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Acid production by $FeSO_4 \cdot nH_2O$ 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 ($FeSO_4 \cdot nH_2O$) 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 $FeSO_4 \cdot nH_2O$. This rapid acidification has previously been attributed to hydrolysis by Fe^{2+}. However, dissolution experiments performed using $ZnSO_4 \cdot nH_2O$, 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 $FeSO_4 \cdot nH_2O$ 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 $Fe_2^{3+}(SO_4)_3$, coquimbite, kornelite, römerite, bilinite, copiapite, or ferricopiapite, all of which are reasonable candidate phases for oxidative breakdown products of $FeSO_4 \cdot nH_2O$. 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