

IDENTIFICATION OF INORGANIC BIOSIGNATURES IN SIMULATED GALE CRATER AQUEOUS ENVIRONMENT STUDIED THROUGH THERMOCHEMICAL MODELLING. S. Cogliati¹, M. C. Macey¹,
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Introduction: Finding evidence of past or present life on Mars is one of the key objectives of the most recent and future space exploration missions [1]. In basaltic aqueous environments, similar to early martian fluvio-lacustrine systems, microbes can modify the fluid chemistry and promote the formation of biosignatures when sourcing bio-essential elements from the rocks [1, 2, 3, 4]. Geomorphological, mineralogical and chemical biosignatures may be particularly suited for assessing whether life existed on early Mars since they may be resistant to the extreme conditions at the present-day surface of Mars and, thus, may be more likely preserved and detectable in martian rocks [1].

Biosignature formation under simulated martian conditions has been investigated over short time frames (months) through experimental microbiology and analytical geochemistry [5, 6, 7, 8], and at geological timescales using thermochemical modelling [5, 6]. Thermochemical modelling is a powerful tool to study processes and products of biotic and abiotic aqueous alteration at timescales relevant to Mars since it allows to predict secondary mineral assemblages and variations in fluid chemistries by assessing reaction pathways of long-term fluid-rock interaction [9, 10].

Here, we use thermochemical modelling to investigate reaction pathways and mineral formation that would occur biotically and abiotically over geological timescales in a chemically accurate water-rock system similar to the Rocknest basalt at Gale crater. We aim to identify mineralogical and geochemical signatures that that may be used as inorganic biosignatures for life detection on Mars.

Methods: Thermochemical modelling was performed using the code CHIM-XPT [9, 10], which has already been used to study water-rock interactions in martian environments and to predict inorganic biosignatures (secondary minerals, fluid chemistries) in basaltic systems under biomediated martian conditions [5, 6]. Rock dissolution was modelled by performing stepwise titration simulations over a range of water/rock ratio $(W/R)_M$ between 10^6 and 1, at 1 bar and 25 °C under 2 different pH conditions: (i) the pH varied in response to the interaction between the rock and the fluid (abiotic model); (ii) the pH was fixed at 7.5 to reproduce the reaction pathways progression in presence of microbes (biotic model). The input data included the composition of a chemically accurate

martian regolith simulant (OUCM-1, 11) and the composition of a thermochemically modelled fluid with chemistry similar to former martian groundwater [8]. These conditions are those used in [8] where experimental microbiology was applied to investigate inorganic biosignature formation in a simulated Gale crater environment over the course of 1 month. Abiotic and biotic models are compared at a specific $(W/R)_M$ range, between 2000 and 250. This corresponds to the actual water/rock interval of the biotic weathering experiments and is equivalent to a fluvio-lacustrine setting, similar to those identified at Gale crater [12].

Results: Figure 1 shows that quartz and phyllosilicates (chlorites, mica, smectite) precipitate in variable amounts at different water/rock ratios in all models; kaolinite precipitates only in the biotic model at water/rock $> 10^2$. Traces of phosphate (apatite) and sulfide (pyrite) are also present in all models.

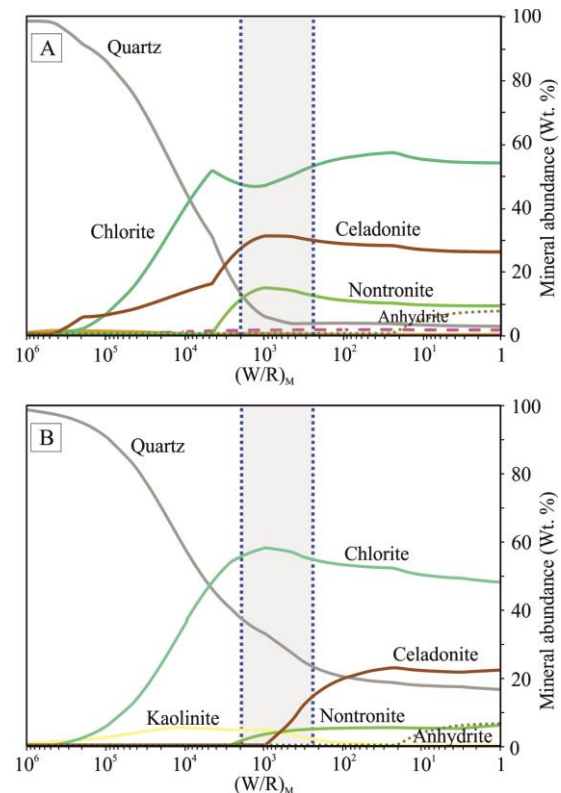


Figure 1: Secondary minerals predicted to form at 25 °C, 1 bar under abiotic (A) and biotic (B) conditions. Pyrite and apatite are < 5 wt. % and are not displayed. The shadowed area in between the two blue dotted vertical lines represent the actual W/R ratio range of the weathering experiments in [8].

Under biomediated fluvio-lacustrine conditions, thermochemical modelling predicts the formation of chlorites (54 - 58 wt. %) together with lower amounts of quartz (23 - 37 wt. %), and minor amounts of mica (6 - 14 wt. %) and traces of (< 5 wt. %) of kaolinite, apatite and smectites, whereas the abiotic system would precipitate mainly chlorites (46 - 52 wt. %), but also mica (26 - 30 wt. %) and smectites (11 - 14 wt. %), minor to trace amounts of quartz (4 - 13 wt. %) and traces (< 5 wt. %) of apatite.

Discussion: Model results suggest that, in a martian-like fluvio-lacustrine setting, a less complex secondary mineral assemblage forms during biotic dissolution compared to abiotic weathering. Chlorites and quartz (and \pm celadonite) are the main precipitates in the biotic model; similarities exist between these results and secondary features that we identified by SEM analysis on the surface of the simulant after biotic experiments performed by [8]. In previous studies this was not observed [5, 6]. Secondary features include honey-comb and tower-like secondary morphologies that we interpreted as phyllosilicate-type minerals (possibly chlorites); we consider these as biosignatures, as nothing comparable was observed in the abiotic controls. We believe that the success of our study lies on the use of fluid and rock chemistry, pH (determined by microbial action in the experiments) and initial oxidation state that accurately mimic the conditions of the Gale crater environment. This has impacted the reaction pathways increasing the correspondence between model and experimental results and, thus, the fidelity of potential biosignatures that could develop under specific martian conditions.

Secondary mineral predicted to form biotically under fluvio-lacustrine conditions (smectites, chlorites, quartz, mica and kaolinite) are all minerals that can precipitate following the action of microbes [e.g., 13, 14] and that have been detected on Mars by orbiters and / or rovers [e.g., 15, 16]. Although chlorites are not common in terrestrial low-temperature aqueous systems, their precipitation at temperature > 20 °C can be still possible through a series of processes [17]. So, their presence in warm superficial (< 60 m) lacustrine settings on Mars should be considered as possible. Considering that two mineralogical associations would form under biotic conditions (chlorite + quartz, $(W/R)_M$ from 2000 to 300; chlorite + quartz + mica, $(W/R)_M$ of < 300), the detection of even minor amounts of secondary phases (e.g. mica) in martian samples could be fundamental to assess mineralogical assemblages that are the expression of a biological activity or supportive environments for preservation of biosignatures. The identification of phyllosilicates

(chlorite, celadonite and nontronite), even in restricted amounts, would be fundamental in this sense since they have a high potential to preserve biosignatures.

Conclusion: this study provide important constraints to distinguish secondary minerals and reaction pathways of abiotic and biotic aqueous weathering processes at Gale crater and are indicative of which mineralogical features may be of interest when screening for biosignatures and searching for evidence of putative life on Mars. Our study strongly supports the necessity to use location-specific simulant and fluid compositions when investigating inorganic biosignatures formation over timescales relevant to Mars. Such information, in conjunction with other geological and geochemical evidence, could support the ongoing sampling activities operated by martian rovers, for planning future life detection missions and for interpreting the results of the analysis of samples recovered by the future Mars sample return missions.

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References: [1] Vago J.L. et al. (2017) *Astrobiology*, 17, 471-510. [2] Vandevivere P. et al. (1994) *Microbial Ecology*, 27(3), 241-251. [3] Uroz S. et al. (2009) *Soil Biology and Biochemistry*, 41(10), 2178-2186. [4] Hays L.E. et al. (2017) *Astrobiology*, 17(4), 363-400. [5] Olsson-Francis K. et al. (2017) *Frontiers in Microbiology*, 8. [6] Cogliati S. et al. (2022) *Front. Astron. Space Sci.*, 9:1062007. [7] Wu L. et al. (2007) *Geochimica Cosmochimica Acta*, 71 (9), 2224-2239. [8] Macey M.C. et al. (2022) *Astrobiology*, 23. [9] Reed M. et al. (2010) Users Guide for CHIM-XPT. [10] Schwenzer S.P. and Kring D.A. (2013) *Icarus*, 226, 487-496. [11] Ramkissoon et al., (2019) *Planetary and Space Science*, 179, 104722. [12] Grotzinger et al., (2014) *Mars. Science* 343 (6169), aac7575. [13] Tazaki K., and Fyfe, W.S. (1992) *Chemical Geology*, 102, 105-118. [14] Lee M.K. et al., (2007) *J. Geophys. Res.* 112, G02026. [15] Ehlmann B.L. et al., (2009) *J. Geophys. Res.* 114, E00D08. [16] Bishop, J.L. et al., (2008) *Mars. Science* 321, 830-833. [17] Grigsby J.D. (2001) *J. Sediment. Res.* 71.