In-situ spectroscopy of sulfur and critical metals in fluid-mineral-melt systems at high temperatures and pressures

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ANR RadicalS, ISIFoR OrPet
**Sulfur and metals on Earth**

- **Ore deposits:**
  - 100,000 ppm S
  - 1-10 ppm Au, Pt
  - 1,000 ppm Mo
  - 10,000 ppm Cu

- **Oceanic crust:**
  - 1,000 ppm S
  - 1.5 ppb Au, Pt
  - 1 ppm Mo
  - 45 ppm Cu

- **Mantle:**
  - 200 ppm S,
  - 1 ppb Au
  - 5 ppb Pt
  - 1 ppm Mo
  - 40 ppm Cu

- **Core:**
  - < 20,000 ppm S (?)
  - 1s ppm Au, Pt (?)
  - 1000s ppm Cu, Mo (?)

- **Continental crust:**
  - 400 ppm S
  - 0.5 ppb Pt
  - 1.3 ppb Au
  - 0.8 ppm Mo
  - 30 ppm Cu

- **Sea water:**
  - 900 ppm S
  - $10^{-5}$ ppb Au, Pt
  - 10 ppb Mo
  - 0.15 ppb Cu

- **Atmosphere:**
  - < 0.1 ppb S
  - < $10^{-6}$ ppb Au, Pt
  - < $10^{-4}$ ppb Mo
  - < $10^{-3}$ ppb Cu
Fluxes of volatile elements through the lithosphere

- Geochemical cycles...
- Dynamics of transfers...
- Volcanic hazard...
- Crust-mantle evolution...
- Climate change...
- Isotope signatures...
- Mineral resources...
- Whatever you want...

> Sulfur state and partitioning in aqueous fluids and silicate magmas at depth

How to form an economic metal deposit?

- Fluids enabling extraction and focused transport and deposition
- Solubility and chemical speciation of sulfur and metals in fluids and magmas

Rock or magma:
- 0.001 ppm Au
- 0.001 ppm Pt
- 1 ppm Mo
- 30 ppm Cu
- 400 ppm S

Deposit:
- 1-100 ppm Au, Pt
- 1,000 ppm Mo
- 10,000 ppm Cu
- 100,000 ppm S

Concentration factor:
\( \times 1,000 \text{ to } 100,000 \)
All existing models of ore deposit formation, magma degassing and isotope fractionation are based on the paradigm of sulfur speciation postulating that $\text{H}_2\text{S}$, $\text{SO}_4^{2-}$ (and $\text{SO}_2$ in gas phase) are the only S forms in fluids and magmas.
Traditional view on sulfur in fluids and magmas

- Sulfur in magmas occurs as sulfate ($\text{CaSO}_4$, $\text{SO}_4^{2-}$) and sulfide ($\text{FeS}$, $\text{H}_2\text{S}/\text{HS}^-$)

- Magmas degas $\text{H}_2\text{S}$ and $\text{SO}_2$

- Most metals are transported by fluids as sulfide and chloride complexes (e.g., $\text{Au(HS)}_2^-$, $\text{Pt(HS)}_2$, $\text{PtCl}_4^{2-}$, $\text{CuCl}_2^-$)

But...

this view is largely based on samples brought to the Earth’s surface...
How to assess the composition and transport capacities of S-bearing fluids (and hydrous melts) at depth if:

- They are not accessible by direct observation
- They are mobile and fugitive, leaving very small traces
- They are extremely chemically reactive
- They are not quenchable
- They are dilute in metals (<100 ppm) and S (<1%) with H$_2$O >99%
Tracking the deep and hot fluids and magmas

High $T$-$P$ reactors

Trace element analyses (ICP-MS, ICP-AES)

Molecular simulations

Cells for in-situ spectroscopy

Synchrotron techniques

$$G_{i,TP} = G_{i,TP}^0 + 2.3026RT \log a_i$$

$$\Delta G_{Born}^0 = \omega_i \times \left( \frac{1}{\epsilon_{mix}} - \frac{1}{\epsilon_{water}} \right)$$

Thermodynamic models
Intermediate-valence sulfur species in hydrothermal fluids at the sulfate-sulfide transition, revealed by in-situ Raman spectroscopy.
Natural and synthetic fluid inclusions

Thermochemical sulfate reduction (TSR)

Equilibrated sub-system

Redox state

Electron donor

Irreversible reaction

Potentials of the bulk reaction

Thermochemical sulfate reduction (TSR)

Sulfate-sulfide solutions in DAC

Ubiquitous $S_3^-$

$2H_2S + SO_4^{2-} + H^+ = S_3^- + 0.75 O_2 + 2.5 H_2O$

Pokrovski, Dubrovinsky (2011) Science 331, 1052


Pokrovski, Dubrovinsky & Dubrovskaya (2011) Earth Planet. Sci. Lett. 396, 190

Truche et al. (2014) Earth Planet. Sci. Lett. 396, 190

0.1 wt% $S_3^-$

1 wt% $S_3^-$

$H_2S$

$HS^-$

$SO_4^{2-}$

$HSO_4^-$

$H_2O$

$NNO$

$QFM$

$HM$

$S_3^-$

$H_2O$

$pH$:

1 2 3 4 5 6 7 8 9 10

$-34$ $-32$ $-30$ $-28$ $-26$ $-24$ $-22$

$log_{10} f_{O_2}$

$S_3^-$

$HSO_4^-$

$SO_4^{2-}$

$H_2S$

$HS^-$

$HM$

$NNO$

$QFM$

$water$

$1$ wt% $10$ wt% $0.1$ wt%

$350 ^\circ C$, $5-15$ kbar

Raman capillary, this study

Raman DAC, Pokrovskii & Dubrovinsky 2011

UV-Vis spectroscopy, Gigenbach 1971

Quantum chemistry, Tossell 2012

HFK model, this study

$q/\bar{q}$

$1000/T(K)$

$1$ $1.5$ $2$ $2.5$ $3$ $3.5$

$-50$ $-45$ $-40$ $-35$ $-30$ $-25$ $-20$ $-15$ $-10$ $-5$ $0$

Stability constant of $S_3^-$

$S_3^-$ (and $S_2^-$) are not quenchable, breaking down to sulfate, sulfide or $S^0$ on cooling

Schmidt, Seward (2017) Chem.Geol. 467, 64

Barré et al. (2017) Chem. Geol. 462, 1

Jacquemet et al. (2014) Amer. Miner. 99, 1109
Predicted abundance of $S_3^-$ (and $S_2^-$) in crustal fluids

Fontboté et al. (2017) Elements 13, 97
Cooling and rise of a fluid degassed from magma at 700°C and 1.5 kbar in equilibrium with Au metal and carrying:
2 wt% S, H$_2$S:SO$_2$ = 1, 10 wt% NaCl, 7500 ppm Fe, 3000 ppm Cu, pH 5-6 (Quartz-Muscovite-K feldspar)

Au + H$_2$S + S$_3^-$ = Au(HS)S$_3^-$ + ½ H$_2$

S$_3^-$ enhances, by a factor of 10 to 100, the fluid capacity to extract Au from magma and to transport it to ore deposition sites at $T > 400$°C, but the effect is weak in epithermal settings (< 300-350°C)

Pokrovski et al. (2015) PNAS 112, 13484
Unique properties of the sulfur radical ions

- High chemical reactivity (unpaired electron)
- Enhanced mobility in fluids and, potentially, magmas
- Strong affinity for metals such as Au and, potentially, PGE, Mo, Re
- Large applications in chemistry (batteries, sensors, colored pigments, borosilicate glasses, gemology)
Sulfur radical ions in fluid-magma systems
Questions for the present study

- What is the true sulfur species in magmatic fluids and silicate melts?
- Are the sulfur radical ions stable at these conditions?
- How do they partition between aqueous fluids and silicate melts at depth?
Looking into magma-fluid systems through diamond glasses

1. Raman bands are known for most S compounds and species
2. They change little with T, P, and composition
3. Resonance Raman is a powerful diagnostic tool

Schmidt & Chou, 2012, EMU Notes in Mineralogy, 12, 247

Max Wilke’s talk tomorrow morning
Raman spectra (473 nm) of melts and fluids at 700°C, 10 kbar

Rhyolite glass (MAC) + 1.9 m Na$_2$S$_2$O$_3$

Alkaline rhyolite glass (NAS 75:75) + 1.9 m Na$_2$S$_2$O$_3$
Determination of fluid/melt partition coefficients for each species

\[ D_{i}^{\text{fluid/melt}} = \frac{C_{i}^{\text{fluid}}}{C_{i}^{\text{melt}}} \approx \frac{I_{i}^{\text{fluid}}}{I_{i}^{\text{melt}}} \]

\( C_{i} \) = concentration of species

\( I_{i} \) = Raman peak integrated intensity of species

corrected for baseline, density, refractive index, absorption

\( D_{i}^{\text{fluid/melt}} \) of sulfate and sulfide are \( \pm 0.3 \) log units

\( D_{i}^{\text{fluid/melt}} \) of S radical ions are minimal values
Results: fluid/melt partition coefficients for each S species

- $S_3^-$ and $S_2^-$ partition into the fluid phase 10-100 times more than sulfate and sulfide.
- Enrichment of more alkaline melts by sulfate and sulfide, but not by $S_3^-$ and $S_2^-$.  
- Our method enables, for the first time, partitioning measurements of each individual S species.
In-situ partition coefficients of sulfate and sulfide are much lower (x10-100) that those measured in most ex-situ experiments, implying much larger sulfur storage capacities of magmas at both reduced and oxidized conditions.

By contrast, large variability and scatter of published $D_S$ at the $S^{2-/S^{6+}}$ transition is likely due to the radical ions that have $D$ values 10-100 times higher than sulfide and sulfate.

10 ppm S as $S_3^-$ or $S_2^-$ in melt will generate >1000 ppm S in the coexisting fluid, largely enough to bind trace metals (Au, Mo, Pt...).
First in-situ measurement of sulfur speciation and partitioning in fluid-magma systems avoiding limitations of previous ex-situ studies

Sulfate, sulfide, and the radical ions $S_3^-$ and $S_2^-$ are stable both in the fluid and melt at the sulfate-sulfide transition.

$S_3^-$ and $S_2^-$ partition in favor of the fluid phase 10-100 times more than sulfate and sulfide.

The radical ions largely enhance sulfur (and metal?) transfers from magma to fluid when magma pass through the redox window of the sulfate-sulfide transition typical of many magmas at convergent margins.
Radical ions and platinum group metals

See also the poster of Clément Laskar
Why platinoids?

1. Critical metals admirably adapted for industry

2. Key tracers in planetary geochemistry and cosmochemistry (metal-silicate-sulfide partitioning; meteorite signature; radioisotope systems: $^{190}\text{Pt}/^{186}\text{Os}$, $^{187}\text{Re}/^{187}\text{Os}$, $^{107}\text{Pd}/^{107}\text{Ag}$)
Why fluids?

1. Hydrous silicates and fluid inclusions in classical magmatic Ni-Cu sulfide/chromitite deposits

   e.g., Bushveld, Norilsk

   Ballhaus et al. 1986; CMP, 94, 193
   Borisova et al. 2012; JPet, 53, 2411
   Arai et al. 2016; Lithos, 264, 277

2. PGE remobilization and concentration in various metal sulfide hydrothermal environments

   Porphyry Cu-Mo-Au (1 ppm Pd, Pt)
   Black shales (500 ppm Pt, Pd, Rh)
   Iron Oxide Copper Gold (100 ppm Pt)
   Serpentinites (1 ppm Pt, 5 ppm Pd)

3. Direct evidence of PGE transport by hydrothermal fluids

   Lac des Iles, Canada (1-10 ppm Pd)
   Hanley, Gladney 2011; Econ. Geol. 106, 33
Major sources of available experimental and theoretical data on Pt aqueous complexes

**Chloride**
- < 1990s (chemical literature)
  - Potentiometry, spectroscopy < 100°C
- 1988-1992 (Wood)
  - Solubility 25-350°C, Psat
- 1992-1995 (Gammons)
  - Solubility 100-300°C, Psat
- 1998 (Sassani, Shock)
  - HKF model predictions
- 2015 (Tagirov)
  - Solubility 400-475°C, 1 kbar
- 2019 (Tagirov)
  - EXAFS, 25-300°C, Psat

**Sulfide**
- 1993 (Gammons)
  - Solubility 200-300°C, Psat
- 1994 (Pan, Wood)
  - Solubility 25-350°C, Psat

PtCl$_4^{2-}$, PtCl$_3^-$

Pt(HS)$_2^-$, Pt(HS)$_3^-$, Pt(HS)$_4^{2-}$
Predicted solubility of Pt in hydrothermal fluids

300°C, 500 bar
10 wt% NaCl+KCl
Quartz-Muscovite-K feldspar (pH 5)

Oxidizing, S-poor
Pyrite-Magnetite-Hematite
0.001m H₂S

Pt(HS)₂ = 3×10⁻³ ppb
PtCl₃⁻ = 4×10⁻⁸ ppb
Pt(SO₄)₁,₂,₃ < 1×10⁻²⁰ ppb

Reducing, S-rich
Quartz-Fayalite-Magnetite
0.3m H₂S (1 wt% S)

Pt(HS)₂ = 1.2 ppb
PtCl₃⁻ = 1×10⁻¹⁰ ppb

Ligands other than Cl and HS and SO₄ are required to account for Pt mobility...
Does $S_3^-$ affect the transport of platinum by hydrothermal fluids?

Pt solubility and local structure in $S_3^-$-bearing model fluids

- Hydrothermal reactors
- In situ X-ray absorption spectroscopy (XAS)
- Molecular dynamics simulations
- Thermodynamic modeling
Gold or titanium flexible-cell hydrothermal reactor

Metal solubility (from <1 ppb to >1000 ppm) in multicomponent mineral-fluid systems to 500°C and 1.5 kbar
FAME cell for X-ray absorption spectroscopy

Metal local atomic structure and total concentrations (>10 ppm) in S-bearing fluids to 450°C and 1.5 kbar

Solubility of Pt in $S_3^-$ - bearing high T-P fluids
PtS solubility is 2 to 5 log units (!!) higher in our experiments than predicted from $S_3^-$-free solutions, and correlates with the $S_3^-$ concentration.
Local atomic structure of Pt in S-rich fluids from in-situ EXAFS spectroscopy
Pt L$_3$-edge EXAFS spectra of $K_2S_2O_3$-HCl and S-NaOH aqueous solutions at 300°C, 500 bar

$K^2\chi(k)$, Å$^{-2}$

$k$, Å$^{-1}$

pH 4.8
pH 5.1
pH 5.3
pH 5.9

~50 ppm Pt
10-20 hours acquisition time

BM30B (FAME)
Fourier Transform of EXAFS spectra from Pt-S aqueous solutions

- $1^{st}$ shell Pt-S$_4$ (square)
- $2^{nd}$ shell S?
- Multiple scattering within $1^{st}$ shell Pt-S$_4$ square

Fourier Transform Magnitude

Radial distance, Å
Fitting EXAFS spectra of Pt-S$_3^-$ bearing solutions

$R_{\text{Pt-S1}} = 2.35 \pm 0.005 \text{ Å}$
$N_{S1} = 4.5 \pm 0.5 \text{ atoms}$

$R_{\text{Pt-S2}} = 3.50 \pm 0.05 \text{ Å}$
$N_{S2} = 2 \pm 1 \text{ atoms}$

Pt(HS)$_2$(S$_3^-$)$_2^{2-}$
(tentative)
“Radical ions and PGE” summary

- Pt forms very stable complexes with the $S_3^-$ ion, greatly enhancing the metal transport.

- Hydrothermal fluid contribution to Pt concentration and remobilization may be much greater than believed.

- Fluid-phase transport of other S-loving metals (e.g., Mo, Re) might also be enhanced in the presence of S radical ions.

- The $S_3^-$ ion makes the formation of ore deposits easier than we thought...
Impact of the sulfur radical ions

Radical ions enhance metal and sulfur transfers in the lithosphere in fluid (-melt) systems, thereby providing metals for ore deposits and sulfur to volcanoes, and “boosting” geological processes.
Perspectives and challenges
Current limitations

• Sulfur species absolute concentrations remain unquantified in fluid(-melt) systems at high T-P (Raman is not really good for that).

• Low concentrations of trace metals (< ppm level) in natural fluids melts (and minerals), complex matrixes, and interfering elements greatly degrade the spectroscopic signal.

• Classical EXAFS and XANES are little sensitive to the exact stoichiometry and beyond-first-shell ligands of aqueous species.

• Few materials can resist to chemically aggressive sulfur-rich fluids and melts at high $T-P$. 
**XANES spectroscopy of sulfur in fluids, melts and minerals at high T-P**

**Advantages**

- Direct and quantitative probe of different S species fractions (in contrast to Raman spectroscopy), owing to the additive nature of the X-ray absorption signal.

**Challenges**

- Strong absorption of X-rays by the cell materials at the low energy of S K-edge.
- Lack of adequate standards for radical ions.
- Constraints on cell heating in the beamline vacuum.
- Contamination of S fluorescence signal.
Sulfur K-edge (2.47keV)
Not possible at any dedicated high-pressure XANES beamline

30µm thin diamond plate
=> pressures up to 100 kbar (cullet 600µm)
=> 20% transmission @ S K-edge

F. Wilhelm et al. 2016, High Pressure Research 36, 445

Fabrice’s talk from this morning
Ultramarines: mineral analogs for sulfur in fluids and melts?

Sodalite-group minerals
\[(\text{Na, Ca})_8 \text{Al}_6 \text{Si}_6 \text{O}_{24} (\text{Cl, S})_2\]

A variety of S species trapped into aluminosilicate cages
\[\text{HS} / \text{S}^{2-}, \text{S}^{0}, \text{S}_3^{2-}, \text{S}_2^{2-}, \text{S}_n^{2-}, \text{SO}_3, \text{SO}_4\]

Lazurite

Precious stones

Plastics

Food

Coatings

Ink

Cosmetics
Ultramarine blue under pressure at S K-edge

295 K

Significant sulfur redox changes under pressure

$S_3^- + SO_4^{2-} \rightarrow S^{2-} + S^0 + SO_3^{2-} + O_2$

Normalized absorbance

Energy, eV

Perforated DAC

sum surface area = 0

1 bar
60 kbar
diff 60 kbar - 1 bar

Significant sulfur redox changes under pressure
High-resolution XANES spectroscopy (HERFD) of metals in fluids at high T-P

**Advantages**

- Gain in spectral resolution compared to conventional XANES,
- Revealing changes in metal coordination, redox state or ligand identity and
- Enabling studies of trace metals in fluids and minerals in the presence of interfering elements with close absorption edges (e.g., Au/Pt versus As).

**Challenges**

- Geometry constraints of the high T-P setup and crystal analyzers.
- Lack of adequate standards for aqueous species and trace metals in minerals.
- Necessity of XANES spectra modeling (e.g., FEFF, FDMNES).
Solid-State detector vs Crystal Analyzer Spectrometer

Denis Testemale’s talk tomorrow

$\Delta E_{\text{emission}} \approx 150-300\text{eV}$

$\Delta E_{\text{incident}} \approx 0.5-1\text{eV}$

Si(220) Double-crystal monochromator

Detector

$\Delta E_{\text{emission}} \approx 1-3\text{eV}$

CAS

$\Delta E_{\text{incident}} \approx 0.5-1\text{eV}$

Si(220) Double-crystal monochromator
High-resolution set up and high T-P autoclave at BM16 (FAME-UHD) for studying metals in hydrothermal fluids
High-resolution set up and high T-P autoclave at FAME-UHD for studying metals in hydrothermal fluids
Spectacular gain in XANES spectra resolution with the HERDFD setup compared to ‘classical’ fluorescence mode

But... How to interpret such spectra in the absence of standards?
Interpreting HERFD XANES spectra in hydrothermal fluids using FDMNES simulations

Experiment, 350°C, 600 bar

0.5 m K₂S₂O₃ + 0.2 m HCl, pH=4.5, Au(HS)S₃⁻ dominant

0.5 m K₂S₂O₃ + 0.3 m KOH, pH=7.5, Au(HS)₂⁻ dominant

Molecular Dynamics simulated Au-S species (Pokrovski et al. 2015, PNAS 112, 13484)

FDMNES code:
Joly 2001, Phys Rev 63, 12120
Bunau et Joly 2009, JPCM 21, 345501
Guda et al. 2015, JCTC 11, 4512
Applications

Formation of mineral resources of critical metals

Evolution of magmas, volcanic degassing

Sulfur and metal isotope tracers

Ore prospection and processing

Hydrothermal synthesis of new nanomaterials

Sulfur and metals on other planets
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