

Equilibrium Tl isotope fractionations of minerals and the constraint on late-veneer

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Thallium (Tl) isotope system can be used as a high-precision isotopic tracer. The variations of Tl isotope composition for terrestrial samples are around 35 $\epsilon^{205}\text{Tl}$ and are thought to be produced by equilibrium fractionation effects, kinetic isotope effects, or the decay of short-lived ^{205}Pb to ^{205}Tl in the early solar system. Equilibrium Tl isotope fractionations include the traditional mass-dependent effect and the nuclear volume effect (NVE). It has been suggested that the magnitude of mass-dependent fractionation is only about a quarter of total isotope fractionation at room temperature. Under high temperature, the NVE dominates the total isotope fractionation. It was found that the ferromanganese sediments concentrate ^{205}Tl most among terrestrial samples (+15 $\epsilon^{205}\text{Tl}$). The reason for the positive anomaly is that Tl^+ is oxidized to Tl^{3+} when manganese oxides absorb Tl^+ from seawater into the vacancy of minerals. We find that the NVE-driven fractionations during the process of exchanging and oxidizing Tl^+ reach 9.57 $\epsilon^{205}\text{Tl}$ through the first-principles based calculation, which explains the positive experimental data. Many Tl-bearing minerals have been calculated here. Among them, the sulfides are generally enrich heavier Tl isotopes than silicates, such as Fe-micas and feldspar. Experimental results indicated that there could be 0.2-0.3 $\epsilon^{205}\text{Tl}$ unit fractionation between sulfides and silicates at 1650°C during the differentiation process. The value of the measurement is consistent with our calculation results of fractionation factors in the range of 0.17 to 0.38 for the coexisting phases of sulfide and silicate. In addition, Tl concentration in bulk silicate Earth (BSE) can constrain the contribution of late veneer. Because the similar Tl isotopic signal between terrestrial samples and chondrites indicates fairly no fractionation during evaporation, we consider that the total content of Tl in the modern BSE derived from the process of late veneer. As a result, the Tl content could challenge the magnitude of late veneer which had been constrained by the amount of highly siderophile elements in BSE. It shows that may need more materials to be delivered in late veneer processes.