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MINERAL SURFACE AND FLUID CHEMISTRY IN NAKHLITE ANALOG WATER-ROCK REACTIONS. M. A. Miller¹, S. P. Schwenzer², J. C. Bridges³, L. J. Hicks³, U. Ott^{4,5}, J. Filiberto^{2,6}, C. Chavez⁷, H. Smith⁷, A. H. Treiman⁸, S. P. Kelley², J. M. Moore⁷, T. D. Swindle⁹, M. A. Bullock¹⁰, R. A. McIntosh¹, – ¹Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas 78228 (mmiller@swri.org); ²The Open University, Milton Keynes, UK; ³Space Research Centre, University of Leicester, UK; ⁴ATOMKI, Debrecen, Hungary, ⁵MPI, Mainz, Germany ⁶Southern Illinois University, Carbondale, IL, USA; ⁷NASA Ames Research Center, Moffett Field, CA USA; ⁸Lunar and Planetary Institute, USRA, Houston, TX, USA; ⁹Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, USA; ¹⁰Southwest Research Institute, Boulder, CO USA.

Introduction: Water and fluid chemistry are central to the question of Martian habitability. On Earth, serpentinization of olivine, especially Fe-bearing fayalite, provides molecular hydrogen as an energy source and as a source of electrons [1-3], which can be efficiently utilized by chemosynthetic organisms [4]. This also holds for Martian rocks [5]. Water serves as the solvent to enable alteration, but its composition matters – even if life can adapt to a wide range of conditions [6-11]. Thus, those factors are a focal point of Martian research including landed missions [12-14], meteorite investigations, analog studies [15-21], and the predictions of possible biomarkers (e.g., [22]). In this study, we conduct experimental and geochemical modeling investigations to study the pairing of mineral surface–fluid chemistry under circumneutral Martian analog conditions, such as those expected on Amazonian Mars based on the nakhlite meteorites [19].

Experiment and methods: Water-rock reaction experiments were conducted in the Aqueous Simulation Facility at NASA Ames [23,24], with alteration experiments at 35 °C under simulated Mars atmosphere (98 % CO₂ and 2 % Ar, 30 ppm Kr and 8 ppm Xe), lasting 1, 3, and 9 months (Run 1, 2, and 3). We used a variety of mineral mixtures to approximate the mineralogies of Martian rocks, including the nakhlite meteorites (Tab. 1). Here we report on newly measured fluids, and mineral surface chemistry and mineralogy. Earlier results were reported by Bullock et al. [25] and Schwenzer et al. [26-28]; further new results are reported in two other LPSC 2018 contributions [29,30]. Analytical methods are as follows. Grains of minerals from the reaction vessels were imaged under a scanning electron microscope (FEI Quanta 650 SEM at SwRI). Elemental abundances were measured with an energy dispersive X-ray spectrometer (EDS, IXRF Systems). Mineral alterations were further examined with Raman spectroscopic microanalysis (Horiba/Jobin-Yvon LabRam HR Evolution Raman Microscope at SwRI). Chemical analyses of fluids of Run 1 were done at University of Colorado Boulder [25], and those of Run 3 at SwRI San Antonio by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES), on a Perkin Elmer Optima (Model 7300DV) and a Thermo Jarrell Ash ICAP (Model 61E)

Trace Purge. Thermochemical modeling was done with CHIM-XPT, see e.g., [26-28].

Table 1. Chemical composition (wt.%) of Ol=forsterite, Pyx=augite, Plag=andesine, Fay = fayalitic glass [26-29]. Our runs contained a variation of combinations from pure minerals, 1:1 mixtures, and mixtures of three or all four phases; also, some mixtures contained trace phases such as apatite or pyrite, or additions such as hydrochloric acid.

	Ol	Pyx	Plag	Fay
SiO ₂	41.8	52.1	63.4	31.84
Al ₂ O ₃		2.4	21.6	4.43
TiO ₂		0.6		0.33
FeO	7.1	9.5	0.06	55.03
CaO	0.1	19.1	2.3	1.48
MgO	56.7	14.6		0.78
Na ₂ O		0.3	8.6	0.38
K ₂ O			3.8	1.23

Results: We report fluid composition and surface chemistry. For clay mineralogy see [30], for noble gases [29].

Fluids. Concentrations of the major elements in the 9 month long run (1 month runs in brackets) cover the following ranges (in mg/L; Fig. 1): sodium 0.4 to 11.8 (0.5 to 5.7), potassium 0.5 to 9.2 (0.5 to 4.6), magnesium 0.07 to 270 (1.6 to 248), calcium 1.72 to 82.6 (6.46 to 99.6), manganese 0.007 to 1.63 (0.12 to 1.21), iron 0.151 to 0.213 but mostly below detection limit (below detection limit), aluminium 0.079 to 3.42 but often below detection limit (~0.11, but mostly below detection limit), silicon 1.16 to 89.9 (12.2 to 56.2), and sulphur 0.071 to 102 (0.478 to 2.14).

Models. Modelling a composition of 30 % Fay, 20 % Ol, 25 % Plag, 25 % Pyx, results in an overlap of Na/Mg ratios between our models and the measured fluids at around W/R of 5000–6000. Taking into account the observation that olivine and plagioclase dissolve more readily than the fayalitic glass, results in a starting composition of 50 % ol, 40 % plag, and 5 % of Fay and Pyx each. In this case, the Na/Mg ratio of the models match the measured fluids at about W/R 3000. However, Ca/Na and K/Na ratios are lower in the models than in the measured fluids, with a lower Ca/Na in the more realistic model due to less Ca in the starting composition.

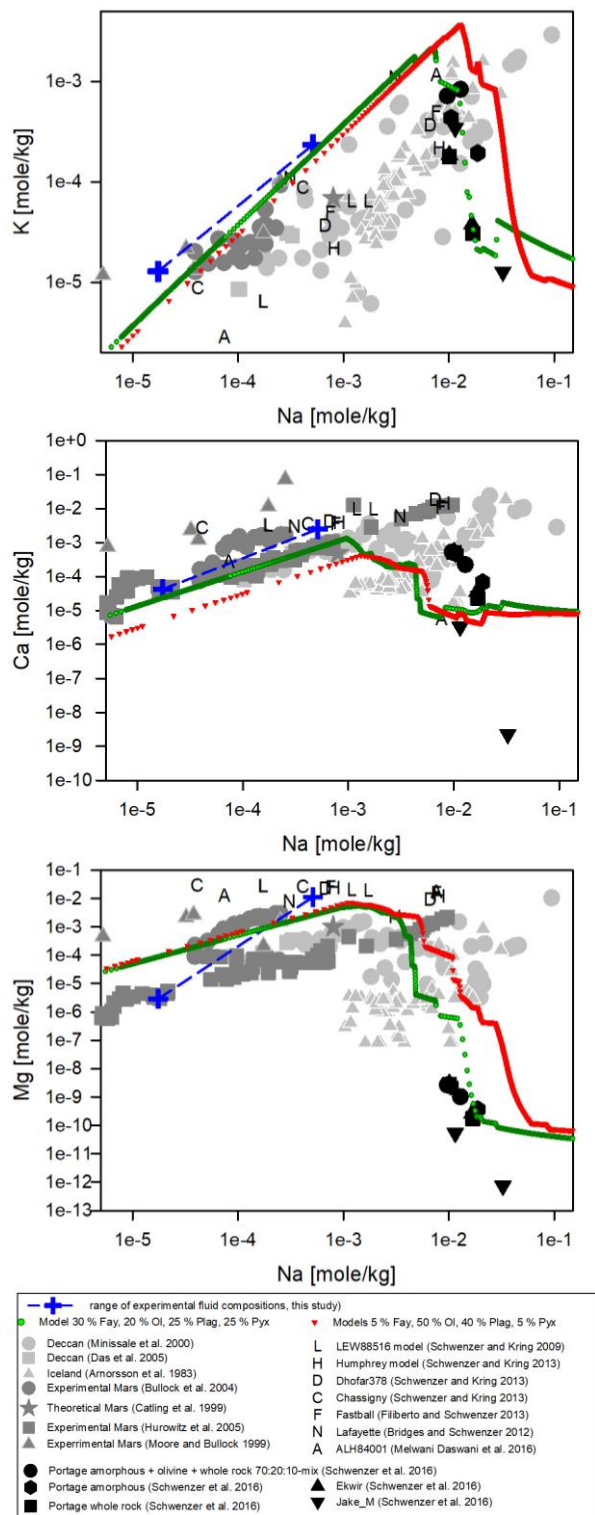


Fig. 1. Plot from [10] with experimental fluids from this study added. a) Na vs K, b) Na vs Ca, c) Na vs Mg. For References in brackets, see [10].

Surface mineralogy. Raman investigation of the mineral surfaces showed compositional alterations after only one month, the most salient of which occurred on

the Ol grains. Other alterations included magnesite and calcite phases, which occurred in mixtures containing Ol+Plag.

Discussion: Fig. 1 shows a comparison of our experimental fluids with a range of terrestrial, Mars analog experimental and modeled fluids, and two models from this study. Our fluids are comparably low in Na, especially compared to Icelandic fluids, but have greater K abundances than fluids with similar Na concentrations (Fig.1a). This is likely due to the nature of plagioclase and the fayalitic glass (Tab. 1), but also suggests that the Icelandic fluids have a sea salt contribution, either by seawater or salt spray. Ca and Mg concentrations are well within the range of other experimental fluids (Fig.1b,c). Our modeled fluids are lower in K and Ca than the measured fluids, which indicates leaching rather than full dissolution and will be investigated further. However, measured Ca concentrations are similar to, but Mg concentrations are higher than modeled Martian fluids, which reflects the clay formation processes, dominated by serpentine in our experiment [19]. In the models Fe-Mg clay are precipitated when modeling the experiments and when modeling Martian fluids [e.g., 8,10]. This will be investigated further.

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