

Silicon Isotope Fractionation During Weathering and Soil Formation: Experimental Results

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"The behavior of silica in water solutions at low temperatures remains one of the most stubborn problems of geochemistry". Despite great progress, these words written by K.B. Krauskopf in 1956 are still true today. When released by weathering, Si is soluble in water but also takes part in a number of inorganic and biologically mediated reactions that lead to secondary precipitates. Knowledge of the Si-isotopic fractionations that take place as Si moves from primary minerals to secondary minerals, biotic products and river water will provide greater specificity to our understanding of the global Si-cycle. Previous applications of silicon stable isotope geochemistry to Si behavior in marine environments (Douthitt, 1982; Ding *et al.*, 1996; De La Rocha *et al.*, 1997), for example, provided better understanding of silicic acid utilization by diatoms, and its spatial and temporal correlation with water-depth, latitude, and past glaciations. On continents, a limited set of measurements suggest that Si-isotopes will help in quantifying the contribution of terrestrial ecosystems to the global biogeochemical Si-cycle. This is of immense importance as we do not understand why dissolved Si in rivers and oceans (+0.4 to +3.4‰) has such a fundamentally different $\delta^{30}\text{Si}$ composition than igneous and metamorphic rocks (-1.1 and +0.4‰) (De La Rocha *et al.*, in press; Ding *et al.*, 1996, 1997). In order to produce a 'positive ocean' from 'negative continents', a major fractionation must take place during the transformation from crystalline Si in rocks to dissolved riverine and marine Si, which also must lead to a residual product with even more negative $\delta^{30}\text{Si}$ values than the parent rocks. Empirical studies by Ding *et al.* (1996, 1997) and Douthitt (1982) demonstrate that weathering-related clay minerals and phytoliths have the most negative surface terrestrial $\delta^{30}\text{Si}$ values (-2.3 to +1.8‰ and -2.2 to +2.8‰, respectively). Aluminosilicate clays and opal phytoliths are the most likely residual products, but their role in Si-isotope fractionation has not been demonstrated on an experimental level.

The main goal of our research is to characterize Si-isotopic fractionation during the partitioning of primary mineral Si into soil clays, phytoliths, and leaching water. In order to determine the magnitude and direction of possible Si-isotopic fractionations, we synthesized clay minerals and phytoliths under controlled conditions. The $\delta^{30}\text{Si}$ values of the clay minerals, phytoliths, and the reaction waters are being monitored.

Allophane ($x^*\text{SiO}_2/y^*\text{Al}_2\text{O}_3/z^*\text{H}_2\text{O}$), a ubiquitous non-crystalline soil mineral, was synthesized at 90 °C and 54% of the initial Si was incorporated into the solid. The source Si has a preliminary $\delta^{30}\text{Si}$ value of -0.88‰. The allophane and the final solution have $\delta^{30}\text{Si}$

values of -1.22‰ and +0.57‰, respectively. Thus, allophane preferentially removes ^{28}Si from solution, enriching the remaining solution in ^{30}Si . The equilibrium fractionation factor α for the system allophane-water is 0.9982; for Rayleigh type fractionation 0.99753. These values compare well with those previously established for opaline marine diatoms (average $\alpha=0.9989$; De La Rocha, 1997), and also with that determined by Li *et al.* (1994) for the precipitation of SiO_2 from monosilicic acid $\text{Si}(\text{OH})_4$ (0.990 to 0.996). Characterization and analyses of solutions and precipitates from a controlled kaolinite synthesis experiment at 25 °C are in progress and will be presented at the meeting.

Opaline phytoliths were synthesized by growing corn and wheat plants in growth-chambers at 29 °C. They were grown in hydroponic solutions that provided a constant supply of Si with a $\delta^{30}\text{Si}$ value of -0.19‰. Phytoliths $\delta^{30}\text{Si}$ values from corn and wheat leaves range between -0.82‰ and -1.82‰. These preliminary results show that biogenic opal formation fractionates Si-isotopes by depleting its parent solution in ^{28}Si . The preliminary $\alpha_{\text{opal-water}}$ is 0.9990 for equilibrium fractionation, and 0.9961 assuming kinetic Rayleigh-type fractionation.

These experimental results demonstrate that the mechanism involved in clay mineral and opal formation do, indeed, fractionate Si-isotopes. Furthermore, the fractionation is in the direction required for explaining the observed isotopic difference between Si fixed in rocks and dissolved Si in waters. They also allow us to hypothesize that in terrestrial weathering systems, we should see opposite $\delta^{30}\text{Si}$ -trends of soil minerals (negative) and soil waters (positive). Those trends should become more pronounced with increasing weathering intensity and soil age. We are testing this hypothesis by sampling minerals, opal phytoliths and stream water from different age landscapes, and hence different weathering intensities.

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