The effect of Al on Si isotope fractionation investigated by silica precipitation experiments

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ABSTRACT

Mass-dependent isotope fractionation occurring during precipitation of solids in low-temperature environments often depends on precipitation rate. Using a series of precipitation experiments in which continuous precipitation and dissolution of Si solids is forced by daily cyclic freezing (solid formation) and thawing (solid re-dissolution), we show this dependence. We conducted six Si precipitation experiments for about 120 days with initial dissolved Si concentration of 1.6 mmol/l Si, at pH values between 4.5 and 7, with additions of 0.1–1 mM of dissolved aluminum (Al), and in the absence of Al. During all experiments increasing amounts of an X-ray amorphous silica-containing solid are formed. No Si isotope fractionation occurs during formation of almost pure Si solids, interpreted as an absence of Si isotope fractionation during polymerization of silicic acid. Si isotope fractionation occurs only in the high-Al concentration experiments, characterized by an enrichment of the light Si isotopes in the solids formed early. With ongoing duration of the experiments, a re-dissolution of these solids is indicated as the Si isotope value of the complementary solution shifts to lighter values and eventually reaches near-initial compositions. Hence, our high-Al experiments are characterized by a gradual shift from a regime that is dominated by unidirectional kinetic isotope fractionation with solids formed that are up to 5‰ lighter in their $^{30}Si/^{28}Si$ ratio than the corresponding solution, to one of steady-state between dissolution and precipitation with the $^{30}Si/^{28}Si$ ratio of the solid being almost identical to the solution ($\Delta_{solid\,-\,solution} \approx 0$). This suggests that the enrichment of light Si isotopes found in natural environments is caused exclusively by a unidirectional kinetic isotope effect during fast precipitation of solids, aided by co-precipitation with Al phases or other carrier phases (e.g. Fe(III)). By contrast, during slow precipitation, or in the absence of a carrier phase like Al, no Si isotope fractionation is expected and solids obtain the composition of the ambient fluid.

1. Introduction

Ratios of stable isotopes of Si have emerged as a powerful proxy to distinguish the reactions involved in low-temperature water–mineral and water–rock interaction. The isotope ratios potentially trace the way Si is released from Si-bearing solids into soil and (diagenetic) interstitial solutions. Si isotopes also trace how silica is precipitated into secondary solids from these solutions. Given the useful information that Si stable isotopes provide along this pathway, the resulting isotope ratios have been increasingly explored as a tool to trace silicate weathering, sediment diagenesis and the associated silicification, precipitation of siliceous sediments from hydrothermal vents, and the genesis of Precambrian cherts and banded iron formation (e.g. Ziegler et al., 2005a; Robert and Chaussidon, 2006; Steinhoefel et al., 2009; van den Boorn et al., 2010; Chakrabarti et al., 2012). In general, dissolved Si in

soil and in river waters is enriched in the heavy isotopes as compared to the primary silicate minerals where Si is sourced from. The corresponding isotopically light reservoir is found in secondary siliceous solid phases (Ziegler et al., 2005a,b; Georg et al., 2007; Opfergelt et al., 2009; Bern et al., 2010; Steinhoefel et al., 2011). Furthermore, siliceous precipitates from hydrothermal solutions enriched in dissolved Si also show the common picture of preferential incorporation of light isotopes in the precipitates (Douthitt, 1982; Ding et al., 1996; de La Rocha et al., 2000). This picture is also inferred from the prevalence of low isotope ratios in Precambrian cherts (Andre et al., 2006; Steinhoefel et al., 2009, 2010; van den Boorn et al., 2010). However, for chert formation, the way in which diagenetic silicification modifies the Si isotope composition from that of the original deposits is far from understood. Basile-Doelsch et al. (2005) found some of the lowest Si isotope ratios in Aptian siliceous cements. Chen et al. (2007) also reported low isotope ratios in *Anabarites celoms* (tubular small shelly fossil), and in quartz occurring in granular phosphates. In contrast, Robert and Chaussidon (2006), Abraham et al. (2011) and Chakrabarti et al. (2012) reported Archean cherts enriched in heavy Si isotopes.

Converting these observations into a quantitative understanding of the movement of silica in low-temperature environments requires knowledge of the isotope fractionation factors associated with precipitation and recrystallization of siliceous solids. However, not only do we lack even first-order experimental estimates of equilibrium isotope fractionation factors, but probably the formation of many siliceous secondary minerals and chemical deposits is affected by non-equilibrium processes, as they are often enriched in light Si isotopes which suggest that the origin of the Si isotope fractionation is mostly kinetic (see e.g. Ziegler et al., 2005a; Georg et al., 2009; DePaolo, 2011). In these conditions, the relative importance of the forward (precipitation) and backward (dissolution) reaction rates determine the net solid formation rate and the associated isotope fractionation factor (DePaolo, 2011). In addition, sedimentary silicates usually do not directly precipitate from aqueous solutions, as documented by the large number of known amorphous silica precursor phases (e.g. Iler, 1979). Therefore the generation of surface area during nucleation, growth and dissolution, and precursor replacement is important as the processes and rates at the mineral–water interface control the isotope composition of the solid material during mineral growth (Cole et al., 1983; Criss et al., 1987; Steefel and Van Cappellen, 1990; Nielsen et al., 2012; Druhan et al., 2013).

To date, only a few notable studies have explored Si isotope fractionation during the fixation of Si from solution under controlled experimental conditions. The Si isotope fractionation during adsorption of Si onto Fe-oxides, the Si isotopic evolution during allophane- and gel-like solid formation and the Si isotope fractionation during abiotic silica precipitation at low temperatures have been experimentally investigated (Li et al., 1995; Ziegler et al., 2005a; Delstanche et al., 2009; Opfergelt et al., 2009; Geilert et al., 2014). Recently, silicon isotope fractionation during adsorption of Si onto Al-hydroxides has been shown to result in a strong rate dependence of silicon isotope fractionation (Oelze et al., 2014). All these studies demonstrate the preferential incorporation of ^{28}Si into the solid, most likely during Si adsorption onto the solid phase. Isotope fractionation factors $10^3 \ln \alpha_{solid/solution}$ range from $-1.0‰$ to $-1.6‰$ for adsorption of Si onto Fe-oxides, $-1.8‰$ up to $-3‰$ for adsorption of Si onto Al-hydroxides and up to $\approx -3.0‰$ for precipitation of allophane- and gel-like solid phases. First-principle calculations predict an enrichment of ^{30}Si in the higher-ordered solid at equilibrium conditions (Ding et al., 1996; Méheut et al., 2007, 2009). However, these predictions suggest that the Si isotope fractionation of the aforementioned experimental studies is dominated by a kinetic isotope effect. Indeed, attaining Si isotopic equilibrium in experimental settings is virtually impossible due to the extremely low exchange rates between solids and fluids in low-temperature processes, especially in the SiO_2–H_2O system. Li et al. (2011) suggested that recrystallization (or re-organization) induced by "Ostwald ripening", the dissolution of small particles and the re-deposition of the dissolved species on the surfaces of larger particles in a saturated solution, is the only way to induce an isotope exchange at low temperature that is not overprinted by kinetic processes. To test whether equilibrium has indeed been attained, experimentalists use the addition of isotopically-enriched species in one of the two compartments (Johnson et al., 2002; Welch et al., 2003; Schuessler et al., 2007). However, this approach is not possible if, as is the case here, Si is precipitated from a homogeneous solution.

A possible experimental approach in which dissolution–precipitation reactions take place is a batch reactor in which solid precipitation is driven by evaporation of the fluid, and solid dissolution driven by dilution of the fluid. However, the slow evaporation rates involved in such an experiment would result in excessively long experimental runtimes. For Si-containing solids, once precipitated, isotopic equilibration times will exceed any feasible experimental runtime due to the slow exchange rates. It is most likely that dissolution is the limiting step to reach full exchange between formed solid products and solution. The low dissolution rate for amorphous silica ($\approx 1 * 10^{-12} \ mol * m^{-2} * s^{-1}$ at 20 °C; Icenhower and

Dove, 2000) will likely impair attainment of equilibrium as in experiments of $CaCO_3$ precipitation (Tang et al., 2008).

To circumvent these difficulties we designed a novel approach. Alternating dissolution–precipitation, implying depolymerization–polymerization of silica, is induced by freezing and thawing for predefined cycle length over a long run duration (Dietzel, 2005). During freezing, only H_2O molecules are captured in the ice lattice and the remaining solution becomes supersaturated in Si and precipitation of solids from the remaining solution occurs as soon as a critical supersaturation is reached. At the end of the freezing time span, temperatures are increased and the ice previously formed melts. Hence the solution is then undersaturated with respect to the formed solids, leading to their partial dissolution during thawing. By continuing these freeze–thaw cycles steady-state conditions between silica precipitation and dissolution are reached, meaning that the dissolution and precipitation fluxes compensate each other at the scale of a freeze–thaw cycle. At this stage concentrations of dissolved Si do not change from a freeze–thaw cycle to the next. Our setup allows us to explore the temporal change in the Si isotope fractionation factor as the system evolves from a state that is characterized by high net Si removal rates (dominated by unidirectional kinetic isotope fractionation), to a state where the net change for precipitation and dissolution is close to zero.

The rationale for this approach becomes apparent from fundamental experimental studies on dissolution–precipitation kinetics of SiO_2 polymorphs. The process of dissolution and precipitation of SiO_2 polymorphs has been described as fully reversible (Rimstidt and Barnes, 1980; Renders et al., 1995; Carroll et al., 1998). Using the empirical relationships of Rimstidt and Barnes (1980) and Dove et al. (2008) for the dependence of the dissolution rate on temperature and saturation state we can estimate the dissolution rate for an experiment maintained far from equilibrium. The dissolution rate and therefore the time needed to reach full exchange is accelerated by a factor of 60 in comparison to experiments close to equilibrium conditions.

Our experimental approach also provides insight into the numerous geological processes associated with water–solid interaction that involve repeated dissolution-precipitating cycles of silica at the water–solid interface, such as for example during mineral replacement in weathering reactions, diagenesis, silicification, or biogenic ooze maturation. In addition, this experimental approach of repeated freeze–thaw cycles can give insights into the formation process of authigenic silicates in polar regions (Tedrow, 1966; Dickinson and Grapes, 1997).

However, in virtually all Earth surface reactions will the release of Si from primary silicates be accompanied by variable amounts of Al. Reactions between Si and Al are hence likely the first crucial reactions. Aluminum in the system not only reduces the solubility of Si in aqueous solutions (Dixit et al., 2001; Van Cappellen et al., 2002), but also further provides surface area for fast adsorption of Si (Hingston and Raupach, 1967; Dietzel and Böhme, 1997). In addition, pH will exert a first-order control over the precipitation kinetics of both elements as the solubility of Al and the solubility of Si are both "pH dependent". Therefore, we performed experiments of Si precipitation from solutions in the presence of variable Al concentrations and different pHs.

In the present study, we conducted six Si precipitation experiments for about 120 days with initial dissolved Si concentration of 1.6 mmol/l Si, with additions of different amounts of Al (0, 0.1, 1 mmol/l dissolved Al) and explored the evolution of the dissolved silicon isotope composition. In all experiments increasing amounts of an X-ray amorphous silica-containing solids are formed. The evolution of the dissolved silicon isotope composition can be explained by the presence or absence of dissolved Al.

2. Framework for isotope fractionation during precipitation

Because of the diversity of isotope fractionation mechanisms encountered in our experiments, we first review the framework of