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Sulfur speciation in hydrothermal fluids probed in situ by synchrotron X-ray energy-loss spectroscopy

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Sulfur is a key element in Earth's redox evolution and ore-forming processes [1]. Its rich geochemistry arises from multiple oxidation states, from sulfate to sulfide, enabling diverse redox behaviors. The intermediate redox range in hydrothermal systems is complex and difficult to investigate in situ [2, 3]. Experimental data are sparse and often cannot be compared directly, reflecting the scarcity of quantitative information on intermediate-valence and polyatomic species. Synchrotron-based X-ray absorption spectroscopy (XAS) at the sulfur K-edge (~2400 eV) – and, more rarely, at the L-edge (~160 eV) under vacuum conditions – has provided valuable insight into solid phases, yet its in situ application to fluids under hydrothermal conditions is extremely challenging. This is because the low incident photon energy of soft X-rays severely limits sample-environment design due to strong absorption by the sample cell materials. To overcome these limitations, coupled with an original spectroscopy autoclave development, we apply non-resonant inelastic X-ray scattering (NRIXS), also known as X-ray energy loss (or X-ray Raman) spectroscopy [4], which enables "indirect" access to soft X-ray absorption edges using hard incident X-rays (~10,000 eV). We probe sulfur $L_{2,3}$-edge and obtain energy-loss X-ray absorption near-edge spectroscopy (XANES) spectra of aqueous S-bearing fluids at 20 – 400°C and 300 – 600 bar. Our data reveal the coexistence of oxidized, reduced, and intermediate-valence species including polysulfides and radical ions. Complementary O and N K-edge spectra acquired at the same time both support the validity of the approach and enable further constraints to be placed on water properties such as hydrogen bonding as well as the fluid redox state. These unprecedented results demonstrate the potential of NRIXS for probing light elements under extreme conditions and highlight the overlooked role of intermediate-valence sulfur in deep geological fluids and prebiotic environments.

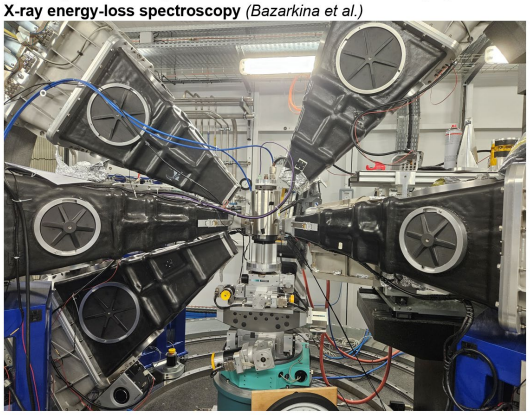
[1] Harlov, D. E. & Pokrovski, G. S. The Role of Sulfur in Planetary Processes: From Cores to Atmospheres. (Springer Cham, 2026).

[2] Pokrovski, G. S. & Dubrovinsky, L. S. *Science* 331, 1052–1054 (2011).

[3] Pokrovski, G. S. & Dubessy, J. *Earth Planet. Sci. Lett.* 411, 298–309 (2015).

[4] Sahle, C. J. et al. *High Press. Res.* 44, 337–360 (2024).

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Experimental setup for *in situ* sulfur $L_{2,3}$-edge measurements in hydrothermal fluids at ID20, ESRF (Grenoble, France). The sulfur-bearing aqueous solution at high temperature and pressure is contained within the original spectroscopy autoclave (center).