THERMOCHEMICAL SIMULATION OF BOCKFJORD VOLCANIC COMPLEX CARBONATES, A TERRESTRIAL MARTIAN ANALOG.

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Introduction: Carbonates in igneous rocks of the Bockfjord Volcanic Complex (BVC), Svalbard, Norway, are a terrestrial analog for Noachian Martian carbonates. The carbonates have a similar chemically zoned, globular appearance; silicate alteration products; and formation fluid redox and pH conditions to those found in the Martian meteorite Allan Hills (ALH) 84001 [1]. The composition and silicate alteration products of BVC carbonates from the Sverrefjell Volcano are also similar to those of Noachian carbonates detected on Mars [1].

BVC carbonates in basaltic breccia from the Sverrefjell Volcano occur either as layered cement covering the surface of the basalt or as globules in vesicles. They contain two distinct ranges of compositions: Mg-Ca and Mg-Fe [1].

Previous modeling studies of other Martian carbonate samples have shown that CO_2 fugacity (fCO_2) and water-to-rock ratio (W/R) can affect carbonate composition [2,3]. Also, starting rock composition is a major difference between ALH 84001 and BVC carbonates [1]. This study aims to understand the possible roles of fCO_2, W/R, and starting rock composition in creating the observed compositional variation of BVC carbonates.

Methods: Thermochemical simulation was conducted using the PHREEQC software [4]. The simulation setup followed the batch model in [2], in which 1 kg of pure water reacted with a certain amount of starting rock according to the desired W/R until equilibrium. CO_2 was added as an equilibrium phase at the desired partial pressure. Magnesite-calcite-siderite solid solution carbonate and a list of 62 possible alteration products were allowed to precipitate (same as [2]).

Input parameters. We ran 18 simulations with differing inputs. Starting rock compositions included unaltered BVC-like and ALH 84001-like compositions. fCO_2 ranged from the terrestrial pre-industrial atmospheric value (280 ppm) to the possible upper limit of ancient Martian atmospheric value (1 bar) [5]. W/R values varied from 50 to 5000 mol/mol.

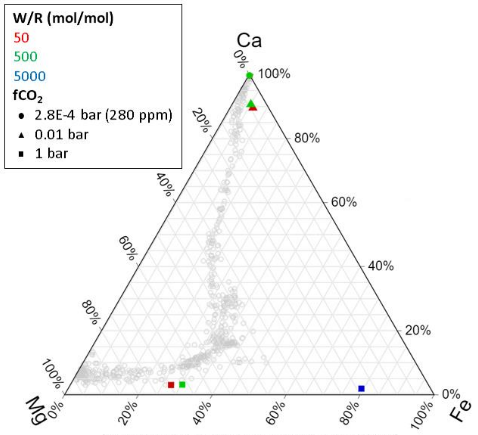
Starting rock composition. The approximate composition of the unaltered BVC igneous rock (Table 1), including basalt and lherzolite xenolith, was calculated from modal mineralogies of rock and lava samples from the Sverrefjell Volcano [1, 6]. The ALH-like starting rock composition was approximated by 100% orthopyroxene ($En_{70}Fs_{27}Wo_3$) [7].

Limitations. Since the formation temperature of BVC carbonates is unknown, the simulations were run at 25ºC, and the effect of temperature was not investigated. Also, kinetic effects were not considered.

Table 1: BVC-like starting rock composition (mineral modes) used in the simulations

Rock	Mineral	mol%
Basalt 70%	Feldspar ($An_{50}Ab_{40}Or_{10}$)	37%
	Olivine ($Fo_{90}Fa_{10}$)	32%
	Clinopyroxene ($En_{35}Fs_{15}Wo_{50}$)	21%
	Magnetite	10%
Lherzolite 30%	Olivine ($Fo_{90}Fa_{10}$)	71%
	Orthopyroxene ($En_{90}Fs_{10}$)	26%
	Clinopyroxene ($En_{50}Wo_{50}$)	2%
	Spinel	1%

Results: The relative abundances of Mg, Ca, and Fe ions in the starting rock affect the resulting carbonate compositions (Fig. 1). When all other inputs are equal, the BVC-like starting rock, richer in Mg and poorer in Fe, produces carbonates that are also more Mg-rich and Fe-poor. fCO_2 influences the Ca content of the carbonates, with higher fCO_2 favoring more Ca-poor carbonates. A higher W/R leads to a higher Fe content, although the effect is pronounced only at high fCO_2 and W/R.



(ALH carbonate data from Corrigan & Harvey, 2004)

ALH-like Starting Rock

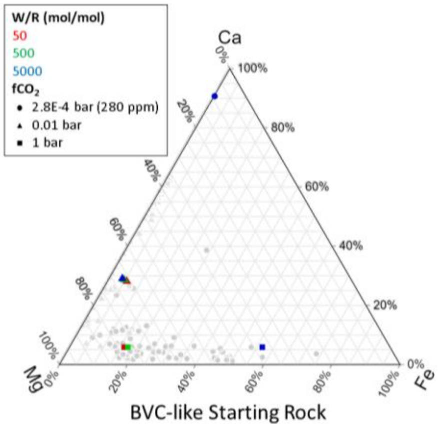


Fig. 1: Ternary diagrams of simulated carbonates with ALH-like (top) and BVC-like (bottom) starting rock compositions (colored symbols) and observed carbonate compositions in ALH 84001 (gray circles, [8]) and a BVC carbonate sample (gray symbols, [1]).

Secondary mineralogy (Fig. 2) depends strongly on fCO_2, especially between the 0.01-bar and 1-bar cases. The more complex composition of the BVC-like starting rock produces more diverse secondary mineralogies. W/R affects the relative abundances of each secondary mineral.

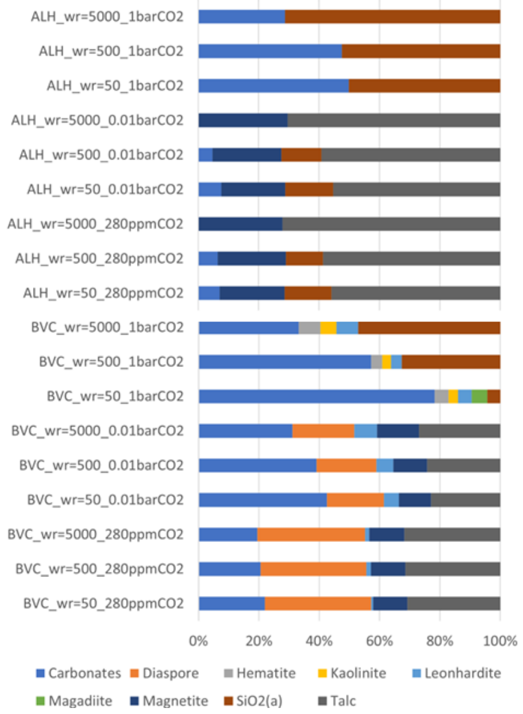


Fig. 2: Simulated secondary mineralogy in mol %. Feldspar, a part of the starting rock, is excluded.

Discussion:

Effects of input parameters. The dependence of carbonate cation composition on starting rock composition can explain the different carbonate compositions found in ALH 84001 and BVC carbonates despite their similar silicate alteration products and alteration fluid pH-Eh conditions. The effects of fCO_2 and W/R are similar to the findings by [2]. By independently varying fCO_2 and W/R, our results show that the effect of W/R is limited to cases where both fCO_2 and W/R itself are high. Therefore, variations in fCO_2 may have played an important role in creating the range of Mg-Ca carbonates while W/R may have had a greater effect on the composition of Mg-Fe carbonates.

Consistency with samples. The simulated compositions for BVC carbonates largely match that of observed carbonates, suggesting the simulated parameter ranges of W/R and fCO_2 would produce the observed BVC carbonates. The simulated non-carbonate alteration products for both ALH-like and BVC-like starting rocks are consistent with the observation of the respective samples. Silica, talc, and magnetite have all been detected in ALH 84001 [7, 8]. Silica-like, talc-like, and zeolite-like phases are the main non-carbonate secondary minerals associated with BVC carbonates [1]. Diaspore is also possibly present as a mixture with talc. Furthermore, the same carbonate-silicate relationship (Mg-Ca carbonates associated with talc, Mg-Fe carbonates associated with silica and zeolite) is present in both the BVC carbonate sample and the simulation results [1].

Possible subglacial hydrothermal origin. The diverse range of Mg- and Fe-rich carbonates observed in the BVC carbonates is only produced by models with much higher fCO_2 than that of the Earth's atmosphere. In contrast, almost pure Ca carbonates occur at lower fCO_2 closer to the terrestrial atmospheric value. The high-fCO_2 condition suggests a non-atmospheric source of CO_2 for BVC carbonates, such as magma degassing. Given the BVC's origin from subglacial eruption [6] and the carbonates' coexistence with phases similar in composition to typical hydrothermal alteration minerals, it is possible that the BVC carbonates were produced by hydrothermal alteration involving magmatic CO_2 dissolved in glacial meltwater following subglacial eruptions.

References:

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