Sulfide oxidation experiments on pyrite, galena, and sphalerite combined with isotope measurements
Motivation

Sulfide oxidation: release of dissolved ions/elements: sulfate, Fe, Zn, Pb, As, Cd...

How and where occurs sulfide oxidation (rates)?

Rate limiting steps?
Himmelfahrt mine:
Solution (oxidation of sulfides) and precipitation (illite, jarosite, anglesite, iron-(oxy)hydrides) – What ions/elements remain in the mine and how?
Oxidation of pyrite:

**by O₂:** \( \text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + \text{Fe}^{2+} + 2\text{H}^+ \)

**by Fe³⁺:** \( \text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 15\text{Fe}^{2+} + 16\text{H}^+ \)

\( \text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + \text{H}^+ \rightarrow \frac{1}{2}\text{H}_2\text{O} + \text{Fe}^{3+} \)

Why isotopes? = fingerprint
Best understood: **Pyrite (FeS$_2$) oxidation**

If no Fe$^{3+}$: oxidation starts only if O$_2$ is available;

O$_2$ adsorbs on pyrite grains – grain size of pyrite is very important (Tichomirowa & Junghans, 2009)

After 100 days oxidation 80-90% oxygen in sulfate stems from the water molecule (Heidel et al., 2009)
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But: even after 150 days some O$_2$ (9%) is permanently incorporated into SO$_4^{2-}$
“anaerobic“: DO (dissolved oxygen) < 0.0005 mmol/L; „low oxygen“: DO = 0.011 mmol/L

Increase of oxidation rate (max = 5 x 10^-9 mmol m^-2 s^-1) with increasing ratio Fe^{3+}/pyrite surface

Fe^{3+}/surface > 3.8 mmol/m^2: 100% oxygen in sulphate from water (anaerobic experiments)
Fe^{3+}/surface < 3.8 mmol/m^2: >0 – 70% oxygen in sulphate from molecular oxygen (anaerobic)
Fe^{3+}/surface 0.001-0.86 mmol/m^2: 20 – 70% oxygen in sulphate from molecular oxygen (low oxygen)

Role of molecular oxygen!

Heidel & Tichomirowa (2011): The isotopic composition of sulphate from anaerobic and low oxygen pyrite oxidation experiments with ferric iron – New insights into oxidation mechanisms. *Chemical Geology* 281, 305-316
Oxidation by Fe$^{3+}$: fractionation of $\delta^{34}$S (ca. -1‰); formation of elemental S
Oxidation by O$_2$: no fractionation of $\delta^{34}$S

Pyrite oxidation

Role of dissolved oxygen (DO):
• Initial adsorption on pyrite surface to start oxidation: pyrite grain size!
• At low Fe$^{3+}$/pyrite surface (natural conditions): 20-70% DO in final sulphate
• Some DO incorporated into water: $0.5 \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O}$

Role of water:
• Without Fe$^{3+}$ oxidation (by DO): after 100 days ca. 90% oxygen of sulphate derived from water
• Anaerobic conditions: only at high Fe$^{3+}$ (Fe$^{3+}$/surface $>3.8 \text{ mmol/m}^2$) all oxygen in sulphate derived from water

Sulphur isotopes;
fractionation (-1‰) only if oxidation by Fe$^{3+}$ (due to formation of elemental S)

Absence/minor amounts of intermediate S-species (elemental S?)
Galena (PbS) oxidation

much slower than pyrite oxidation;
Pyrite (DO+H₂O): $6 \times 10^{-11}$ to $2 \times 10^{-10}$ mmol m⁻² s⁻¹
Pyrite (Fe³⁺): $10^{-9}$ to $10^{-7}$ mmol m⁻² s⁻¹
Galena (DO+H₂O): $10^{-10}$ – $10^{-12}$ mmol m⁻² s⁻¹, fastest during first 10 days.
pH evolves towards 4 – 5
No faster dissolution with lower grain sizes

Different dissolution mechanisms:
• pH =2: „non-oxidative dissolution“
  very low sulphate production but release of Pb (and Fe) into solutions
  after 10 days no increase of concentrations
  no isotope measurements because of low sulphate
• pH = 6, 8: „oxidative dissolution“
  higher sulphate concentrations (but lower Pb, no Fe) in solution;
  thiosulfate ($S₂O₃^{2-}$) < $SO₄^{2-}$ concentrations
  traces of sulphite
  ca. 75% oxygen in sulphate from water fractionation of S isotopes (anglesite formation)

Isotopes in Environmental and Health Studies; Vol. 47, No. 2, 169–188
Galena Oxidation:

- much slower
- many intermediate sulfur species
- passivation products like angesite (PbSO₄)
- Oxidation not faster with Fe³⁺

Sphalerite (ZnS) oxidation

\[
\begin{align*}
\text{ZnS} + 2 \text{O}_2 & \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-} \\
\text{ZnS} + 8 \text{Fe}^{3+} + 4 \text{H}_2\text{O} & \rightarrow \text{Zn}^{2+} + 8 \text{Fe}^{2+} + \text{SO}_4^{2-} + 8 \text{H}^+
\end{align*}
\]

much slower than pyrite oxidation;
Pyrite (DO+H₂O): 6 x 10⁻¹¹ to 2 x 10⁻¹⁰ mmol m⁻² s⁻¹
Pyrite (Fe³⁺): 10⁻⁹ to 10⁻⁷ mmol m⁻² s⁻¹
sphalerite (DO+H₂O): 10⁻¹⁰ – 10⁻¹² mmol m⁻² s⁻¹, fastest during first 2-5 days.

pH evolves towards 7 (= proton consumption!)

Different dissolution mechanisms:
- pH = 2: „non-oxidative dissolution“
  very low sulphate production but release of Zn and Fe into solutions (first 5 days)
  loss of H₂S
- pH = 6 (also pH 2 after 5 days)
  sharp decrease in reaction rate after 2-5 days
  up to day 20: all oxygen in sulphate derived from DO (reaction 1)
  from day 50-100: more and more oxygen in sulphate produced by Fe³⁺ (dissolved from sphalerite) = reaction 2

Sphalerite Oxidation:
• much slower
• many intermediate sulfur species (polysulfides and thiosulfates)
• passivation products like polysulfides, Zn deficit due to adsorption to ferric oxyhydroxides)

After 3 years

- preferential oxidation of galena and sphalerite (over pyrite)
- first 30 days: oxidation mainly by O₂
- afterwards oxidation mainly by Fe³⁺
- formation of intermediate soluble S species (thiosulfates, sulfite)
- formation of anglesite (Pb+S)
- in difference to single Sphal- and Ga-experiments: no sharp decrease of reaction rate
- complex behaviour of isotopes: different fractionation and isotope exchange processes (sulphite-water) in addition to varying chemical processes

back to nature...
Probenteilung
Zugabe von destilliertem Wasser (100 bzw. 400 ml): Bestimmung von pH, Eh, Leitfähigkeit

Leitfähigkeit (mS/cm)

Jarosit auf Galenit

Sphalerit (ZnS)
Pyrit (Fe₃S)
Galenit (PbS)
Gneisfragmente

> 2mm  2mm - 200 μm  200 - 63 μm  63 - 20 μm

Jarosit auf Galenit
Tichomirowa & Heidel (2012): Regional and temporal variability of the isotope composition (O, S) of atmospheric sulphate in the region of Freiberg, Germany, and consequences for dissolved sulphate in groundwater and river water. *Isotopes in Environmental and Health Studies* Vol. 48, 118–143
less than one year (10 month): sulphate from precipitation through mine into river
NOT 100 YEARS

Tichomirowa & Heidel (2012): Regional and temporal variability of the isotope composition (O, S) of atmospheric sulphate in the region of Freiberg, Germany, and consequences for dissolved sulphate in groundwater and river water. *Isotopes in Environmental and Health Studies* Vol. 48, 118–143
Summary: Oxidation experiments

**Role of O₂:**
- for initializing the oxidation:
  - initial sorption on pyrite grains (grain size)
  - initial oxidation on ZnS, PbS and sulfide mixes
  - later as an electron acceptor

**Very slow oxidation of single PbS and ZnS,**
- increase of pH
- stop after a few days

**Role of intermediate S species and anglesite (PbS, ZnS, and sulfide mix):**
- fractionation of S- and O-isotopes (complex)
- passivation of surface (anglesite, jarosite)
- preferential oxidation of PbS and ZnS (to FeS₂) results in much slower oxidation rates than single pyrite oxidation
Summary: Himmelfahrt Fundgrube

Schematischer Schnitt durch den zentralen Grubenbereich:
Freiberg (aus HAUBRICH 2000)

flooded area (500 m depth):
- fixation of Fe$^{3+}$ (oxyhydrides, jarosite)
- consumption of O$_2$: very low DO in flooded water until 2002, stratified water column

aerated area above Rotschönberger Stolln (200 m):
- sphalerite already mainly dissolved
- galena surface passivated by anglesite
- today mainly oxidation of pyrite (acid pH)
- „Letten“: jarosite + illite (fixation of Pb)
- upper 100 m already oxidised, another 100 m left for oxidation
- decreasing sulphate from industrial source
- decreasing sulphate from soil (former brown coal combustion)

flooded area (500 m depth):
- fixation of Fe$^{3+}$ (oxyhydrides, jarosite)
- consumption of O$_2$: very low DO in flooded water until 2002, stratified water column
References:
HEIDEL C., TICHOMIROWA M. (2010): The role of dissolved molecular oxygen in abiotic pyrite oxidation under acid pH conditions - experiments with $^{18}$O-enriched molecular oxygen. Appl. Geochem. 25, 1664-1675