

LABORATORY SIMULATIONS OF MARS EVAPORITE GEOCHEMISTRY: EVAPORATION OF MODERN BRINES UNDER VARIOUS HEADSPACE GAS MIXTURES.

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Introduction: This abstract reports on laboratory experiments that generated Mars-analog evaporites under simulated Mars conditions. First, we produced small amounts of dilute brines from the interaction of water with an SNC-derived mineral mixture under present day Mars conditions. Synthetic versions of this brine were then evaporated under two different conditions: Under a modern-Mars gas mixture, and under a gas mixture with added acidic gases. Compositional differences in the laboratory evaporites produced under these two conditions show how atmospheric chemistry may influence the deposition and composition of evaporites on Mars. The spectacular discoveries of the MER rovers and the infrared spectrometers aboard *Mars Express* and *Mars Reconnaissance Orbiter* both illustrate the relevance, as well as guide the future direction, of this work.

Evaporite-rich sedimentary deposits on Mars were formed under chemical conditions quite different from those on the Earth. Their unique chemistries record the chemical and aqueous conditions under which they were formed, and possibly subsequent conditions to which they were subjected. We have reported our results from experiments performed using precursor brines formed under acidic atmospheric conditions that were then desiccated under both acidic and modern atmospheric composition head gases [4]. In this abstract we provide initial analysis of evaporates precipitated using precursor brines formed under modern martian atmospheric conditions that were then desiccated under both types of head space gases as were used in previous runs [4].

Evaporite Experiments: Small amounts of brines formed by the interaction of water with an SNC-derived synthetic Mars mineral mix were produced under the modern Mars atmospheric gas mixture [1]. We then produced a synthetic brine (Table 1) with the same composition, for the evaporation experiments. The brine was desiccated under simulated Mars conditions in the evaporite apparatus. We synthesized two atmospheric compositions for these experiments: Present-day Martian conditions and a more acidic, ‘paleo-Mars’ gas mixture with trace amounts of SO₂ (100 ppm), N₂O (10 pm), and HCl (10 ppm) to simulate an atmosphere influenced by volcanic emissions.

Evaporites Experiment Apparatus: See Fig 1 for overview. Formation of the evaporites are carried out in thin, conical 50 cc teflon sample holders that sit inside and line cylindrical receivers. Precipitation occurs at the bottom of each sample holder on a gold-

plated TEM sample grid with a holey-carbon thin film, which is removed at the conclusion of a run and placed directly into an XRD sample chamber. Each receiver contains a conical cavity for supporting the teflon sample holders, a helical path about the outside diameter, and two O-rings to contain coolant. The helical path provides efficient circulation of the coolant near each sample for temperature stability. The sample holders and receivers are mounted into a stainless steel cooling block that is itself fitted with coolant lines to further ensure an isothermal environment.

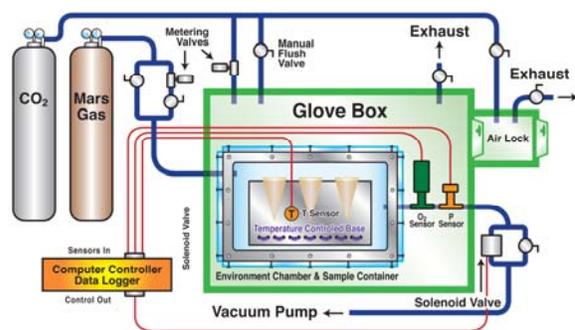


Fig. 1. Schematic diagrams of the Mars Evaporites Experimental Apparatus. (a) The environmental chamber encloses the sample vessel container block. Computer-controlled closed-loop circuits maintain pressure and temperature within the environment chamber. An O₂ sensor monitors the system for contamination. (b) Nine conical Teflon sample holders sit within cylindrical receivers outfitted with helical grooves through which a coolant is circulated for maintaining a constant temperature. The Plexiglas and steel environment chamber has gas, coolant, and electrical feed-throughs.

The entire assembly (9 flasks within a block) resides within a vacuum desiccator chamber. The desiccator has been fitted with two gas valves; one for flushing its interior with a synthesized Mars gas, and the other for pumping the desiccator down to pressures as low as 1 mbar when required. The gas input and output valves are teflon solenoids which can be actuated both manually and by the computer-controller. A pressure sensor feeds information back to the computer to ensure appropriate pressure in the chamber. Cambridge Sensotec Rapidox 200 O₂ sensors (capable of detection of O₂ down to 10⁻¹⁷ ppm) have been fit into the vacuum lines. These are constantly monitored by the computer-controller in order to detect any oxygen contamination. An electrical feed-through allows signals from thermistors attached to the sample flasks to be passed to the computer controller. A laptop com-

| | Ion | K | Fe | Al | Mg | Ca | Na | Cl | NO3 | SO4 | CO3 |
|-----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Salt | [M] | 1.79E-05 | 5.37E-07 | 3.45E-04 | 2.01E-03 | 1.42E-03 | 1.44E-04 | 5.36E-05 | 8.06E-06 | 2.45E-04 | |
| KCl | 1.79E-05 | 1.79E-05 | | | | | | | | | |
| FeCl2 | 5.37E-07 | | 5.37E-07 | | | | | | 1.79E-05 | | |
| Al2(SO4)3 | 8.15E-05 | | | 1.63E-04 | | | | | 1.07E-06 | | |
| MgNO3 | 8.06E-06 | | | | | | | | | 2.45E-04 | |
| MgCO3 | 2.01E-03 | | | | 2.01E-03 | | | | | | 2.01E-03 |
| Na2CO3 | 7.18E-05 | | | | | | 1.44E-04 | | | | 7.18E-05 |
| CaCO3 | 1.42E-03 | | | | | 1.42E-03 | | | | | 1.42E-03 |
| HCl | 3.46E-05 | | | | | | | 3.46E-05 | | | |

Table 1. Synthetic Mars-Analog Brines Recipe for an modern Mars atmosphere. The second row lists the ion concentrations of the experimental brine, while the second column shows the concentration of salt used in the synthetic brine.

puter using Labview and a PCMCIA data acquisition card serves as the controller, measuring temperature and pressure in the chamber, logging data and controlling the vacuum pressure in the chamber.

Experimental Procedure: The four-run experiment set we are reporting here involved the fast (days) and slow (weeks) evaporation of our brine once under the “modern Mars” head gas composition and again under the “paleo-Mars” composition. The rate of evaporation was controlled by the temperature and pressure of the samples. The slow evaporation temperature and pressure was held just above 0°C and 10 mbar, while the fast evaporation temperature and pressure was held at 25°C and 500 mbar. Also the gas flow rate was constant for all runs.

Brines were placed into 9 sample holders (in the amounts of 20 ml), and desiccated. The desiccation of liquid samples was followed by visual (video monitoring) inspection. The thoroughly dry precipitate samples were removed in an oxygen and moisture free glove box, sealed, and sent for SEM and FTIR analyses.

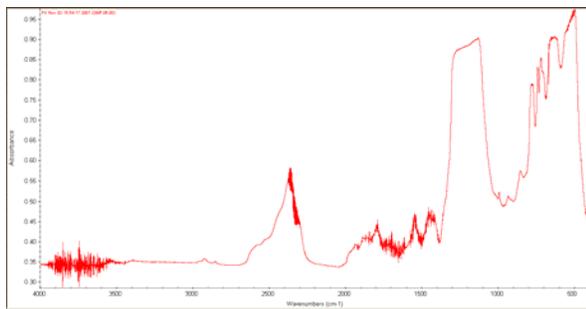


Fig. 2. FTIR reflectance spectrum of evaporite formed by fast evaporation of Mars-analog brine under simulated acidic conditions on Mars. Peaks at 1250 and 1160 cm^{-1} are diagnostic of sulfates. Comparison with the ASU library shows the presence of Ca and Mg sulfates

Results: Microscopy of the resulting salts showed significant differences in appearance and crystallinity between evaporites produced under the simulated present Mars conditions, and those produced under the more acidic conditions. Infrared reflectance spectroscopy of evaporites produced under the ‘paleo-Mars’

atmosphere show clear evidence of sulfates, most likely hexahydrate and epsomite (Fig 2). These are calculated to be stable under present Mars conditions (Fig 3). Reflectance spectra of the evaporites produced under simulated present-day Mars have proven more difficult to obtain, however, due to their lack of obvious crystallinity. It is likely that these are primarily anhydrous carbonates, with small amounts of sulfates. We will report on the ongoing effort to identify and quantify the evaporites produced under modern Mars conditions.

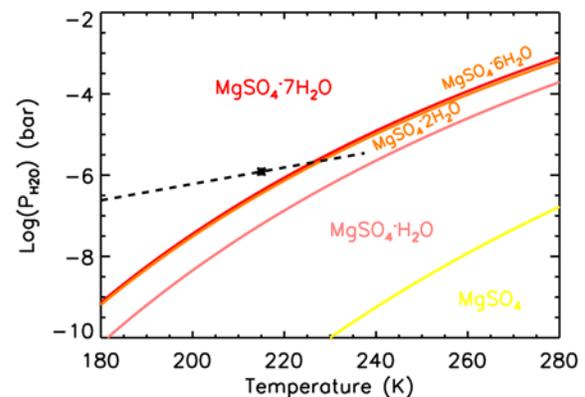


Fig. 3. Stability fields for hydrated states of magnesium sulfates. The black dashed line shows surface conditions on Mars, from 15 km to -5 km altitude. At the globally averaged temperature and water vapor pressure, epsomite and hexahydrate are stable. Data from [5]

References: [1] Bullock M.A. et al. (2004) *Icarus*, 170, 404-423. [2] Bullock M.A. and Moore J.M. (2004) *GRL*, 31, L14701. [3] Bullock M.A. and Moore J.M. (2007) *GRL*, 34, L19201. [4] Moore, J.M. et al (2010) *JGR*, 115, E06009. [5] Fegley, B., and Treiman, A.H., (1992) *Venus and Mars: Atmospheres, Ionospheres and Solar Wind Interactions*. AGU, 1992, pp. 7-71.

This research was supported by NASA’s Planetary Geology & Geophysics Program and Mars Fundamental Research Program.