Thermodynamics and crystal chemistry of rhomboclase, (H$_2$O)$_2$Fe(SO$_4$)$_2$·2H$_2$O, and the phase (H$_2$O)Fe(SO$_4$)$_2$ and implications for acid mine drainage

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ABSTRACT

The system Fe$_3$O$_4$·SO$_4$·H$_2$O contains the most important minerals of acid mine drainage (AMD), iron oxides, and iron sulfates. For geochemical modeling of the AMD systems, reliable thermodynamic data for these phases are needed. In this work, we have determined thermodynamic data for the most acidic sulfates rhomboclase [(H$_2$O)$_2$Fe(SO$_4$)$_2$·2H$_2$O or (H$_2$O)Fe(SO$_4$)$_2$·3H$_2$O] and the phase (H$_2$O)Fe(SO$_4$)$_2$. The actual compositions of the studied phases are (H$_2$O)$_{1.18}$Fe(SO$_4$)$_{2.17}$ (molecular mass of 344.919 g/mol) and (H$_2$O)$_{1.36}$Fe(SO$_4$)$_{2.17}$ (289.792 g/mol). Structural details for both phases were refined from synchrotron powder X-ray diffraction data. Enthalpies of formation were determined by acid-solution calorimetry. Low-temperature heat capacity was measured for rhomboclase by relaxation calorimetry but a critical analysis of entropies for several oxysalts showed that these data are too high. Entropies for both phases were estimated from a Kopp-rule algorithm. The enthalpies of formation and entropies were combined with previously published temperature-relative humidity brackets to generate an internally consistent thermodynamic data set for rhomboclase: $\Delta H^\circ = -3202.03$ kJ/mol, $S^\circ = 378.7$ J/(mol·K); and for (H$_2$O)$_{1.34}$Fe(SO$_4$)$_{2.17}$: $\Delta H^\circ = -2276.25$ kJ/mol, $S^\circ = 253.2$ J/(mol·K). Solubility experiments at room temperature and at $T = 4^\circ$C agree well with previously reported data in the system Fe$_3$O$_4$·SO$_4$·H$_2$O. An inspection of the extended Pitzer model for Fe$^{3+}$·SO$_4$ solutions shows that this model reproduces the general topology of the phase diagram, but the position of the calculated solubility curves deviates substantially from the experimental data. Solid-state $^3$H MAS NMR spectra on deuterated rhomboclase show two isotropic chemical shifts $\delta_{iso}(^3H) = 8 \pm 1$ and 228 ± 1 ppm, assigned to D$_2$O and Fe-OD$_2$ groups, respectively. Canonical ensemble (NVT) molecular dynamics simulations for (H$_2$O)Fe(SO$_4$)$_2$ at $T = 300$ K showed that the H$_2$O groups maintain their trigonal pyramidal geometry and perform different types of motion.

Keywords: Rhomboclase, acid mine drainage, thermodynamics, hydrogen mobility

INTRODUCTION

The system Fe$_3$O$_4$·SO$_4$·H$_2$O comprises the most common and important minerals of acid-mine drainage (AMD), a global environmental problem related to mining of ores of metals (e.g., Au, Cu), metalloids (e.g., Sb), and coal, polluting thousands of kilometers of rivers worldwide (Blowes et al. 2003). Several remediation options have been proposed for various AMD systems, ranging from large volumes with intermediate pollution to relatively small volumes with extreme water compositions (Nordstrom et al. 2000; Johnson and Hallberg 2005; Sheoran and Sheoran 2006; Byrne et al. 2012; Anawar 2015). Early recognition of the vital role of microorganisms in the sustainable formation of AMD (Lacey and Lawson 1970; Nordstrom 1982; Nordstrom and Southern 1997) led to several studies on the geochemistry of these systems (Hallberg 2010; Klein et al. 2014; Garris et al. 2016). Significant attention is paid to the possibility of predicting the development of AMD (Parbhakar-Fox and Lottermoser 2015) so that measures can be taken before the problem unfolds in a way that is difficult and costly to manage and remediate.

An integral part of the research and remediation of AMD systems is geochemical modeling (Perkins et al. 1995), using the known thermodynamic and kinetic parameters for the phases involved in the AMD systems. Forward simulations can predict the time evolution of an AMD system or the performance of a remediation measure. Inverse simulation can explain the path of the aqueous fluids between uncontaminated surface or underground water or precipitation and acidic, metal-loaded fluids. For such simulations, the information about the solids forming or dissolving is crucial. Mineralogy of the AMD systems is well known from both laboratory (Bigham et al. 1996; Sejkora et al. 2015) and field studies (Nordstrom et al. 2000; Buckby et al.

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