THE FATE OF MANGANESE: FRACTIONATION OF MN AND FE DURING THE KINETIC ALTERATION PROCESS.

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Introduction: Since 2012, the MSL mission has been exploring Gale Crater, Mars. The ascension of Mount Sharp by the MSL *Curiosity* rover has shown that sediments were deposited in a fluvio-lacustrine environment and that water-rock interactions, often accompanied by oxidation state changes in redox-sensitive elements, were occurring [1]. One such redox-sensitive element, Mn, is commonly involved in biochemical reduction-oxidation on Earth. Mn-bearing minerals are most often formed in oxidative environments and its oxidation may be catalyzed by bacterial activity [2].

Across the traverse, the ChemCam and APXS instruments have discovered localized enrichment in Mn [3, 4, 5]. Recently, Mn caused much interest as it was found across the Murray formation in association with P, Fe and Mg. Both reduced and oxidized Mn material are still possible to explain these enrichments and might reflect several different fluid events. Drilling was attempted on the Mn-enriched Ayton/Groken location to sample the Mn-rich material, but the Mn-bearing phase or amorphous material remained unknown [6]. Even more recently, after more than 10 years of traverse, ChemCam and APXS measured high Fe, Mn, and Zn concentrations in a remarkable sedimentary feature on the Marker Band [7]. As this abstract is written, attempts to drilling the Marker band and hopefully identifying the long-awaited Mn-bearing phase(s) are still ongoing.

Overall, the Gale sediments are depleted in Mn compared to the Martian crust. This depletion is most likely caused by rock leaching and linked to the localized enrichment of Mn by weathering fluids [3]. In previous works, the enrichment of Mn as oxide material was proposed to be a marker of oxidizing conditions [4,5]. It could also be linked to more reducing conditions if found as reduced phases [8]. In this work, we use a kinetic dissolution/oxidation model of the weathering process to suggest that Mn behaves like a mobile element even under oxidative conditions, hence remaining in the fluid until water removal from evaporation, freezing or hydrated phases precipitation creates late-stage brines. We also show that Fe/Mn fractionation highlighted by APXS [3] could also happen in more oxidative environment and would not be restricted to Eh-pH space where oxidized Fe and reduced Mn species coexist.

Modelling of the alteration process: For modelling the alteration process, we used the USGS's PHREEQC batch reaction code. This computer program can perform a variety of operations such as dissolution, precipitation and more [9]. We compute the weathering process as a simultaneous kinetic dissolution of primary phases, kinetic oxidation of Fe and Mn species in the fluid by O_2 and a thermodynamic (instantaneous) precipitation/re-dissolution of secondary phases based on their saturation index. For the thermodynamic parameters, we used the Thermoddem database [10], including corrected Mg/Mn phosphates from our previous work [11] as well as some LLNL database consistent phases [10]. For most of the phases, we implemented the dissolution rates parameters from [12] and for others (e.g., magnetite) from [13]. The parameters were chosen to be as best cases for Mn and Fe oxidation: the atmospheric parameters were set to a 0.5 bar CO_2 atmosphere, and 0.05 bar of O_2 [14]. Rate parameters for the oxidation of Fe are computed for a surface self-catalysis, and Mn oxidation is also computed as surface catalyzed by the lepidocrocite Fe-oxyhydroxide [15]. For the initial solid, we based our calculation on the Rocknest (RN) sample amorphous-free normalized composition, based on CheMin results. This sample could be representative of one of the sediments sources of the Gale crater [16]. From this composition, we removed the remaining secondary phases except magnetite and ilmenite. We created custom solid solutions matching those reported by CheMin, adjusting the thermodynamic and kinetic parameters accordingly. Mn was added as a minor element in the olivine composition, as well as minor amounts of fluorapatite and pyrite to provide a P and S sources. The reactive surface is representative of non-clay minerals in basaltic sediments and is based on terrestrial modeling and experimental study [17].

Results: We observed a fractionation between Fe and Mn during the kinetic weathering process (Fig. 1). For the iron species, we observe an initial spike of Fe(II), and continuous precipitation of Fe-oxide. For Mn, the Mn(II) total first quickly increase and later stabilize in a slow increase. At t=100y, total concentration of Mn(II) is more than an order of magnitude higher than that of Fe(II).
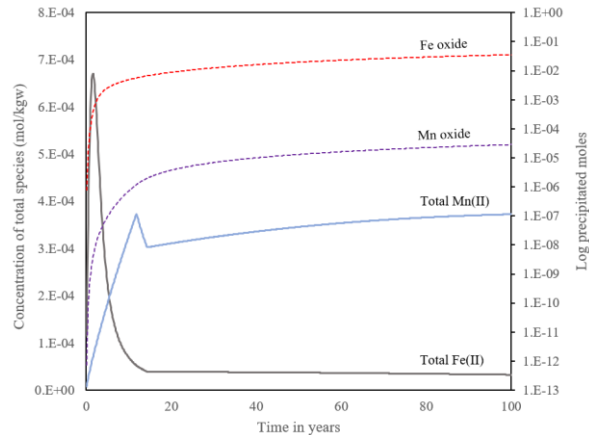
Fig. 1 - Run of the kinetic weathering and oxidation at t=3°C and W/R = 10

Discussion: As the solution is buffered by mineral dissolution, oxidation rate increases while dissolution rate lowers until the oxidation becomes faster than dissolution. The initial spike of Fe(II) is therefore resulting of the competition between the dissolution rate (mainly of olivine), and the oxidation rate of Fe. The precipitation of Fe-oxide follows the process as Fe(III) is supplied to the solution. For Mn, we observe mostly a continuous increase in dissolved Mn(II), as the dissolution rate is faster than oxidation rate. Precipitation of Mn-phosphate and Mg-clays occurs quickly but in negligible proportion. The increasing concentration of Mn(II) under a CO_2 atmosphere triggers the precipitation of Mn-carbonates, shortly decreasing Mn concentration until Mg-carbonates precipitation occurs and slows the production of Mn-carbonates, hence stabilizing the Mn concentration. The timescale of the model is only indicative. Many parameters such as reactive surfaces can drastically affect it. It's important to notice that timescale vary depending on the system: in this modeled atmosphere open system, the same body of water stays in equilibrium with the atmosphere and the exact same rock, which is unlikely to happen for an extended period, because of fluid renewal (run-off) and rock burial. For longer-lived, lower W/R and higher temperature scenarios, typically closed systems, removal of dissolved O_2 in ground water by Fe oxidation would quickly consume the dissolved O_2 limiting even more Mn oxidation, therefore increase the fractionation. In these conditions, carbonates would be naturally inhibited and other phases such as clays would precipitate [18]. Precipitation of rhodochrosite is interesting as the pH is always lower than 6.4 during the initial kinetic surface alteration process. As we did not observe Mn-carbonates *in situ*, it is likely that: 1) Mn-carbonates could reach saturation, but at this low pH, its sluggish precipitation rates would limit its formation, both in weathering and evaporation scenarios, hence

increasing the fractionation process by preventing Mn-carbonate formation and 2) The weathering process never reached this advancement, hence Mn-carbonates never reached saturation because dissolved Mn concentration was too low. Low temperature, run-off, sedimentation rate, short-lived hydrological system or shielding of the primary minerals by iron-oxide and/or amorphous silica can prevent further advancement and high concentration. Overall, the Mn oxidation rate is extremely optimistic, probably overestimating the final Mn(II) [15,19]. During the runs we performed at lower pO2, we found out that when dynamically weathering and oxidizing, primary minerals dissolution mostly controls the oxidation rate trough pH variation.

Therefore, removal of Mn(II) species by oxidation remains unlikely, forming Mn-rich brines in the later stage. A recent modeling and experimental study confirmed that Mn-oxide could be formed by oxyhalogen species [19]. Another possibility would be to form Mn-phosphates or Mn-chloride during evaporation, but more modeling and experimental works remain to assess this hypothesis.

Conclusion: During the alteration process, a fractionation between Mn and Fe is triggered by differential in oxidation rates. Oxidation rates are mostly dynamically pH controlled by the dissolving minerals, rather than controlled by O_2. We showed the importance of computing kinetics of dissolution and oxidation simultaneously, as even strictly thermodynamically favored phases can be difficult to form. This restrict Mn-oxides as a proxy for oxygen levels, as they could likely not be formed even under high O_2 pressures and are also likely oxidized by other agents. Fe-oxide is likely a better O_2 proxy. In an article in preparation, we will develop the model outcome using a different set of parameters.

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