# MANGANESE ENRICHMENT PATHWAYS RELEVANT TO GALE CRATER, MARS: EVAPORATIVE CONCENTRATION AND CHLORINE-INDUCED PRECIPITATION

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**Introduction:** The *Curiosity* rover has discovered localized Mn enrichments in Gale crater on Mars with the APXS and ChemCam geochemical instruments [1,2]. Mn enrichment is remarkable for an aqueous system in Gale because, at neutral to low pH, the Mn oxidation reaction:

$$Mn^{2+} + 2H_2O \rightarrow Mn^{IV}O_2 + 4H^+ + 2e^- \ (E° = -1.23V)$$
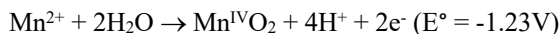
is non-spontaneous with a negative electrochemical potential (E° at STP); an oxidant is necessary to induce precipitation of Mn as an oxide. Here, we explore two pathways for Mn enrichment relevant to Gale crater: evaporative concentration and redox precipitation by Cl-species.
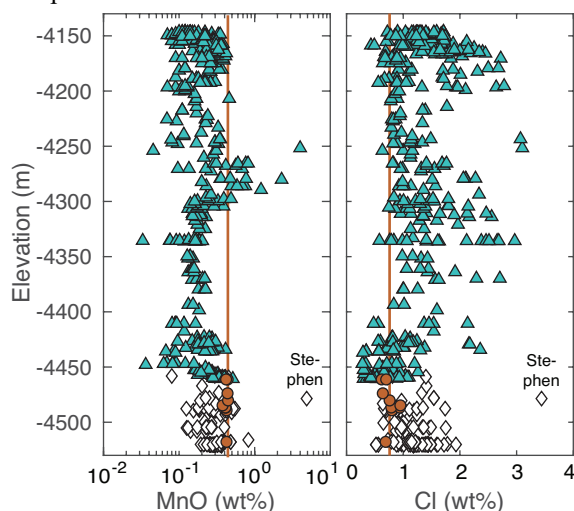


**Fig. 1:** *Log MnO and linear Cl concentrations in APXS targets in Gale crater, with elevation as a proxy for stratigraphic position. All targets in the Bradbury group (diamonds) and Mt. Sharp group (triangles) are shown with average Mars soil (brown circles and vertical line).*

**Mn and Cl in Gale Crater:** *Curiosity's* APXS quantifies Cl and Mn at all relevant concentrations, and here we present an overview of Gale crater results. The rover's traverse has been up a sequence of sedimentary strata. Thus, plots of MnO and Cl concentrations versus elevation provide a rough chemostratigraphic profile (Fig. 1).

In the APXS data set, Mn enrichments are very limited spatially. ChemCam has detected a larger number of localized Mn enrichments because they have probed 3–4 times more targets, most with 3–5 small ~350 μm spots each; nonetheless the stratigraphic locations cor-

respond with those found by the APXS [2]. In the Bradbury group, one vein target, Stephen, is highly enriched in MnO (4.1 wt%). In the Mt. Sharp group, a number of Mn-rich diagenetic features were found near the Sutton/Blunt's Point member contact at -4300 to -4250 m elevation.

Chlorine concentrations in Gale crater vary over one order of magnitude, ranging from 0.3 wt% in the Buckskin drill fines up to 3.4 wt% in the unusual vein Stephen. The median Cl concentration in drilled material ($0.56 \pm 0.28$ wt%) is about half of the median Cl concentration in unbrushed surfaces ($1.23 \pm 0.51$ wt%) and brushed surfaces ($1.06 \pm 0.54$ wt%).

**Evaporative Concentration:** In a closed basin, dissolved constituents will necessarily be deposited as solids when 100% of the water is removed by evaporation and/or freezing and sublimation. To approximate the fate of Mn in an evaporitic scenario relevant to Gale crater, which is a closed basin, we ran a *simple* thermochemical evaporation model with PHREEQC [3]. The dilute starting composition was adapted from analyses of a basaltic aquifer in the Snake River basalt (Table 1). The assumptions include (1) charge is balanced by pH, (2) carbonates do not form (because they have not been found in Gale), and (3) the system is closed, except for the removal of pure $H_2O(g)$. $SO_4^{2-}$ was increased to the lowest concentration such that (2) was satisfied, and the resulting value is plausible for a S-rich Martian system. The model was run in 12 steps to simulate the evaporation of 95% of the initial water. Non-ideal behavior in very high ionic strength brines results in unreliable thermochemical models, thus we did not model higher percentages of evaporation.

**Table 1:** *Initial concentrations of dilute aquifer water*

| temp | 25 | K | 5 mg/L |
|---|---|---|---|
| pH | 7 | Mg | 17 mg/L |
| C(4) | 222 mg/L | Mn | 29 μg/L |
| Ca | 51 mg/L | Na | 43 mg/L |
| Cl | 32 mg/L | S(6) | 185 mg/L |
| Fe | 60 μg/L | Si | 37 mg/L |

The results of the model indicate that $Mn^{2+}$ is still soluble with 5% of the initial water remaining (Fig. 2). Being undersaturated in all phases, $Mn^{2+}$ is thus concentrated in the brine.

Ferric iron phases are supersaturated starting with 99%-91% water remaining. Amorphous silica becomes saturated with 37%-28% water remaining, and gypsum is saturated with 8%-6% water remaining. Halides are still undersaturated in the brine, and are thus enriched.
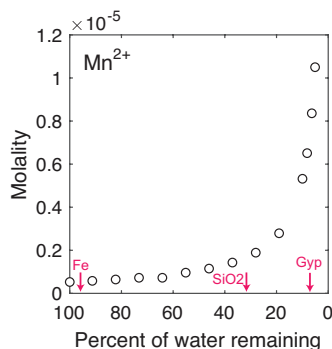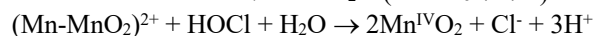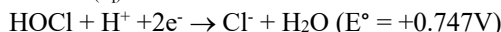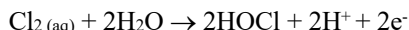
**Fig. 2:** *Concentration of $Mn^{2+}$ in modelled solution as evaporation proceeds to 5% of the initial amount (1 L). Saturation points of ferric oxides, amorphous silica, and gypsum are shown.*



**Fig. 3:** *Predicted Mn-species ($MnCl_2$-aq) and phases for $\log a(Mn)=0$, $aH_2O=1$, $\log a(Cl)<0$, 25 species and minerals. $ClO_3^-$ is not in the database.*

**Redox Precipitation:** Chlorine has multiple valence states and it may oxidize dissolved $Mn^{2+}$. For example, $Cl_2$ added to water supplies as a disinfectant causes Fe- and Mn-oxide scaling in water treatment processes [e.g., 4]. Cl oxidation is exploited to intentionally remove undesirable Fe and Mn from water by adding excess free $Cl_2$ and a colloidal adsorption site, $(Mn-MnO_2)^{2+}$ [5-7], and the product oxide is filtered [4-5]:

$$Cl_{2\,(aq)} + 2H_2O \rightarrow 2HOCl + 2H^+ + 2e^-$$
$$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O \ (E° = +0.747V)$$
$$(Mn-MnO_2)^{2+} + HOCl + H_2O \rightarrow 2Mn^{IV}O_2 + Cl^- + 3H^+$$

This oxidation process is spontaneous and efficient at pH 6 – 8 [4-7] and reaction rates are sufficiently fast to be useful for water treatment plants ($\sim$4x$10^6$M$^{-2}$s$^{-1}$) [6]. On Mars, $Cl_2$ may be derived from volcanism and impact events, and abundant nanophase Fe-(Mn) particles are present to provide adsorption sites.

Other Cl-species may induce redox reactions, for instance, perchlorate ($Cl^{VII}O_4^-$) and chlorate ($Cl^{IV}O_3^{2-}$) species identified in Gale crater bedrock [8]. Perchlorate oxidizes $Mn^{2+}$ spontaneously via:

$$ClO_4^- + Mn^{2+} + 4H^+ + 6e^- \rightarrow Mn^{IV}O_2 + Cl^- + 2H_2O$$
$$(E° = +0.11V)$$
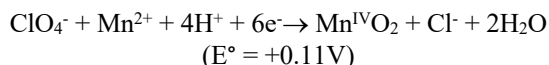
Our thermodynamic models show that $MnO_2$ is stable at a range of pH >1 for $\log(Cl/ClO_4^-) < 55$, with other Mn-phases stable at higher $\log(Cl/ClO_4^-)$ (Fig. 3). However, perchlorate is kinetically inhibited at low temperatures common on Mars and it may be inert as an oxidant, as seen in experiments with Fe [9]. Oxidation by chlorate is favored because the reaction is spontaneous with higher E°:

$$ClO_3^- + Mn^{2+} + 2H^+ + 4e^- \rightarrow Mn^{IV}O_2 + Cl^- + H_2O$$
$$(E° = +0.185V)$$
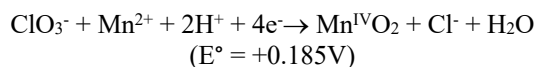
Chlorate is kinetically reactive at low temperatures; for example, it oxidizes $Fe^{2+}$ in experimental setups at pH 3-7 [9].

**Discussion:** The modelling presented here is simplified, but it demonstrates a possible fate of dissolved $Mn^{2+}$ in Gale crater. Mn was mobile in Gale, as evident in depleted alteration haloes [10], enriched diagenetic
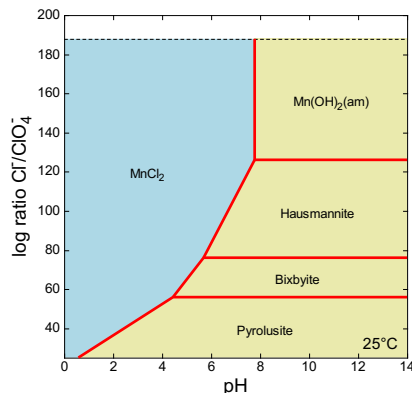
features (Fig. 1), and the wide range of FeO/MnO in the Mt. Sharp bedrock (35-250) relative to basaltic sand and soil (50). $Mn^{2+}$ was likely released into fluids via alteration of a basaltic precursor, and then subsequently concentrated in brine that resulted from evaporation of Gale crater fluids, such that $Mn^{2+}$ would be highly enriched when >90% of the water was removed. The evaporative concentration of $Mn^{2+}$ in brine would also lead to the enrichment of Cl species in the fluid, particularly chlorate, which is highly concentrated at saturation [11]. Oxidation of $Mn^{2+}$ by Cl-species would likely be favored in the brine; alternatively, the $Mn^{2+}$ would necessarily precipitate when 100% of the water was removed. This scenario is consistent with the highly localized, Mn-rich features and the apparent Mn depletions in Mt. Sharp bedrock. The ultimate Mn phase is unknown, but we speculate that Mg-chlorate is important or possibly $MnCl_2$ and Mg-perchlorate, as suggested by the 3.4 wt% Cl in the Mn-rich target Stephen.

**Conclusion:** Two plausible pathways are available for the enrichment and precipitation of Mn without free $O_2$: (1) evaporative concentration in a closed-basin brine and precipitation and (2) oxidation of $Mn^{2+}$ by chlorate or possibly hydrochlorous acid and/or perchlorate. We suggest that both of these processes acted in concert to form the highly localized Mn-enrichments in Gale crater.

**References:** [1] Lanza et al. (2016) *GRL 43*, 7398-7407. [2] Gasda et al. (2018) *49th LPSC* #2483. [3] Parkhurst and Appelo (2013) *USGS* 6:A43:497. [4] Deborde and von Gunten (2008) *Water Research 42*, 13-51. [5] Morgan (1967) in Faust & Hunter (eds.) *Principles and Applications of Water Chemistry*, Wiley, NY. [6] Hao et al. (1991) *J. Environ. Eng. 117*(3), 359-374. [7] Knocke et al. (1988) *Am. Water Works Assc.* [8] Sutter et al. (2018) *JGR* 122-12. [9] Mitra & Catalano (2018) *49th LPSC* #1031. [10] Yen et al. (2017) *EPSL 471*. [11] Toner and Catling (2018) *EPSL 497*.