(H₂O)Fe(SO₄)₂ formed by dehydration rhomboclase and its potential existence on Mars

WENQIAN XU,¹,* JOHN B. PARISE,¹,² AND JONATHAN HANSON³

¹Department of Geosciences, Stony Brook University, Stony Brook, New York 11794-2100, U.S.A.
²Department of Chemistry, Stony Brook University, Stony Brook, New York 11794-3400, U.S.A.
³Department of Chemistry, Brookhaven National Laboratory, Upton, New York, 11793-5000, U.S.A.

ABSTRACT

Rhomboclase, (H₂O₂)Fe(SO₄)₂·2H₂O, a common secondary iron sulfate mineral found in acid mine drainage (AMD) regions (Nordstrom and Alpers 1999; Jambor et al. 2000; Keith et al. 2001; Buckby et al. 2003; Hammarstrom et al. 2005), has also been suggested as a potential hydrated iron sulfate in the sulfur-rich soils at Gusev Crater on Mars (Johnson et al. 2007; Lane et al. 2008; Yen et al. 2008). In laboratory studies, rhomboclase was found in evaporites of a brine from chemically weathering synthetic martian basalts (Tosca et al. 2004; Hurowitz et al. 2005; Tosca and McLennan 2009). Iron sulfates are sensitive to environmental changes such as relative humidity (RH) and T and can thus act as mineral indicators of current and past sedimentary environments. Precipitates from aqueous Fe(III)-SO₄-H₂O systems have been previously studied (King and McSween 2005; Jonsson et al. 2006; Tosca et al. 2007; Marion et al. 2008). Rhomboclase precipitates at pH ≤ –1.8 (Marion et al. 2008), lower than the pHeq for ferricopiapite [Fe₄Fe₂(SO₄)₆(OH); 20H₂O] precipitation (–1 < pHeq < 1) and jarosite [(K,Na,H₃O)₃Fe₂(OH)₆(SO₄)]; precipitation (1 < pH < 3) (Jonsson et al. 2006; Tosca et al. 2008). Though primarily precipitating at different pH conditions, the laboratory study has shown rhomboclase and ferricopiapite can co-precipitate by evaporation of a ferric sulfate solution (molar ratio Fe³⁺/SO₄²⁻ = 2/3) (Xu et al. 2009). The mixture of rhomboclase and ferricopiapite may combine to form kornelite [Fe₂(SO₄)₆·7.25H₂O] and paracoquimbite [Fe₄(SO₄)₆·9H₂O] in the diagenesis process (Xu et al. 2009). Conversion of ferricopiapite to rhomboclase was also observed during the dehydration of ferricopiapite, probably due to a subtle change of environmental acidity (Freeman et al. 2009). Thermodynamic data for these iron sulfates are recently reported by J. Majzlan and colleagues (Majzlan et al. 2004, 2005, 2006; Ackermann et al. 2009) and these data help understand the phase stability relations in the Fe(III)-SO₄-H₂O system. Here we evaluate the stability of rhomboclase with changes of RH and T, and find a transition to a dehydrated phase, (H₂O)Fe(SO₄)₂. Powder XRD shows the dehydrated phase has the same structure as that recently reported from a single crystal (H₂O)Fe(SO₄)₂ (Peterson et al. 2009), synthesized hydrothermally at 140 °C. Further experiments under simulated martian conditions suggested the dehydrated phase may exist on the current martian surface.

Keywords: Rhomboclase, sulfate, hydrate, humidity, Mars, ferric sulfate

INTRODUCTION

Rhomboclase, (H₂O₂)Fe(SO₄)₂·2H₂O, a common secondary iron sulfate mineral found in acid mine drainage (AMD) regions (Nordstrom and Alpers 1999; Jambor et al. 2000; Keith et al. 2001; Buckby et al. 2003; Hammarstrom et al. 2005), has also been suggested as a potential hydrated iron sulfate in the sulfur-rich soils at Gusev Crater on Mars (Johnson et al. 2007; Lane et al. 2008; Yen et al. 2008). In laboratory studies, rhomboclase was found in evaporites of a brine from chemically weathering synthetic martian basalts (Tosca et al. 2004; Hurowitz et al. 2005; Tosca and McLennan 2009). Iron sulfates are sensitive to environmental changes such as relative humidity (RH) and T and can thus act as mineral indicators of current and past sedimentary environments. Precipitates from aqueous Fe(III)-SO₄-H₂O systems have been previously studied (King and McSween 2005; Jonsson et al. 2006; Tosca et al. 2007; Marion et al. 2008). Rhomboclase precipitates at pH ≤ –1.8 (Marion et al. 2008), lower than the pHeq for ferricopiapite [Fe₄Fe₂(SO₄)₆(OH); 20H₂O] precipitation (–1 < pHeq < 1) and jarosite [(K,Na,H₃O)₃Fe₂(OH)₆(SO₄)]; precipitation (1 < pH < 3) (Jonsson et al. 2006; Tosca et al. 2008). Though primarily precipitating at different pH conditions, the laboratory study has shown rhomboclase and ferricopiapite can co-precipitate by evaporation of a ferric sulfate solution (molar ratio Fe³⁺/SO₄²⁻ = 2/3) (Xu et al. 2009). The mixture of rhomboclase and ferricopiapite may combine to form kornelite [Fe₂(SO₄)₆·7.25H₂O] and paracoquimbite [Fe₄(SO₄)₆·9H₂O] in the diagenesis process (Xu et al. 2009). Conversion of ferricopiapite to rhomboclase was also observed during the dehydration of ferricopiapite, probably due to a subtle change of environmental acidity (Freeman et al. 2009). Thermodynamic data for these iron sulfates are recently reported by J. Majzlan and colleagues (Majzlan et al. 2004, 2005, 2006; Ackermann et al. 2009) and these data help understand the phase stability relations in the Fe(III)-SO₄-H₂O system. Here we evaluate the stability of rhomboclase with changes of RH and T, and find a transition to a dehydrated phase, (H₂O)Fe(SO₄)₂. Powder XRD shows the dehydrated phase has the same structure as that recently reported from a single crystal (H₂O)Fe(SO₄)₂ (Peterson et al. 2009), synthesized hydrothermally at 140 °C. Further experiments under simulated martian conditions suggested the dehydrated phase may exist on the current martian surface.

EXPERIMENTAL METHODS

Synthesis

Rhomboclase was synthesized according to methods described in the literature (Majzlan et al. 2006): mixing 2 g of anhydrous ferric sulfate, 2.5 g of water, and 2.5 g of sulfuric acid (95.9% H₂SO₄ by mass) to produce a solution. Anhydrous ferric sulfate was made by baking ferric sulfate hydrate [Baker Analyzed, Assay Fe₃(SO₄)₂ > 97.0%] at 300 °C for 2 h to remove all the water content. XRD analysis confirmed the product of this treatment was pure trigonal Fe₃(SO₄)₂. The solution was evaporated at ambient conditions (20 °C, 10–30% RH). A white solid forming after three days was confirmed as rhomboclase by XRD. The product was vacuum-filtered and rinsed with deionized water and ethanol to remove any surface H₂SO₄. The yield was calculated as 68% based on the amount of Fe used in the synthesis.

Thermal analysis

Thermogravimetric and differential scanning calorimetric analysis (TG and DSC) was performed on a Netzsch STA 449C Jupiter. A 7.7 mg powdered sample of freshly prepared rhomboclase was loaded in an alumina crucible with a hole in the cover and heated from room temperature to 300 °C at a rate of 3 °C/min under N₂ flow.