

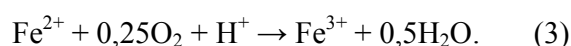
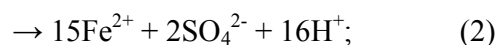
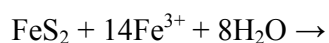
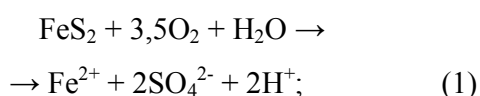
THE ISOTOPIC COMPOSITION OF SULPHATE FORMED BY PYRITE OXIDATION EXPERIMENTS – THE INFLUENCE OF PYRITE GRAIN SIZE

Oxygen and sulphur isotopes of sulphate formed by oxidation of different pyrite grain size fractions were investigated to understand oxidation mechanisms and their dependency on grain size. Both oxygen and sulphur isotope compositions indicate different oxidation mechanisms for fine and coarser pyrite grain sizes. Oxidation mechanisms with atmospheric oxygen as the oxidant seem to be more important for the finest grain size fraction < 63 µm compared to coarser grain sizes. The isotopic composition of sulphate formed by experiments with the coarser grain size fractions 63-100 µm, 100-140 µm, and 140-180 µm do not differ among each other in spite of varying surface areas. Presumably, the lack of highly reactive fine material results in similar oxidation mechanisms.

Для понимания механизмов окисления и их зависимости от гранулометрического состава были проведены исследования кислородных и серных изотопов сульфатов, образовавшихся в результате окисления пирита различного гранулометрического состава. Изотопы как кислорода, так и серы демонстрируют различные механизмы окисления в зависимости от размеров зерен пирита. Представляется, что окислительные механизмы в присутствии атмосферного кислорода в качестве оксиданта играют более важную роль для тонкодисперсных материалов (< 63 мкм), чем для зерен более крупных размеров. По изотопному составу сульфаты, полученные в результате экспериментов с материалом более крупного гранулометрического состава (63-100, 100-140 и 140-180 мкм), не отличаются друг от друга, несмотря на различную площадь поверхности. Вероятно, отсутствие химически высокоактивных тонкодисперсных элементов приводит к возникновению аналогичных окислительных механизмов.

Introduction

Pyrite is one of the most common sulphide minerals in mine wastes. Water and air supply results in aerobic oxidation of pyrite which is a complex reaction with several intermediate sulphur species. It can be described by the simplified chemical equations (1)-(3). Pyrite oxidation results in acid mine drainage with release of protons, iron and sulphate into waters and soils.



Investigations of the oxygen and sulphur isotope composition of the produced sulphate can help to understand oxidation mechanisms. The oxygen isotope composition of sulphate reflects the contribution of the two oxygen sources (water and dissolved atmospheric oxygen) which vary in their oxygen isotope signatures. Furthermore, kinetic isotope fractionation effects occur during the incorporation of oxygen from water or atmospheric oxygen into sulphate. In contrast, sulphur in sulphate origi-

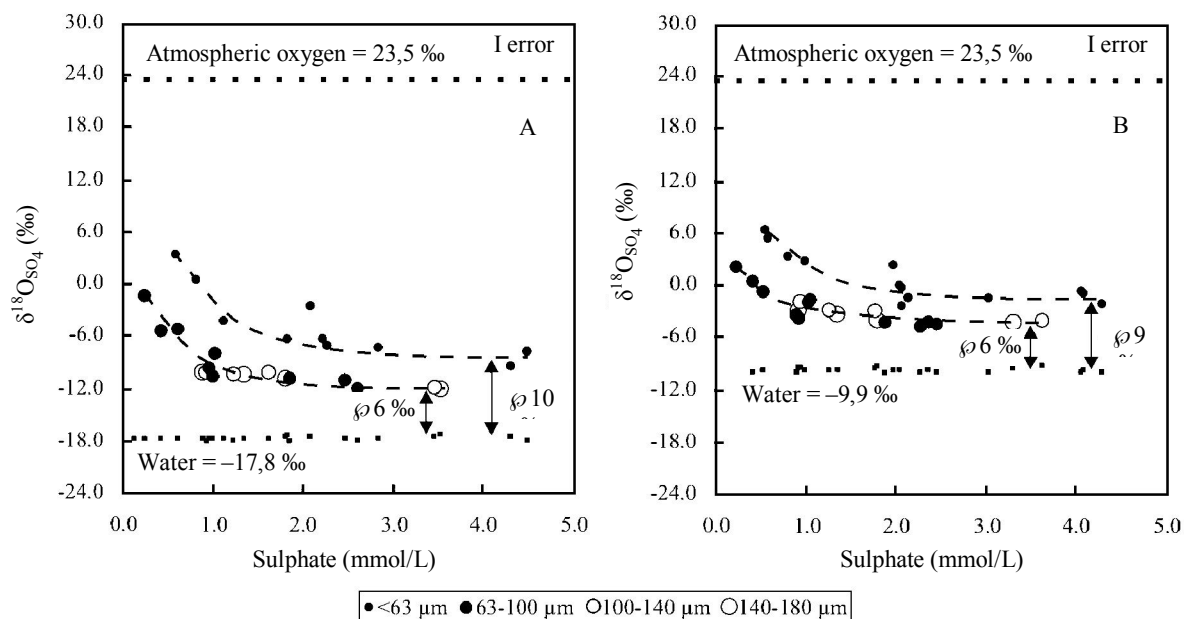


Fig. 1. Plot of $\delta^{18}\text{O}_{\text{SO}_4}$ vs. sulphate concentration for experiments with different grain size fractions and water with $\delta^{18}\text{O}_{\text{H}_2\text{O}} = -17,8\text{‰}$ (A) and $\delta^{18}\text{O}_{\text{H}_2\text{O}} = -9,9\text{‰}$ (B)

nates from only one source (pyrite). Hence, sulphur isotopes of sulphate and pyrite should agree under aerobic acidic conditions.

Several factors that may influence the isotopic composition of sulphate have been already studied, e.g., the influence of oxidant, microorganisms, pH value, temperature. We investigated the relationship between the grain size (i.e., specific surface area) and the isotopic composition of sulphate because to date there is only little literature data about this topic.

Material and methods

Four different pyrite grain size fractions were used: $< 63 \mu\text{m}$, $63\text{-}100 \mu\text{m}$, $100\text{-}140 \mu\text{m}$, and $140\text{-}180 \mu\text{m}$. As expected, the largest specific surface area results from the smallest grain size fraction. All experiments were carried out in duplicate with waters with different oxygen isotope composition at pH 2 for different lengths of time. After finishing the experiments, pH value and concentrations of dissolved oxygen, ferrous iron, total iron, sulphate, sulphite, and thiosulphate were measured.

Oxygen isotopes of water and sulphate and sulphur isotopes of sulphate were measured by gas mass spectrometry. The δ -notation is used for the isotopes, this means that the isotope ratios are normalised to standards. Errors were

better than 0,2 ‰ for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, 0,5 ‰ for $\delta^{18}\text{O}_{\text{SO}_4}$, and 0,3 ‰ for $\delta^{34}\text{S}_{\text{SO}_4}$.

Results and discussion

Hydrochemical measurements. Observed pH values slightly decreased from about 2 to about 1,9 in the course of time because of the release of protons. Despite oxygen-limited conditions, the DO concentrations remained constant until the end of the experiments.

Iron concentrations increased over time in all experiments. However, iron concentrations of experiments with grain size fractions $< 63 \mu\text{m}$ and $63\text{-}100 \mu\text{m}$ did not differ despite large differences in their specific surface areas.

Sulphate concentrations also increased over time in all experiments. But in contrast to iron concentrations, sulphate concentrations of experiments with grain size fraction $< 63 \mu\text{m}$ were distinctly higher than those of grain size fraction $63\text{-}100 \mu\text{m}$. However, the differences in sulphate concentrations between both grain size fractions were not as high as expected from the different surface areas. Sulphate concentrations of both coarser grain size fractions did not differ among each other although their surface areas differed by about 20 %. Maybe the lack of highly reactive fine material caused similar oxidation properties.

By the way, the sulphur intermediate species sulphite and thiosulphate could not be detected in any experiment.

Oxygen isotope composition of sulphate. $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values remained constant in the course of time. Hence, no isotope fractionation effects due to evaporation or oxygen consumption occurred.

Experiments with grain size fractions $< 63 \mu\text{m}$ and $63\text{-}100 \mu\text{m}$ showed a decrease of $\delta^{18}\text{O}_{\text{SO}_4}$ values with increasing sulphate concentrations during the first days (figure 1). This means that oxygen isotopes of sulphate became more similar to those of the used waters. Experiments with the coarser grain size fractions $100\text{-}140 \mu\text{m}$ and $140\text{-}180 \mu\text{m}$ were first sampled after 50 days, where a considerable decrease of $\delta^{18}\text{O}_{\text{SO}_4}$ values during the first days of the experiments was probably already finished. In the course of the experiments $\delta^{18}\text{O}_{\text{SO}_4}$ values decreased only slightly with increasing sulphate concentrations for all grain size fractions. This means that the contribution of oxygen from both sources (dissolved atmospheric oxygen and water) became more or less constant and sulphate was predominantly composed of water-derived oxygen as shown by $\delta^{18}\text{O}_{\text{SO}_4}$ values more similar to those of water.

At the end of the experiments $\Delta^{18}\text{O}_{\text{SO}_4-\text{H}_2\text{O}}$ ($= \delta^{18}\text{O}_{\text{SO}_4} - \delta^{18}\text{O}_{\text{H}_2\text{O}}$) of grain size fraction $< 63 \mu\text{m}$ accounted for about 9-10 ‰ and were

about 3-4 ‰ higher than those of the other three grain size fractions which agreed within errors. One reason for higher $\delta^{18}\text{O}_{\text{SO}_4}$ values of grain size fraction $< 63 \mu\text{m}$ is a higher proportion of atmospheric-derived oxygen in sulphate because more dissolved atmospheric oxygen can be adsorbed on the larger surface area. Another reason may be a dependency between the kinetic isotope fractionation effects and the grain size fraction leading to larger fractionation effects for finer grain size fractions.

Sulphur isotope composition of sulphate. $\Delta^{34}\text{S}_{\text{SO}_4-\text{FeS}_2}$ ($= \delta^{34}\text{S}_{\text{SO}_4} - \delta^{34}\text{S}_{\text{FeS}_2}$) remained more or less constant for experiments with grain size fractions $63\text{-}100 \mu\text{m}$, $100\text{-}140 \mu\text{m}$, and $140\text{-}180 \mu\text{m}$. Furthermore, $\delta^{34}\text{S}_{\text{SO}_4}$ values agreed within errors with the $\delta^{34}\text{S}_{\text{FeS}_2}$ value of the oxidized pyrite because fractionation effects should be negligible under aerobic acidic conditions (figure 2).

Unexpectedly, during the first days $\delta^{34}\text{S}_{\text{SO}_4}$ values of sulphate formed by oxidation of grain size fraction $< 63 \mu\text{m}$ showed negative isotope fractionation effects compared to the $\delta^{34}\text{S}_{\text{FeS}_2}$ value of the pyrite. It is known that fractionation effects result from reactions between pyrite and the sulphur intermediate species sulphite. But sulphite could not be detected in any experiment. In addition, the existence of sulphite should also cause oxygen isotope fractionation

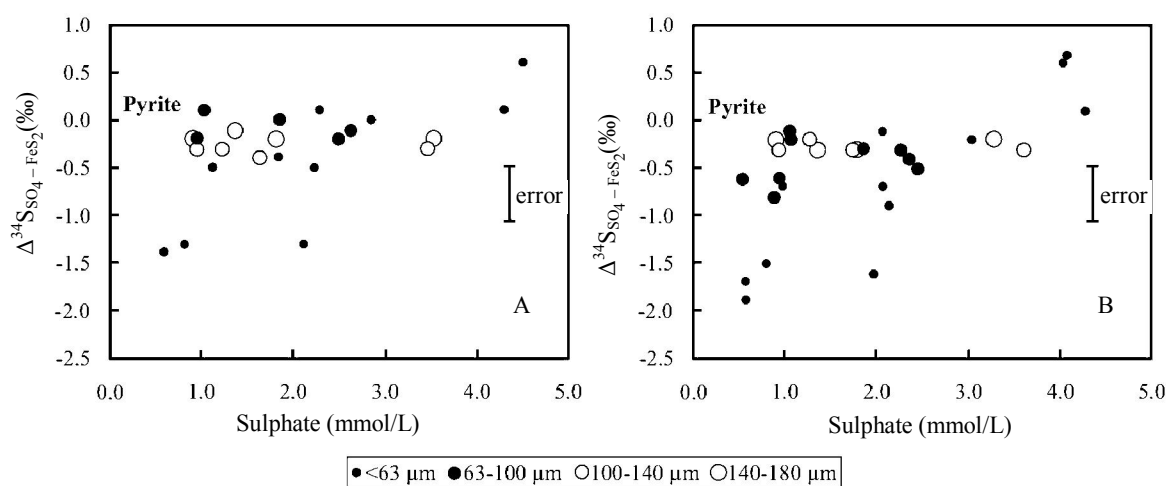


Fig.2. Plot of $\Delta^{34}\text{S}_{\text{SO}_4-\text{FeS}_2}$ vs. sulphate concentration for experiments with different grain size fractions and water with $\delta^{18}\text{O}_{\text{H}_2\text{O}} = -17,8\text{‰}$ (A) and $\delta^{18}\text{O}_{\text{H}_2\text{O}} = -9,9\text{‰}$ (B)

effects that were not observed. Furthermore, literature data show that the oxidation of dissolved sulphide results in greater sulphur isotope fractionation effects than the oxidation of solid sulphide. Hence, it is possible that the isotope fractionation effects are caused by oxidation of very fine dissolved material.

Conclusion

The pyrite oxidation experiments with different grain size fractions indicate different reaction mechanisms for fine and coarser grain size fractions. Oxygen isotopes of sulphate show that more dissolved atmospheric oxygen can be adsorbed on the larger surface area of grain size fraction $< 63 \mu\text{m}$. Furthermore,

oxygen isotope fractionation effects may be different for different grain size fractions. Despite differences in their specific surface areas, the three coarser grain size fractions show similar oxygen isotope compositions of sulphate. Maybe the lack of very fine material results in similar reaction mechanisms.

Furthermore, a time-dependent decrease of oxygen isotopes indicates changing reaction mechanisms when the oxidation progresses.

The fractionation effects of sulphur isotopes of sulphate that is formed by oxidation of grain size fraction $< 63 \mu\text{m}$ also indicate different oxidation mechanisms for fine and coarser pyrite grain sizes.