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TRANSIENT ALKALINE LAKES ON MARS: THE KEY TO RAPID OXIDATION ?. M. Loche¹, S. Fabre¹, B. M. Tutolo², A. Cousin¹, D. Camila Jaimes Fajardo³, V. Chevrier³ and O. Gasnault¹, ¹Institut de Recherche en Astrophysique et Planétologie, Université Toulouse 3 Paul Sabatier, CNRS, CNES, 9 avenue du colonel Roche, 31400 Toulouse, France ; matteo.loche@irap.omp.eu, ²Department of Geoscience, University of Calgary, ³Arkansas Center for Space and Planetary Sciences, UARK.

Introduction: In situ missions have been observing carbonates and oxides deposit both in Jezero and Gale crater [1, 2]. In particular, the observation made by *Curiosity* at the Amapari Marker Band (AMB) and above showed the presence of closely related Fe-carbonate and probable Fe/Mn oxides [3, 4]. These secondary phases are best suited to understand Mars' carbon cycle, and assess its impact on the greenhouse effect and climate. Similarly, the redox potential of Mars' ancient atmosphere has been the subject of many debates, and could potentially be reconstructed using these phases [5]. Fe-oxyhydroxides and Mn-oxides, most typically observed in Earth environments exposed to atmospheric oxygen, have been previously interpreted to be an evidence of oxygenation of Mars' early atmosphere [6]. However, because of the even higher dependency of aqueous oxidation rates on pH than pO_2 , more recent studies have shown that the inherent acidity of surficial Martian fluids precludes sufficiently fast oxidation and that other oxidants might be needed [5, 7]. Here, we investigated the possibility that a common but overlooked mechanism at the surface of Mars could help to overcome the pH threshold to enhance oxidation rates, so that oxygen could remain a potential oxidant to consider. Thus, our investigation has led us to think that evaporation, when considering precipitation kinetic inhibitions and initial redox disequilibrium of the fluid, might result in transient alkaline conditions that accelerate oxidation on Mars.

The oxidative-evaporation pathway: Many of the geologic and mineralogical features of the Martian surface are interpreted to have been formed in evaporative settings [8, 9]. On Earth, evaporitic environments are thoroughly studied and can generally be explained by a stoichiometry-solubility framework known as the "chemical divides" theory [10]. This theory predicts the sequence of evaporitic minerals that will precipitate during evaporation, based on the initial water composition and mineral solubility. Within this theory, evaporation can lead to alkaline (high pH) or acidic lakes [11]. If no phases are able to precipitate, evaporation will lead to an increase in pH due to the increased concentration of alkalinity shifting the carbonate buffer system [12]. However, in natural waters, the evaporative concentration triggers carbonate precipitation, ultimately removing alkalinity from the system and lowering the pH. The criterion to determine if a

solution will ultimately become alkaline depends on the ratio between the alkalinity and the concentration of carbonate-forming elements. When this ratio equals $ALK > 2 [CFE]$ (Carbonate Forming Elements) the carbonate formation is limited and the alkalinity and pH increase as evaporation progresses further. This theory generally works well but overlooks kinetic effects such as the precipitation rate of secondary minerals. In the field, some observations have already shown that some lakes are alkaline under steady-state conditions despite having $ALK < 2 [CFE]$, probably because of kinetic inhibition of carbonate precipitation [11]. In addition, the evaporation of initial solutions under redox disequilibrium, i.e. solutions containing Fe^{2+} being oxidized while evaporation progresses, was never considered. Previous studies suggest that solutions on the surface of ancient Mars would often be under redox disequilibrium (oxidative atmosphere, but partially reduced species in the fluid) because of low pH, low temperature, and limited time causing sluggish oxidation kinetics [5, 13]. Moreover, Mars, with its predominantly basaltic crust whose minerals have rapid dissolution kinetics, is probably the site of carbonate inhibition due to high Mg and P concentrations [5].

Modeling Methods For modeling the evaporation process, we used the USGS's PHREEQC batch reaction and its Python module, PhreeqPY [14]. This computer program can perform a variety of operations such as dissolution, precipitation and more. PHREEQC can handle kinetic calculation, notably with the support of user-described rate laws for a variety of processes. For the thermodynamic parameters, we are using a custom modified version of the Thermochem database that can handle aqueous oxidation kinetics [5, 15]. In our model, after the calculation of the initial speciation of the solution, we simulate evaporation, oxidation, and precipitation as a simultaneous process. Evaporation is mimicked with the removal of H_2O at a constant rate using a custom rate law. At each time step, the Fe and Mn species in the solution are kinetically oxidized by O_2 following custom rate laws. Mineral precipitation or re-dissolution is governed by supersaturation or undersaturation. We are also currently implementing precipitation rate laws for carbonate precipitation for the next version of the model. The starting solution is composed of respectively of $[Fe]$ and $[Mg] = 1 \times 10^{-4} \text{ mol L}^{-1}$, $[Mn]$ and $[Ca] = 1 \times 10^{-5} \text{ mol L}^{-1}$. Initial alkalinity

produced from weathering under CO_2 is mimicked by adding $2 \times 10^{-4} \text{ mol L}^{-1}$ of NaHCO_3 ($\text{ALK} < 2$ [CFE]). Precipitation of carbonates is active in A and deactivated in B (Figure 1). The evaporation is then simulated for 14 days under an atmosphere with $p\text{O}_2 = 10$ mbar $p\text{CO}_2 = 990$ mbar.

Results: As expected when $\text{ALK} < 2$ [CFE], the evaporation in Figure 1 - A shows an initial increase in pH as concentration increases, enhancing initial oxidation rates. When carbonates start to precipitate, the alkalinity is depleted and the pH decreases, inhibiting further oxidation of Mn oxides. In Figure 1 - B, carbonates cannot precipitate, which results in a drastic increase in pH as evaporation progresses. Unlike case A, Mn is oxidized more rapidly and Mn-oxide precipitates in larger quantity, despite conditions that should not be favoring its oxidation.

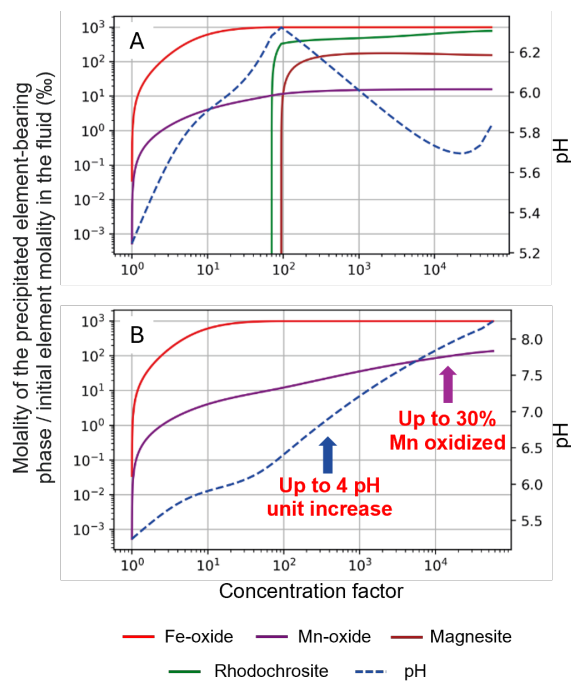


Figure 1 – Evaporation models results with: (A) carbonates can precipitate; (B) carbonates removed.

Experiments To confirm these initial models and our hypothesis, an experimental setup is currently being built. The evaporation will be carried out in a glove-box with a controlled CO_2 - O_2 gas mixture, while the solution is stirred and the weight is monitored. The setup will mimic the evaporation of a weathering solution with different starting fluid compositions and gas ratios. Samples will be frequently taken to closely measure changes in alkalinity and pH and quantify rates of carbonate or oxide precipitation.

Determination the oxidation window: From the experimental results, a new model that includes refined

precipitation kinetics of carbonates will be added to determine the extent of the pH and oxidation rate increase between the ideal case (B) and the case with only solubility-based carbonate precipitation (A). Using multi-parameter sensitivity tests, we will explore a wide range of $p\text{O}_2$, $p\text{CO}_2$, evaporation rates, and initial solution composition (species concentration, alkalinity). The results of this simulation will allow the quantification of the parameter window where Fe and/or Fe and Mn oxidation is possible. This means that the type of paleoenvironments could be reconstructed with the estimation on evaporation rates, notably when compared to estimated evaporation rates on Mars. It is also probable that lower limits on $p\text{O}_2$ could be determined to allow efficient oxidation of Fe and Mn. The determination of the parameters window compatible with carbonates precipitation as well as their effective precipitation rates will be precious to understand the spatial and temporal distributions of paleo-environments on Mars. Going further, this approach could be integrated on a steady-state model of a large endorheic lake: the water compositions and flux of rivers entering a lake within evaporation rates compatible with a stable lake could be tested. The results would also have an impact at the global scale, where evaporative environments might be linked to oxide deposits. This will also need to be considered when modeling large scale climate and carbon cycle models, as it could significantly alter the carbon budget compared to solubility-based approaches. Finally, the results would provide a new answer to a long-standing debate about the presence of Fe and Mn oxides on ancient Mars and their significance.

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