

Acid production by $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$ 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 Fe^{2+} -sulfate minerals ($\text{FeSO}_4 \cdot n\text{H}_2\text{O}$) is caused by Fe^{3+} hydrolysis, which occurs when low levels (<1 mol%) of a contaminant Fe^{3+} -sulfate phase are dissolved along with the $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$. This rapid acidification has previously been attributed to hydrolysis by Fe^{2+} . However, dissolution experiments performed using $\text{ZnSO}_4 \cdot n\text{H}_2\text{O}$, in which the Zn^{2+} cation has a higher hydrolysis constant ($\log K = -8.96$) than Fe^{2+} ($\log K = -9.5$), failed to produce significant changes in solution pH. We present the results of geochemical modeling simulations confirming that $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$ 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 Fe^{2+} to Fe^{3+} in solution. Instead, our experimental results can be best explained by modeling the incorporation of <1 mol% Fe^{3+} contamination from any number of Fe^{3+} or mixed valence Fe-sulfate phases, including anhydrous $\text{Fe}_2^{3+}(\text{SO}_4)_3$, coquimbite, kornelite, römerite, bilinite, copiapite, or ferricopiapite, all of which are reasonable candidate phases for oxidative breakdown products of $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$. Laboratory Mössbauer spectra are consistent with up to 0.6 mol% of the total Fe in the sample to be present as Fe^{3+} . Although the doublet has parameters that are not diagnostic of any specific Fe^{3+} -sulfate, they do help constrain its identification. These results demonstrate that minor contamination of labile Fe^{2+} sulfates by Fe^{3+} can have dramatic 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