ANHYDRITE NUCLEATION AND GROWTH AT LOW TEMPERATURES: EFFECTS OF FLOW RATE, ACTIVITY OF WATER, AND MINERAL SUBSTRATES. K. M. Miller¹, C. M. Phillips-Lander¹, J. L. Bishop², A. S. Elwood Madden¹, M. E. Elwood Madden¹, ¹School of Geology and Geophysics, University of Oklahoma, 100 E. Boyd St., Rm 710 Norman, OK, ²SETI Institute, 189 Bernardo Ave, Suite 200 Mountain View, CA 94043  
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Introduction: Calcium sulfate minerals anhydrite and gypsum have been historically used to interpret temperature and salinity conditions experienced during diagenesis, as anhydrite commonly forms at temperatures > 50°C in high salinity waters, while gypsum commonly forms in closed systems at lower temperatures across a wide range of water activities. However, previous experiments comparing jarosite dissolution in semi-open (flow-through) and closed system (batch) experiments with high salinity CaCl₂ brine (activity of water 0.5) observed anhydrite forming at <25°C in semi-open flow-through experiments [1], while gypsum formed in batch reactors with otherwise identical conditions.

Dixon et al. [1] hypothesized that anhydrite may form at low temperatures in flow-through experiments due to the constant source of high salinity, low-water-activity brine, while gypsum initially nucleates in the batch reactors, increasing the activity of water as calcium and sulfate ions are consumed. Other workers have suggested that anhydrite, bassanite, and gypsum form via complex nucleation, aggregation, and growth processes [2] that may also be affected by hydrologic flow rates, as well as different mineral substrates present in the system.

Here, we test Dixon’s hypothesis that sustained low activity of water permits anhydrite nucleation and growth in low temperature flow-through experiments 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 for comparison with flow-through results.

Methods: We conducted flow-through experiments with synthetic K-jarosite + 5 wt % (αw = 0.98), 20 wt % (αw = 0.8), or 50 wt % (αw = 0.5) CaCl₂ brine at room temperature and pressure over 10 and 22 days to test the effects of brine concentration on mineral reaction products. We also conducted closed system batch reactor experiments under otherwise identical conditions to compare mineralogy with flow-through experiments by combining 150 mL of CaCl₂ brine with 0.5 g of synthetic K-jarosite. We used volumetric flasks covered with parafilm and left them to react on an oscillating shaker table for 10 days, sampled them, and then returned the reactors to the shaker table until the experiment reached 22 days. We vacuum filtered the brine + mineral slurry samples prior to analysis.

We employed powder x-ray diffraction (XRD) to identify the mineral phases present in both flow-through and batch reactor experiments. We analyzed all samples on zero-background holders with Bragg-Brentano geometry using a Rigaku Ultima IV X-Ray diffractometer at the University of Oklahoma. Due to the relative insensitivity of XRD to poorly crystalline or nanocrystalline phases within the jarosite matrix, we used Raman spectroscopy as a secondary analytical technique to identify and map mineral phases present in the samples, employing a Renishaw inVia confocal Raman microscope located at the University of Oklahoma. We also conducted visible/near-infrared spectroscopy (VNIR: 0.35-2.5 μm) at the SETI Institute to test the possibility of detecting and resolving Ca-sulfate phases in these samples.

Finally, we examined the textural relationships in the reaction products using transmission electron microscopy (TEM) to evaluate possible nucleation pathways leading to anhydrite precipitation in flowing brines. We ultrasonicated experimental samples with isopropyl alcohol for 10 minutes before pipetting 7 ml of the solution onto lacy carbon formvar TEM grids. We then analyzed the experimental samples using 80kV Zeiss10 and 200kV JEOL 2000FX TEMs.

Results: XRD and Raman: Akaganeite (FeO(OH), Cl) is observed as a reaction product across all experiments. Antarcticite (CaCl₂·6H₂O) is also observed in most experiments, but is considered to be present in reaction product specimens due to precipitation of residual brine in the samples and was likely not present in the dissolution reactors. Gypsum is present across all flow-through and batch experiments. Bassanite may be present in trace amounts (less than 1 weight percent) in two flow-through experiments, but is not observed in any of the batch experiments. We observed anhydrite in flow-through experiments but not in batch experiments.

VNIR: VNIR spectra of the samples are dominated by jarosite bands with some gypsum features. The strongest gypsum signatures are observed for the samples in the longer experiments. Anhydrite does not have features in this spectral region.
TEM: Gypsum is the only Ca-sulfate phase identified in batch reactor experiments, forming as relatively large (>1μm) lath-shaped crystals (Figure 1a). Though gypsum and anhydrite are both present in flow-through experiments, the large lath-shaped particles were not observed in any of the flow-through experiments. Instead, Ca-sulfate phases seem to be associated with akageneite, both of which grow as nanoscale crystals around the edges of microscale jarosite grains (Figure 1b), but more x-ray mapping is needed to confirm this.

Discussion: The presence of anhydrite in flow-through experiments with higher activities of water negates Dixon’s hypothesis that anhydrite nucleates due to sustained low water activity in high salinity, flowing brine. Instead, anhydrite was observed forming in all three brine concentrations after 22 days of reaction, despite significantly higher water activities in the 20 and 5 wt.% brines. Again, no anhydrite was observed in any of the batch reactor experiments, suggesting hydrodynamic effects are key for anhydrite formation and growth at low temperatures in the presence of jarosite. Since jarosite and abundant salts have been extensively documented on the martian surface by both orbiters and rovers [3-12], this is particularly relevant to interpreting anhydrite observed on the surface of Mars.

At Gale Crater, anhydrite had been observed in association with jarosite [9, 10, 13]. While previous studies have interpreted these anhydrite veins as forming at depth indicating significant burial had occurred prior to diagenesis [9, 14], our experimental results demonstrate that anhydrite may also form at lower temperatures if there is significant groundwater flow. Indeed, the co-location of anhydrite and gypsum suggests varying hydrodynamic conditions may have existed within these formations. Linking Ca-sulfate phase nucleation to specific hydrodynamic conditions gives us information about the open or closed nature of the aqueous system in which the observed Ca-sulfate minerals may have formed. Ultimately, our findings can provide much needed data for interpreting the timing and evolution of depositional environments and diagenetic conditions for the sedimentary rocks at Gale Crater and other locations where Ca-sulfate minerals have been observed [15-19]. For example, in the Sheepbed Mudstone, the mineralogical assemblage jarosite, anhydrite, bassanite, and akageneite is observed, which might suggest that this formation experienced flowing chloride brines in a near-surface diagenetic environment [20].

Ongoing and Future Work: We are currently conducting further TEM analyses and X-ray mapping at the edge of jarosite grains in the flow-through dissolution experiments to investigate the hypothesis that Ca-sulfates preferentially nucleate on Fe-sulfate phases in flow-through experiments. If this is the case, we will be one step closer to understanding the mechanisms involved in the nucleation and growth of anhydrite at low temperature, which will aid in interpreting the complex network of Ca-sulfate veins observed at Gale Crater and, more specifically, the diagenetic history of the Sheepbed Mudstone.


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Figure 1. a) Gypsum lathe observed in batch reactor experiment b) Edge of jarosite grain in flow-through dissolution experiment covered with secondary phases – possibly Ca-sulfates and akageneite