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A NEW FE-CARBONATE FORMATION WINDOW ON MARS M. Loche¹, S. Fabre¹, A. Cousin¹, A. Proietti², A. Benmamar³, W. Rapin¹, B. M. Tutolo⁴, P.Y. Meslin¹, F. Dimitracopoulos⁵, R.C Wiens⁶, 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, ²Centre Castaing, Toulouse, France, ³GéoSciences Réunion, St Denis, France, ⁴University of Calgary, Calgary, Canada ⁵University of New Mexico, Albuquerque, USA ⁶Purdue University, Lafayette, USA.

Introduction: A number of missions have reported secondary minerals that preserve environmental records of multiple water-rock-atmosphere interactions early in Mars' history. The MSL and M2020 missions in Gale and Jezero craters have identified, among other secondary phases, numerous Fe-bearing secondary phases [1,2]. In Gale crater, several occurrences of minerals bearing different valence states of iron have been reported throughout the traverse: nontronite and Fe oxides, as well as potential Fe / Mn phosphates [1,3]. Recently, Fe-carbonates were detected in the Gale crater sulfate unit [4], and Fe-Mg carbonates and variable Fe valence states in sedimentary layers were observed in Jezero crater [5,6]. If these carbonates are authigenic, they could have formed directly from the alteration of the primary rock, or by chemical sedimentation. During alteration of the primary minerals, divalent Fe cations are released in the solution and form phases such as carbonates, sulfides or sulfates or can be aqueously oxidized to the higher valence state and form oxides and oxyhydroxides. Thus, Fe is used as a tracer for the redox conditions on both Earth and Mars. Aqueous oxidation of Fe requires oxidant sources, such as photo-oxidation or oxidants like oxygen. Finding a lower or higher valence state in secondary phases helps quantify the eH-pH space and derives pO₂ using equilibrium models. However, this purely thermochemical boundary does not account for other processes such as joint alteration, oxidation and precipitation, and ignores potential kinetic effects. As Mars aqueous activity, especially in direct contact with the atmosphere, could have been rather short lived, and at low temperature, kinetics might be a controlling parameter. Moreover, even if Mars' most likely low pH alteration fluids would favor faster dissolution rates, it would also hinder oxidation rates [7].

In this study, we focus on modeling results based on a kinetic weathering experimental setup under Mars-like conditions. With these models, we aim to enhance our ability to interpret the redox and hydrological conditions when finding Fe-oxides or carbonates on Mars.

Methods: *Experimental setup* Experiments were carried out at various pO₂, pCO₂, temperatures and starting solutions [8]. For the scope of this abstract we will only focus on the experiments at 23°C with 1 or 10 % O₂ and 99 or 90 % CO₂ (AO₂- and AO₂+) with a total

pressure of 1.2 bar. We used an olivine bearing basalt of Réunion Island (Indian Ocean, French) as the starting material. This basalt is composed of relatively ferroan olivine (Fo 75) close to Martian composition measured in situ [1]. The rock was thoroughly characterized using EDS-EBSD to determine the composition of every mineral and their proportion in the rock. After being sieved at 100-200 µm, 50g of starting solid and 500 ml of pure water are mixed in the reactor, for an initial W/R of 10. These experiments lasted for 80 days, with regular fluid sampling for major-element analysis with ICP-OES and analysis of the final altered powders with SEM-EDS.

Geochemical Modeling For modeling the weathering process, we used the batch reaction code PHREEQC from the USGS [9]. This code can perform various calculations including equilibrium with solid, fluid and gas and kinetic calculations. Using our new thermo-kinetic calculator (Solver for pHase Kinetic RatEs or SHAKER), the starting rock is modeled with the description of all minerals with their custom solid solutions, individual derived geometric surface area, initial molar quantity and their calculated custom thermodynamic and kinetic parameters. Along with the Thermodem [10] database, we used a combination of the two main kinetic compilations [11,12] for the dissolution rate expression and parameters. At each time step, the kinetic dissolution and kinetic aqueous oxidation are computed, and the precipitation/dissolution of secondary phases occurs on a saturation-based criterion. The fluid is equilibrated at all times with an infinite source of gases defined by its partial pressure (atmosphere). The Fe and Mn oxidation rate law and parameters were based on literature [13,14]. From the experimental results and comparison with models, we updated the required siderite saturation for precipitation [15]. Using PhreeqPy [16], a large parametric exploration was conducted with 3600 simulations in the pCO₂ / pO₂ space through time. The range of pO₂ was set from 10 ppm oxygen to 300 mbar (10 % at 3 bar total pressure) and the pCO₂ from the present-day Martian pressure (6 mbar) to 3 bars. Two sets of runs were performed: one parametric exploration with the same experimental condition, and another with a reduction in the reactive surface area (SA) by two orders of magnitude and an increase in time of around two orders of magnitude, lasting 20 years, reasonably

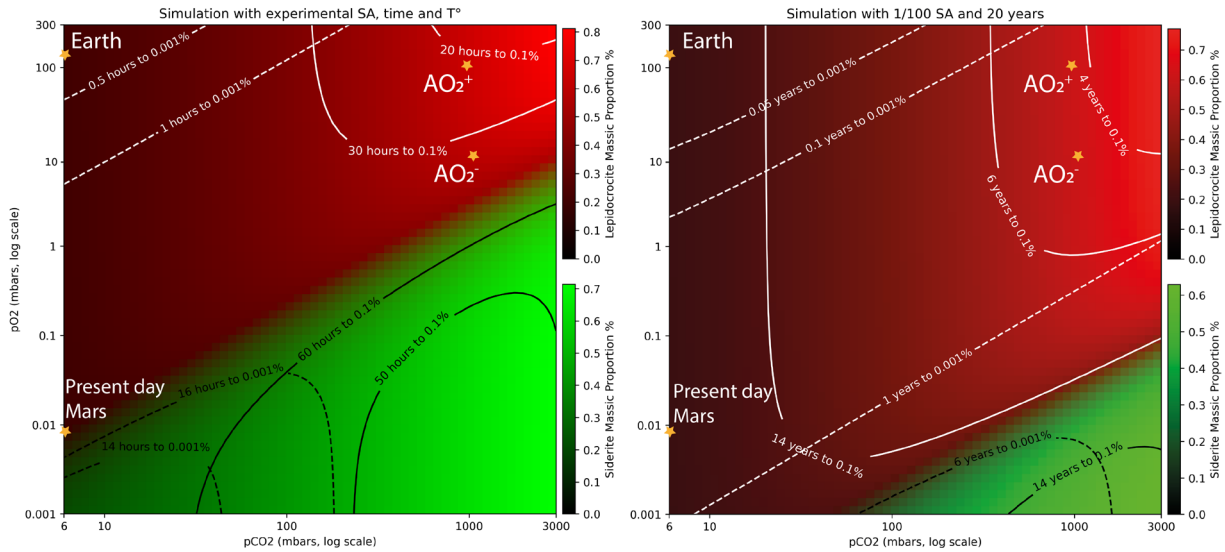


Fig.1. Results from the parametric exploration of the kinetic weathering model. The heatmap represents the final bulk mass proportion (all primary and secondary phases) of siderite and Fe-oxide. The isochrones represent the area where a given proportion of siderite or oxide is reached at a given time during the weathering.

representing what could be a maximum residence time at the surface (time with the same rock and same reacting fluid).

Results: The parametric exploration revealed a new pO_2 , pCO_2 and reactive surface-controlled boundary for the precipitation of siderite or Fe-oxide. Unlike thermodynamic models that mostly prevent siderite formation because of Fe oxidation down to at least $\log pO_2 = -50$, siderite can form up to $\log pO_2 > -2$ (or 10 mbar at 3 bar CO_2). Consistent with the parametric exploration, the AO_2^- and AO_2^+ altered products only showed the presence of iron oxide and no carbonates. Although the final bulk proportions are highest at high pCO_2 , precipitation of Fe-oxides or siderite occurs first at the lower part of their pCO_2 precipitation domain (0.001 % bulk isochrones in the left side of their color area, Fig. 1) and then transition to higher proportions only after longer times at higher pCO_2 (0.1 % bulk isochrones). For Fe-oxides, this shows that initial precipitation is favored by higher pH (enhanced oxidation rates), but higher proportions are produced only when weathering rates are higher (at higher pCO_2) and after longer times (higher buffering). Siderite precipitation also requires higher pH, which is reached faster when pCO_2 is lower, but also only increases in greater proportion with higher pCO_2 and longer times (weathering rates and buffering). The initial precipitation of siderite and oxide is separated by 1 order of magnitude in time, as shown by 0.001 % isochrones. In Fig. 1, the isochrones in the heatmap at 1/100 SA and 20 years show that almost all the final Fe-oxide pCO_2 and pO_2 domain have already seen Fe-oxide precipitation after 1 year while 6 years are needed to have precipitation in only a fraction of the siderite

domain. At experimental conditions, this separation is even greater, at 1 hour and 14 hours respectively to reach similar fractions in their domains.

This is particularly important because it shows that below a certain residence time (buffering, thus activities and pH), only Fe-oxides will be able to form, while siderite will not form under any conditions.

Conclusion: We determined a new Fe-carbonate formation window, even under oxidizing conditions from a thermodynamic standpoint, redefining the significance of “reducing” or “oxidizing” conditions on Mars. Additionally, because of the different residence time required to form Fe-oxides and Fe-carbonate, we interpret that Fe-carbonate would be primarily a clue for a different hydrological regime (chemical sedimentation or higher weathering rates) and only then a redox marker. At a global scale, the formation of authigenic siderite and even other carbonates (for example, when accounting the Mg-inhibition of calcite precipitation) during rock weathering would be rather limited without long residence times or later evaporation.

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