Acid production by FeSO$_4$$\cdot$$n$H$_2$O dissolution: Comment

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ABSTRACT

Dissolution of natural and commercial melanterite generates a significant decrease in pH that is not thermodynamically explained by Fe$^{2+}$ hydrolysis. It has been recently proposed that the production of acidity is actually caused by hydrolysis of Fe$^{3+}$ occurring in trace amounts in melanterite. Following this finding, the experiments of melanterite dissolution previously conducted by the author have been reviewed and modeled with PHREEQC. Without invoking oxidation of Fe$^{2+}$ to Fe$^{3+}$, modeling results indicate that the amount of Fe$^{3+}$ needed to significantly decrease solution pH is low (0.16–0.20 wt%) and already contained in melanterite in the form of contaminant.

Keywords: Melanterite, dissolution, acidity, modeling

INTRODUCTION

Hurowitz et al. (2009) have conducted a combined experimental and modeling study to evaluate the mechanism of rapid production of acidity during dissolution of melanterite FeSO$_4$$\cdot$7H$_2$O by dilute waters, also discussing potential implications for martian aqueous systems. Their study is based on previous results from the literature; in particular, Hurowitz et al. (2009) consider the mechanism suggested by Frau (2000), i.e., Fe$^{2+}$ hydrolysis, successively also indicated by Jerz and Rimstidt (2003). Frau (2000) highlighted the importance of melanterite dissolution in negatively affecting the quality of waters and indirectly providing a supply of Fe$^{3+}$ for intense oxidation of pyrite and consequent generation of hyper-acidic, saline waters (pH = 0.6, total dissolved solids = 300 g/L) in an abandoned mine in Sardinia, Italy. Hurowitz et al. (2009) have proposed that the production of acidity by Fe$^{2+}$-sulfates dissolution is actually caused by Fe$^{3+}$ hydrolysis occurring when trace amounts of a contaminant Fe$^{3+}$-sulfate of some sort are simultaneously dissolved. Following these results, the experiments of melanterite dissolution conducted by Frau (2000) are hereafter reviewed and modeled to verify the findings of Hurowitz et al. (2009).

METHODS

Modeling was carried out using PHREEQC ver. 2.15.0 (Parkhurst and Appelo 1999) with the included “lii.dat” thermodynamic database, which corresponds to the “thermo.com.V8.R6.230” database prepared at the Lawrence Livermore National Laboratory (California, U.S.A.) and contains the “Bi-dot” aqueous model parameters for calculating activity coefficients in solutions with ionic strength up to 1 molal. According to the experimental observations by Frau (2000) and Hurowitz et al. (2009), which rule out significant oxidation of Fe$^{2+}$ to Fe$^{3+}$ during the time span of the dissolution experiments, the kinetic mode was not used and dissolved oxygen was set at zero to prevent any oxidation. Pure water at 20 °C in equilibrium with atmospheric CO$_2$ (log fugacity = −3.5) was considered as initial batch solution, resulting in an initial pH of 5.64 for all simulations. The following equilibrium reaction for schwertmannite precipitation from Majzlan et al. (2004) was included in the database:

FeO(OH)$_{0.5}$(SO$_4$)$_{1.25}$ + 2.75H$^+$ = Fe$^{3+}$ + 0.125SO$_4^{2-}$ + 1.75H$_2$O log K = 1.2.

The catalog of the manufacturer (Carlo Erba) of the commercial melanterite used in the experiments (RPH Code n. 344957, CAS n. 7782-63-0) indicates that synthetic melanterite may contain up to 0.5 wt% of Fe$^{3+}$. Since melanterite tends to oxidize when exposed to air, the amount of Fe$^{3+}$ could increase with time. However, melanterite oxidation is not so fast, often prevailing dehydration to rozenite FeSO$_4$·H$_2$O and szomolnokite FeSO$_4$·H$_2$O (Frau 2000). Moreover, the bottle of commercial melanterite was opened just in the time sufficient to pick up the amount of salt needed for the experiments, the melanterite was visually inspected for possible color changes attributable to oxidation, and experiments were immediately conducted without leaving melanterite exposed to air.

Another piece of information reported by the manufacturer is that the pH of a 5% melanterite solution (50 g/L melanterite) ranges from 3.0 to 4.0. More details on experimental conditions are reported in Frau (2000).

RESULTS

The plots “pH vs. elapsed time” of Figure 1 show the results of PHREEQC simulations for different amounts of dissolved melanterite (0.4, 2, 10, 25, and 50 g/L). Each plot reports: (1) the experimental observation; (2) the simulation with pure melanterite; (3) the simulation with melanterite containing 0.5 wt% Fe$^{3+}$; (4) the simulation with melanterite containing the amount of Fe$^{3+}$ needed to reach the observed pH; and (5) the latter simulation with schwertmannite precipitation allowed. The phase Fe$_2$(SO$_4$)$_3$ was chosen as the Fe$^{3+}$-bearing contaminant of melanterite. The elapsing time is different in each plot and corresponds to the time for complete melanterite dissolution.

According with Hurowitz et al. (2009), dissolution of pure melanterite results in an insignificant decrease in pH. On the other hand, dissolution of melanterite containing 0.5 wt% Fe$^{3+}$ always generates a decrease in pH greater than that experimentally observed. The amount of Fe$^{3+}$ needed to reach the observed pHs varies between 0.16 and 0.20 wt%. Except for simulations with pure melanterite, batch solutions result to be oversaturated with respect to schwertmannite (saturation index from 2.6 to 2.9) and, thus, when precipitation of schwertmannite is allowed, a further decrease in pH is obtained (2.75 moles H$^+$ generated for 1 mole schwertmannite precipitated). However, batch solutions remained clear during the time span for complete melanterite dissolution so that precipitation of schwertmannite or other Fe$^{3+}$-bearing phases can be discounted.

Summarizing, modeling results indicate that hydrolysis of Fe$^{3+}$, instead of Fe$^{2+}$, is the mechanism for acidification of dilute aqueous solutions, such as rain water, when rapidly dissolving...