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Abstract

A study conducted in a French alpine basin, in an unsaturated zone, exhibits total Arsenic concentrations [As] in water higher than the WHO guideline fixed at 10 µg/l. New tools are used to study As at low concentrations where many processes may be masked. [As], As speciation (As^V/As^{III}), isotopic compositions of pyrites (δ³⁴S), sulfate (δ³⁴S_{SO4}, δ¹⁸O_{SO4}) and water (δ¹⁸O_{H2O}) show a geogenic source of arsenic linked to the dissolution of pyrite. The negative correlation between δ³⁴S_{SO4} and [As] is interpreted as successive fractionations during pyrite dissolution. Oxygen isotopes are good tools to retrieve both initial redox and aerobic/anaerobic conditions. A 3-year monitoring at high-resolution showed that droughts enhance pyrite dissolution.

Origin of Arsenic

Type of Minerals	As content (mg/Kg)	δ ³⁴ S _{mineral} (‰ VCDT)	ε ³⁴ S _{sulfate-mineral} (‰ VCDT)	As concentration in water (µg/l)
Arsenopyrite FeAsS	19.6	8.25	-2	5.16
Chalcopyrite CuFeS ₂	4.20	7.8	-1.55	5.16
Pyrite FeS ₂	4.40	15	-15.1	14.85

Table 1. Comparison of isotopic signature, As content of three sulfides minerals with As concentration in water dripping from this zone and computed fractionation factors between sulfates and minerals.

→ The **ORIGIN OF AS mobilization** are **SULFIDES MINERALS**.

→ **SUCCESSIVE OXIDATIONS** of intermediate sulfoxy species during pyrite dissolution may be responsible for **CUMULATED FRACTIONATIONS**.

→ The **NEGATIVE CORRELATION** can be explained by **APPARENT FRACTIONATION FACTORS** that become progressively larger as **DISSOLUTION OF PYRITE PROGRESSES** and **MORE ARSENIC IS RELEASED**.

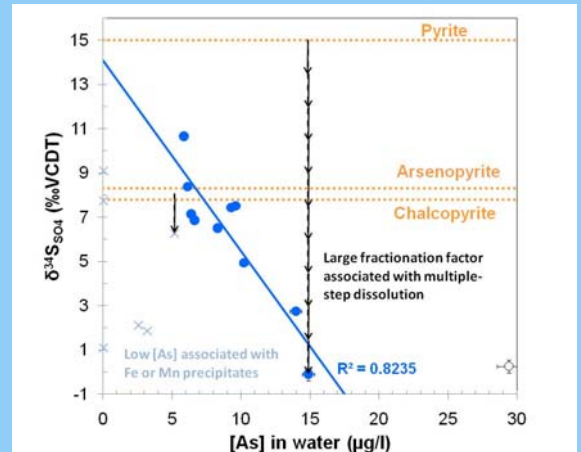


Figure 1. Negative correlation of δ³⁴S_{SO4} with [As]

Exceptions are samples where precipitates of Fe or Mn oxides are observed. A high As mobilization is associated with cumulative fractionations during pyrite dissolution.

Conditions of Pyrite Dissolution

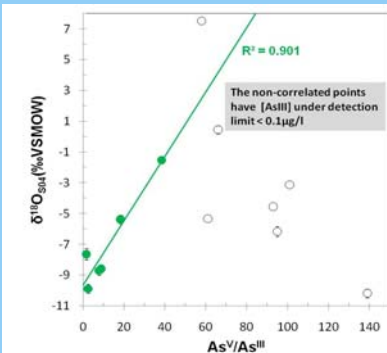


Figure 2. δ¹⁸O_{SO4} correlates positively with As^V/As^{III} ratio

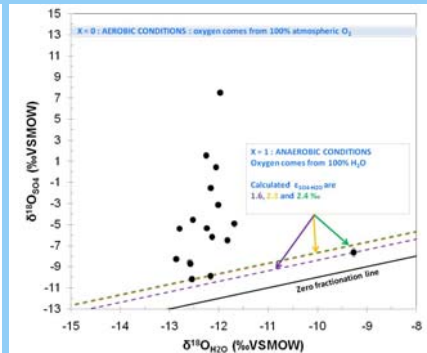


Figure 3. δ¹⁸O_{SO4} versus δ¹⁸O_{H2O}

On a Pourbaix diagram, measured Eh and pH show As under HAsO₄²⁻ (As^V) form whereas As^{III} and As^V are detected. δ¹⁸O_{SO4} value is a good tool to keep the memory of As^V/As^{III} in water at depth.

δ¹⁸O_{SO4} = X(δ¹⁸O_{H2O} + ε_{SO4-H2O}) + (1-X)(δ¹⁸O_{O2} + ε_{SO4-O2})
 ε_{SO4-H2O} = 1.6‰, 2.3‰, 2.4‰ are for samples in **strong reducing conditions**.
 ε_{SO4-O2} taken at -10.2 +/- 0.5‰ and δ¹⁸O_{O2} = 23.5‰
 → **Upper limit for Aerobic conditions.**

→ **AS SPECIATION** keeps in memory the more reducing conditions of pyrite oxydation.
 → **Pyrite dissolution** lies within a range of **AEROBIC/ANAEROBIC** conditions.

Temporal evolution

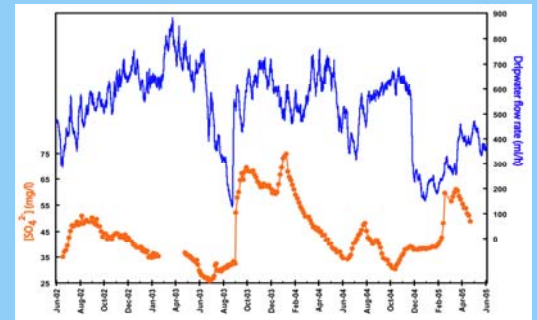


Figure 4. [SO₄²⁻] and flow rates monitored over a [2002-2005] period

The 2003 summer and 2004-2005 winter droughts enhanced pyrite dissolution and produced a high increase of [SO₄²⁻] due to water recharges (high flow rates).

→ **[SO₄²⁻] and consequently [As] mobilized are higher during summer drought than winter drought.**
 → **TEMPERATURE effect and/or better NUTRIENT availability.**

Acknowledgments

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Conclusions

1. **Pyrites dissolutions** are at the origin of As mobilization in a range of **aerobic to anaerobic** and **more reducing conditions** compared to measured Eh in water.
2. Sulfate and oxygen isotopes enable to know (1) the **[As] initially mobilized** in the absence of precipitation, (2) the memory of initial redox conditions considering **As^V/As^{III}** and (3) the part of **water-derived oxygen proportion** in sulfate.
3. Drought waves enhance pyrite dissolution resulting in an increase of [As] in waters due to water recharges.

References :

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