Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.26178

Quantifying the transfers of metals and sulfur by geological fluids using in-situ spectroscopy

GLEB S. POKROVSKI[1], DR. MARIA A. KOKH, PHD[2,3], ELENA F. BAZARKINA[4], ELSA DESMAELE[5], DR. CLÉMENT LASKAR[1,6], ERIC LAHERA[7], OLIVIER PROUX[8], DENIS TESTEMALE[9,10], JEAN-LOUIS HAZEMANN[10] AND RODOLPHE VUILLEUMIER[5]

[1]Géosciences Environnement Toulouse - CNRS - Université Toulouse III
[2]Universität Potsdam
[3]Institut für Mineralogie - WWU
[4]European Syncrotron Radiation Facility, ESRF and Institut Néel
[5]Ecole normale supérieure - PSL Université - Sorbonne Université - CNRS
[6]Laboratoire de Génie Chimique - CNRS - Univ Toulouse III - INP
[7]Univ. Grenoble Alpes, CNRS, IRD, INRAE, Météo France, OSUG-FAME
[8]OSUG, CNRS-Univ. Grenoble Alpes, Saint Martin d'Hères
[9]FAME beamline - ESRF
[10]Institut Néel - CNRS - Univ Grenoble Alpes - FAME beamline - European Synchrotron Radiation Facility

Our society needs metals, but recycling alone will be unable to meet the economy growth and energy transition demand for most of them. To better manage known mineral resources and to find new ones in the Earth's crust, we need to understand their formation that is largely controlled by hydrothermal fluids. These fluids extract metals from rocks or magmas and transport and deposit them in concentrated form in the right place at the right moment, to create an ore deposit. The key point is to know the solubility and chemical speciation of metals and their ligands in the fluid phase at elevated temperatures and pressures. However, this knowledge cannot be acquired by exclusively studying minerals and ore - the natural end products of fluid reactions occurring at depth. Quantifying such fugitive metal species and complexes in a multi-ingredient hydrothermal soup requires in-situ spectroscopic approaches combined with thermodynamic analyses and molecular simulations.

In this contribution, we show how in-situ synchrotron X-ray absorption spectroscopy, coupled with other experimental and theoretical methods, has allowed us to gain a quantitative vision of the role of sulfur in the concentration and transport of chalcophile metals (Au, PGE, Mo) by hydrothermal fluids in the Earth's crust. These studies used a unique optical hydrothermal autoclave (Figure) developed and installed at FAME and FAME-UHD beamlines at the ESRF [1], along with high energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD-XAS) setups [2]. The combination of spectroscopic data with in-situ solubility measurements and molecular modeling tools allows the quantification of both identity and stability of metal complexes with the major sulfur ligands - hydrogen sulfide and trisulfur ion [3-6], enabling the construction of more accurate thermodynamic models for metal transport across the lithosphere [7].

[1] Testemale et al (2024) *High Pres Res* 44, 277.
[2] Proux et al (2017) *J Env Qual* 46, 1146.
[3] Pokrovski et al (2015) *PNAS* 112, 13484.
[4] Pokrovski et al (2021) *PNAS* 118, e2109768118.
[5] Laskar et al (2022) *GCA* 336, 407.
[6] Pokrovski et al (2022) *Am Mineral* 107, 369.
[7] He et al (2024) *PNAS* 121, e2404731121.

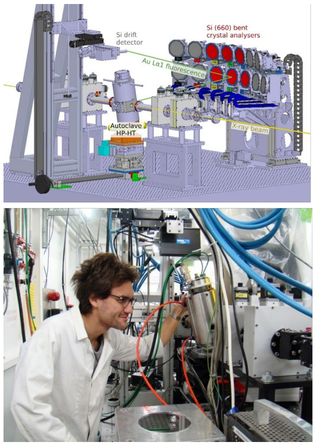

Figure. HERFD-XAS setup with a technical scheme and a photo of an experiment, at FAME-UHD (BM16) beamline at the ESRF combining a high-resolution crystal analyzer spectrometer with the hydrothermal reactor for in situ measurements of metal speciation and solubility in aqueous fluids at elevated temperatures and pressures. The autoclave is tilted from the vertical axis to match the required Bragg angle of the crystals to selectively probe the Au $L\alpha1$ fluorescence line.