Acid production by FeSO₄·nH₂O dissolution and implications for terrestrial and martian aquatic systems

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ABSTRACT

Combined experimental, modeling, and analytical results indicate that the rapid acidification of dilute waters in contact with nominally Fe²⁺-sulfate minerals (FeSO₄·nH₂O) is caused by Fe³⁺ hydrolysis, which occurs when low levels (<1 mol%) of a contaminant Fe³⁺-sulfate phase are dissolved along with the FeSO₄·nH₂O. This rapid acidification has previously been attributed to hydrolysis by Fe³⁺. However, dissolution experiments performed using ZnSO₄·nH₂O, in which the Zn²⁺ cation has a higher hydrolysis constant (log K = –8.96) than Fe³⁺ (log K = –9.5), failed to produce significant changes in solution pH. We present the results of geochemical modeling simulations confirming that FeSO₄·nH₂O dissolution alone cannot explain the experimentally observed change in pH from 5.65 to 3.50. Nor can the experimental observations be explained by oxidation of Fe²⁺ to Fe³⁺ in solution. Instead, our experimental results can be best explained by modeling the incorporation of <1 mol% Fe³⁺ contamination from any number of Fe³⁺ or mixed valence Fe-sulfate phases, including anhydrous Fe₃⁺(SO₄)₃, coquimbite, kornelite, römerite, bilinite, copiapite, or ferricopiapite, all of which are reasonable candidate phases for oxidative breakdown products of FeSO₄·nH₂O. Laboratory Mössbauer spectra are consistent with up to 0.6 mol% of the total Fe in the sample to be present as Fe³⁺. Although the doublet has parameters that are not diagnostic of any specific Fe³⁺-sulfate, they do help constrain its identification. These results demonstrate that minor contamination of labile Fe²⁺ sulfates by Fe³⁺ can have drastic effects on solution chemistry that should be considered when studying reactions relevant to acid mine drainage waste sites and other localities where Fe-sulfate minerals occur, such as the surface of Mars.

Keywords: Mars, AMD, melanterite, pH, Mössbauer

INTRODUCTION

The formation and paragenesis of Fe-sulfate minerals has proven to be a topic of considerable interest for both the terrestrial and martian surface environments. On Earth, Fe-sulfates are most commonly found as oxidative weathering products of Fe-sulfide minerals associated with acid mine drainage (AMD) sites (e.g., Jambor and Blows 1994). Fe-sulfates may also be found in natural environments such as those associated with magmatic degassing of SO₂/H₂S into near-surface waters (e.g., Dutrizac and Jambor 2000). It is well known that the generally low pH and high toxic metal content of fluids associated with AMD sites can have a deleterious effect on natural surface waters (Frau 2000; Hammarstrom et al. 2005; Jerz and Rimstidt 2003; Nordstrom and Alpers 1999a, 1999b). On Mars, Fe-sulfate minerals are generally thought to originate from weathering of the basaltic martian crust in the presence of sulfuric acid-rich surface waters in a relatively water-limited, oxidizing, and evaporative surface environment (Banin et al. 1997; Burns 1987; Tosca et al. 2004). Recent mineralogical data returned by the ongoing Mars Exploration Rover (MER), Mars Express (MEx), and Mars Reconnaissance Orbiter (MRO) missions have confirmed that the martian surface environment is indeed rich in various sulfate minerals, including Fe-sulfates (Gendrin et al. 2005; Klingelhofer et al. 2004; Milliken et al. 2008; Yen et al. 2008).

In almost every environment where Fe-sulfate minerals are found, one of the first minerals to form will be a hydrated Fe²⁺-sulfate (hereafter referred to as HFS), with a general formula of Fe²⁺SO₄·nH₂O. This hydration series is important because the majority of iron in the protolith phases from which Fe-sulfates are derived is in the ferrous state [e.g., pyrite = FeS₂, pyrrhotite = Fe₇(S,S)₇, fayalite = Fe₅SiO₄, ferrosilite = Fe₃Si₂O₆, etc.]. Subsequent transformations of HFS minerals occur by a combination of dehydration, oxidation, and neutralization reactions, generating a complex suite of mixed-valence sulfate minerals [e.g., copiapite, Fe₅Fe³⁺(SO₄)₃(OH)₂·20H₂O], Fe³⁺-sulfate minerals