

EVAPORATION OF FE(II)- AND FE(III)- SULFATE BRINES UNDER CO₂ AND ULTRAVIOLET LIGHT: IMPLICATIONS FOR FE REDOX AND FE MINERAL ASSEMBLAGES ON MARS. Xiyu WANG^{1,2}, Disheng ZHOU^{1,2}, Yu-Yan Sara ZHAO¹, Dongdong LI³, Xiongyao LI¹, Shijie WANG¹. ¹Center for Lunar and Planetary Sciences, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550081, China (wangxiyu@mail.gyig.ac.cn), ²University of Chinese Academy of Sciences, Beijing, 100049, China, ³Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining, 810008, China.

Introduction: Sulfates and oxides have been identified on Mars from both orbital and in-situ observations [1]. In Ca-, Mg- and Fe- sulfates, Fe-sulfate is indeed important due to Fe redox and hydrolysis, that not only link sulfates- and oxides- assemblages on Mars, but also control the brine chemistry in a multi-component system. Fe³⁺-sulfates were detected in the sedimentary records at Meridiani Planum and Gale Crater [2, 3], and the possible presence of Fe²⁺/Fe³⁺ redox is also suggested at these two sites [4, 5]. The Fe chemistry on the Martian surface may hold key information of the ancient environments and habitability on Mars.

Despite its importance, there are currently lack of constraints regarding Fe-sulfate brine evolution under Mars CO₂ atmosphere. What are the Fe assemblages produced with or without UV irradiation under Mars atmosphere? What are the nature and compositions of amorphous components forming by evaporation of Fe-sulfate brines?

In this work, we investigate Fe-sulfate brine evolution and final products during evaporation under CO₂ Mars-like atmosphere. Ambient light and ultraviolet (UV; 254 nm) light are both examined to compare the possible difference in final assemblages. Initial Fe-sulfate brine with various Fe²⁺/Fe³⁺ molar ratios (Fe²⁺/Fe_T = 0, 0.25, 0.5, 0.75, 1; Fe_T = 500 mM) are used to simulate various oxidation states.

Experimental Methods:

Evaporation under CO₂ and ambient light. The evaporation chamber is illustrated in Fig. 1. Purified CO₂ (>99.99%) was continuously bubbled into the brine at the chamber bottom, and the gas flow was set at 0.5 L/h. Vacuum pump was continuously pumping throughout the experiment to facilitate evaporation and the condenser was able to collect the evaporating components out of the chamber so the system was mass-balanced and the brine evolution can be closely monitored. Circulating water in the outer jacket of the chamber was maintained at 25°C for all experiments. The starting brines were prepared using ultrapure (18.2 MΩ), deoxygenated water (dissolved O₂ < 2 ppm), and Fe²⁺ and Fe³⁺ were added as FeSO₄·7H₂O and Fe₂(SO₄)₃, respectively. In each run, an aliquot of the evaporating brine were sampled every 6 h, and the pH, ORP, Fe²⁺, Fe_T, SO₄²⁻, HCO₃⁻, CO₃²⁻ were determined

immediately. The condensed evaporating solutions were also collected and analyzed for cation and anion compositions. By the end of each run (~120 h), the formed solids were collected, isolated from ambient atmosphere for further analysis.

Evaporation under CO₂ and UV₂₅₄ light. The apparatus can be modified to accommodate the UV photooxidation experiments, with the mercury UV₂₅₄ light source inserted directly into the chamber. Initial brine was placed in a quartz beaker evaporated to dryness by intermittently pumping. The chamber was first filled with CO₂ (loaded at 1 bar; not bubbling into the brine) and sealed for 12 h without pumping ("reaction period"), then pump was on for 12 h to facilitate evaporation. UV light was continuously on for 120 h. After 5 such reaction-pump cycles, the final products were removed from the chamber for phase characterization. Aliquots of solid mixtures were dissolved in ultrapure water for soluble components analyses. During the experiments, the chamber was fully covered with heavy duty aluminum foil to eliminate UV leaks and prevent interference by other wavelength light sources.

Characteristics of solid and solution samples. Evaporative solids were characterized by X-ray Diffraction (XRD), infrared, Raman spectrometry and Scanning Electron Microscope (SEM) with EDS.

The solution samples were filtered with a 0.2 μm membrane. The pH and ORP of solution were monitored by WTW electrodes, Fe²⁺, Fe_T, SO₄²⁻ were measured immediately after sampling using a HACH DR 6000 UV/VIS Spectrophotometer, HCO₃⁻ and CO₃²⁻ were determined by titration. Total Fe and SO₄²⁻ concentration were also cross checked by Atomic Absorption Spectrophotometer (AAS) and Ion Chromatography (IC), respectively.

Results: Evaporation under CO₂ and ambient light.

Systematic difference in brine evolution and final products correlating to initial Fe²⁺/Fe³⁺ was observed. As increasing the initial proportion of Fe³⁺ (Fe_T remains constant), the starting pH of brines decreasing systematically due to Fe³⁺ hydrolysis. During the evaporation, pH of the brines keep decreasing in all experiment with Fe³⁺ added. In contrast, the Fe²⁺-only brine has a lightly increase of pH towards the end of the experiment.

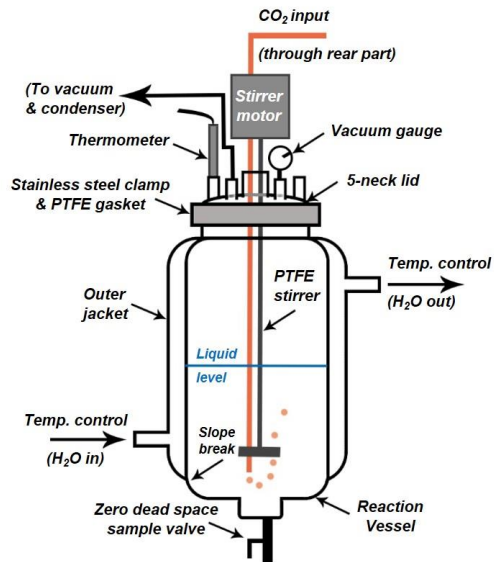


Fig. 1. The experimental apparatus used for brine evaporation under ambient light.

The elevated pH in the Fe^{2+} -only system is probably caused by slight oxidation of Fe^{2+} . The pH of Fe^{2+} -sulfate brine is likely controlled by competition of Fe(II) oxidation (production of OH^-) and Fe(III) hydrolysis (production of H^+), if no Fe mineral with hydroxyl precipitates. We are currently characterizing the suspension materials, and to see if the pH increase relates to evaporation or not.

In addition, for the three experiments that Fe^{3+} consist of 50% or higher initially, colloids forms by the end of evaporation when the brines get very concentrated. But colloids were not observed in experiments with Fe^{3+} of 25% or lower.

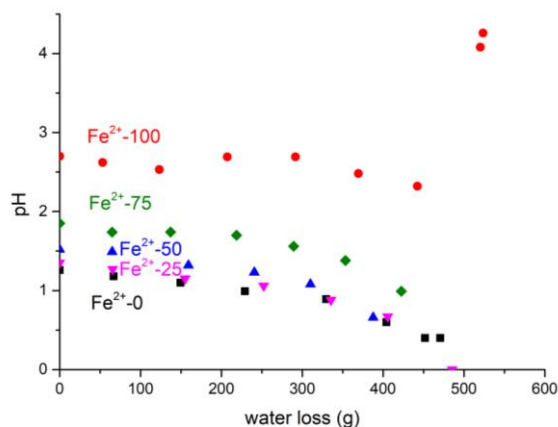


Fig. 2. pH change during evaporation. Numbers following Fe^{2+} represent Fe^{2+} molar proportion in Fe_T .

The final evaporative products are shown in Fig. 3. Amorphous components were identified in XRD pat-

terns but will need further characterization. In general, the higher the Fe^{3+} proportion, the degree of crystallinity is improving. In Fe^{2+} -only experiment, melanterite is the only crystalline phase and a growth of melanterite particle can be seen. In Fe^{3+} -only experiment, rhomboclase and copiapite are precipitated. In the experiments with mixing Fe^{2+} and Fe^{3+} , rozenite is the major Fe^{2+} phase, and rhomboclase is the Fe^{3+} phase. One exception is that in the Fe^{2+} -50% condition, amarantite rather than rhomboclase precipitates. Thermodynamics modeling is being conducted to compare with experimental results to see if any kinetics factors influencing the final evaporites.

Due to acidic conditions of our brines, bicarbonate is of limited in the evaporating system. Diluted Fe^{2+} -only brine ($\text{Fe}_T < 50 \text{ mM}$) is currently being examined under ambient light to see how the CO_2 would interact with a less acidic Fe-sulfate system.

Dissolved CO_2 is expected and might be picked up by the precipitates. The EDS detected relatively high C contents in the evaporating solid samples. Additional analyses are needed to rule out the possible contaminations during the pretreatment of SEM analysis. The UV experiments are now being conducted and we will report further results at the conference.

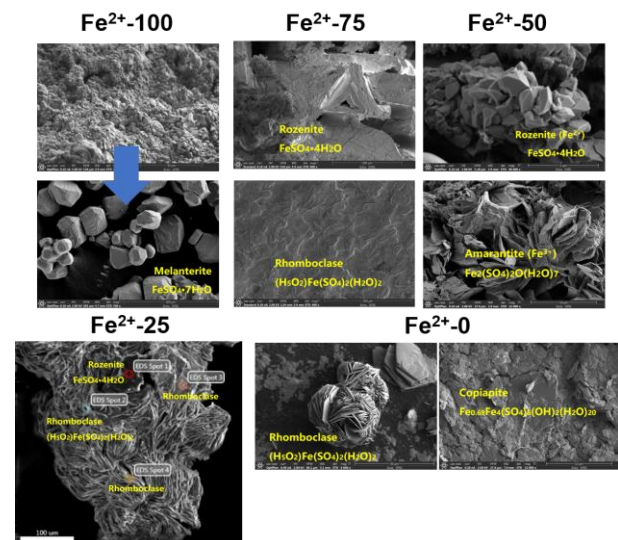


Fig. 3. SEM images of final evaporative products identified by XRD and EDS.

Funding: This work is supported by West Light Foundation of Chinese Academy of Sciences and National Natural Science Foundation of China (No. 41673072) to Y.Y.S.Z.

References: [1] Ehlmann, B.L. and Edwards, C.S. (2014) *Annu. Rev. Earth Planet. Sci.*, 42, 291-315. [2] Klingelhofer, G., et al. (2004) *Science*, 306, 1740-1745. [3] Rampe, E.B., et al. (2017) *Earth Planet. Sci. Lett.*, 471, 172-185. [4] Tosca, N.J., et al. (2008) *JGR-planet*, 113(E5). [5] Hurowitz, J.A., et al. (2017) *Science*, 356(6341).