

Accurate bromine isotope analysis and implications of multiple isotope tracers for origin and evolution of rare metal resources in hydrothermal brines in Tibet

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Halogens are major anions in geological fluids and natural waters, and their isotopes (e.g. $\delta^{37}\text{Cl}$, $\delta^{81}\text{Br}$) together with other geochemical tracers are indicative of fluid sources, water-rock interactions, and magmatic and hydrothermal processes [1]. In an attempt to identify the origin and evolution processes of abundant rare metal resources (e.g. Li, Rb, Cs) in hydrothermal brines in typical tectonic belts (Tibet Plateau, China), a preliminary investigation using multiple geochemical tools is carried out in this work. A two-stage ion exchange procedure is established for effective bromine separation from various geological matrices (e.g. brines, hydrothermal springs, evaporites and river water). The external reproducibility better than $\pm 0.10\%$ is achieved with modified bromine isotope analysis procedure by MC-ICP-MS. The evaluation on potential diffusive bromine isotope fractionation shows that the Br isotope fractionation factor of $\alpha_{\text{NaBr-HBr}}$ increases from 1.0001 to 1.0141, associated with around ~28% Br loss in aerosol when changing the cation from Na^+ ions to H^+ ions. It would be due to the higher diffusion coefficient of $3.15 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ for HBr than that of $1.48 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ for NaBr in solution [2].

An extraordinarily high bromine abundances (generally higher than 0.5 mg/L) in hydrothermal springs in this area are observed, which is several orders of magnitude higher than that in seawater and surface water in nature ([Br] of 0.05-55 $\mu\text{g/L}$). The boron isotopes display depleted $\delta^{11}\text{B}$ values from -21.3 ‰ to -8.4 ‰. Taking all evidence together, we suggest that the abundant rare metal resources were likely derived from residual magmatic fluids of crustal partial remelting.

[1] Eggenkamp et al. (1995) *Geochim. Cosmochim. Acta* 59, 5169-5175. [2] Eggenkamp et al. (2009) *Geochim. Cosmochim. Acta* 73, 3539-3548.