

GEOCHEMICAL MODELING OF BASALT-BRINE INTERACTIONS AS AN ANALOG FOR MARS NEAR-SURFACE PROCESSES. M. E. Elwood Madden¹ and R. J. Bodnar, Virginia Tech, Department of Geological Sciences, 4044 Derring Hall, Blacksburg, VA 24061 (¹melwood@vt.edu)

Introduction: Geochemical thermodynamic reaction modeling allows one to predict the equilibrium composition of fluid and rock resulting from water-rock interactions. Geochemical modeling has been used here to predict fluid compositions resulting from brine-basalt interactions as analogs for possible liquid water-rock interactions near the surface of Mars. Given the low temperatures and pressures at the surface of Mars, pure water is not stable in its liquid state. However, the addition of salts to liquid water depresses the triple point, allowing liquid to be stable at lower temperatures and pressures. Salts have been reported to be important components in Mars surface chemistry based on evidence from lander soil analyses [1],[2],[3],[4],[5] as well as Mars meteorites [6]. Water-salt brines could form near the surface of Mars through dissolution of soil duricrusts, input of volcanic salts from the atmosphere and/or through water-rock interactions.

Description of Model: The numerical equilibrium model REACT [7] was chosen to predict a possible Mars near-surface fluid composition by calculating the fluid composition that would result from brine reacting with basalt. High salinity NaCl and MgSO₄ aqueous solutions were equilibrated with basalt to predict possible fluid compositions at or near the surface of Mars. In the initial model one liter of 4 molal NaCl brine was reacted with 100 g of basalt to match the water/rock ratios of Rosenbauer et al. [8]. NaCl was chosen as the salt component in these experiments because it is a geologically important salt on Earth, has been predicted as a soil constituent on Mars, and can be compared with previously published data in the basalt-H₂O- NaCl system.

The mineral components of the initial, unreacted basalt were calculated as a CIPW norm from the weight percent oxides reported in [8] (Table 1). The ratio of Fe₂O₃/FeO weight percent was calculated as 0.52 for an average basalt composition [9].

Table 1: Basalt CIPW Norm Mineral Composition

Mineral	Mole Fraction
Albite	0.14
Anorthite	0.17
Diopside	0.32
Enstatite	0.17
Ferrosilite	0.08
K-feldspar	0.04
Magnetite	0.08
Quartz	0.01

The equilibrium fluid composition of the basalt-NaCl brine system was calculated at a series of temperatures from 300° to 0°C. Differences in fluid composition between a closed, gas-free system and an

open system buffered by CO₂ gas were also examined. MgSO₄-- cited as a significant portion of Mars soil [1], [2],[3],[4]-- was also used as the salt component in brine interaction models with basalt.

Results:

NaCl Brine: As a test of our model, we first reproduced the basalt-4 molal NaCl brine experiment at 350°C described by [8]. We initially modeled the experiment at high temperature (300°C due to the temperature restrictions of the thermodynamic database), to test the accuracy of our model. The results of the model calculations appear to be in agreement with the experimental results, despite the 50° difference in temperature (Table 2). While the absolute values of cation concentrations from the model are differ significantly from the experimental results, the relative values of cation concentration demonstrate that the model accurately predicts which cations will be major components in the fluid.

Table 2. Fluid Components (ppm change from initial fluid composition)

Component in Fluid	300°C Experiment	300°C Model
Ca ⁺⁺	262	1728
Fe ⁺⁺	15	56.4
K ⁺	100	8031.5
Mg ⁺⁺	0.15	1.5
Na ⁺	-350	-4820

To approximate Mars near-surface conditions, the basalt-NaCl brine model was evaluated at 25°C. Reacting the same basalt composition and 4 molal NaCl brine as was used in the 300°C model, the results predict Na⁺ and Ca⁺⁺ as the dominant cations in the low temperature fluid (Table 3). A series of equilibrium calculations of the basalt-NaCl brine system were made ranging from 300 to 0°C, changing the temperature in 25° increments for each calculation. As the temperature of the system was lowered, K⁺ concentration in the product fluid decreased, while Ca⁺⁺ increased. Mg⁺⁺ and Fe⁺⁺ concentrations always remained several orders of magnitude lower than Ca⁺⁺ over the range of temperatures. This suggests that while hot NaCl brines equilibrated with basalt result in fluids dominated by Na⁺, K⁺, and Ca⁺⁺ (in order of decreasing concentration), at lower temperatures Na⁺ and Ca⁺⁺ are the main cations since the concentration of K⁺ in the fluid is greatly reduced.

The low temperature interaction of basalt and NaCl brine was also calculated as an open system buffered by CO₂ (*f*CO₂ = .001, approximating the CO₂ partial pressure of Mars' present surface atmosphere). By adding CO₂ to the system, the Ca⁺⁺ concentration in the equilibrated fluid is further increased

compared to the CO₂-free system at the same temperature. K⁺, Fe⁺⁺, and Mg⁺⁺ concentrations in the equilibrium fluid remain low. The results of the open system calculation are very similar to the CO₂-free fluid at the same temperature (Table 3).

Table 3. Equilibrium Fluid Components (ppm change from initial fluid composition)

Ion	NaCl 25°C No CO ₂	NaCl 25°C Open to CO ₂	MgSO ₄ 25°C
Ca ⁺⁺	4662	5341	568
Fe ⁺⁺	0.0011	0.0013	-717
K ⁺	5.47	6.27	1.14
Mg ⁺⁺	0.034	0.039	-57100
Na ⁺	390	-6110	2430
Cl ⁻	8900	0	0
SO ₄ ⁼	0	0	-219000

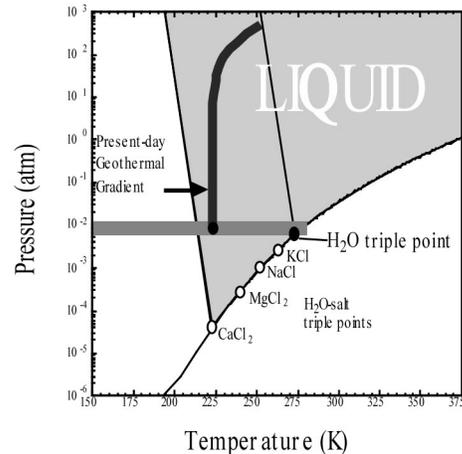
MgSO₄ Brine: Further modeling experiments were conducted using MgSO₄ as the primary dissolved salt. The basalt composition remained the same as in the NaCl experiments; only the initial composition of the brine was altered to 4 molal MgSO₄. As expected, the dominant anion in solution is SO₄⁼. However, a significant portion of the SO₄⁼ precipitates as gypsum, lowering the SO₄⁼ concentration in the brine. Na⁺ and Ca⁺⁺ are the dominant cations in solution following precipitation of Mg⁺⁺ out of the fluid phase. This results in a Na⁺-Ca⁺⁺-SO₄⁼ brine. The basalt-MgSO₄ brine reaction was calculated with and without CO₂ as a buffer. Just as in the basalt-NaCl reactions, the dominant cations and anions remain the same.

Discussion: The results of the thermodynamic equilibrium models predict that both NaCl brine and MgSO₄ brine-basalt interactions will produce fluids dominated by Na⁺ and Ca⁺⁺. The Cl⁻ brine produced by the NaCl interactions is likely to be stable as a fluid at low temperatures. However, due to the relatively low solubility of sulfates at low temperatures the SO₄⁼ brine will become saturated and will precipitate sulfates under Mars conditions, leaving any Cl⁻ in solution as the dominant anion. Therefore, low-temperature NaCl and mixed NaCl-MgSO₄ brines interacting with basalt will generate similar fluid compositions—Na-Ca-Cl solutions—as temperature decreases.

The predicted near-surface fluid compositions with significant amounts of dissolved Ca⁺⁺ and Cl⁻ suggest that aqueous fluids could be stable at the requisite low temperature and pressure conditions at or near the martian surface. The eutectic temperature for the CaCl₂-H₂O system is -49.8°C, lowering the stability field of an aqueous liquid phase well into the Mars' temperature/pressure field. Figure 1 shows the triple point depression associated with four major chloride salts in water. By adding CaCl₂ to the system, the liquid field is expanded to encompass the largest range of Mars surface temperatures and pressures. Adding other salts to the system decreases the

triple point even further, although the effect is small compared to the already low freezing point of CaCl₂-solutions. CaCl₂ dominated fluids are likely to be stable as "groundwater" as well, since the geothermal gradient expected on Mars lies within the CaCl₂-water liquid stability field [10].

Figure 1. Brine P-T Diagram



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