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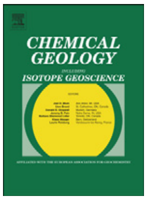

Oxygen and sulfur isotope investigations of the oxidation of sulfide mixtures containing pyrite, galena, and sphalerite

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ABSTRACT

Laboratory investigations of sulfide oxidation may help to understand data from Acid Mine Drainage (AMD) field sites. Although numerous oxygen and sulfur isotope studies of sulfide oxidation have been performed with single sulfides, isotopic data from oxidation experiments with sulfide mixtures are lacking. Due to the common occurrence of sulfide parageneses in nature, aerobic abiotic experiments were performed with mixtures of pyrite, galena, and sphalerite at initial pH 2 and 6 for different lengths of time (5 to 100 days). The oxygen and sulfur isotopes as well as surface and geochemical features were studied in order to obtain similarities and/or differences compared to data from single sulfide experiments.

The oxidation of sulfide mixtures cannot be simply derived from previously performed single sulfide oxidation experiments. The experiments showed that pyrite was galvanically protected whereas galena and sphalerite were preferentially dissolved during the whole time period of 100 days. Geochemical and isotopic data indicated that the dissolution mechanisms of the acid-soluble sulfides galena and sphalerite are controlled by the concurrent attack of protons and molecular oxygen (or ferric iron, if available) on sulfide surfaces. The non-oxidative dissolution of galena and sphalerite followed by hydrogen sulfide oxidation dominated under acid pH conditions. When the concentration of DO or ferric iron exceeded the proton concentration, galena and sphalerite were dissolved oxidatively by molecular oxygen or ferric iron. The relatively large $\Delta^{34}S_{SO4-sulfide}$ values gave evidence that pyrite was not measurably oxidized during sulfide mixture experiments. Sulfide mixture experiments indicated that oxidation rates of waste rock of polymetallic sulfide ore deposits depend on pH conditions, the minerals present and their iron content, the abundance of the minerals, and their grain size (i.e., specific surface area). The $\delta^{18}O_{SO4}$ values indicated that an oxygen isotope exchange between dissolved intermediate sulfur species (e.g., sulfite, thiosulfate) can occur during the oxidation of galena and sphalerite. The observed $\varepsilon^{18}O_{SO4-H2O}$ value was 16.1–18.9‰ at a pH of about 5. The results from these experiments indicate that pyrite oxidation may be substantially reduced under AMD conditions as long as galena and/or sphalerite are not completely decomposed. Large $\delta^{18}O_{SO4}$ and $\Delta^{34}S_{SO4-sulfide}$ values in combination with only slightly acid pH conditions are indicators of the preferential oxidation of galena and/or sphalerite.

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1. Introduction

Dissolution mechanisms of single sulfides (especially pyrite) have been extensively studied by means of oxygen and sulfur isotopes and, thus, are well understood. However, reaction rates and dissolution mechanisms of sulfide mixtures are expected to differ from those of single sulfides due to galvanic interactions.

Sulfide minerals can be oxidized if oxidizing agents (e.g., molecular oxygen, ferric iron) are present. The aerobic oxidation of the sulfide minerals pyrite (FeS_2), galena (PbS), and sphalerite (ZnS) can be described by the following simplified reaction equations (e.g., Singer and Stumm, 1970; Seal and Hammarstrom, 2003):

$$FeS_2 + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{1}$$

$$PbS + 2\ O_2 \rightarrow Pb^{2+} + SO_4^{2-} \tag{2}$$

$$ZnS + 2\ O_2 \rightarrow Zn^{2+} + SO_4^{2-}. \tag{3}$$

The ferric oxidation of sulfide occurs especially in the presence of iron-oxidizing microorganisms and can be described as follows (e.g., Singer and Stumm, 1970; Seal and Hammarstrom, 2003):

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{4}$$

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$$PbS + 8\ Fe^{3+} + 4\ H_2O \rightarrow Pb^{2+} + SO_4^{\ 2-} + 8\ Fe^{2+} + 8H^+ \tag{5}$$

$$ZnS + 8\ Fe^{3+} + 4\ H_2O \rightarrow Zn^{2+} + SO_4^{\ 2-} + 8\ Fe^{2+} + 8H^+. \tag{6}$$

The oxidation of monosulfides (S^{-2}) and disulfides ($S_2^{\ 2-}$) to sulfate ($SO_4^{\ 2-}$) requires the transfer of eight and seven electrons per mole of sulfur, respectively. Because only one or two electrons can be transferred in one step (Basolo and Pearson, 1967), multiple intermediate sulfur species, which are not represented in Reactions (1)–(6), should be formed. Furthermore, the catalytic effect of sulfur-oxidizing microorganisms cannot be displayed in these overall reaction equations. In the absence of sulfur-oxidizing bacteria, both galena and sphalerite tend to generate primarily elemental sulfur (S^0) rather than sulfate (e.g., Schippers and Sand, 1999).

Under acid pH conditions, acid-soluble sulfides such as galena and sphalerite are dissolved non-oxidatively generating dissolved hydrogen sulfide which can be oxidized to sulfate or may escape as gaseous hydrogen sulfide (Seal and Hammarstrom, 2003; Cama and Acero, 2005). Therefore, dissolution pathways differ for acid-insoluble (e.g., pyrite) and acid-soluble (e.g., galena, sphalerite) sulfides (e.g., Schippers and Sand, 1999). However, Thurston et al. (2010) observed that oxidation mechanisms of the acid-soluble sulfide chalcopyrite ($CuFeS_2$) proceed more like those of the acid-insoluble pyrite than those of the acid-soluble sphalerite. These findings indicate that there might be no general dissolution mechanism for all acid-soluble sulfides.

In sulfide mixtures, the sulfide with the higher rest potential is galvanically protected by acting as the cathode on which the reduction of the oxidant (molecular oxygen or ferric iron) takes place; while the sulfide with the lower rest potential dissolves rapidly by acting as the anode (e.g., Mehta and Murr, 1982). Pyrite should be galvanically protected in the presence of other sulfides due to its high rest potential ($E = 0.55$–0.65 V *vs.* Standard Hydrogen Electrode (SHE), Biegler and Swift, 1979). Chizhikov and Kovylina (1956) observed a higher rest potential for galena ($E = 0.28$ V *vs.* SHE) compared with sphalerite ($E = -0.24$ V *vs.* SHE). In contrast, Majima (1969) and da Silva et al. (2003) obtained a slightly lower rest potential for galena ($E = 0.33$–0.40 V *vs.* SHE) compared with sphalerite ($E = 0.37$–0.46 V *vs.* SHE).

Oxygen and sulfur isotopes of dissolved sulfate are useful tools to investigate the oxidation of sulfide minerals (e.g., Taylor et al., 1984; Van Stempvoort and Krouse, 1994; Seal, 2003; Nordstrom et al., 2007). The oxygen isotope signature of the sulfate may reflect the relative contribution of molecular oxygen and water (according to Reactions (1)–(6)) and may indicate oxygen isotope enrichment processes which occur during the incorporation of molecular oxygen or water-derived oxygen into sulfate (Lloyd, 1967):

$$\delta^{18}O_{SO4} = X\left(\delta^{18}O_{H2O} + \varepsilon^{18}O_{SO4-H2O}\right) + (1\text{–}X)\left(\delta^{18}O_{O2} + \varepsilon^{18}O_{SO4-O2}\right). \tag{7}$$

$\delta^{18}O_{SO4}$, $\delta^{18}O_{H2O}$, and $\delta^{18}O_{O2}$ are the oxygen isotope compositions of sulfate, water ($\delta^{18}O_{H2O} < 0$‰ for meteoric waters), and molecular oxygen ($\delta^{18}O_{O2} = 23.5$‰, Kroopnick and Craig, 1972), respectively. X and $(1 - X)$ are the relative proportions of water-derived and molecular oxygen in sulfate, respectively. The $\varepsilon^{18}O_{SO4\text{–}H2O}$ and $\varepsilon^{18}O_{SO4\text{–}O2}$ values are the oxygen isotope enrichment factors for the incorporation of oxygen from water and molecular oxygen, respectively, into sulfate. Likewise, sulfur isotopes of sulfate may reflect the sulfur source (sulfide) and sulfur isotope enrichment effects between sulfate and the sulfide. Therefore, the isotopic composition of sulfate may allow conclusions concerning possible oxidation reactions and the formation of intermediate sulfur species (e.g., Van Stempvoort and Krouse, 1994; Seal, 2003; Böttcher et al., 2005; Nordstrom et al., 2007).

Numerous oxygen and sulfur isotope studies on the oxidation of single sulfides have been published (pyrite: e.g., Taylor et al., 1984; Balci et al., 2007; Heidel et al., 2009; Tichomirowa and Junghans, 2009; Heidel and Tichomirowa, 2010, 2011b; galena: e.g., Toran, 1986; Heidel and Tichomirowa, 2011a; sphalerite: e.g., Heidel et al., 2011; Balci et al., 2012; chalcopyrite: Thurston et al., 2010). However, only two isotope studies deal with the oxidation of mixtures containing different sulfides. Toran (1986) carried out abiotic experiments with a mixture of pyrite, sphalerite, and minor galena. The oxygen isotope composition of sulfate in experiments like these has not been determined presumably due to low sulfate amounts. Because of the similar sulfur isotope composition of pyrite and sphalerite, sulfur isotopes of the produced sulfate could not indicate which sulfide was oxidized preferentially. Gould et al. (1989) performed biotic experiments with a mixture of pentlandite ($(Fe,Ni)_9S_8$) and chalcopyrite ($CuFeS_2$). They observed that oxygen in the produced sulfate originated from both water (ca. 71%) and molecular oxygen (ca. 29%). The dominant sulfur source could not be identified due to the lack of sulfur isotope measurements. Thus, combined oxygen and sulfur isotopic data from oxidation experiments with sulfide mixtures are needed to better understand oxidation mechanisms of sulfide mixtures.

2. Approach

Aerobic abiotic experiments were performed under varying conditions. Experiments were started at two different pH (initial pH 2 and initial pH 6) and performed for different lengths of time (5 to 100 days) to investigate the pH and time dependence of geochemical and isotopic parameters and, thus, dissolution mechanisms.

The minerals originated from the same specimens used for oxidation experiments with single sulfides (Heidel and Tichomirowa, 2011a,b; Heidel et al., 2011). Sulfide mixtures with two different weight-based ratios were prepared. The same pyrite mass was used for both sulfide mixtures because pyrite was expected to be galvanically protected. In contrast, galena and sphalerite masses were varied in order to investigate their reactivity. Sulfur isotopes were used as an additional parameter for the sulfide reactivity. Therefore, sulfides with significantly different $\delta^{34}S$ values ($\delta^{34}S_{FeS2} = 2.6$‰, Heidel and Tichomirowa, 2011b; $\delta^{34}S_{PbS} = 9.9$‰, Heidel and Tichomirowa, 2011a; $\delta^{34}S_{ZnS} = 0.4$‰, Heidel et al., 2011) were oxidized.

Corrosion pits and secondary phases were checked by surface investigations (SEM, EDX, XRD) to assess the weathering degree and the reactivity of the sulfides. Geochemical measurements were performed in order to control the experimental conditions (pH, DO) and to determine dissolved oxidation products (sulfur species, metals).

Experiments were performed with two isotopically different waters in order to calculate oxygen source ratios in final sulfate from rearrangement of Eq. (7):

$$\delta^{18}O_{SO4} = X\left(\delta^{18}O_{H2O}\right) + \left[(1\text{–}X)\left(\delta^{18}O_{O2} + \varepsilon^{18}O_{SO4-O2}\right) + X\left(\varepsilon^{18}O_{SO4-H2O}\right)\right]. \tag{8}$$

Accordingly, the slope (multiplied by 100) in a plot of $\delta^{18}O_{SO4}$ *vs.* $\delta^{18}O_{H2O}$ values equals the water-derived proportion of oxygen in sulfate (X) (e.g., Gould et al., 1989; Balci et al., 2007; Nordstrom et al., 2007), i.e., X can be determined without knowledge of $\varepsilon^{18}O_{SO4\text{–}O2}$ and $\varepsilon^{18}O_{SO4\text{–}H2O}$. The isotope composition of molecular oxygen in the headspace can give information on oxygen-consuming processes. The oxygen isotope enrichment factor associated with the reduction of molecular oxygen can be determined because $\delta^{18}O_{O2}$ values and DO concentrations are expected to follow a Rayleigh fractionation trend (Oba and Poulson, 2009a,b):

$$\ln\left(\frac{\delta^{18}O_{O2} + 1000}{\delta^{18}O_{initialO2} + 1000}\right) = (\alpha\text{–}1)\ln\ F, \tag{9}$$

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