

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:
 100,000s 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

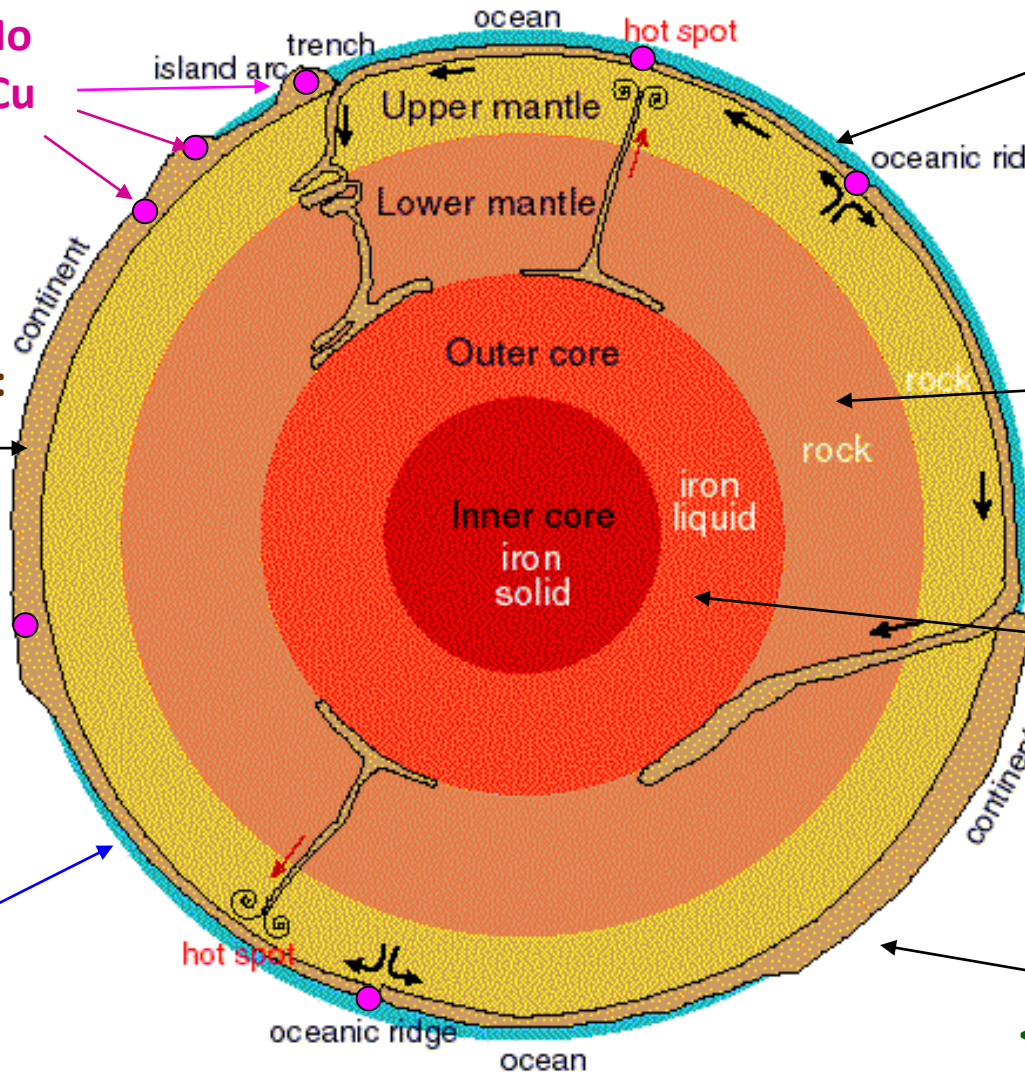
Mantle:
 200 ppm S,
 1 ppb Au
 5 ppb Pt
 1 ppm Mo
 40 ppm Cu

Core:
 $\leq 20,000$ ppm S (?)
 1s ppm Au, Pt (?)
 1000s ppm Cu, Mo (?)

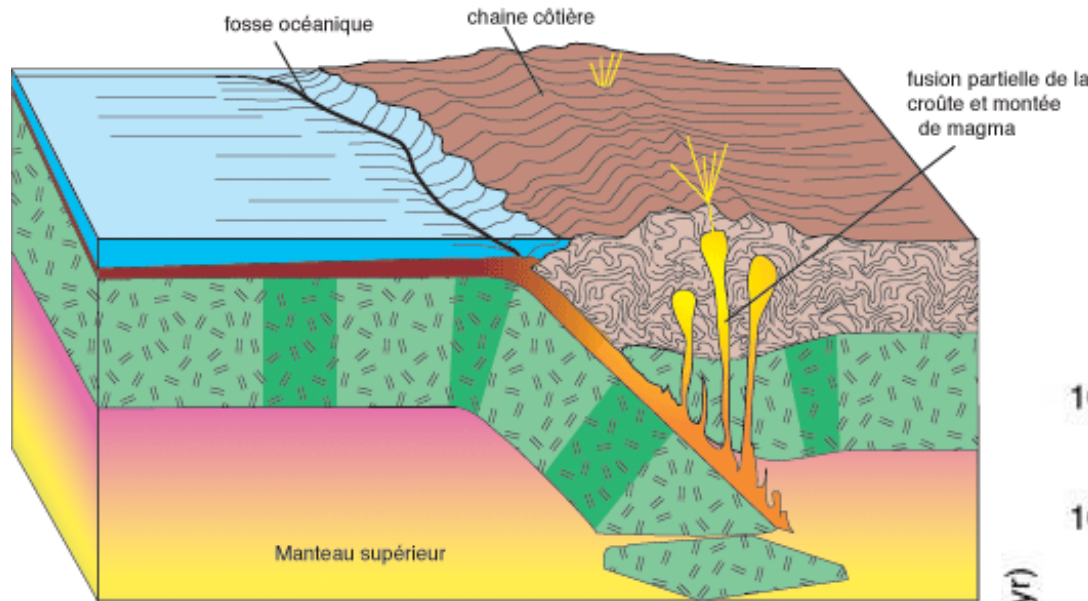
Atmosphere:
 < 0.1 ppb S
 $< 10^{-6}$ ppb Au, Pt
 $< 10^{-4}$ ppb Mo
 $< 10^{-3}$ ppb Cu

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



Fluxes of volatile elements through the lithosphere



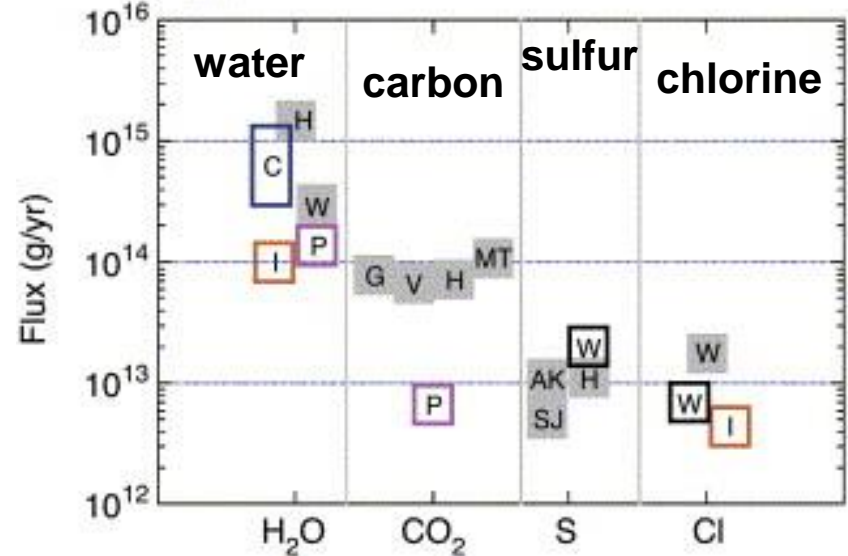
- ❖ Geochemical cycles...
- ❖ Dynamics of transfers...
- ❖ Volcanic hazard...
- ❖ Crust-mantle evolution...
- ❖ Climate change...
- ❖ Isotope signatures...
- ❖ Mineral resources...
- ❖ Whatever you want...

Gas Flux & Composition

SJ	Stoiber & Jepsen
V	Varekamp et al.
G	Gerlach
MT	Marty & Tolstikhin
AK	Andres & Kasgnoc
H	Hilton et al.
W	This study

Magma Flux & Volatile Content

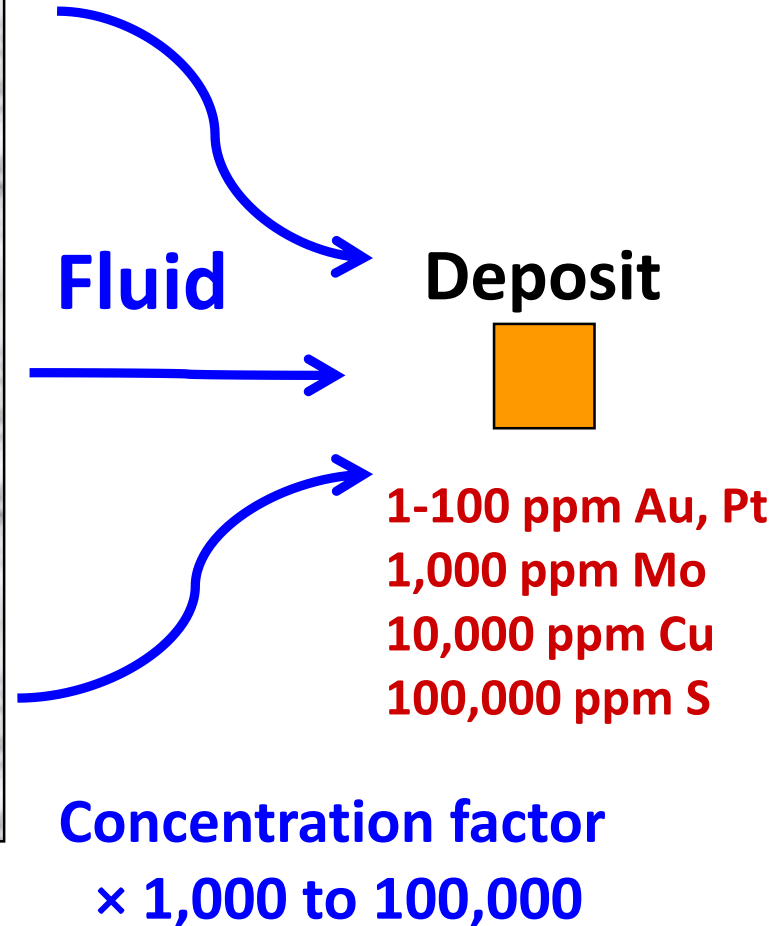
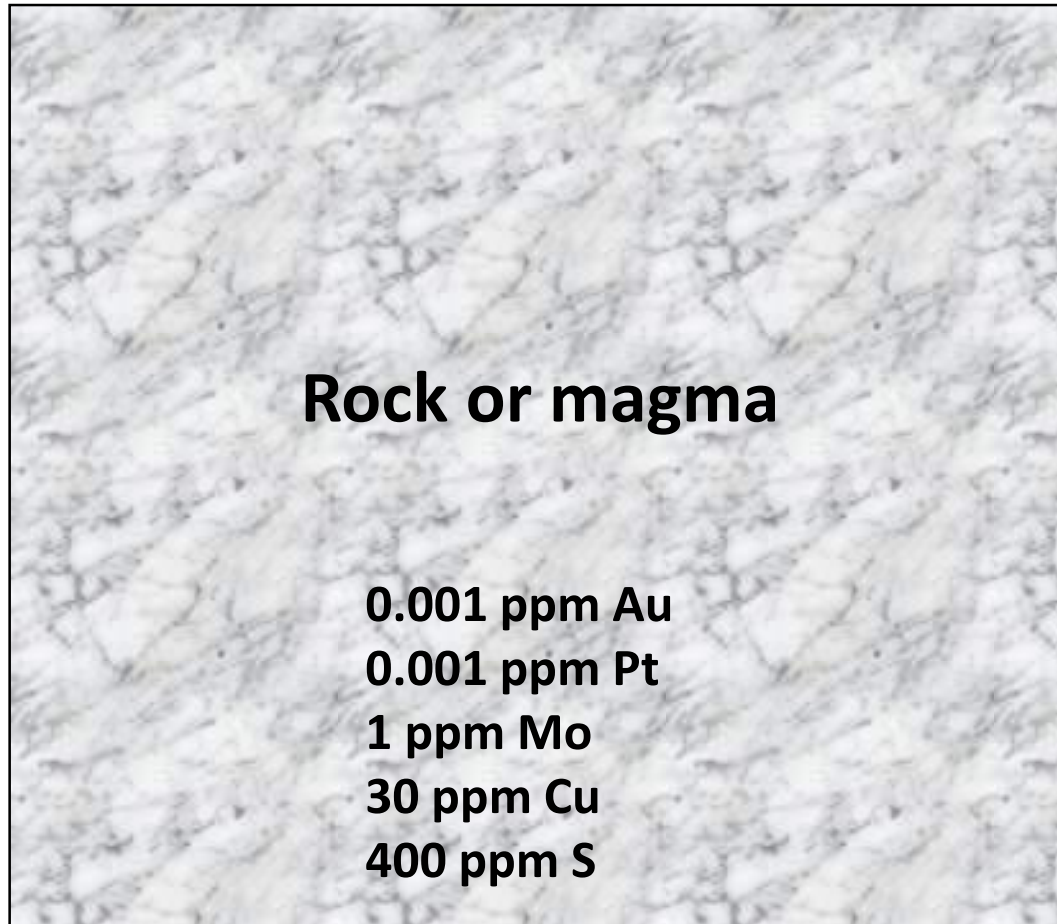
I	Ito et al.
P	Peacock
C	Carmichael
W	Assuming 2.5 km ³ /yr magma flux



Wallace (2005) *J. Volcanol. Geotherm. Res.* 140, 217

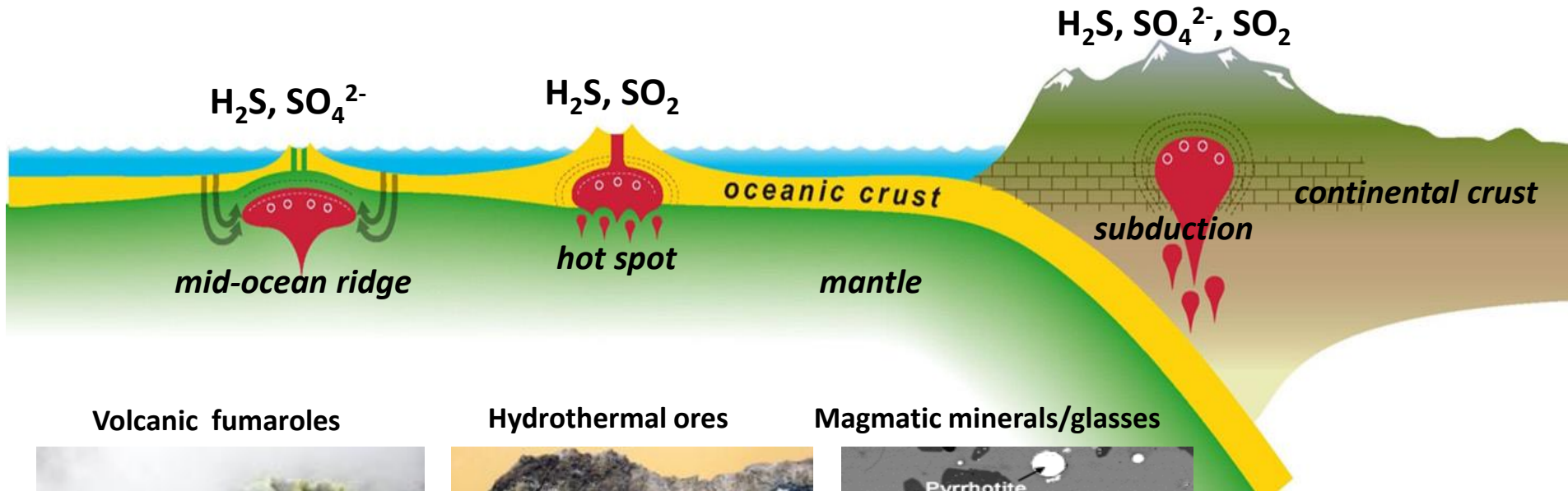
➔ **Sulfur state and partitioning in aqueous fluids and silicate magmas at depth**

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

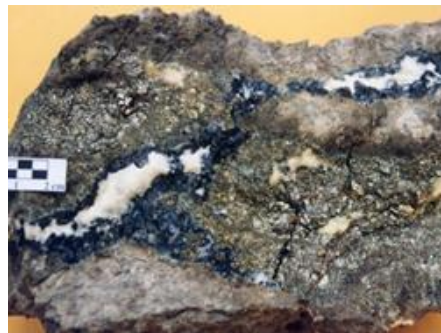
Sulfur in fluids, vapors and melts: what do we know?



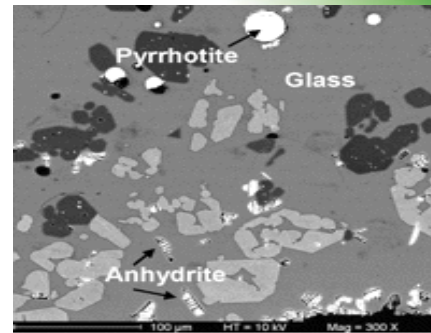
Volcanic fumaroles



Hydrothermal ores



Magmatic minerals/glasses



All existing models of ore deposit formation, magma degassing and isotope fractionation are based on the paradigm of sulfur speciation postulating that H_2S , SO_4^{2-} (and 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 (CaSO_4 , SO_4^{2-}) and sulfide (FeS , $\text{H}_2\text{S}/\text{HS}^-$)
- ❖ Magmas degas H_2S and SO_2
- ❖ Most metals are transported by fluids as sulfide and chloride complexes (e.g., $\text{Au}(\text{HS})_2^-$, $\text{Pt}(\text{HS})_2$, PtCl_4^{2-} , CuCl_2^-)

But...

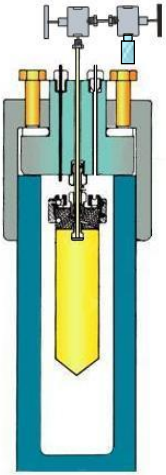
this view is largely based on samples brought to the Earth's surface...



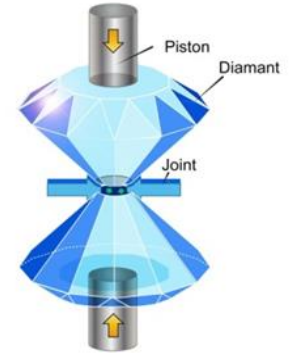
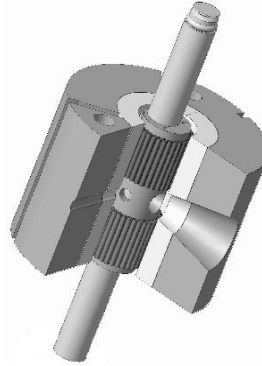
How to assess the composition and transport capacities of S-bearing fluids (and hydrous melts) at depth if:

- 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 H₂O >99%

Tracking the deep and hot fluids and magmas



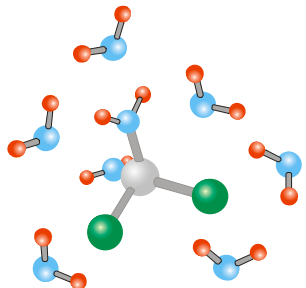
High T - P reactors



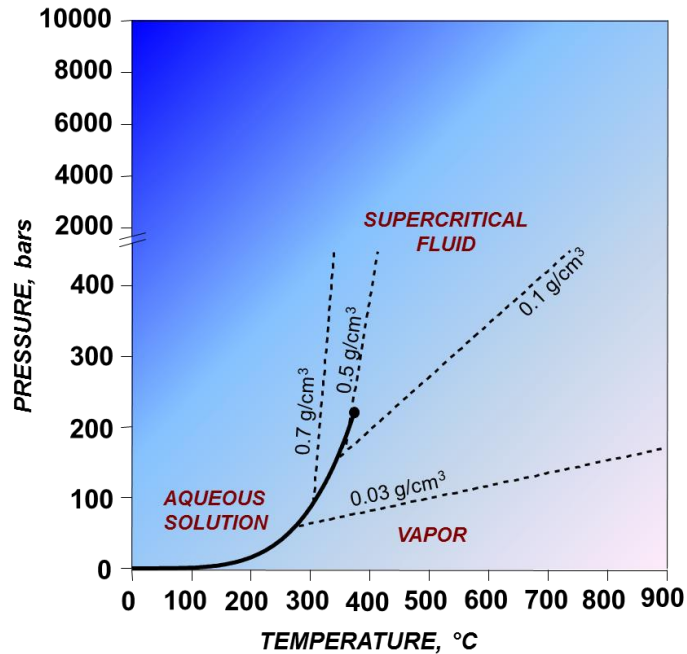
Cells for in-situ spectroscopy



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



Molecular simulations



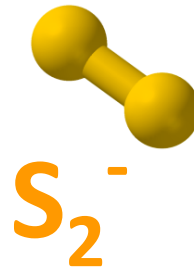
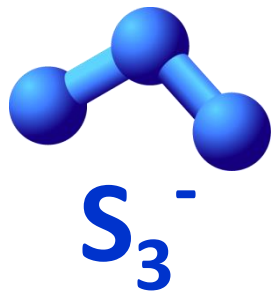
Synchrotron techniques

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

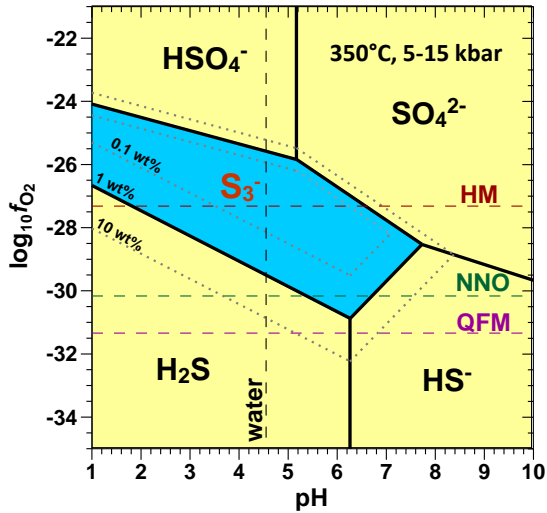
$$\Delta G_{Born}^0 = \omega_i \times \left(\frac{1}{\epsilon_{mix}} - \frac{1}{\epsilon_{water}} \right)$$

Thermodynamic models

**Intermediate-valence sulfur species
in hydrothermal fluids
at the sulfate-sulfide transition,
revealed by in-situ Raman spectroscopy**

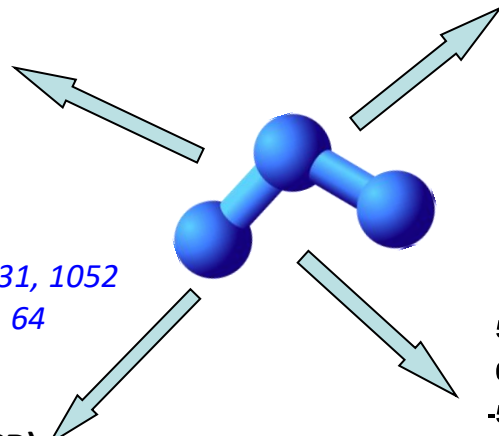


Sulfate-sulfide solutions in DAC

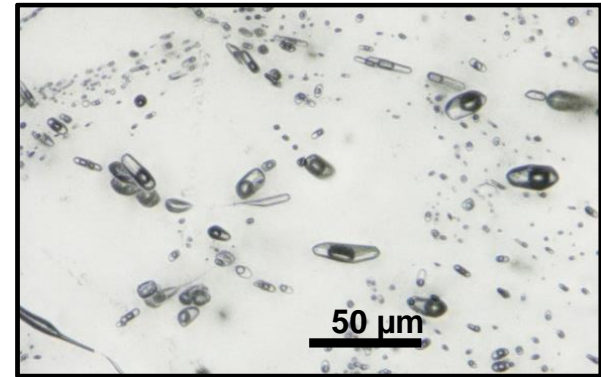


Pokrovski, Dubrovinsky (2011) Science 331, 1052
Schmidt, Seward (2017) Chem. Geol. 467, 64

Ubiquitous S_3^-

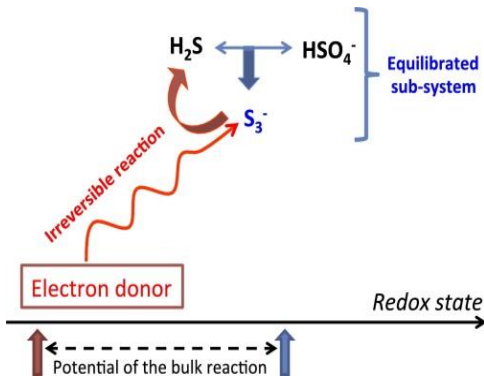


Natural and synthetic fluid inclusions

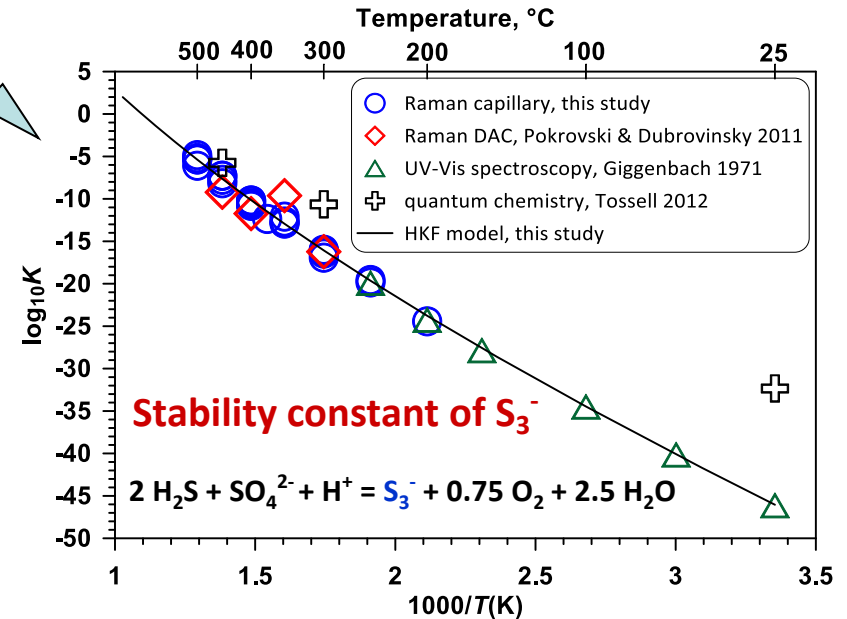


Jacquemet et al. (2014) Amer. Miner. 99, 1109
Barré et al. (2017) Chem. Geol. 462, 1

Thermochemical sulfate reduction (TSR)



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

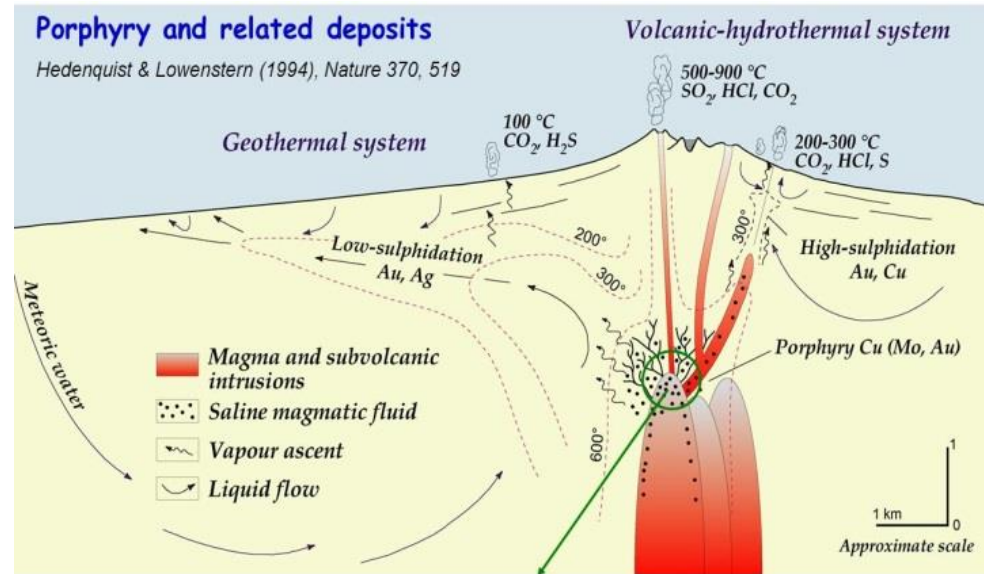
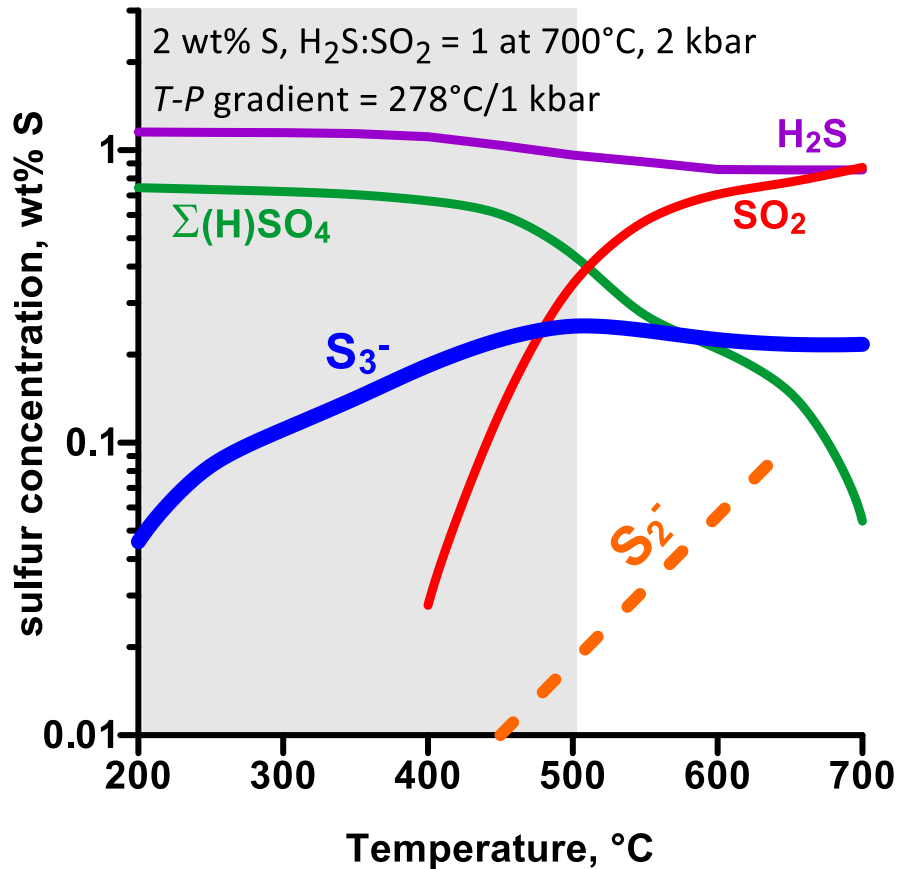


Pokrovski, Dubessy (2015) Earth Planet. Sci. Lett. 411, 298

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

Predicted abundance of S_3^- (and S_2^-) in crustal fluids

Magmatic-hydrothermal fluid
(0.2-2.0 kbar)

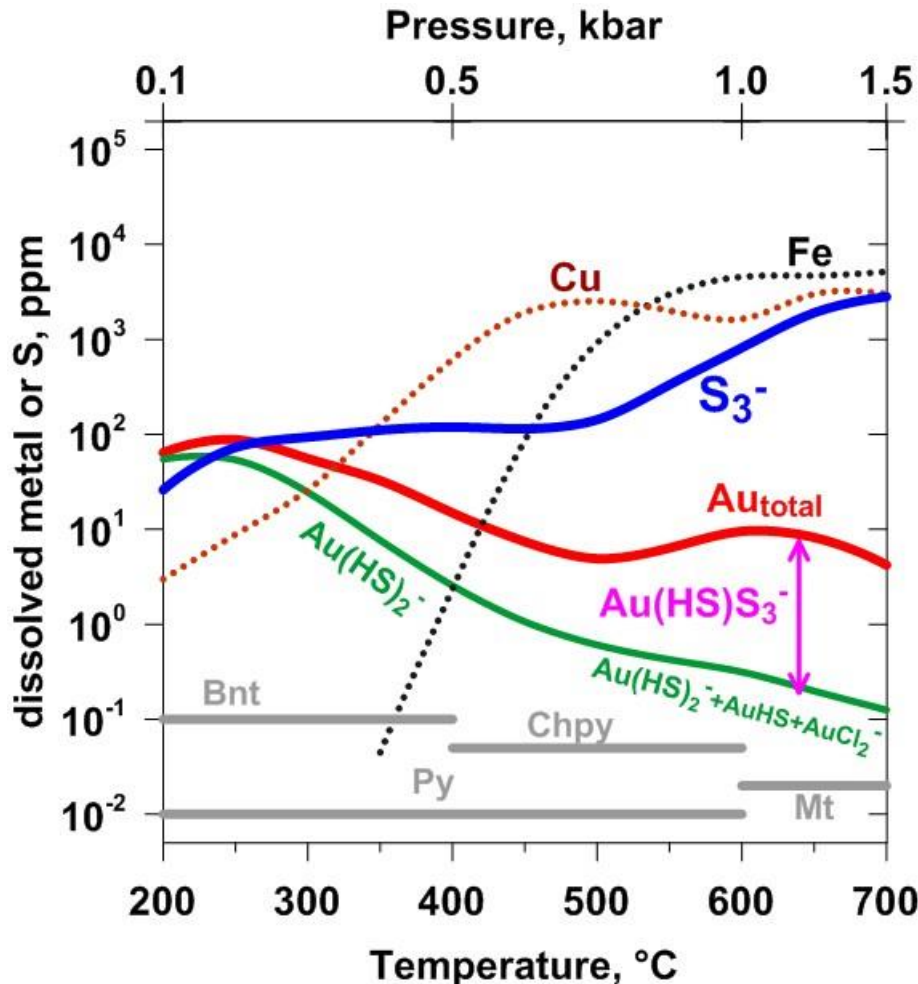
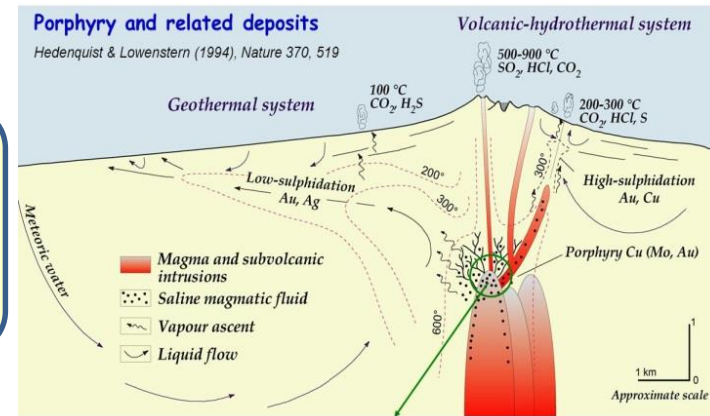


75% Cu, 50% Mo, 90% Re, 20% Au production

Fontboté et al. (2017) Elements 13, 97

Gold in porphyry-epithermal fluids

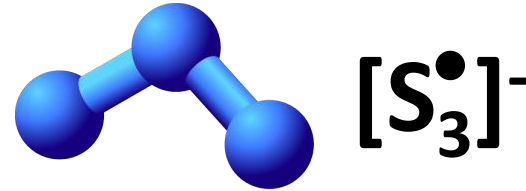
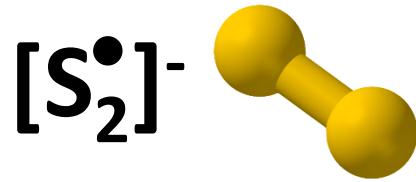
Cooling and rise of a fluid degassed from magma at 700°C and 1.5 kbar in equilibrium with Au metal and carrying:
 2 wt% S, H₂S:SO₂ = 1, 10 wt% NaCl, 7500 ppm Fe, 3000 ppm Cu,
 pH 5-6 (Quartz-Muscovite-K feldspar)



S₃⁻ 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 $T > 400^\circ\text{C}$, but the effect is weak in epithermal settings ($< 300\text{-}350^\circ\text{C}$)

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)

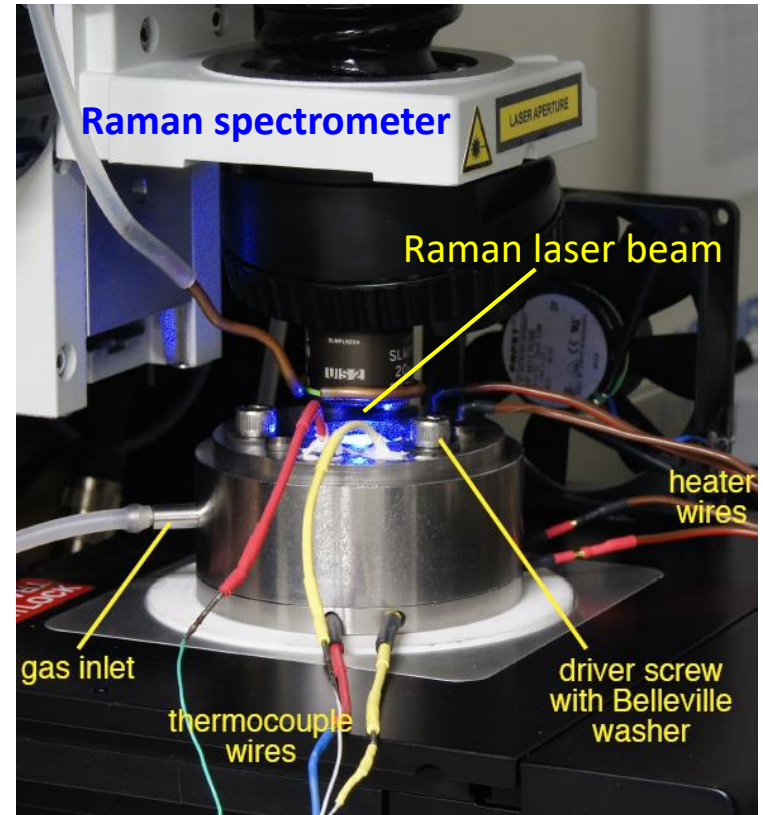
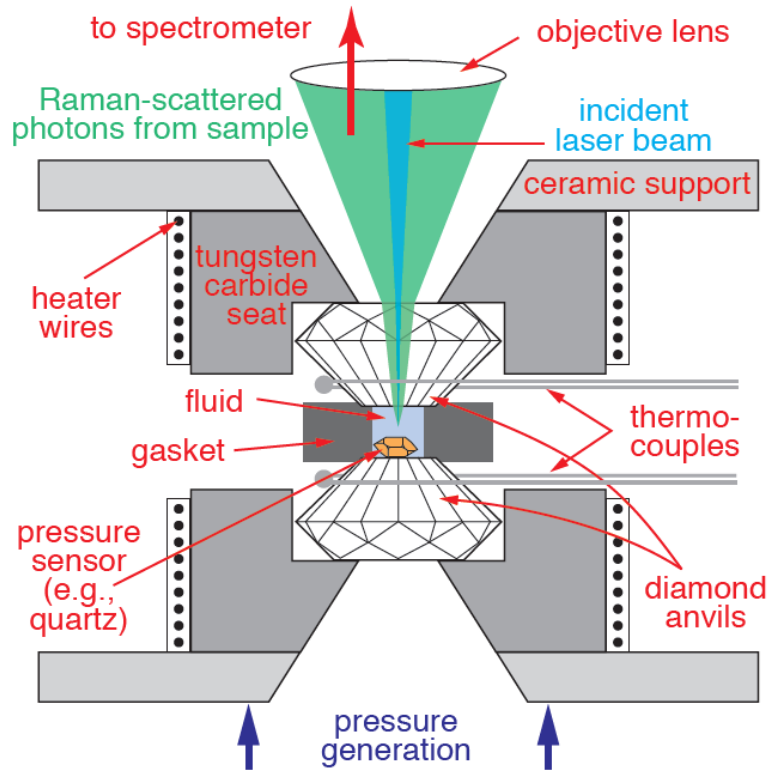
Sulfur radical ions in fluid- magma systems

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

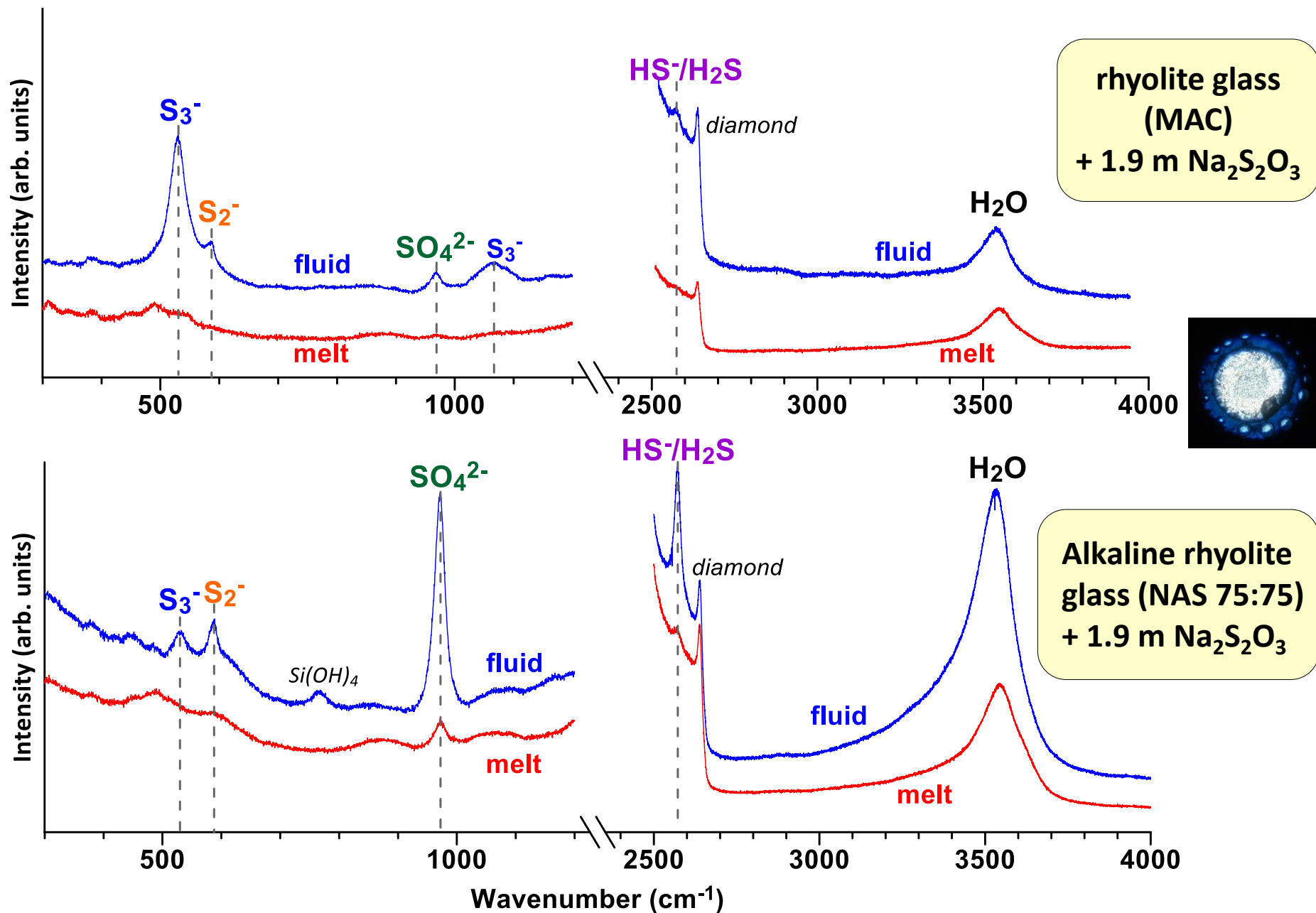


Schmidt & Chou, 2012, EMU Notes in Mineralogy, 12, 247

Max Wilke's talk tomorrow morning

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

Raman spectra (473 nm) of melts and fluids at 700°C, 10 kbar




Determination of fluid/melt partition coefficients for each species

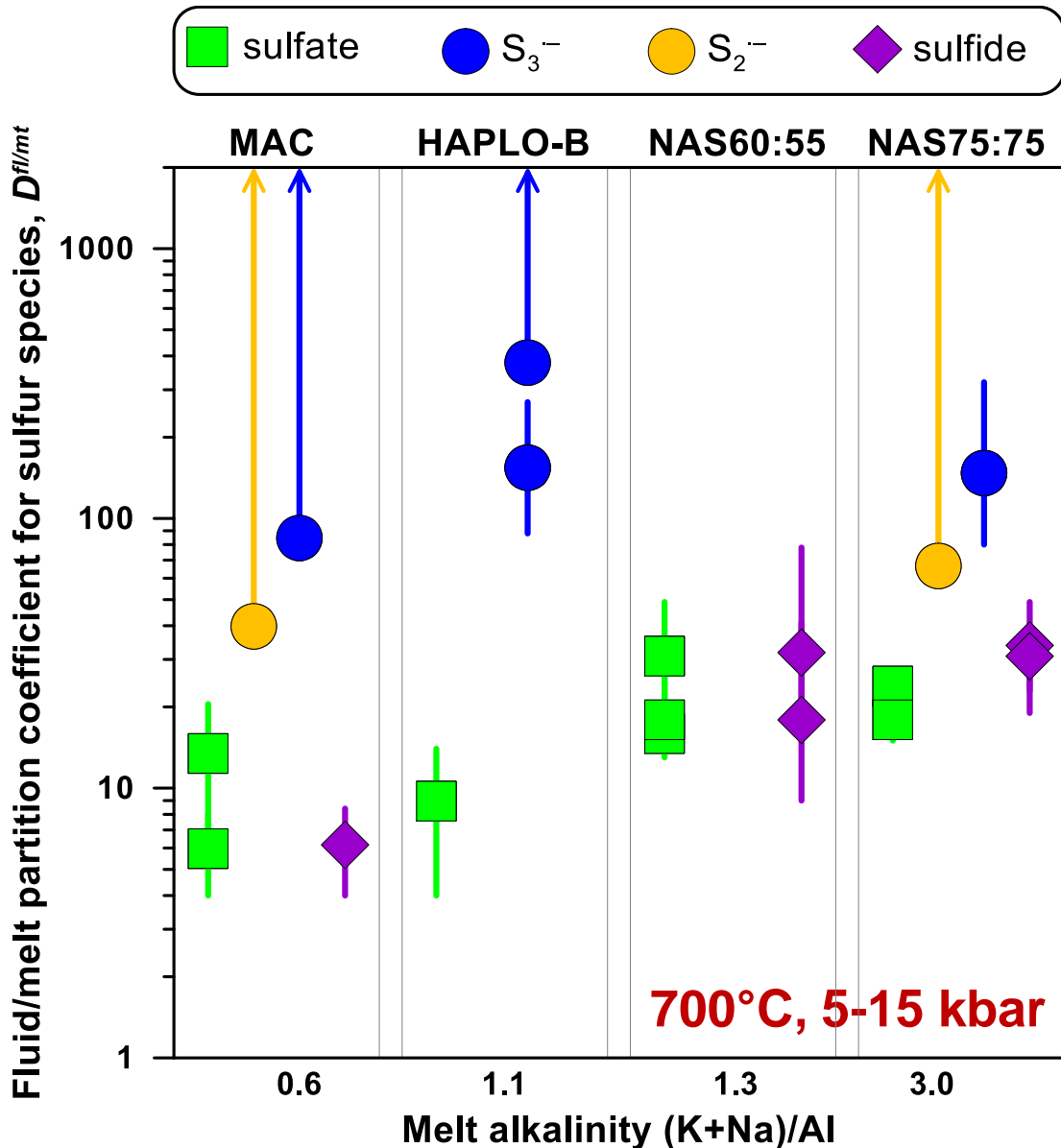
$$D_i^{fluid/melt} = C_i^{fluid} / C_i^{melt} \approx I_i^{fluid} / I_i^{melt}$$

C_i = concentration of species

I_i = Raman peak integrated intensity of species
corrected for baseline, density, refractive index, absorption

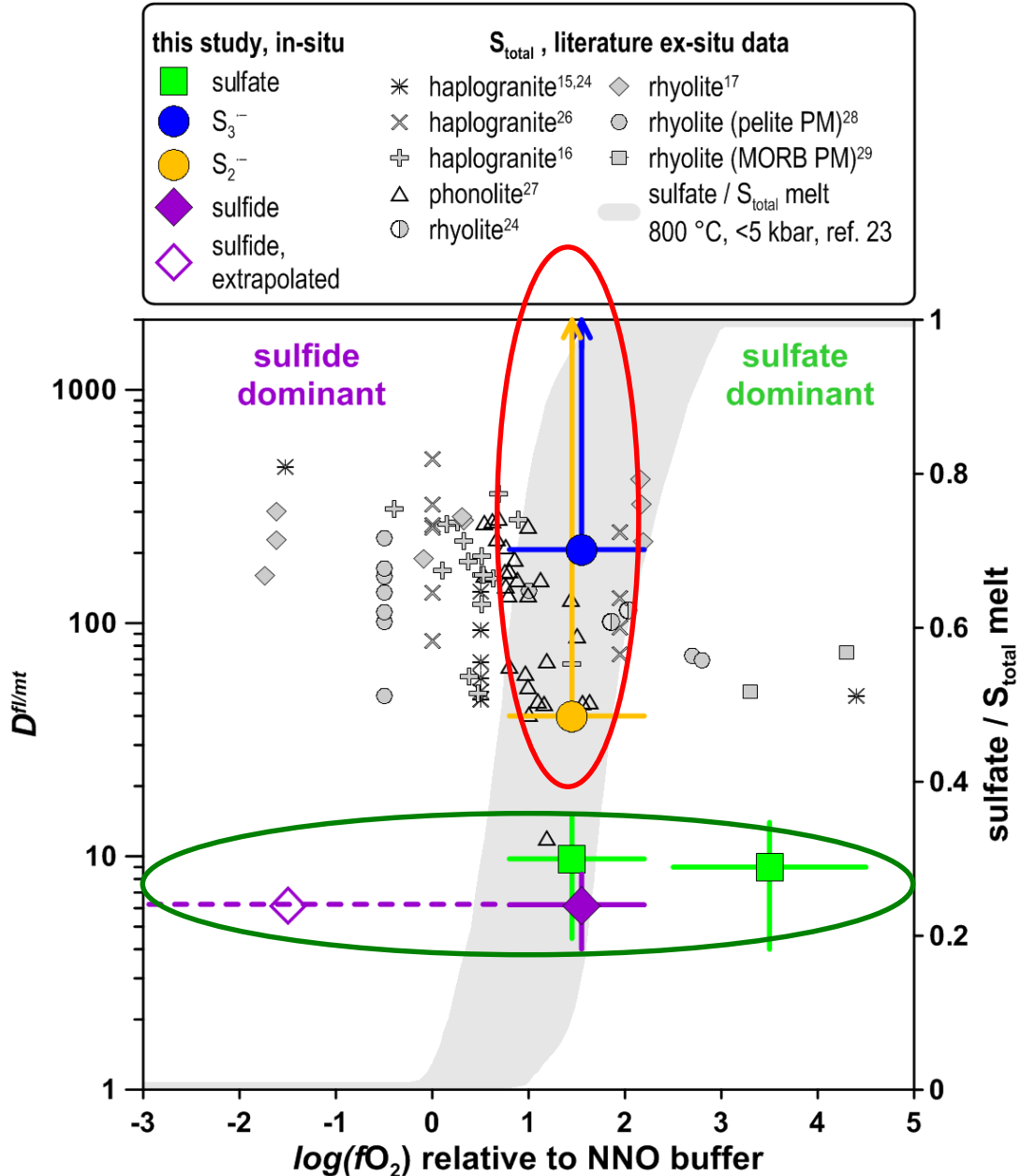
 $D_i^{fluid/melt}$ of sulfate and sulfide are ± 0.3 log units
 $D_i^{fluid/melt}$ of S radical ions are minimal values

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.

Comparison of our in-situ DAC data with available ex-situ data on quenched glasses for felsic melts ($\text{SiO}_2 > 65 \text{ wt}\%$)



- In-situ partition coefficients of sulfate and sulfide are much lower (x10-100) than 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 $\text{S}^{2-}/\text{S}^{6+}$ 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...).

“Sulfur radical ions in magmas” summary

- 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

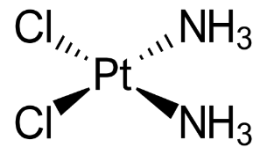
Why platinoids?



1. Critical metals admirably adapted for industry



Anticancer drugs



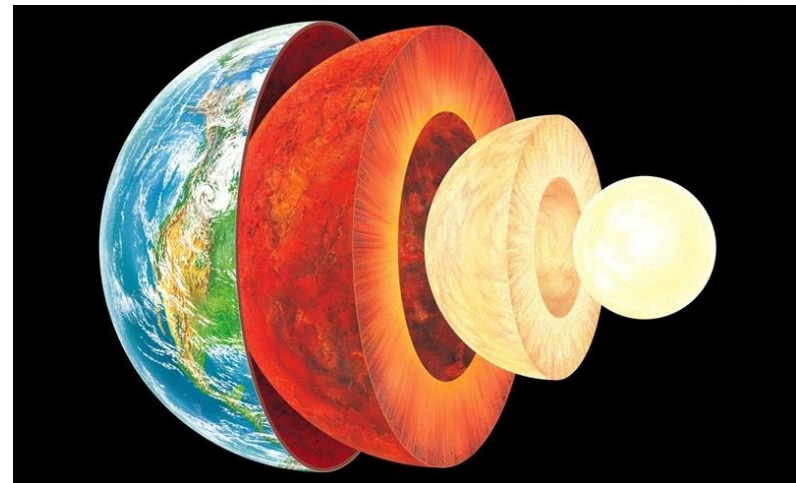
Jewelry



Materials



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

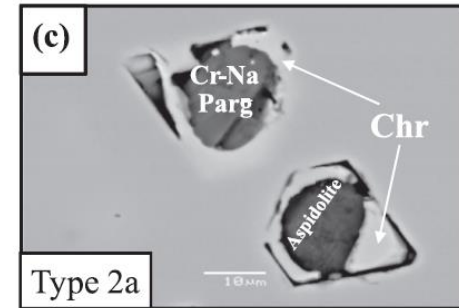


Why fluids?

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

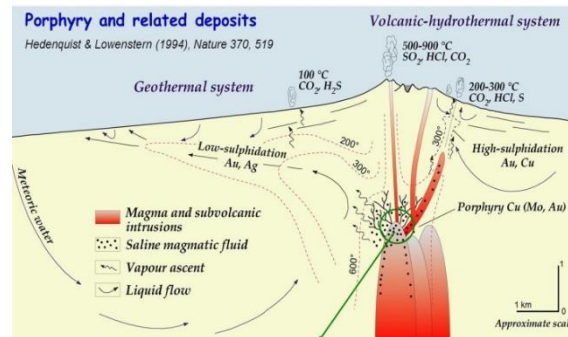


e.g., Bushveld, Norilsk



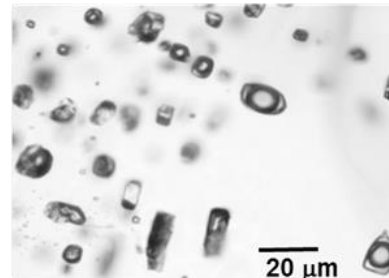
Ballhaus et al. 1986; CMP, 94, 193
Borisova et al. 2012; JPet, 53, 2411
Arai et al. 2016; Lithos, 264, 277

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)
Serpentinities (1 ppm Pt, 5 ppm Pd)

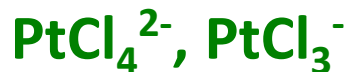
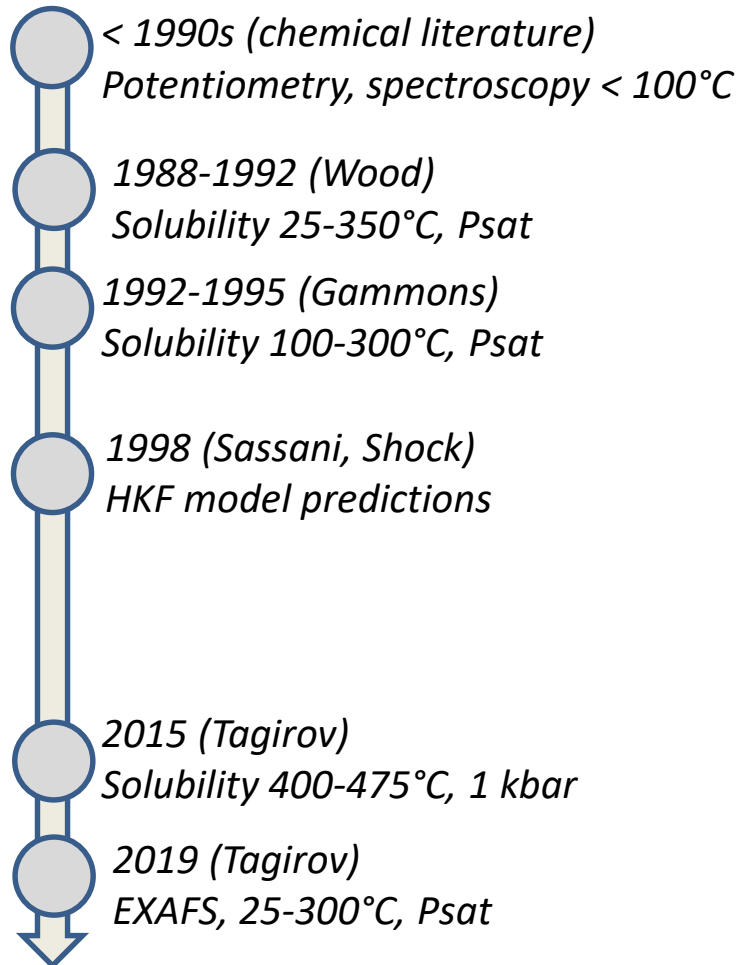
3. Direct evidence of PGE transport by hydrothermal fluids



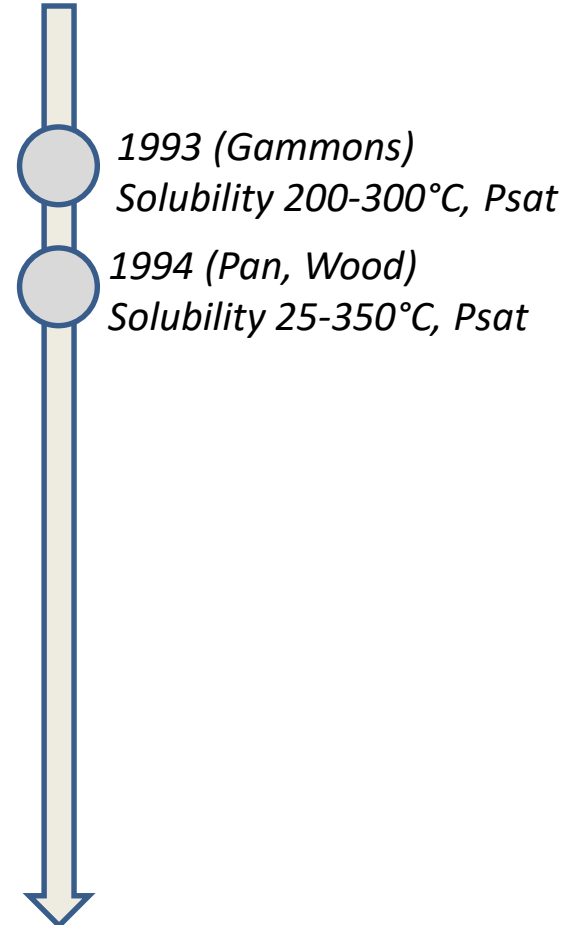
Lac des Iles, Canada (1-10 ppm Pd)
Hanley, Gladney 2011; Econ. Geol. 106, 33

Major sources of available experimental and theoretical data on Pt aqueous complexes

Chloride



Sulfide



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

$\text{Pt}(\text{HS})_2 = 3 \times 10^{-3}$ ppb

$\text{PtCl}_3^- = 4 \times 10^{-8}$ ppb

$\text{Pt}(\text{SO}_4)_{1,2,3} < 1 \times 10^{-20}$ ppb

Reducing, S-rich

Quartz-Fayalite-Magnetite

0.3m H₂S (1 wt% S)

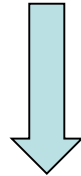
$\text{Pt}(\text{HS})_2 = 1.2$ ppb

$\text{PtCl}_3^- = 1 \times 10^{-10}$ ppb



Ligands other than Cl and HS and SO₄ are required to account for Pt mobility...

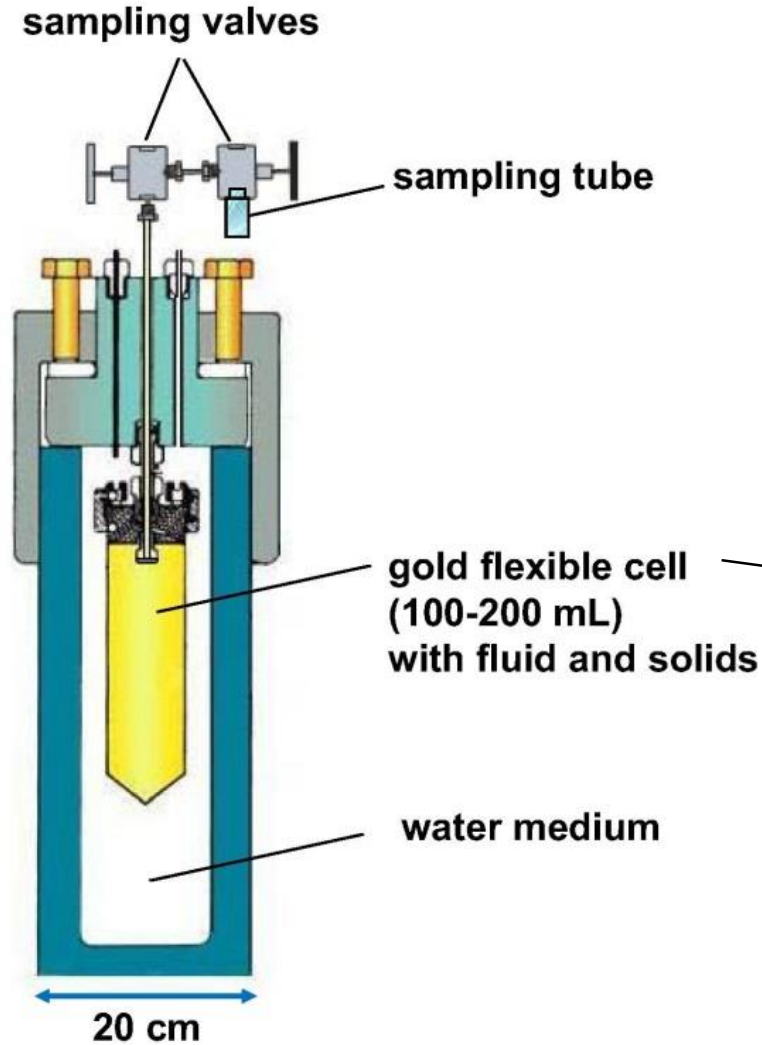
Does S_3^- affect the transport of platinum by hydrothermal fluids?



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

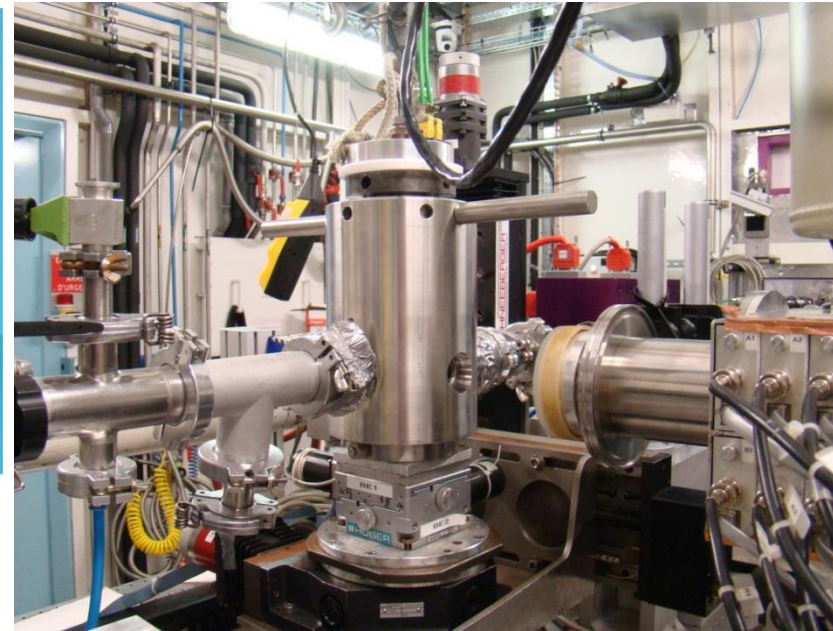
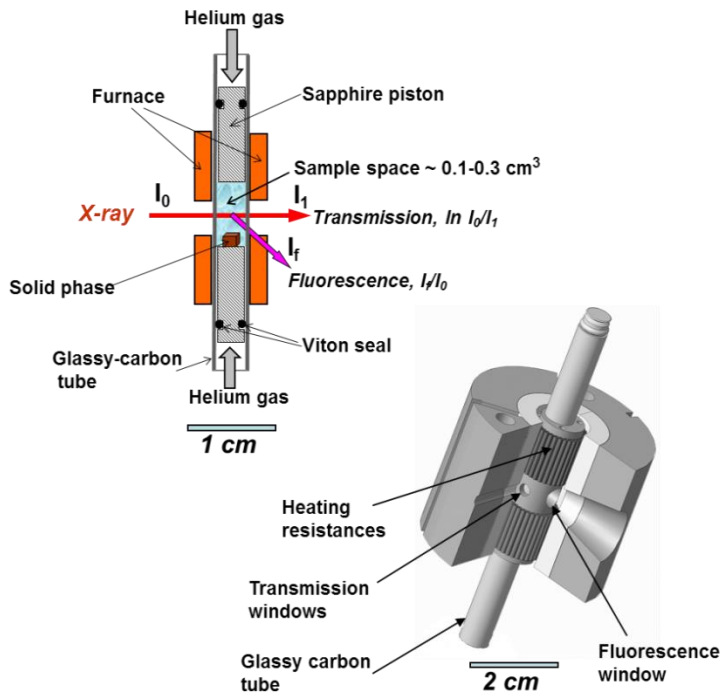
- ❖ Hydrothermal reactors
- ❖ In situ X-ray absorption spectroscopy (XAS)
- ❖ Molecular dynamics simulations
- ❖ Thermodynamic modeling

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

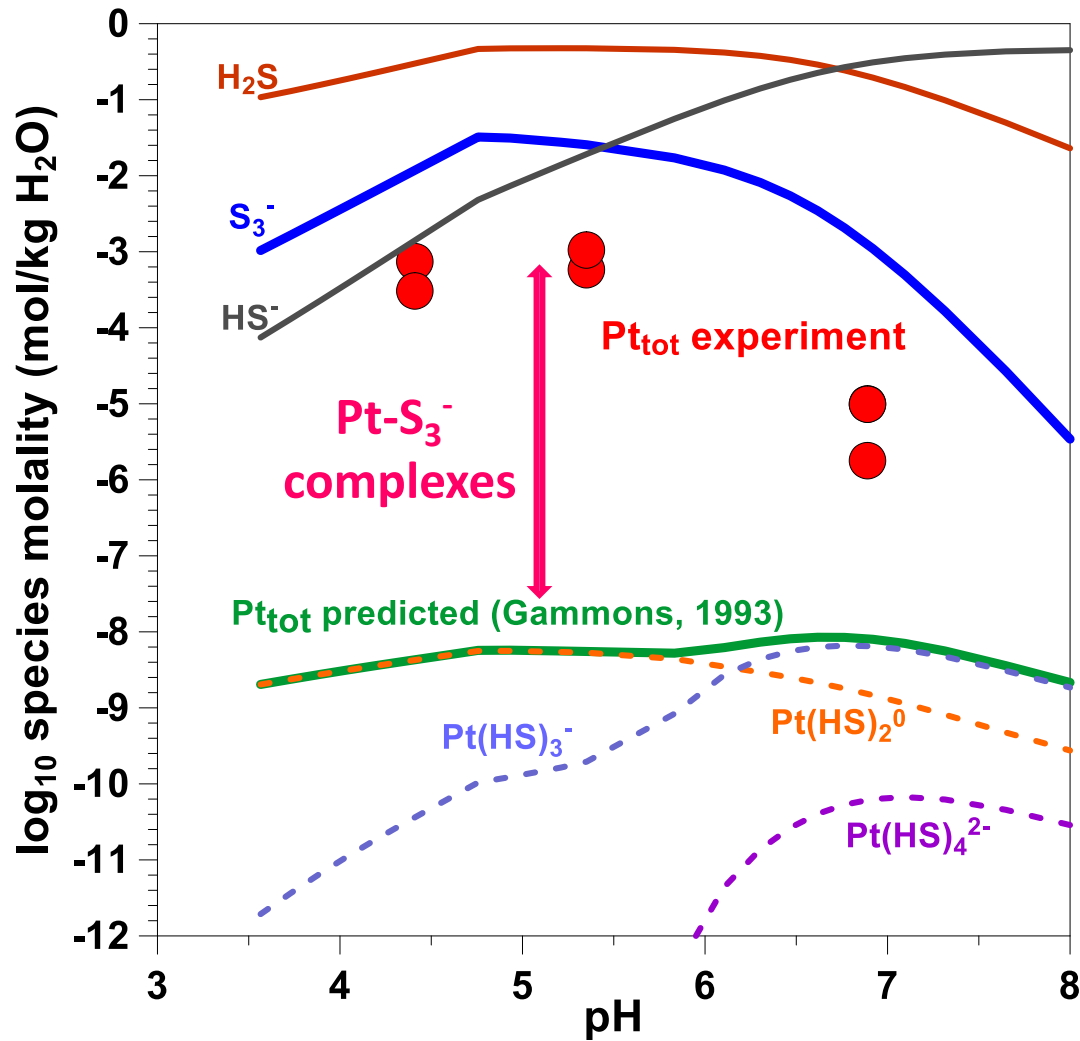


D. Testemale et al. (2005) Rev. Sci. Instrum. 76, 043905

➔ 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**

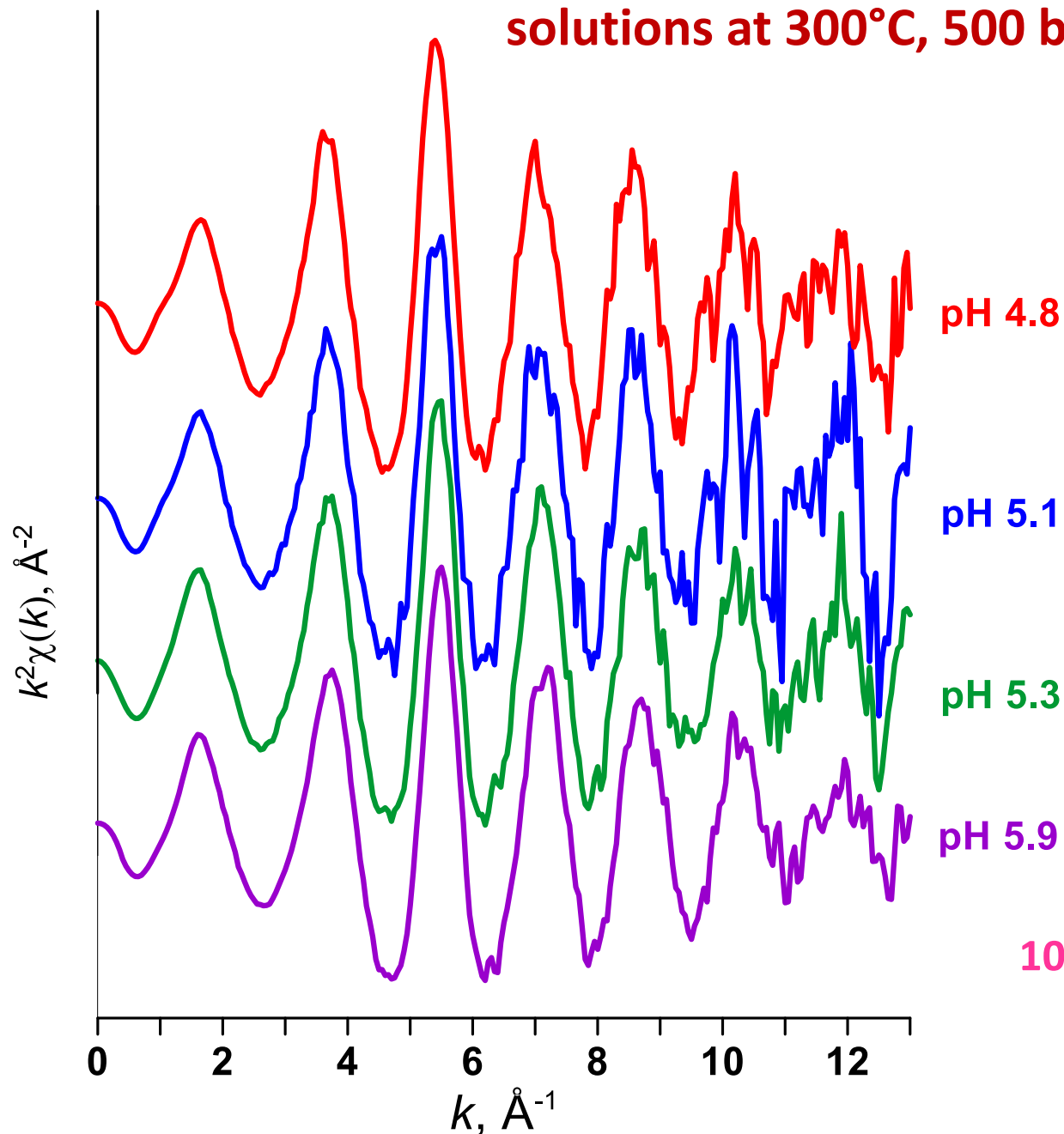
Solubility of PtS in 0.5 m $\text{K}_2\text{S}_2\text{O}_3$ (-HCl-KOH) solutions at 300°C, 500 bar



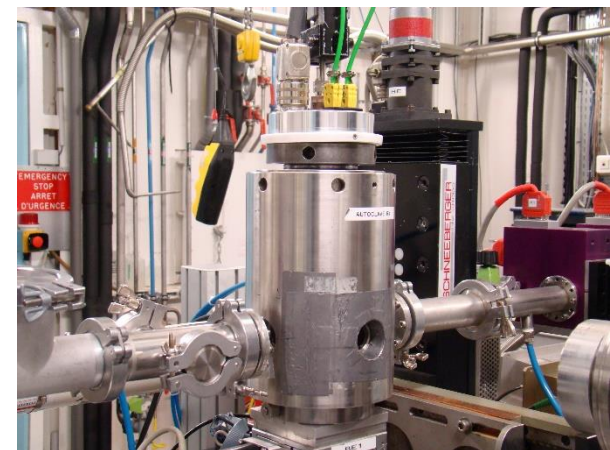
➔ PtS solubility is 2 to 5 log units (!!) higher in our experiments than predicted from S_3^- -free solutions, and correlates with the S_3^- concentration.

**Local atomic structure of Pt
in S-rich fluids from in-situ EXAFS
spectroscopy**

Pt L₃-edge EXAFS spectra of K₂S₂O₃-HCl and S-NaOH aqueous solutions at 300°C, 500 bar



BM30B (FAME)



pH 4.8

pH 5.1

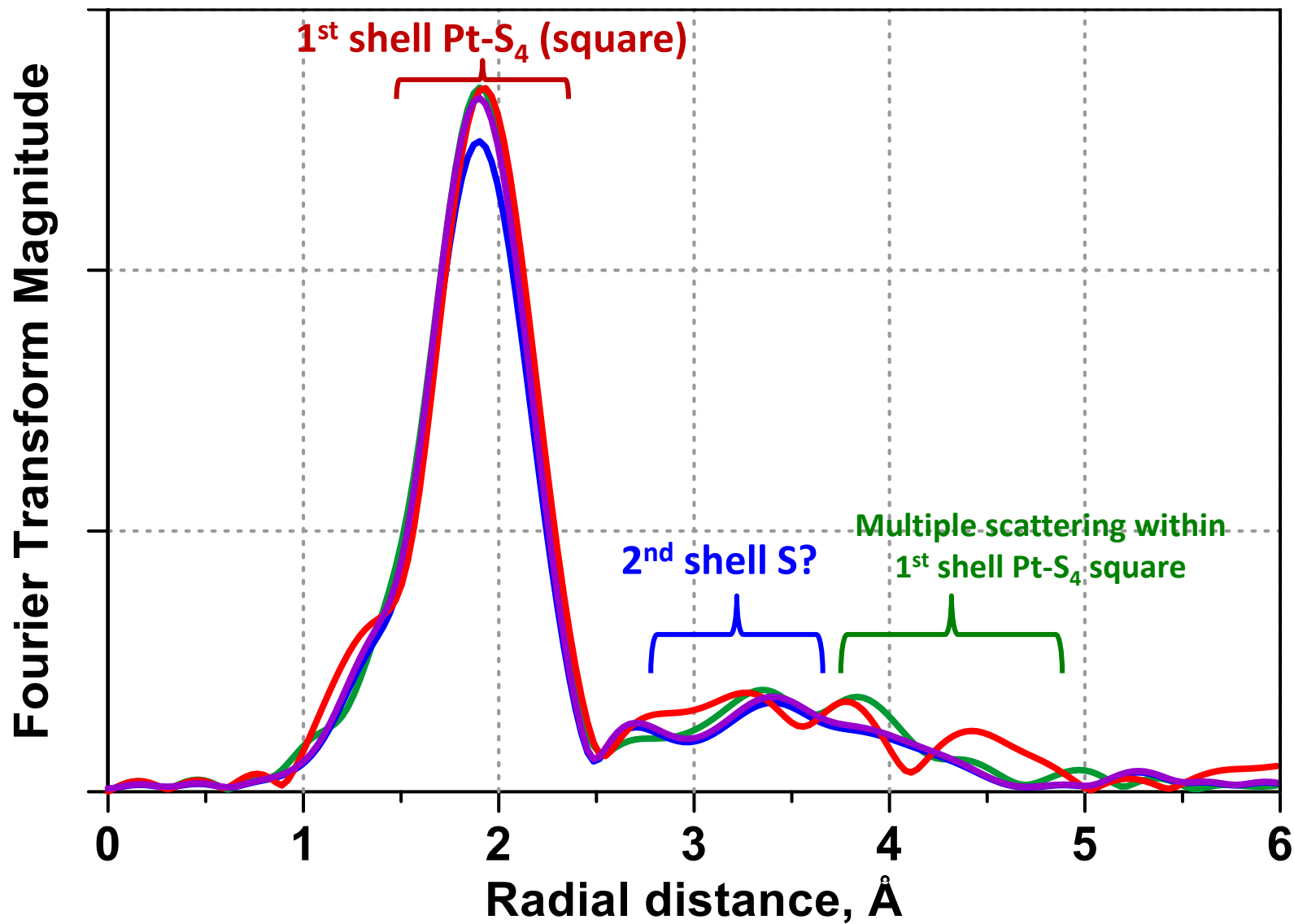
pH 5.3

pH 5.9

~50 ppm Pt

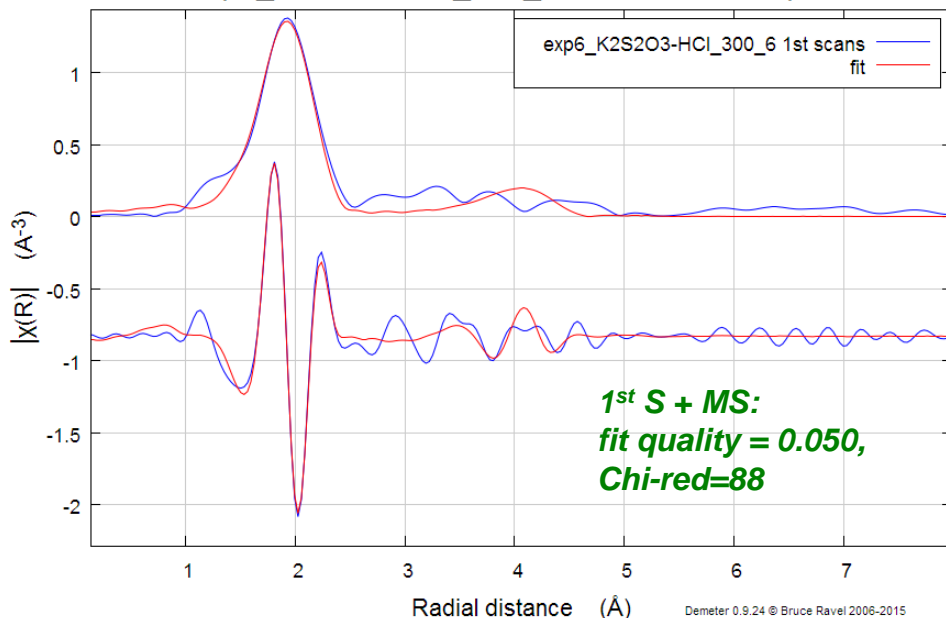
10-20 hours acquisition time

Fourier Transform of EXAFS spectra from Pt-S aqueous solutions

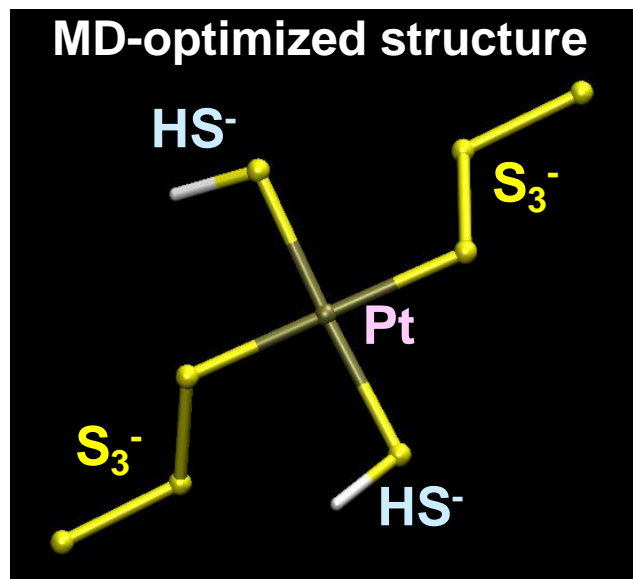
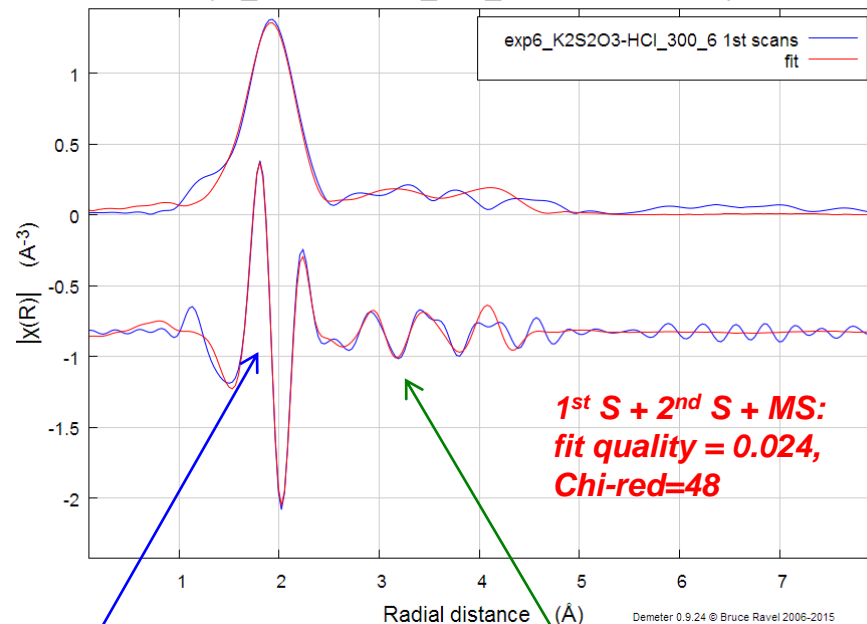


Fiting EXAFS spectra of Pt-S₃⁻ bearing solutions

exp6_K2S2O3-HCl_300_6 1st scans in R space



exp6_K2S2O3-HCl_300_6 1st scans in R space



$$R_{\text{Pt-S1}} = 2.35 \pm 0.005 \text{ \AA}$$

$$N_{\text{S1}} = 4.5 \pm 0.5 \text{ atoms}$$

$$R_{\text{Pt-S2}} = 3.50 \pm 0.05 \text{ \AA}$$

$$N_{\text{S2}} = 2 \pm 1 \text{ atoms}$$

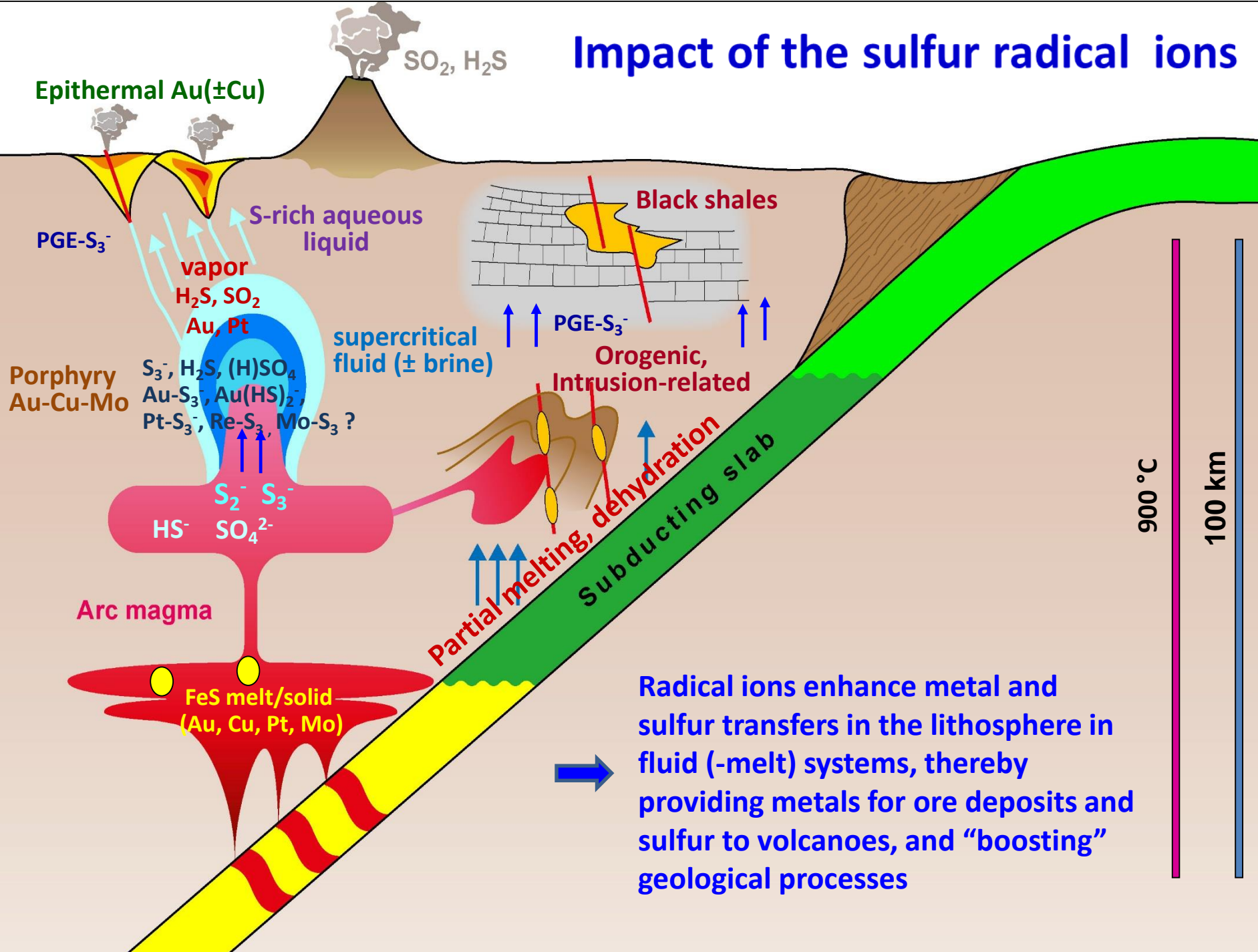


(tentative)

“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

Pespectives 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

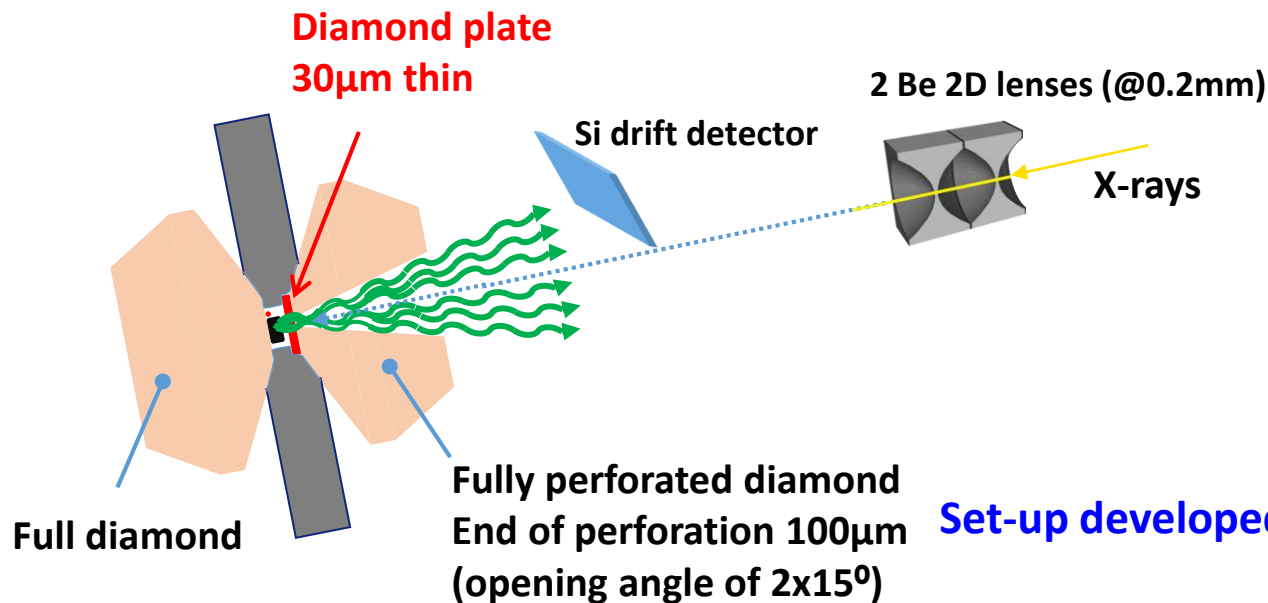
- ✓ Direct and quantitative probe of different S species fractions (in contrast to Raman spectroscopy), owing to the additive nature of the X-ray absorption signal.

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

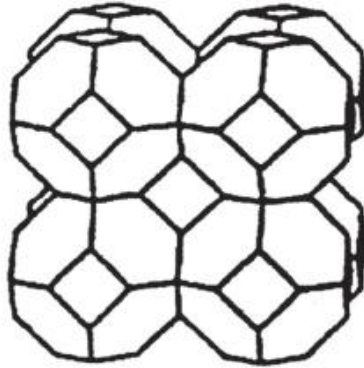
=> pressures up to 100 kbar (culet 600µm)

=> 20% transmission @ S K-edge

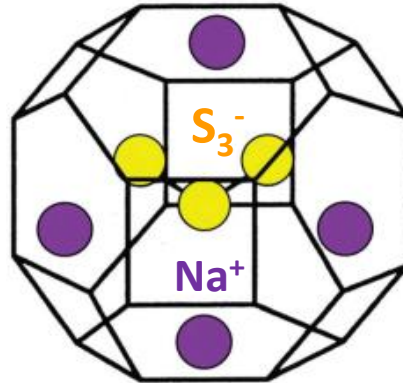
Set-up developed at ID12 beamline:

- Focalization with Be 2D lenses
- Partial Fluorescence Detection
- Helium pressure transmitting medium
- In-situ pressure measurements by ruby luminescence
- Ambient temperature conditions

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
 $\text{HS/S}^{2-}, \text{S}^0, \text{S}_3^-, \text{S}_2^-, \text{S}_n^{2-}, \text{SO}_3, \text{SO}_4$



Precious stones



Plastics



Food



Coatings

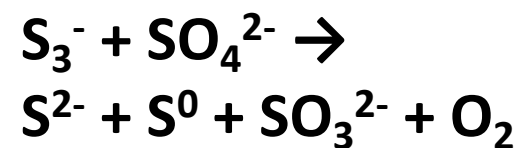
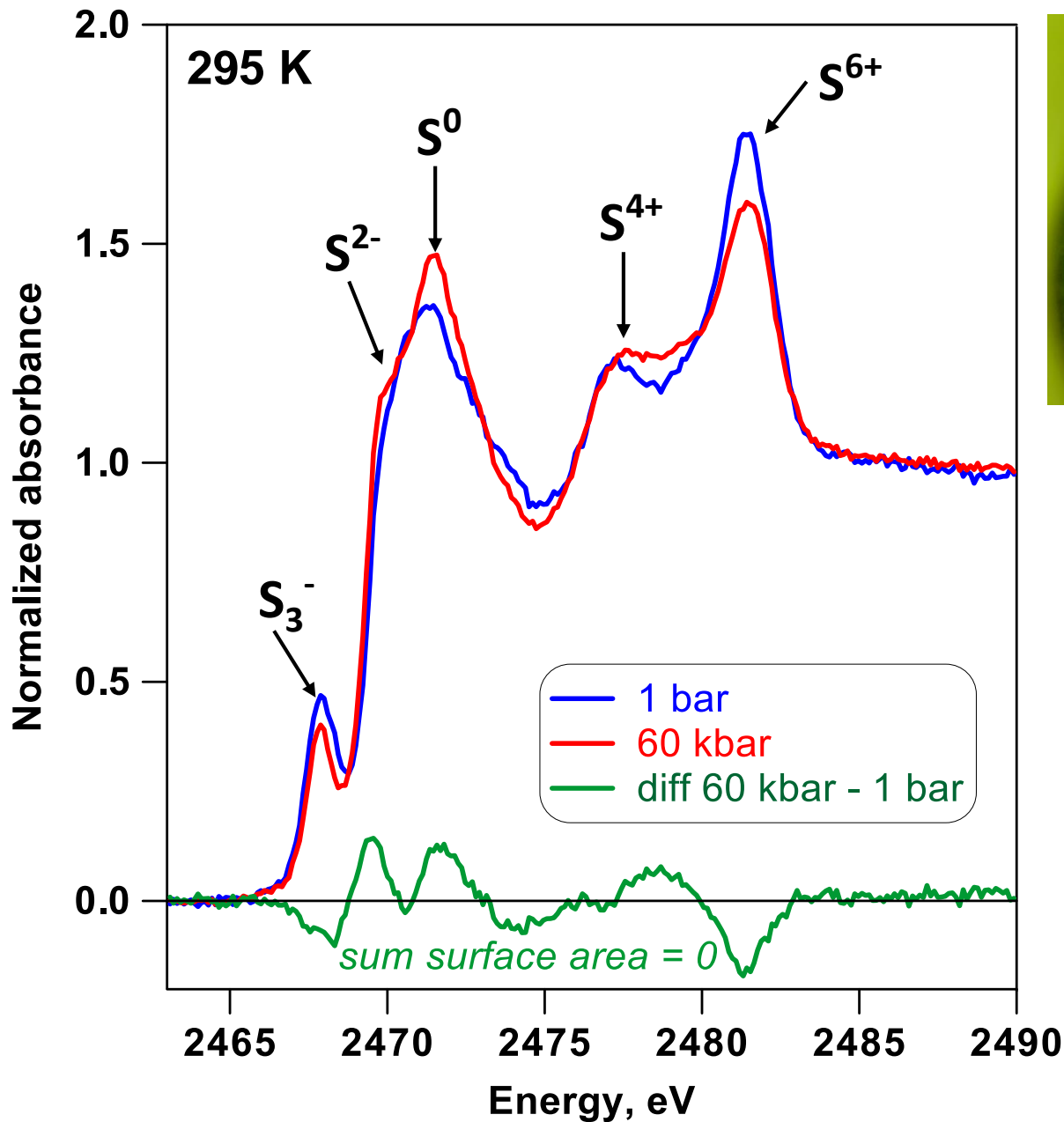


Ink



Cosmetics

Ultramarine blue under pressure at S K-edge



→ Significant sulfur redox changes under pressure

High-resolution XANES spectroscopy (HERFD) of metals in fluids at high T-P

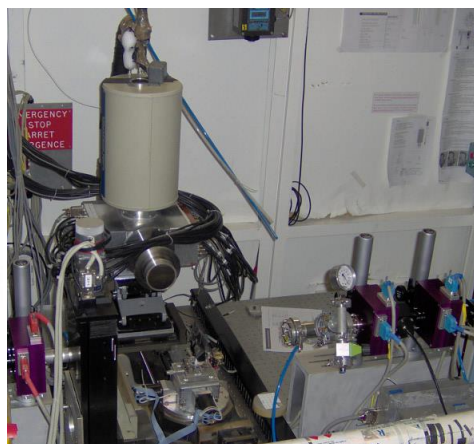
Advantages

- ✓ 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).

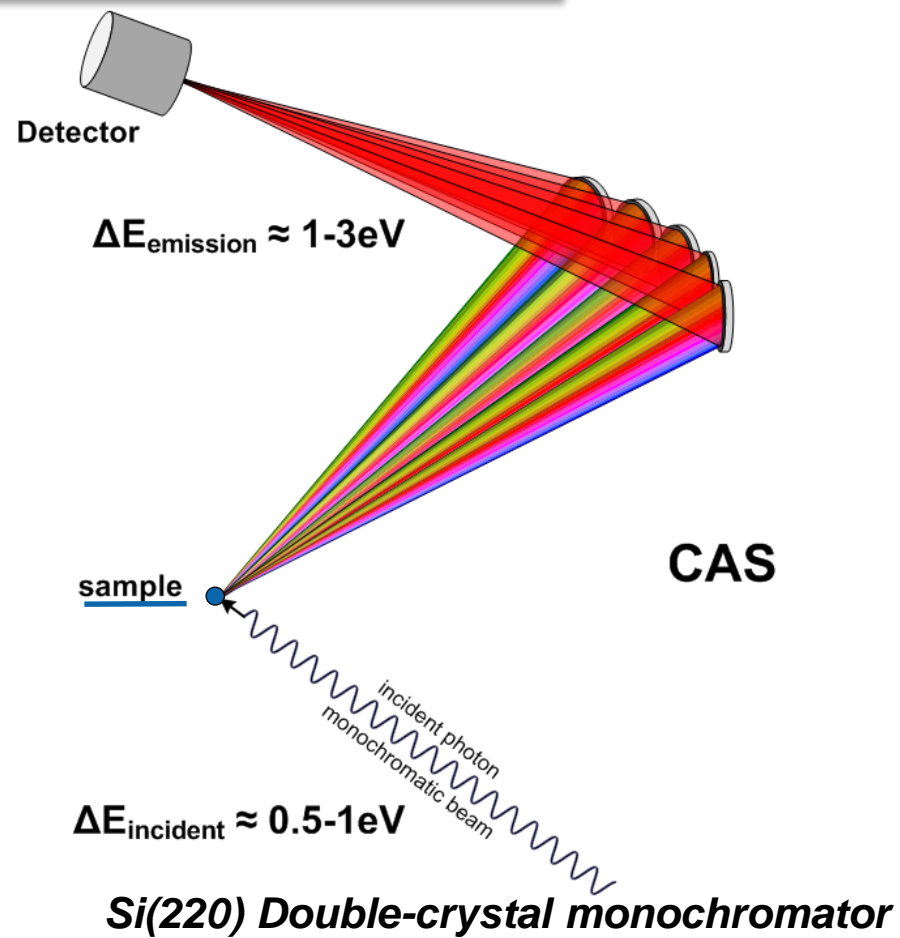
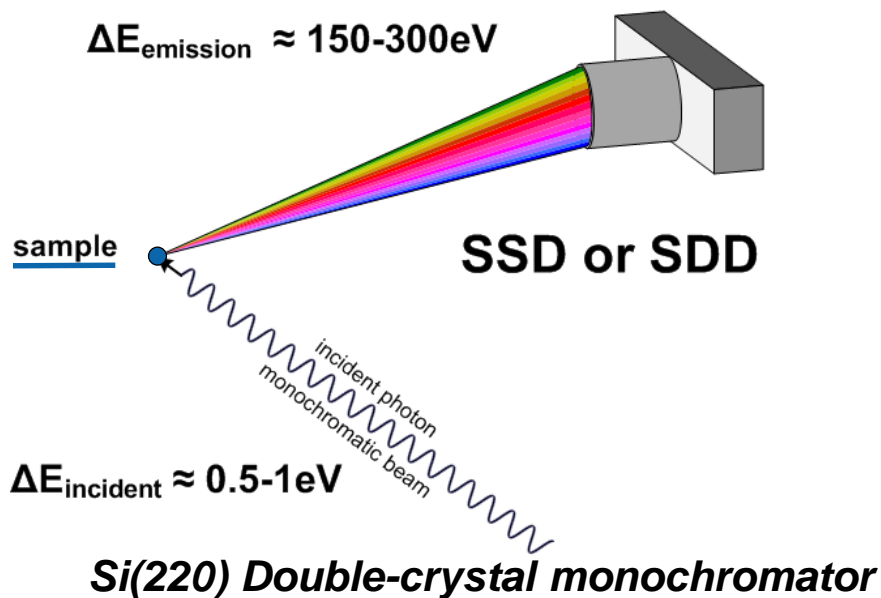
Challenges

- ❖ 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).

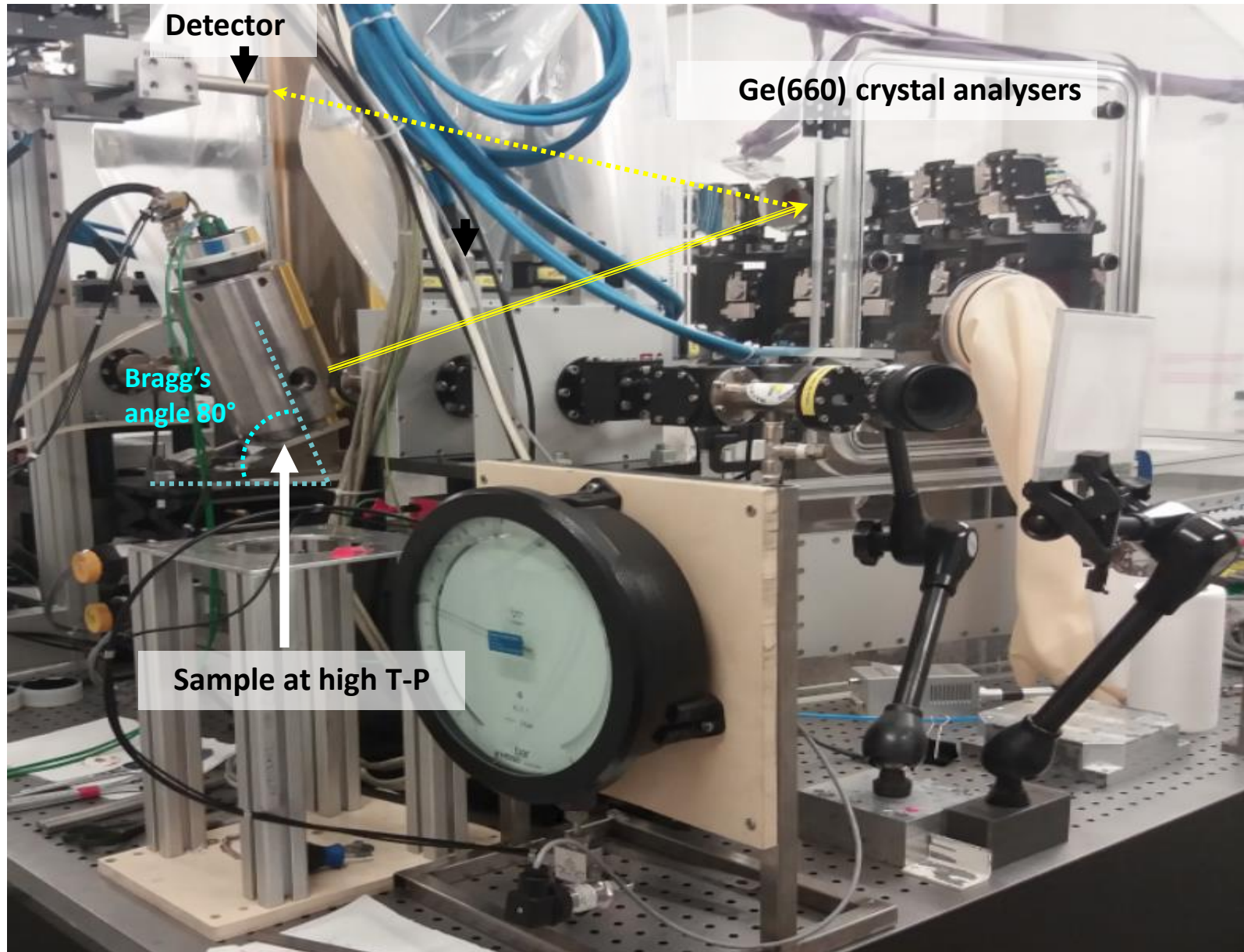
Solid-State detector vs Crystal Analyzer Spectrometer



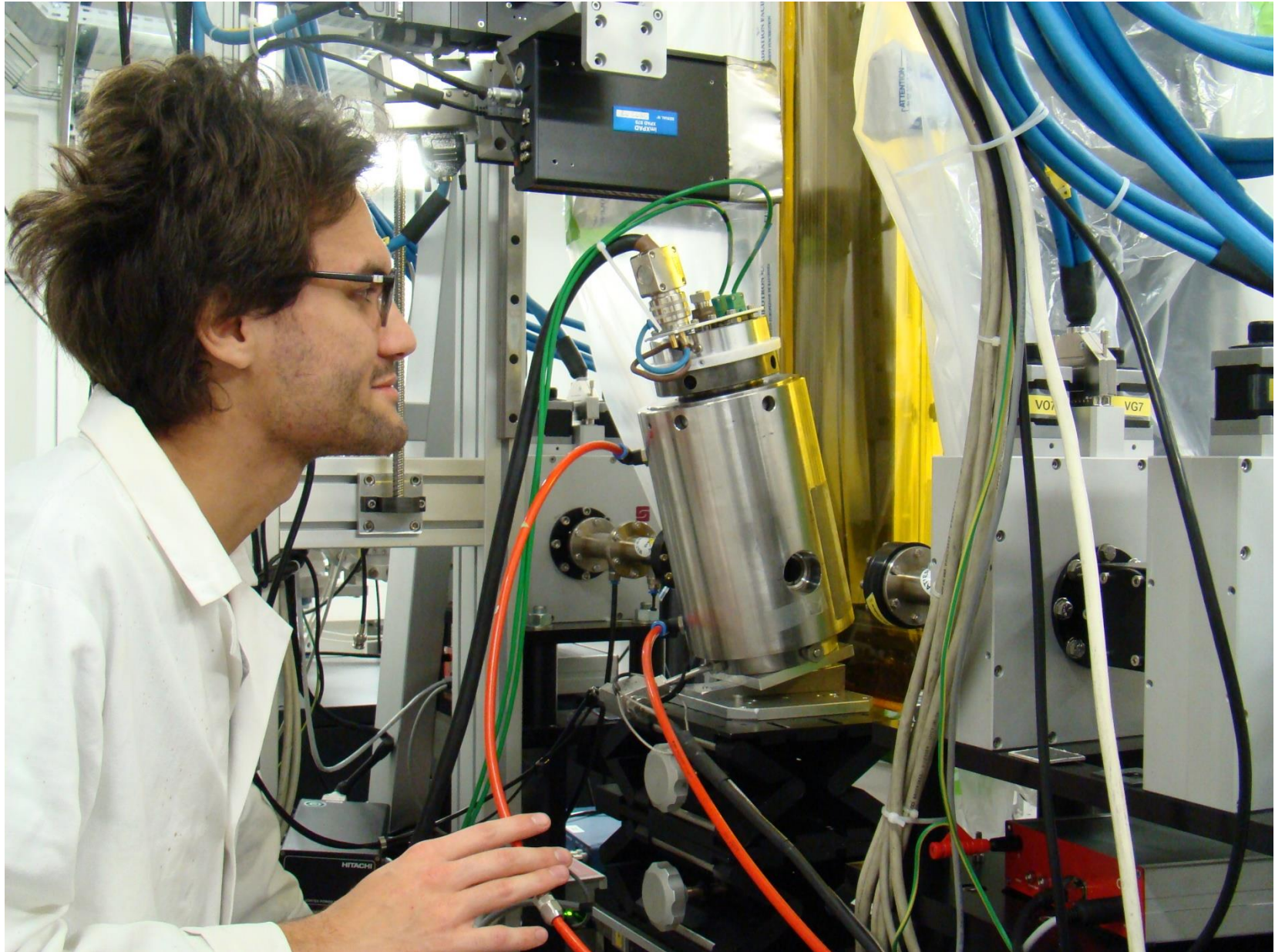
Denis Testemale's talk tomorrow



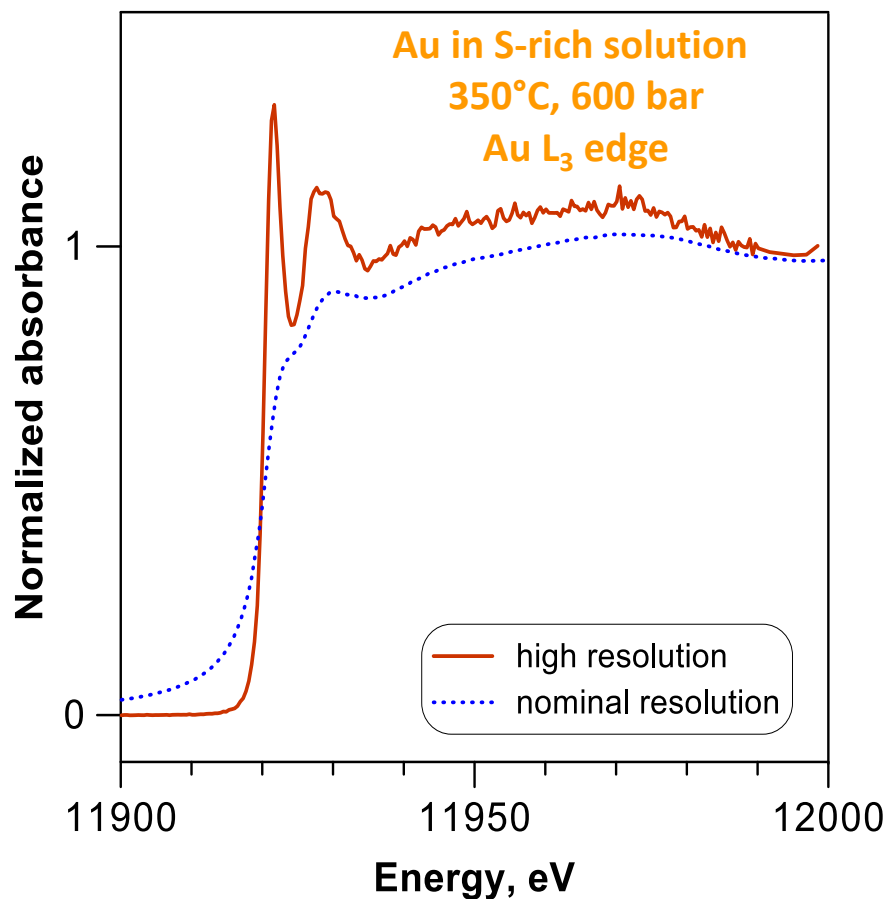
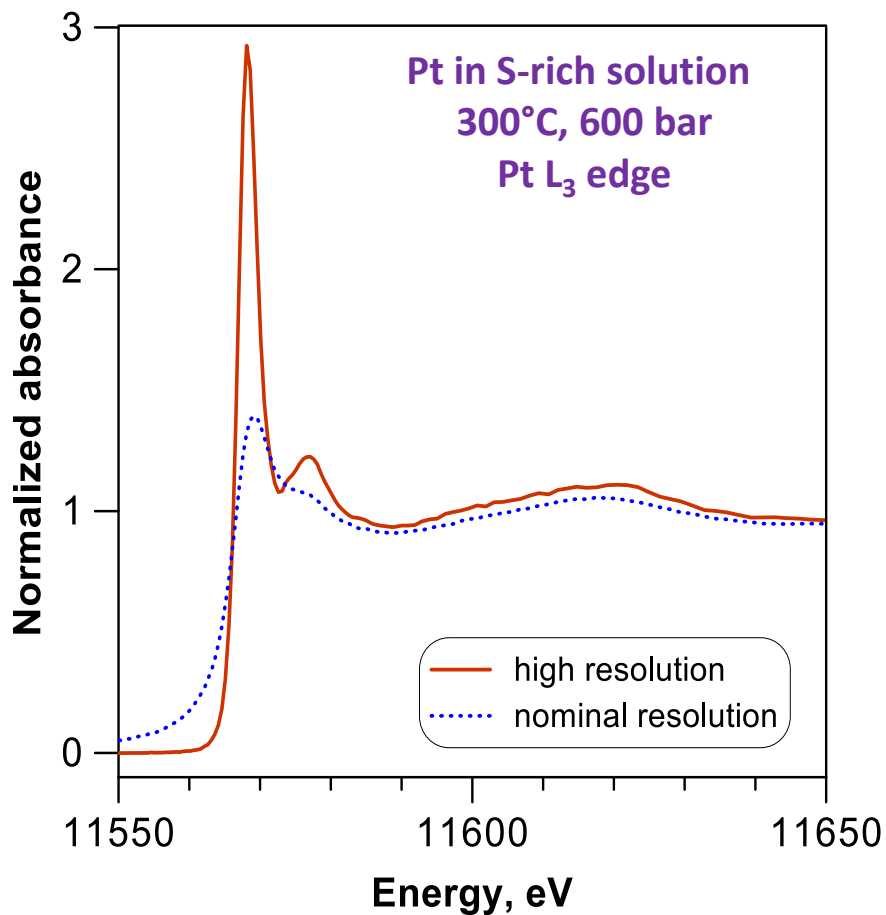
High-resolution set up and high T-P autoclave at BM16 (FAME-UHD) for studying metals in hydrothermal fluids



High-resolution set up and high T-P autoclave at FAME-UHD for studying metals in hydrothermal fluids

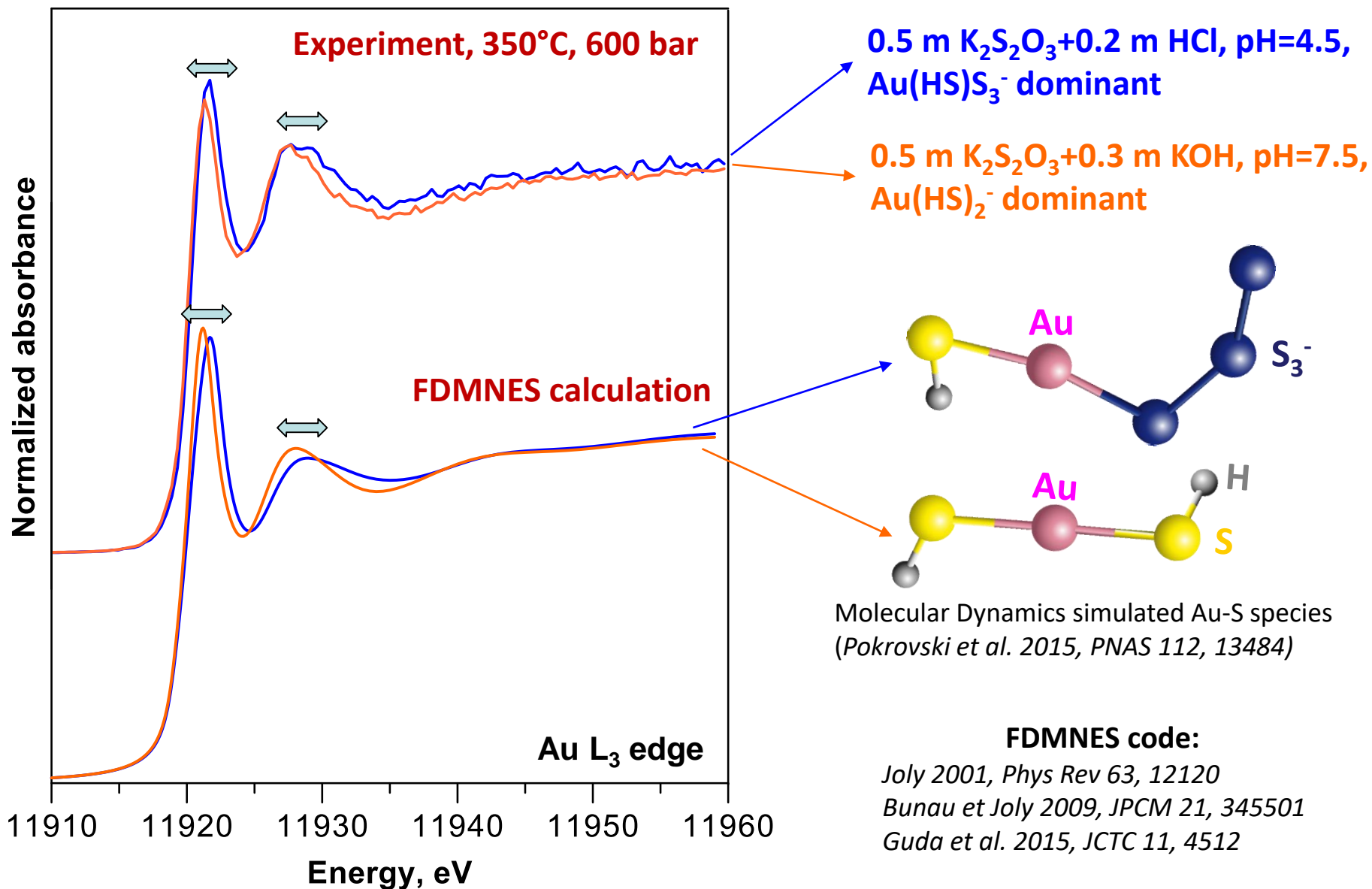


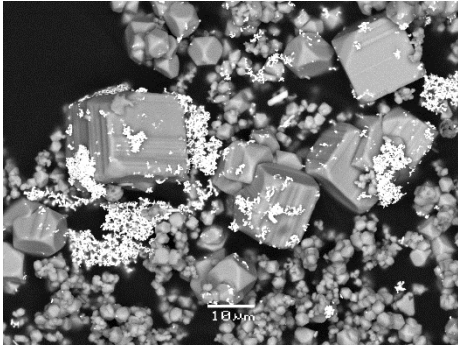
Spectacular gain in XANES spectra resolution with the HERDFD setup compared to 'classical' fluorescence mode



But... How to interpret such spectra in the absence of standards?

Interpreting HERFD XANES spectra in hydrothermal fluids using FDMNES simulations

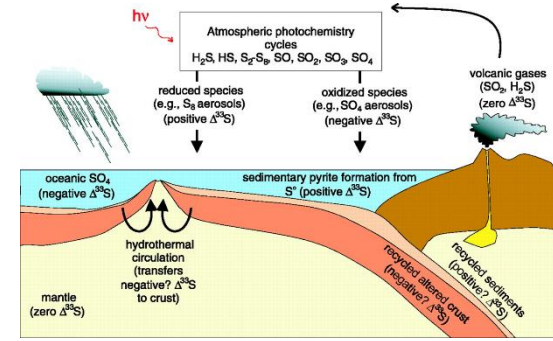




Formation of mineral resources of critical metals



Evolution of magmas, volcanic degassing

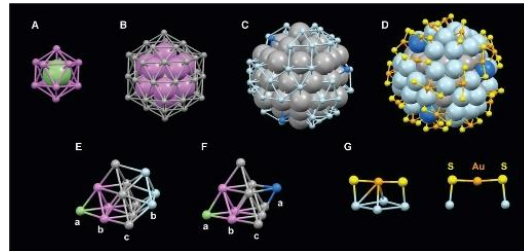


Sulfur and metal isotope tracers

Applications



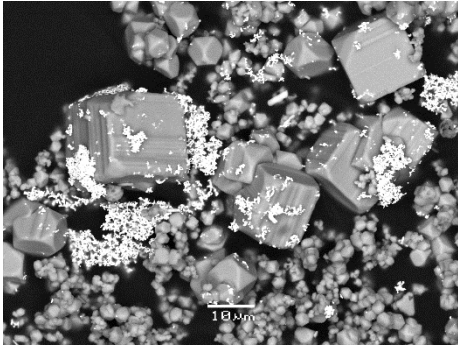
Ore prospection and processing



Hydrothermal synthesis of new nanomaterials



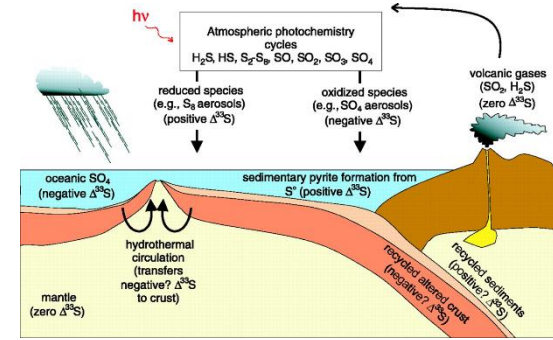
Sulfur and metals on other planets



Formation of mineral resources of critical metals



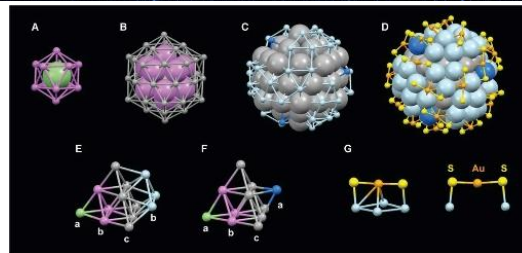
Evolution of magmas, volcanic degassing



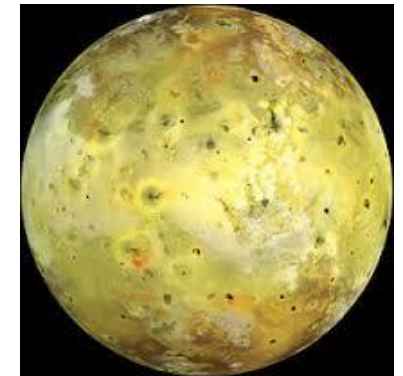
Sulfur and metal isotope tracers



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Sulfur and metals on other planets