Sulfur speciation matters

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Geochemical cycling in subduction zones affects the atmosphere and sub-surface environments. Insights from experiments under relevant conditions suggest which sulfur species contribute to the formation of metallic ore deposits below arc volcanoes.

Subducting plates link the deep Earth to the near-surface environment. Chemical elements transferred from subducting plates to the magmas feeding overlying arc volcanic systems are thought to contribute to providing an atmosphere that is benign to life through geologic time. High temperature, high pressure chloride-bearing aqueous fluids, termed hydrothermal fluids, have long been suggested as a key agent in transferring elements from subducting plates to the source region of arc magmas. Sulfur transfer from a slab in aqueous fluids is thought to be particularly important because it has multiple oxidation states resulting in numerous very different aqueous sulfur species. However, identifying the S-species in high temperature-pressure fluids has been experimentally difficult. Writing in *Nature Geoscience*, Farsang and Zajacz[1] report novel experiments establishing the main sulfur species in an aqueous fluid at magmatic arc conditions to be sulfur dioxide, hydrogen sulfide (H_2S), and bisulfide (HS^-).

It has long been established that volcanic arc magmas produce lavas that are more oxidized than those generated at the mid-ocean ridges. As a consequence, arc volcanoes degas species including sulfur dioxide or sulfate, instead of more toxic compounds such as methane (CH_4) or hydrogen sulfide. Furthermore, arc magmas are often associated with large copper sulfide ore deposits termed porphyry copper deposits. These ore deposits have been the main source of the world's

copper for over a hundred years. The origin of porphyry copper deposits involves the role of magmatic hydrothermal fluids in transporting copper and sulfur to form deposits in the subsurface below arc volcanoes. However, the principal sulfur species in hydrothermal fluids at magmatic conditions have been controversial.

For decades, thermodynamic modelling and solubility experiments have been used to predict sulfur species and their complexes in both low and high pressure environments. The properties of these species were extrapolated to elevated temperatures and pressures using equations of state. However, in situ documentation of sulfur species was limited, owing to the complexities of controlling the oxidation state and pH in experiments. Starting in 2011, the sulfur species S^{2-} and S^{3-} were reported from in situ experiments and the S^{3-} species was subsequently suggested to be of major importance in subduction zone fluids and in hydrothermal fluids forming ore deposits of platinum and gold[2–4]. However, concern has arisen that the importance of S^{3-} has not been reliably demonstrated experimentally[5].

Farsang and Zajacz[1] use a new experimental apparatus to identify the sulfur species in re-heated synthetic hydrothermal fluid inclusions in situ. The oxidation state of the fluids in the experiments was varied to investigate the nature of oxidizing versus reducing sulfur species at fixed temperature and pressure. The solubility of gold under variable redox conditions was also assessed. The novelty of these experiments lies in the use of a saline (NaCl) fluid and control of the oxidation state. In addition, Farsang and Zajacz[1] use in situ analysis of the synthetic fluid inclusions using Raman spectroscopy — a vibrational spectroscopic technique used to identify the species present — with specially chosen wavelengths. This revealed very low concentrations of the sulfur species S^{2-} and S^{3-}; instead, the sulfur species detected were SO_2, H_2S, and HS^- at 875 °C and 2.0 kbar (Fig. 1a). At the lowest oxidation states studied, represented by values of ΔNNO of 0.0 to −1.0, H_2S and HS^- were predominant, and these correlated with the highest solubilities of gold,
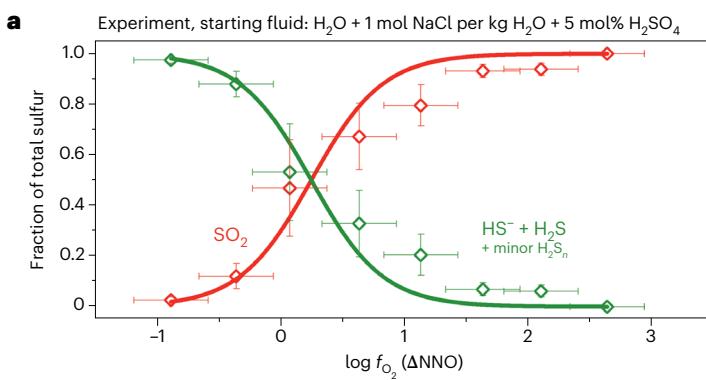

Fig. 1 | Comparison of the sulfur speciation in a magmatic arc hydrothermal fluid and in a deep subduction zone fluid as a function of oxidation state. **a**, Experimentally determined S-speciation[1] at 875 °C and 2.0 kbar as a function of oxidation state represented by the index ΔNNO. **b**, Model prediction of S-speciation[6] at 650 °C and 30.0 kbar as a function of oxidation state represented
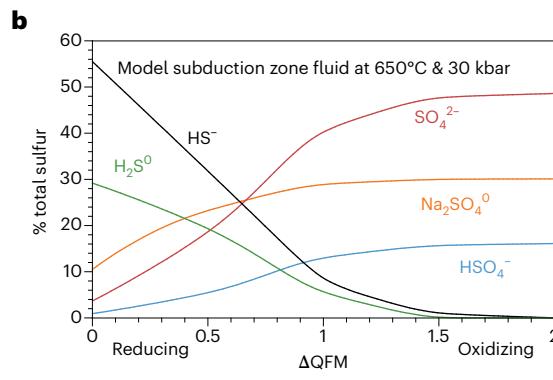
by the index ΔQFM. In both figures, oxidation state increases on the *x* axis. The indices ΔNNO and ΔQFM represent similar oxidation states. At the highest oxidation states shown, the sulfur species in the lower pressure magmatic fluid is completely different to the expected species in the subduction zone fluid. Part **a** adapted from ref. 1, Springer Nature Limited.

strongly suggesting gold complexes with HS^-. At high oxidation states, represented by values of ΔNNO of +1.0 to +3.0, SO_2 was predominant.

The high temperature, low pressure, and NaCl content of the current experimental study serve as a model of a magmatic arc hydrothermal system relevant to hydrothermal ore deposits. Knowledge of the sulfur speciation in hydrothermal ore-forming fluids is of paramount importance in assessing the abilities of such fluids to transport critical metals such as copper, which can govern the potential size and richness of a porphyry copper ore deposit. The most reducing fluids studied carried both H_2S and HS^-, relevant to possible metal transport in magmatic hydrothermal ore deposits.

However, the relative amounts of HS^- established in the experiments are surprisingly higher than predicted by thermodynamic models[1]. It is possible that HS^- in the experimental fluids was stabilized by Na^+ as a complex, or, substantially ionized at the particular pH of the experiments, which was not controlled. The issue of pH certainly needs more investigation. Such experiments would enable recalibration of the thermodynamic properties of HS^-, and most importantly connect sulfur speciation to variations in the silicate mineral assemblages found in natural systems. Finally, at subduction zone temperatures and pressures, and in equilibrium with a simple pH buffer (K-feldspar+muscovite+coesite) conditions are more favourable to ionic species (Fig. 1b). Here, it can be seen that at high oxidation states represented by values of ΔQFM (a similar index of oxidation state as ΔNNO) of +1.0 to +2.0, several sulfate species are predicted to be predominant[6].

Overall, the current study of sulfur species at magmatic hydrothermal conditions has newly demonstrated the importance of SO_2, H_2S, and HS^- relative to the previously recognized species S^{2-} and S^{3-}. This result has important implications for metallic hydrothermal ore deposits related to arc magmatism and the sulfur species emitted at volcanic arcs. The study lays the foundation for connecting sulfur speciation in hydrothermal fluids and the complexities of fluctuations of temperature, pressure, oxidation state, and pH relevant to natural mineral assemblages and the origins of metallic ore deposits.

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