

# Thermochemical Aqueous Alteration Simulations to Explore the Relationship between Protolith Composition and Carbonates on Mars

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Ca/Fe carbonates on Mars are less studied compared to their Mg-rich counterparts, which have been investigated by both rover missions [e.g., 1] and modelling studies [e.g., 2], but they are important because Ca/Fe carbonates exposed in craters may represent a major sink of ancient atmospheric CO<sub>2</sub> [3]. The distribution of observed Ca/Fe carbonates on Mars roughly coincides with “chemically striking regions” with more felsic surface compositions than that of the average, mafic Martian surface [3,4], but whether the Ca/Fe composition and the more felsic surface are related is still unclear [3]. In this study, we use thermochemical modelling to test whether there may be a causal link between felsic protolith composition and Ca/Fe carbonates.

Aqueous alteration of a 100-m deep column of igneous rock immersed in pure water, whose top is exposed to atmospheric CO<sub>2</sub>, was simulated in PHREEQC using a similar basic setup as [2], in which water-rock reactions proceeded by diffusive transport until thermodynamic equilibrium over 100,000 Earth years. To test the effect of protolith composition, two simulations were conducted, one with a mafic protolith similar to that of the Séitah formation in Jezero Crater [5], and the other with a felsic protolith similar to that of the Meetinghouse rock in Gale Crater [6]. (Parameters used in the simulations are summarized in Table 1.)

The simulation with felsic protolith produced mostly Ca/Fe carbonates while the one with mafic protolith produced mostly Mg/Fe carbonates. Since all other parameters were constant, this result suggests that it is possible for protolith composition alone to determine whether Ca/Fe or Mg-rich carbonates are produced. If the felsic surface composition of the “chemically striking regions” reflects primary rock composition, the difference in protolith composition may explain the different carbonate compositions.

The mafic protolith produced amorphous silica and carbonates in the shallower part of the column and a mixture of phyllosilicates and oxides in the deeper part. Carbonate formation was largely limited to the shallower part. In contrast, the felsic protolith produced fewer secondary phases, dominated by amorphous silica and smectites except near the bottom of the column. Carbonates were produced in lower quantities throughout the column except at the very top. The lower amounts of carbonates and other secondary minerals in the felsic case is possibly due to the lower solubility of felsic minerals in acidic fluid, reducing the concentration of cations (Ca, Mg, Fe) available. This is also consistent with the shallower drop in CO<sub>2</sub> and the presence of carbonates deeper down the column, since less CO<sub>2</sub> would have been consumed in the shallower part.

The results were compared with remote sensing studies. The association of Ca/Fe carbonates with Fe/Mg smectites in the felsic simulation roughly agrees with the mineralogy of Ca/Fe carbonate outcrops in or near the felsic “chemically striking regions” (Western Noachis Terra [3], Huygens Crater [3], and Capri Chasma [7]. Mineralogy in Leighton Crater may have been similar before metamorphism [8]). On the other hand, Ca/Fe carbonates detected beyond the felsic regions (Robert Sharp Crater [9] and Terra Tyrrhena [10]) are often associated with olivine, a mafic mineral, so a different explanation for their composition is needed.

## References

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Keywords: Mars, carbonates, thermochemical simulation

Table 1: Input parameters

|                            | Mafic | Felsic |
|----------------------------|-------|--------|
| Albite (mol%)              | 6.59  | 36.67  |
| Anorthite (mol%)           | 2.38  | 1.93   |
| K-Feldspar (mol%)          | 0.68  | 15.30  |
| Diopside (mol%)            | 1.09  | 3.43   |
| Enstatite (mol%)           | 30.56 | 4.22   |
| Ferrosilite (mol%)         | 18.10 | 7.50   |
| Forsterite (mol%)          | 24.73 |        |
| Fayalite (mol%)            | 14.65 |        |
| Magnetite (mol%)           | 1.22  |        |
| Quartz (mol%)              |       | 30.95  |
| Water/Rock Ratio (mol/mol) | 500   | 500    |
| Temperature (°C)           | 5     | 5      |
| pCO2 (bar)                 | 1     | 1      |

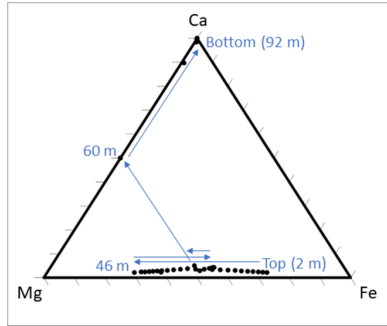


Figure 1: Simulated carbonate compositions from the mafic protolith. Arrows show the trend from top to bottom.

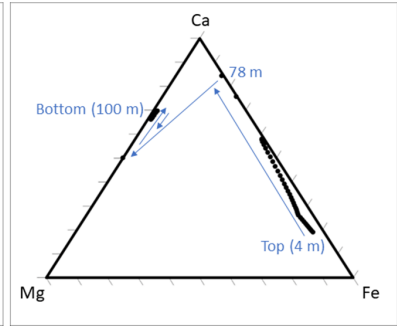


Figure 2: Simulated carbonate compositions from the felsic protolith. Arrows show the trend from top to bottom.

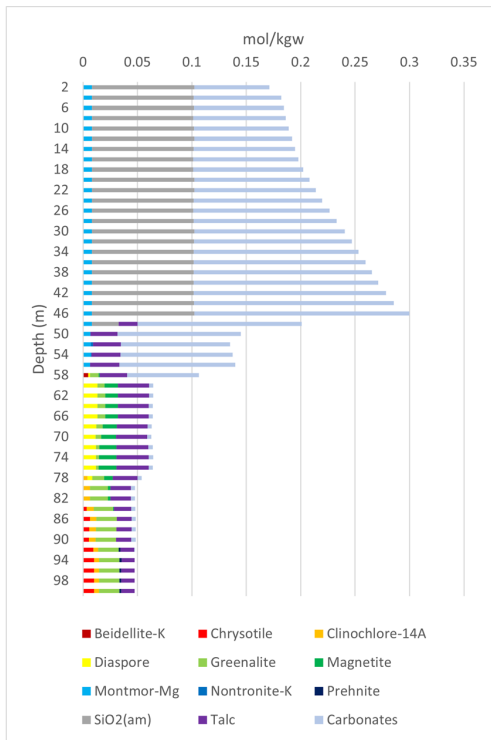


Figure 3: Simulated vertical profile of secondary phases from the mafic protolith. Feldspars, present at the start of the simulation, are not shown for clarity.

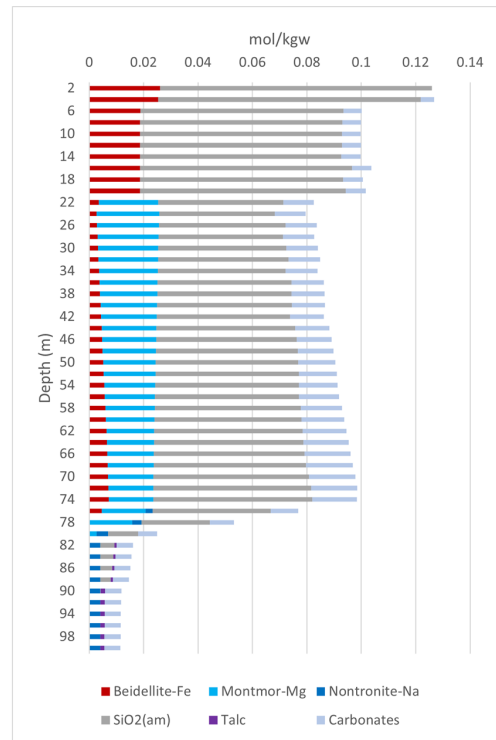


Figure 4: Simulated vertical profile of secondary phases from the felsic protolith. Feldspars, present at the start of the simulation, are not shown for clarity.

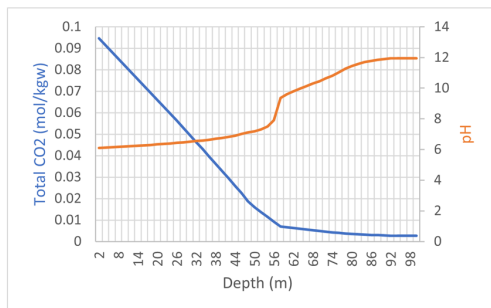


Figure 5: Total CO2 and pH vs. depth for the simulation with mafic protolith.

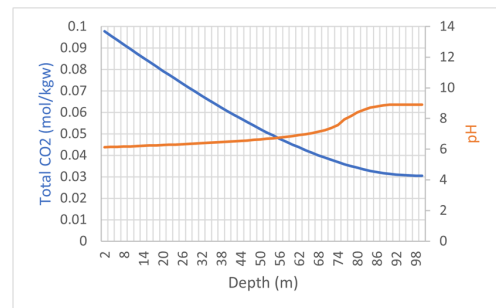


Figure 6: Total CO2 and pH vs. depth for the simulation with felsic protolith.