

**EXPERIMENTAL STUDIES OF BRINES AND EVAPORITES AS APPLIED TO MARS: INITIAL RESULTS FROM 1998-1999 RUNS** J.M. Moore<sup>1</sup>, M.A. Bullock<sup>2</sup>, M.T. Mellon<sup>3</sup>, C.R. Woosley<sup>1</sup>, and A.P. Zent<sup>1</sup> <sup>1</sup>NASA Ames Research Center, MS 245-3, Moffett Field, CA 94035; <sup>2</sup>SwRI, 1050 Walnut St., Boulder, CO 80302; <sup>3</sup>LASP CB 392, University of Colorado, Boulder, CO 80309 (jmoore@mail.arc.nasa.gov) (bullock@sunra.colorado.edu)

**Introduction:** We are performing laboratory experiments to determine the concentrations and rates of dissolution of ions that could occur in closed, juvenile groundwater systems on Mars. Our approach is to incubate unaltered Mars-analog minerals in initially pure liquid water in contact with a Mars gas mixture for one year. At exponentially increasing time intervals, aliquots of the solutions at three different temperatures are extracted and analyzed using standard terrestrial laboratory geochemical techniques. Ultimately, our experiments will produce Mars analog brines which will be freeze dried to create evaporites. The physical and chemical properties of these evaporites will be compared with spacecraft remote sensing and *in situ* compositional and physical data.

Evaporite deposits may represent significant sinks of mobile cations (e.g. Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>) and anions (e.g. CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>) among the materials composing the martian surface and upper crust. Carbon and nitrogen are especially interesting because of their role as atmospheric gases which can become incorporated into crustal rocks. The nature of evaporite-precursor brines formed under martian conditions is poorly understood. Our laboratory studies investigating the formation of brines will greatly aid in improving our understanding of both the fluids and their precipitates (evaporites). The modeling of "warm, wet Mars" alteration and precipitate mineralogies will benefit from laboratory data of the type we discuss here.

**Approach and Experimental Technique:** To generate brines, samples of unaltered mineral mixtures, which are thought to represent the rock in the upper martian crust were ground, sorted, and mixed with doubly-distilled water. Individual pristine minerals were used to simulate martian rocks and have been chosen on the basis of SNC meteorite mineralogy [1]. The slurries were placed in an environment (pressure 1 bar, temperatures set a several values: 3°, 25°, and 35° C) which represent the conditions within the martian subsurface where brines might reside. The atmospheric gases in the sample chambers were mixed to match the present composition of the martian atmosphere -- (CO<sub>2</sub> 95.50%, N<sub>2</sub> 2.70%, O<sub>2</sub> 0.13%). Within a set of runs, specific samples are being collected after durations of 1, 21, 42, 84, 168 and 336 days. The individual sample durations have been chosen on the basis that most chemical reaction rates (including those that are grain-rind diffusion limited) decay exponentially with time. At the end of the exposure, the identity and abundances of water soluble ions in the fluid are being determined, and the rock samples are examined for the presence of precipitates and weathering products. Anion concentrations are determined to ppb levels using a Dionics 4500I Ion Chromatograph (IC) using EPA 300 protocols. Cations are also determined at ppb levels with an ARL 3410 Plus Inductively Coupled Plasma/Atomic Emission Spectrometer (ICP/AES), following the EPA 6010 protocol. Controls of two types are also incubated during the experiment: (a) chambers with fluid and Mars-analog minerals with Earth gas in the headspace, and (b) chambers

with fluid, no rock, but with the Mars analog gas in the headspace.

**Results to Date:** The experiments began on November 7, 1998 and will continue for nine months. To date, aliquots at 1 day, 21 days, 42, days and 90 days have been extracted and analyzed. Anion and cation concentrations vs. time for fluid samples extracted from runs at 3, 25 and 35° C are shown in Figures 1 - 6. Only the four most abundant cations and five most abundant anions are plotted. Also plotted on these charts are pH, with the scale on the right-hand vertical axes. Total dissolved carbon was calculated for each sample from measured pH and the carbon dioxide pressure in the headspace. Debye-Huckel theory was used to account for the activities of other ions in solution; total dissolved carbon was then calculated from equilibrium between H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. Figure 7 shows the anion dissolution rates as functions of temperature. Note that in general, anion concentrations increase with temperature, but dissolution rates decrease with temperature. Most of the ion dissolution occurs nearer the beginning of the higher temperature experiment, and is subsequently controlled and limited by the higher pH. Figure 8 shows the cation dissolution rates as functions of temperature. We have modeled the precipitation of salts that would occur during evaporation of the fluids generated in this experiment. For this we used the computer code PHREEQ, a standard geochemical modeling package from the USGS [2]. PHREEQ is based on an ion-association aqueous model and has capabilities for (1) speciation and saturation-index calculations, (2) reaction-path and advective-transport calculations involving specified irreversible reactions, mixing of solution, mineral and gas equilibria, surface-complexation reactions, and ion-exchange reactions, and (3) inverse modeling, which finds sets of mineral and gas mole transfers that account for composition between solutions, within specified compositional uncertainties. This modeling shows that the primary evaporites produced from our Mars brines precursor at all temperatures would be gypsum, anhydrite and fluorite. Recent findings by the Mars Global Surveyor (MGS) Thermal Emission Spectrometer (TES) indicate that carbonates are in undetectable abundances while there is some evidence that sulfates appear as a ubiquitous component of atmospheric dust (P.R. Christensen, personal communication), consistent with the findings of Pollack et al. [3]. Smaller amounts of calcite and dolomite would subsequently precipitate out as the brines became more concentrated.

**References:** [1] McSween, H.Y., *Rev. Geophys.* 23, 391-416, 1985. [2] Parkhurst, et al., PHREEQ -- A computer program for geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 80-96, (Revised and reprinted 1990.) [3] Pollack, J.B. et al., *J. Geophys. Res.* 95, 14,595-14,627, 1990.

Fig.1

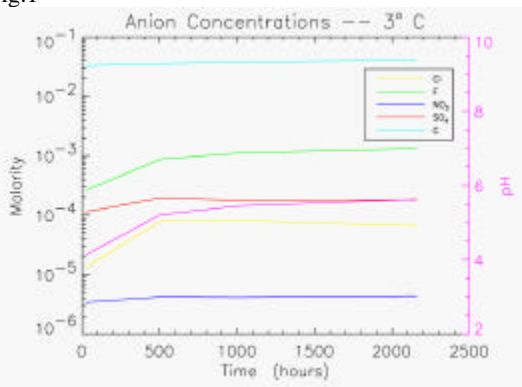


Fig. 4

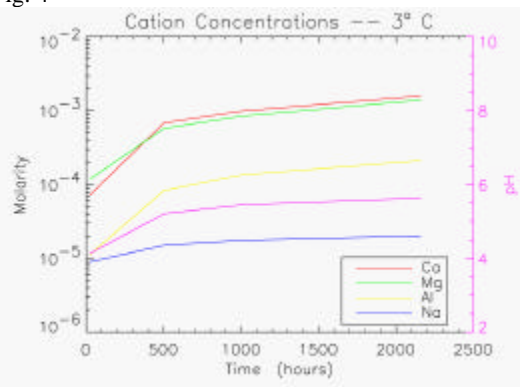


Fig. 2

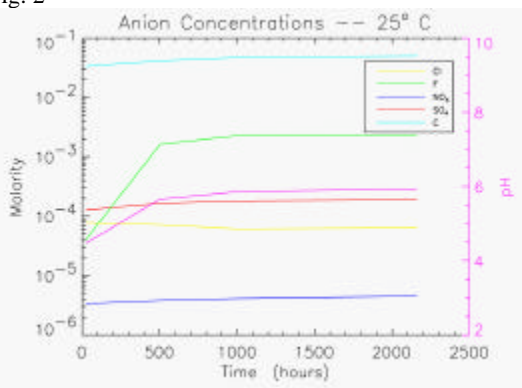


Fig. 5

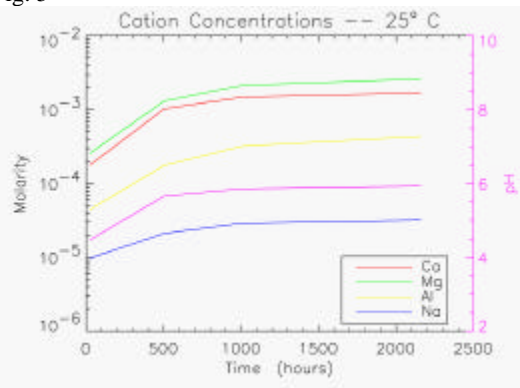


Fig. 3

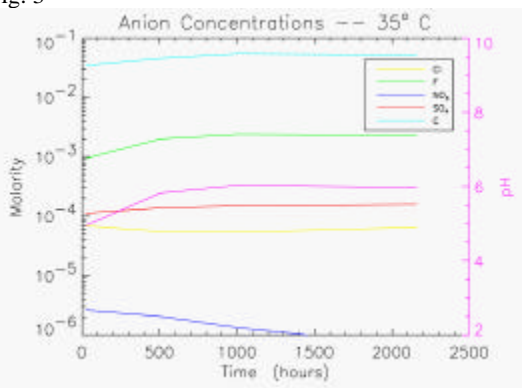


Fig. 6

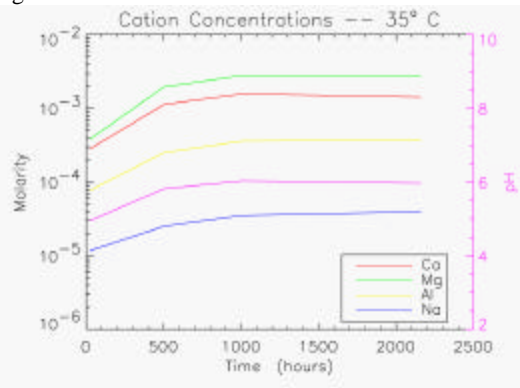


Fig. 7

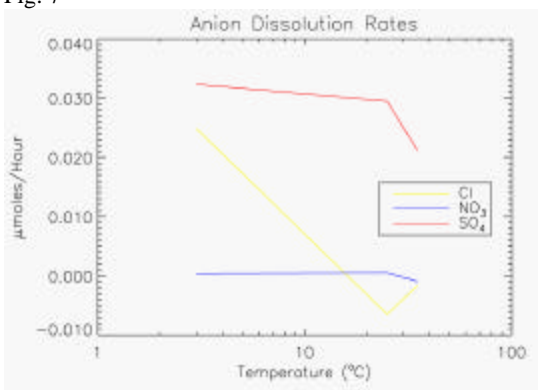


Fig. 8

