



## Fluid speciation controls of redox-sensitive non-traditional stable isotope systems

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The classic study of Ohmoto (1972) on the sulfur isotope system demonstrated that mass-balance among reduced and oxidized solution species potentially exerts a strong control on the isotopic composition of hydrothermal sulphide ore minerals. In the present study, we extend this approach to redox-sensitive non-traditional stable isotope systems. In such systems, significant isotopic fractionation occurs between reduced and oxidized species ( $\sim 3$  to  $12\text{\textperthousand}$ ), with the heavy isotope being enriched in the oxidized species. The fluid speciation calculations are first applied to copper isotopes in the sedimentary and hydrothermal Cu-S-H<sub>2</sub>O-Cl system. The basic model assumptions are that the  $\delta^{65}\text{Cu}$  values of Cu-sulphides reflect the isotopic composition of the Cu(I) species in the solution, and the mole fraction and type of Cu(I) solution species (CuCl, CuCl<sub>2</sub><sup>-</sup> and CuCl<sub>3</sub><sup>2-</sup>) is a function of thermo-chemical variables (Eh, pH, T and aCl). Under thermo-chemical conditions where the Cu(I) complex is the dominant species in solution (>99%), the  $\delta^{65}\text{Cu}$  of the copper sulphide will reflect that of the bulk solution. However, as the Cu(I) complex becomes less abundant relative to Cu(II) solution species (e.g., Cu<sup>++</sup>, CuCl<sup>+</sup> and CuCl<sub>2</sub>), the isotopic composition of the copper sulphide becomes lighter with respect to the bulk solution, as the heavier isotope becomes concentrated in the oxidized species. In Eh-pH diagrams the size of the Cu(I) chloride species field governs the extent to which copper sulphides will have the bulk solution  $\delta^{65}\text{Cu}$  value. Thermodynamic calculations using GWB.4 database and software show that as aCl<sup>-</sup> increases, the [Cl]/[Cu] ratios of copper chloride complexes increases, and also that the Cu(I) chloride complexes become increasingly dominant in solution. Likewise, at higher temperatures the Cu(I) complex becomes more dominant and at hydrothermal temperatures >200°C, it occupies almost all of the water stability field. Thus, as a result of higher aCl<sup>-</sup> values and temperatures, the isotopic composition of the reduced complex and that of the precipitated Cu-sulphide, becomes closer to that of the bulk isotopic composition for a wide range of redox conditions. The dominance of Cu(I) complexes at high temperatures may contribute to the relative uniform  $\delta^{65}\text{Cu}$  values of primary copper minerals from igneous and hydrothermal systems.

The fluid speciation approach can also be applied to other redox sensitive systems such as those of Mo, Cr and Se. Certain systems show very sharp redox boundary. This is the case of the Mo-S-H<sub>2</sub>O system, which will show complete mass transfer at the MoO<sub>4</sub> to MoS<sub>4</sub> boundary. No fractionation will be observed between the MoO<sub>4</sub> and MoS<sub>4</sub> species, unless the system is H<sub>2</sub>S limited ( $[\text{H}_2\text{S}] \leq 30\mu\text{M}$ ). Other systems (e.g. Cr-Cl-H<sub>2</sub>O and Se-SO<sub>4</sub>-H<sub>2</sub>O) show broader redox transitions, which can be used to quantify reduction and as paleoredox tracers.

Ohmoto, H., 1972. Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. *Economic Geology*, 67(5): 551-578.