

Kinetic Si isotope fractionation parameters in weathering processes

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The silicon element, only second in abundance to oxygen in Earth's crust, is one of the most dominant constituents in silicates. However, there are many unexplained observations about Si isotope distributions in Earth's surface systems (i.e., in soil, water or plants) (Opfergelt and Delmelle, 2012). For example, the deduced Si isotope equilibrium fractionation factors by Rayleigh model at ambient temperature between clay and the solution $\Delta^{30}\text{Si}_{\text{clay-solution}} = -1.5\text{‰}$ (Georg et al., 2007) and -2.05‰ (Hughes et al., 2013) obviously disagree with common sense, which dictates that stiffer chemical bonds will enrich heavier isotopes, i.e., the precipitated minerals will preferentially incorporate heavy isotopes relative to aqueous H_4SiO_4 due to their shorter Si-O bonds. Another similar case is the fractionation between quartz and solution. Most field observations suggested that solution will be enriched with heavier Si isotope compared to quartz (e.g., Douthitt, 1982; Basile-Doelsch et al., 2005), conflicting to the fact that quartz is the one with much shorter Si-O bonds than aqueous H_4SiO_4 (ca. 1.610\AA vs. 1.639\AA).

Those strange Si isotope behaviors can be explained by knowing basic Si isotope fractionation parameters related to equilibrium and kinetic processes of Si cycling in surface systems. This study will focus on providing the most important Si kinetic isotope fractionation (KIE) factors associated with the formation of amorphous quartz and other secondary minerals in hydrolysis, polymerization, co-precipitation and adsorption processes. Previous studies (e.g., Geilert et al., 2014) probably could not distinguish the above processes and assigned their net fractionation results to a single cause. The lacking of Si KIE factor has limited further investigation of Si isotope distributions at surface systems. For natural Si weathering processes, hydrolysis, polymerization, co-precipitation and adsorption processes are happened simultaneously in one system. Therefore, without the knowledge of KIE of these coupled or competing pathways, we cannot quantitatively evaluate the net Si isotope fractionation during such complicated process and cannot discover the dominant driving forces of isotope fractionation. With the basic KIE factors provided here, Si isotope method can be significantly improved for the investigation of Si isotope variations in natural environments.