the Endeavour rim materials. It is unclear how the fluids became enriched in S, however, the same process responsible for the formation of the Burns fm may be the S source [7]. Mn, S, Ni, and other ions (e.g., Ca²⁺) precipitated in Matijevec fm veins and Island rocks fractures, although, the Island rocks were float so their origin is uncertain. Mn may have precipitated as a sulfate, and over time Mn oxidized to form Mn-oxides [1]. Potential reactions for Mn precipitation are shown in Fig. 4.

Implications for Fe/Mn Redox Reactions. Fe/Mn is a sensitive indicator for redox reactions. Redox reactions have played an important role in the mobilization and transportation of redox sensitive elements in the Endeavour rim deposits. Redox pairs are essential for metabolic systems and thus Endeavour rim may have provided suitable habitats for life.

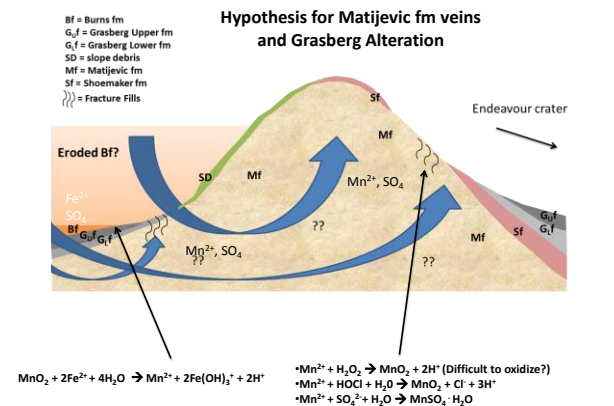


Figure 4. Model for mobilization, movement, and precipitation of Mn in Endeavour crater rim materials.

References: [1] Arvidson R.E. et al. (2014) *Science*, 343, DOI: 10.1126/science.1248097. [2] Crumpler L.S. et al. (2015) *JGR-Planets*, in revision. [3] Squyres S.W. et al. (2012) *Science*, 336, 570-576. [4] Arvidson R.E. et al., (2015), this volume; [5] Mittlefehldt D.W. et al. (2015) this volume. [6] Postma D. and Appelo C.A.J. (2000) *GCA*, 64, 1237-1247. [7] Hurowitz J.A. et al. (2010) *Nature Geo*, 3, 323-326; [8] Andrews-Hanna J. et al. (2010) *JGR-Planets*, 115, DOI: 10.1029/2009JE003485; [9] Grant J.A. et al. (2015), this volume.