Temperature and humidity effects on ferric sulfate stability and phase transformation

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ABSTRACT

Evolution of concentrated Fe₂(SO₄)₃ solution, a process including both evaporation of the solution and post-evaporation aging of the precipitates, was studied at 2 and 50 °C under controlled relative humidity (RH). At 50 °C and 42–47% RH, ferricopiapite [Fe₄(SO₄)₃(OH); 2H₂O] and rhomboclase [(H₂O)₂Fe₂(SO₄); 2H₂O] first crystallized from the starting solution, and then combined to form kornelite [Fe₄(SO₄)₃; 7.5H₂O] at 42% RH or to paracoquimbite [Fe₂(SO₄)₃; 9H₂O] at 46–47% RH. At 2 °C and 34–43% RH, initially crystallized ferricopiapite and rhomboclase appeared to be stable and did not proceed to form a single ferric sulfate hydrate phase over 385 days. At both 2 and 50 °C and RH ≤ 31%, an amorphous ferric sulfate formed. The amorphous ferric sulfate was preserved longer at low RH conditions, e.g., RH ≤ 11%, than higher RH, at which it slowly transformed to crystalline phases of rhomboclase and ferricopiapite, as observed at 31% RH and 50 °C. Combining the results from this study and those from our previous study at 25 °C, the ferric sulfate phase evolution at 2, 25, and 50 °C were mapped and compared. Temperature shows a strong effect on the evolution kinetics; low T may inhibit the evolution from reaching an equilibrium state. Also, an RH and T-controlled in situ X-ray diffraction (RH–T–XRD) method was used to study phase transitions of ferric sulfate hydrates at temperatures from 25 to 80 °C. A dehydration of paracoquimbite to ferric sulfate pentahydrate [Fe₂(SO₄)₃; 5H₂O] was identified at 80 °C. The results are discussed with a previously constructed ferric sulfate RH–T phase diagram by Ackermann et al. (2009).

Keywords: Ferric sulfate, humidity, phase diagram, ferricopiapite, sulfate, paracoquimbite, amorphous sulfate

INTRODUCTION

Ferric sulfate minerals are suspected to occur at several localities on the surface of Mars, including at the Meridiani planum (Farrand et al. 2007; Klingelhoefer et al. 2004; Poulet et al. 2008), Gusev crater (Johnson et al. 2007; Lane et al. 2008; Yen et al. 2008), and Juventae Chasma (Bishop et al. 2009; Milliken et al. 2008), and may be more widely distributed within or near Valles Marineris (Milliken et al. 2008). On Earth, ferric sulfates are mostly found at acid mine drainage (AMD) regions as secondary minerals deposited from acidic sulfate waters formed by the oxidation of sulfide minerals (Hammarstrom et al. 2005; Jambor et al. 2000; Nordstrom and Alpers 1999). Many ferric sulfates are hygroscopic and display complex phase transitions with change of relative humidity (Xu et al. 2009). These minerals exhibit the potential to be used to extract detailed information on depositional and post-depositional environments; this utility requires a comprehensive knowledge of the mineral stability and transitions as a function of environmental variables including temperature (T), relative humidity (RH), redox conditions, etc. To date, most of the relevant phase relations are still to be established. Majzlan and colleagues reported thermodynamic data for a series of ferric sulfate minerals (Ackermann et al. 2009; Majzlan et al. 2006, 2005) and constructed an RH–T phase diagram (Ackermann et al. 2009). Wang and Ling (2011) have been studying phase transitions of various ferric sulfates and their spectroscopic signatures in conjunction with mission data analysis. In a previous study, we reported the ferric sulfate phase transitions at room temperature (22–25 °C) under different RH conditions investigated with both ex situ and in situ X-ray diffraction (XRD) methods (Xu et al. 2009). In this study, we continued to explore precipitation from ferric sulfate solutions and subsequent phase changes at 2 and 50 °C using similar methods, and built phase evolution maps as a function of time and RH at the three temperatures, 2, 25, and 50 °C.

EXPERIMENTAL METHODS

Sample preparation and the ex situ humidity-buffer cell method

Concentrated ferric sulfate solution was prepared by deliquesceing anhydrous ferric sulfate at 84% RH and 25 °C in a potassium chloride humidity buffer cell, a diagram of which could be found in the previous work (Xu et al. 2009). Humidity buffers are saturated solutions of a salt that produces a constant RH in a closed space at equilibrium. The equilibrium RH is specific to the salt, and varies with temperature (Greenspan 1977). The anhydrous ferric sulfate was prepared by heating the ferric sulfate hydrate from J.T. Baker [Baker Analyzed, Assay Fe₂(SO₄); > 73.0%] at 350 °C for 2 h. The purity and the anhydrous state of the prepared samples were further confirmed by XRD and thermogravimetric analysis (TGA). The anhydrous ferric sulfate was hydrated and turned to slurry after a few hours at 84% RH, and finally turned to a clear amber solution after 7 days. The concentration of the solution was calculated to be 40 wt% Fe₂(SO₄)₃ by measuring the weight of the starting sample and the produced solution. The solution was then stored in a series of humidity buffer cells in a laboratory refrigerator and in an oven set to 50 °C. The weight of the starting solution in each humidity buffer cell was 1.5–2.0 g.