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## ► To cite this version:

M. Loche, S Fabre, P.-Y Meslin, A Cousin, N Lanza, et al.. Exploring the formation of the mn-p-fe-mg enrichment of the groken nodules in gale crater with source-to-sink geochemical modeling. Lunar and Planetary Science Conference, Lunar and Planetary Institute, Mar 2022, The Woodlands, TX, United States. pp.1274. hal-03847199

**HAL Id: hal-03847199**

**<https://hal.science/hal-03847199>**

Submitted on 10 Nov 2022

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**EXPLORING THE FORMATION OF THE MN-P-FE-MG ENRICHMENT OF THE GROKEN NODULES IN GALE CRATER WITH SOURCE-TO-SINK GEOCHEMICAL MODELING.** M. Loche<sup>1</sup>, S. Fabre<sup>1</sup>, P.-Y. Meslin<sup>1</sup>, A. Cousin<sup>1</sup>, N. Lanza<sup>2</sup>, L.C. Kah<sup>3</sup> O. Gasnault<sup>1</sup>, S. Maurice<sup>1</sup>, R. Wiens<sup>2</sup>. <sup>1</sup>Institut de Recherche en Astrophysique et Planétologie, Université de Toulouse, UPS, CNRS, CNES, 9 avenue du Colonel Roche, 31400 Toulouse, [matteo.loche@irap.omp.eu](mailto:matteo.loche@irap.omp.eu), <sup>2</sup>Los Alamos National Laboratory, <sup>3</sup>University of Tennessee.

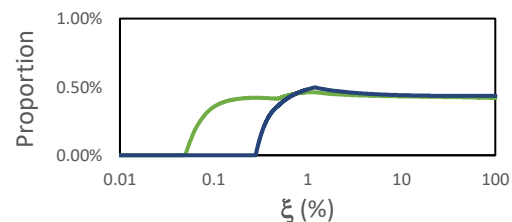
**Introduction:** Gale crater on Mars is being explored by the Curiosity rover since 2012. Sedimentary deposits show an intermittent fluvio-lacustrine activity between 3.8 Ga and 3.4 Ga before present [1], and observation of secondary phases proves that water-rock interaction was occurring [2]. Across Curiosity's traverse of the Murray formation, a variety of facies enriched in Mn, P, Fe and Mg were observed by the ChemCam instrument. Recent observations of the Groken target [3,4] led to the discovery of a facies composed of manganese-phosphorus-rich nodules in the Glen Torridon region, leading to samples' collection and more detailed analyses. The dark toned sub-millimetric nodules are composing up to 50% of thin laminae, with an alternance of nodule rich and nodule poor beds. Manganese and phosphorus are extremely important because on Earth they are closely associated with biological processes. Finding them on Mars could be a clue for the emergence of a biosphere or instead, for abiotic processes obscured by biological overprint on Earth. Observation of the mineralogical nature of the enrichment would be the best clue to reconstruct a story of the deposition through thermodynamic inverse modeling. Unfortunately, the only potential crystalline candidate detected, the Mn phosphate jahnsite-whiteite [6], was ruled out by a thermodynamic study [5] and by a refined analysis of the CheMin data [7]. It is now thought to be part of the amorphous component detected in the rock sample [7]. Therefore, given the lack of mineralogical constraints, we changed our modelling approach toward a source-to-sink and ab initio model, producing fluids and solids from an initial weathering stage, and then making them evolve in several scenarios to explore possible syndepositional formation processes at the water-sediment interface. We first tested our scenarios with a thermodynamic-only weathering model, and we are now developing an improved kinetic-thermodynamic model to feed the same scenarios and bring more realistic constraints.

**Thermodynamic model for weathering:** For the modeling, we mainly used the USGS PHREEQC program, a thermodynamic batch reaction code, which can perform a variety of operations such as dissolution, precipitation, evaporation and more [8]. For the thermodynamic parameters, we used the Thermoddem database [9] as well as some phases from the LLNL database [8]. In the first stage of the model, we performed a weathering reaction in an open system,

typically happening in rivers, lakes, or shallow sediments. A starting rock was dissolved in an initial fluid in equilibrium with an hypothetical ancient Mars atmosphere (30 ppm of O<sub>2</sub>, 95% of CO<sub>2</sub>, 500 mb total pressure). Our thermodynamic model used the chemical composition of the Darwin conglomerates found in Gale crater as the starting rock composition [10]. This starting material was dissolved by increments following a stoichiometric ratio. Like similar models, our starting fluid was pure water and temperature was relatively low, at 3°C [11,12]. Scenarios using our modeled surface fluid were performed at a 1% dissolution rate, simulating a moderate surface weathering.

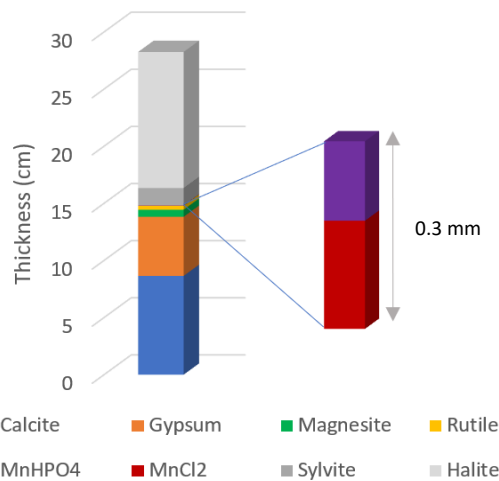
**Scenarios of formation:** Our scenarios of formation mainly focused on a precipitation at or near the water-sediment interface, a choice driven by the observed beds/nodules relationship. We developed these scenarios and tested them with our thermodynamic weathering model. We considered 5 scenarios: 1/lacustrine oxidation and precipitation of dissolved Fe/Mn, 2/long standing ice-covered lake with oxidation and precipitation of Fe/Mn oxides from a limited supply of dissolved O<sub>2</sub> and sediments, 3/evaporation in a steady-state regime in an equilibrated evaporitic lake, 4/full evaporation of a lake, and 5/steady-state lacustrine photo-oxidation of Fe/Mn. Steady-state models are based on previous estimations of sedimentation rates, water flow, and lifetime of the Gale Lake system [13,14]. In these models, we can directly calculate a proportion of precipitated materials in the detrital sedimentary column.

**Results:** The preliminary results from the thermodynamic model showed that we were able to produce MnHPO<sub>4</sub> and chlorapatite. Unfortunately, their proportion were far too low to explain the observed



**Fig. 1.** Proportion of MnHPO<sub>4</sub> (green) and chlorapatite (Blue) deposited during the surface weathering process (dissolution rate =  $\xi$ ). Even if precipitation of Mn-phosphate occurs, an enrichment process is still needed to explain the Groken facies.

facies (Fig.1). In the different scenarios that we explored, the oxidation and deposition of observable proportion of Fe-oxide was possible by both atmospheric O<sub>2</sub> and photo-oxidation within a realistic timescale. On the other hand, the production of Mn oxide was completely negligible, mainly due to the natural circum-neutral pH of weathering fluids and because of the low rate of photo-oxidation. Evaporation in steady-state, while effectively precipitating Mn-phosphate, was unable to form any observable deposit. The complete evaporation of the lake produced a thin sulfates/carbonates dominated evaporites column with a very low proportion of Mn-phosphate and Mn-chloride (Fig.2).



**Fig. 2.** Evaporites column formed after a full evaporation of a surface weathering fluid at 1% dissolution rate in a 300m deep lake. Even if the thickness of Mn phosphate and chloride formed is compatible with the Groknen facies, the greater proportion of the other evaporites in this scenario is not compatible with the observations.

**Discussion:** Even though we formed Mn-phosphate or apatite, the scenario explored here could not explain the observed facies at Groknen because of the low proportion produced. In addition, Groknen nodules material seems to be poorly crystallized and therefore these phases would not be identified by CheMin. The implementation of a kinetic model of weathering could increase their proportion by passively increasing Mn-Fe-P-Mg concentrations in limited alteration scenarios. In all our scenarios, all the potential phases included in the database were considered, and not only the Mn-P-Fe-Mg phases. This is particularly interesting because we can track and quantify the formation of every other phase (sulfates, carbonates, phyllosilicates, chlorides, etc.) allowing a direct confrontation with the observations. With the new kinetic model currently being implemented, we will be able to generate more evolved fluids in closed systems scenarios, to simulate early and late diagenesis. Early results showed that it

can be a powerful tool to explore the formation of other phases such as sulfates or carbonates, and weathering trends (Fig. 2).

**Model in progress:** Our new kinetic model is keeping the same initial parameters than our thermodynamic model, except the starting rock composition, which is based on the mineralogy of the John Klein lacustrine mudstone analyzed by CheMin [15], and sulfur and chlorine are supplied by the atmosphere. We removed the secondary minerals and the amorphous component and only kept the pristine igneous part and normalized it to obtain the whole-rock composition. We included 0,15 %wt of a Mn rich olivine (tephroite), as the source of Mn, corresponding to the MnO content in the amorphous component. Kinetic parameters for mineral dissolution are coming from a compilation of rate parameters [16].

With this set of parameters, we will calculate dynamic kinetic dissolution-oxidation and thermodynamic precipitation rates. At each time step, initial minerals are dissolved and provide elements to the solution, while dissolved Fe and Mn are kinetically oxidized. Then thermodynamic calculations are made based on updated dissolved concentrations to precipitate (or re-dissolve) secondary phases. Unlike previous weathering kinetic models [11,12], the precipitation is a relatively free parameter, meaning that all the phases in our wide database that are possible to form with the dissolved species in the system are computed. In addition, the implementation of Mn oxidation kinetic will allow us to track more realistically the fate on Mn in ancient Mars conditions. We are also looking toward a fully kinetic model including precipitation kinetics, becoming the first fully kinetic model.

**Acknowledgments:** The engineers and scientists who operate the Curiosity rover are thanked for their generous contributions to this work. We thank C. Drouet from the CIRIMAT for using his tools for estimating thermodynamic parameters.

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