

Chlorine isotope fractionation during metal-chloride complexation: Implications for metallogenic processes

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Ore-forming hydrothermal fluids transport metals in the Earth's crust by forming complex ionic and molecular species involving ligands such as Cl⁻, HS⁻, and OH⁻ (Seward et al., 2014) [1]. The most important of these ligands is Cl⁻, which in HSAB theory is a borderline base that can be complexed with both hard and soft cations (metal ions). Thus, its behavior during complexation is of great importance for understanding metal mobilization by hydrothermal fluids (e.g., Williams-Jones and Migdisov, 2014[2]). In order to quantify the extent of chlorine isotope fractionation in hydrothermal fluids, we have investigated the behavior of aqueous Zn²⁺, Pd²⁺, Cu⁺, Ag⁺, Au⁺, Ni²⁺, Pb²⁺, Fe²⁺-chloride complexes at elevated temperature and pressure.

The complexes with higher Cl⁻/cation molar ratios have smaller reduced isotopic partition function ratio (i.e., β -factors), preferring to enrich the light isotope (³⁵Cl) in the complexes. For the same metal-chlorine complex configuration but differing coordination number (CNs), the metal-chlorine bond length increases with an increase in the coordination number (CNs), resulting in a decrease in the 1000ln β value. Furthermore, a comparison of the fractionation of chlorine isotopes in CuCl(H₂O) and CuCl(HS) reveals that sulfur donor ligand systems with longer bonds have lower 1000ln β values, which is in good agreement with results of the study of Fujii and Albarede (2018)[3].

The metal-chloride complexes in hydrothermal fluids vary depending on temperature, pressure, pH, salinity and redox state. This study helps explain the variability of chlorine isotopic compositions of fluid inclusions in ore deposits.

[1] Seward, T. M., William-Jones, A. E., Migdisov, A. A. (2014). *Treatise on Geochemistry* (Second Edition) (ed. K. K. Turekian). Elsevier, Oxford. 29-57.

[2] Williams-Jones, A. E., Migdisov, A. A. (2014). *Society of Economic Geologist, Special Publication*, 18, 77-95.

[3] Fujii, T., Albarede, F. (2018). *Geochimica et Cosmochimica Acta*, 234, 37-49.