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Sulfur in hydrothermal fluids: what we don't know

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Sulfur, sulfur, sulfur... There is unlikely another volatile element that attracts so much attention and engenders so much debate among geochemists, volcanologists, magmatic petrologists, ore deposit geologists, and planetary scientists. This is because sulfur is a key element in the processes that govern the formation and distribution of ore deposits, magma evolution and degassing, volcanic hazard and isotope fractionation. For technological applications, sulfur is an important player in chemical catalysis, nanotechnology, and materials science. Critical to all these aspects is understanding the chemical speciation, transport and partitioning of sulfur in aqueous fluids typical of those natural and industrial systems, across a wide range of temperatures, pressures, and physical-chemical environments. In addition to sulfate and sulfide, commonly referred as the dominant sulfur redox states found in natural samples, suflur speciation is controlled by the coexistence of a multitude of intermediate-valence polyatomic aqueous species (Figure 1). The abundance, stability and interactions with metals of these fascinating species at elevated temperatures and pressures are among the major unknowns of sulfur geochemistry [1].

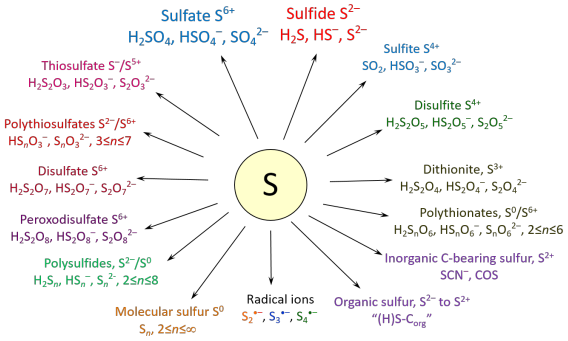

Figure 1. Chemical forms of sulfur known in aqueous solution, solid or gas phases (formal redox state of sulfur is indicated).

Nowadays, we know fairly well how to analyze total sulfur concentrations, chemical forms and isotopes in materials at ambient conditions such as natural fluid, gas, or mineral samples brought to the Earth surface and accessible to collection and observation. However, the fundamental question that yet remains unanswered is the following: do all these samples and data collected therefrom correctly reflect the true sulfur speciation and partitioning in fluid(-melt-mineral) systems at elevated temperatures and pressures? The answer to this key question requires a combination of in situ experimental and analytical approaches coupled with physical-chemical modeling. Over the last 20 years, these approaches have seen significant progress that led to paradigm changes about sulfur chemical speciation in hydrothermal fluids and its role in metal transport and ore deposit formation. These changes will be emphasized in this contribution.

[1] Pokrovski GS, Kouzmanov K, Stefánsson A (2026) Sulfur in hydrothermal fluids. In: *The Role of Sulfur in Planetary Processes: From Cores to Atmospheres,* DE Harlov and GS Pokrovski (eds.), Springer Geochemistry, https://link.springer.com/book/9783032077042