

LOW TEMPERATURE ANHYDRITE FORMATION IN FLOW-THROUGH DISSOLUTION EXPERIMENTS. K. M. Miller,¹ C. M. Phillips-Lander¹, A. S. Elwood Madden¹, and M. E. Elwood Madden¹,
¹School of Geology and Geophysics, University of Oklahoma, 100 E. Boyd St., Rm. 710 Norman, OK 73019
 kayla.m.miller@ou.edu

Introduction: Sulfate minerals, including jarosite, are common on the martian surface [1-8]. Flowing brines have recently been documented on the surface of Mars as well [9]; therefore, understanding the reaction products formed when sulfate minerals react with brines can inform interpretations of Mars' hydrologic system, both past and present.

In this study, flow-through dissolution experiments simulated one-directional, semi-open systems analogous to hydrological environments proposed at Meridiani Planum, Mars, where jarosite was first observed [10]. Previous experiments comparing jarosite dissolution in semi-open (flow-through) and closed system (batch) experiments observed anhydrite forming at low temperatures in semi-open flow-through experiments [11]. Dixon et al. [11] hypothesized that anhydrite may form at low temperatures in flow-through experiments due to the constant source of high salinity, low-water-activity brine.

Here, we test this hypothesis by examining jarosite and brine reaction products in semi-open flow-through experiments using CaCl₂ brines of varying salinity and, therefore, water activity. Batch reactor experiments – analogous to closed evaporite basins or freezing groundwater systems on Mars – were also conducted. In these experiments, we quenched samples by adding isopropyl alcohol during vacuum filtration to examine whether drying methods affect sulfate mineralogy [12-16].

Methods: Flow-through experiments were conducted with synthetic K-jarosite + 5%, 20%, or 50% weight (wt.) CaCl₂ brine at room temperature and pressure over 10 days to test the effects of brine concentration on mineral reaction products (Figure 1).

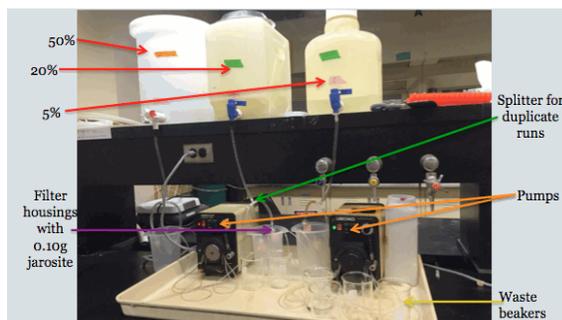


Figure 1. Full flow-through experimental setup.

Closed system batch reaction experiments were conducted to investigate the effect of sample quenching on sulfate mineralogy by combining 150 mL of 50 % wt. CaCl₂ brine with 0.5 g of synthetic K-jarosite. Two volumetric flasks were covered with parafilm and left to react on an oscillating shaker table for 10 days, sampled, and then returned to the shaker table until the experiment reached 22 days. The sampled brine-jarosite slurries were vacuum filtered, then either quenched with isopropyl alcohol or air dried to test the effects of chemical quenching on the mineral reaction products.

Powder X-ray diffraction was employed to identify the mineral phases present in both flow-through and batch reactor experiments. All samples were analyzed on zero-background holders with Bragg-Brentano (BB) geometry using a Rigaku Ultima IV X-Ray diffractometer with a Cu tube operated at 40kV and 44mA and a curved graphite monochromator that passes predominantly Cu K α radiation. Data were collected over 2-70 degrees at 4s/step then analyzed and processed with MDI Jade 10 software with the ICDD (International Centre for Diffraction Data) PDF4+ database.

Results:

Flow-through experiments: Powder X-ray diffraction (XRD) analysis of the flow-through dissolution experiment samples indicates that jarosite was preserved across all three concentrations. Anhydrite, akaganeite, gypsum, and antarcticite were observed in all of the flow-through experiments, regardless of the brine concentration.

Effects of quenching in batch experiments: Batch experiments, reacting synthetic K-jarosite with saturated CaCl₂ brine samples, were also analyzed by the XRD following isopropyl alcohol quenching or air drying. XRD analysis of both quenched and unquenched samples indicated jarosite was preserved in all the batch experiments. Akaganeite, gypsum, and antarcticite were also observed in all of the batch experiments. Bassanite was only definitively observed via XRD in one 10-day quenched sample and is thought to have formed during the quenching process. Bassanite may also be present in the replicate 10-day quenched experiment, but is absent in both 22-day runs, regardless of the drying technique. Anhydrite was not observed as a reaction product in any of the batch experiments (Table 1).

Table 1. Mineral phases observed across all experiments. “?” indicates phase identification was dubious. Ja=jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$); Anh=anhydrite (CaSO_4); Ba=bassanite ($\text{Ca}(\text{SO}_4)(\text{H}_2\text{O})_{0.67}$); Ak=akaganeite ($\text{Fe}_8\text{O}_8(\text{OH})_8\text{Cl}_{1.35}$); Gy=gypsum ($\text{Ca}(\text{SO}_4)(\text{H}_2\text{O})_2$); Ant=antarcticite ($\text{CaCl}_2(\text{H}_2\text{O})_6$).

Experiment	Ja	Anh	Ba	Ak	Gy	Ant
10d 50 wt. % CaCl_2 Batch, dried	YES	NO	NO	YES	YES	YES
10d 50 wt. % CaCl_2 Batch, quench	YES	NO	YES	YES	YES	YES
10d 50 wt. % CaCl_2 Batch dup., dried	YES	NO	NO	YES	YES	YES
10d 50 wt. % CaCl_2 Batch dup., quench	YES	NO	?	YES	YES	YES
22d 50 wt. % CaCl_2 Batch, dried	YES	NO	NO	NO	YES	YES
22d 50 wt. % CaCl_2 Batch, quench	YES	NO	NO	YES	YES	?
22d 50 wt. % CaCl_2 Batch dup., dried	YES	NO	NO	YES	YES	YES
22d 50 wt. % CaCl_2 Batch dup., quench	YES	NO	NO	YES	YES	?
10d 50 wt. % CaCl_2 Flow-through	YES	YES	NO	YES	YES	YES
10d 20 wt. % CaCl_2 Flow-through	YES	YES	NO	YES	YES	YES
10d 5 wt. % CaCl_2 Flow-through	YES	YES	NO	YES	YES	YES

Discussion: Significant differences in reaction products observed in the batch reactor and flow-through experiments can guide our interpretations of semi-open and closed system aqueous alteration on Mars based on the mineral phases present. Both gypsum and jarosite were observed across all flow-through dissolution and batch reactor experiments. However, anhydrite only formed in the semi-open system flow-through experiments, suggesting that, though this mineral phase readily forms at low temperatures in relatively short periods of time in flowing, open systems, it does not readily precipitate in closed systems. Anhydrite was also notably observed in 50%, 20%, and 5% brines, negating the hypothesis that sustained high salinity (low water activity) conditions are necessary to its formation. Instead, the calcium sulfate nucleation mechanism may differ between these open and closed hydrologic systems.

Akaganeite and antarcticite were formed in most experiments. Akaganeite contains iron and chloride and was, thus, not unexpected as a reaction product here. Antarcticite is present as a consequence of using high salinity brines and not thoroughly rinsing the samples. Their presence or absence does not seem to correlate well with experimental condition variations

or sample preparation variations. Bassanite was only observed in quenched samples from one of the 10-day batch runs. The absence of bassanite in both quenched 22-day indicates that further investigation into the mineralogical implications of quenching samples is needed.

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