

Humidity-induced phase transitions of ferric sulfate minerals studied by in situ and ex situ X-ray diffraction

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ABSTRACT

Phases encountered in the hydration of monoclinic and trigonal anhydrous $\text{Fe}_2(\text{SO}_4)_3$ and evaporation of $\text{Fe}_2(\text{SO}_4)_3$ solutions at room temperature were determined using in situ and ex situ X-ray diffraction (XRD) under dynamic relative humidity (RH) control at room temperature (22–25 °C). Both monoclinic and trigonal forms of $\text{Fe}_2(\text{SO}_4)_3$ remain anhydrous at 11% RH or below, and undergo the following phase evolution sequence: anhydrous $\text{Fe}_2(\text{SO}_4)_3 \rightarrow$ (ferricopiapite, rhomboclase) \rightarrow kornelite \rightarrow paracoquimbite at RH between 33 and 53% as a function of time. Evaporation of aqueous $\text{Fe}_2(\text{SO}_4)_3$ solutions at $40\% < \text{RH} < 60\%$ results in precipitation of ferricopiapite and rhomboclase during evaporation, followed by a transition to kornelite and then paracoquimbite. Evaporation at $\text{RH} < 33\%$ produced an amorphous ferric-sulfate phase. The presence of some iron sulfate hydrates and their stability under varying RH are not only determined by the final humidity level, but also the intermediate stages and hydration history (i.e., either ferricopiapite or paracoquimbite can be a stable phase at 62% RH depending on the hydration history). The sensitivity to humidity change and path-dependent transitions of ferric sulfates make them potentially valuable indicators of paleo-environmental conditions and past water activity on Mars. The phase relationships reported herein can help in understanding the diagenesis of ferric sulfate minerals, and are applicable to geochemical modeling of mineral solubility in multi-component systems, an endeavor hindered by the need for fundamental laboratory studies of iron sulfate hydrates.

Keywords: Ferric sulfate, humidity, ferricopiapite, rhomboclase, kornelite, paracoquimbite