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The silicon isotope record of early silica diagenesis

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ABSTRACT

The heavy isotopes of silicon are strongly enriched in some of the youngest, early diagenetically formed porcellanite layers from the Southwest Indian Ridge (Pleistocene) and the Maud Rise (Pliocene). These porcellanite layers are composed of opal-CT and were formed by the conversion of amorphous silica (opal-A) from siliceous sediment via dissolution–reprecipitation. Their bulk δ^{30}Si values range between 1.7 and 2.3‰. Detritus-poor siliceous sediment surrounding these layers is significantly lower at −0.3 to 1.5‰. Sequential chemical extractions of bulk siliceous sediment show (i) preferential dissolution of diatoms featuring higher δ^{30}Si than radiolaria and Al–Si components. The detailed investigation of porcellanite layers by micro-scale Si isotope and Al/Si analyses using UV femtosecond laser ablation ICP mass spectrometry show that (ii) precipitation of authigenic aluminum silicates enriched in light Si isotopes drives pore waters to even higher δ^{30}Si. We suggest that the same processes redistributed stable silicon isotopes in precursor siliceous sediments of ancient chert. We infer that past environmental conditions can be reconstructed with high fidelity from the stable Si isotope composition of chert when initial seawater Si concentrations were high (such as in the Precambrian). Exchange of Si between layers during phase transformation (from opal-A to opal-CT and from opal-CT to quartz) is impeded when variable amounts of detrital minerals are present, because they control rates of silica phase transformation and hence the timing of dissolution–reprecipitation during burial.

1. Introduction

Today the stable isotopes of silicon are successfully employed to quantify the present and past oceans' environmental conditions and marine biogeochemical cycles. In the modern ocean for example biological silicic acid utilization is inferred from the Si isotope composition of seawater (Cardinal et al., 2005; De la Rocha et al., 1997; Reynolds et al., 2006) or from biogenic silica in diatoms sampled in core top sediments (Egan et al., 2012). This information is crucial for estimating export rates of organic carbon from surface waters and its burial that affects atmospheric carbon dioxide concentrations. In the geologic record the stable Si isotope composition of chert and silicified rocks is used to reconstruct for example the weathering and hydrothermal sources of Si and the distribution of sedimentary Si sinks (e.g., André et al., 2006; Van den Boorn et al., 2007, 2010; Steinhoefel et al., 2009, 2010; Marin-Carbonne et al., 2011, 2012, 2013; Chakrabarti et al., 2012; Fan et al., 2013). In spite of this progress we lack an understanding of whether the measured isotope compositions of sedimentary chert deposits do indeed record primary environmental conditions. This difficulty arises because chert forms by diagenetic dissolution–reprecipitation reactions. The effect of diagenetic overprint on sedimentary Si isotope compositions was testified for example in a study of the Miocene Monterrey Formation. There, Ziegler et al. (2011) found that the stable Si isotope composition (δ^{30}Si) of diagenetic quartz ($\delta^{30}\text{Si} = 0$‰) was much lower than that of the amorphous silica in associated diatoms ($\delta^{30}\text{Si} = 1.4$‰). The authors attributed this difference to a late diagenetic fluid that had equilibrated with the Monterrey shales. Another result of such dissolution of amorphous precursor silica and reprecipitation of quartz was found in the form of highly variable Si and O isotope compositions measured by micro-scale SIMS analyses of micro-quartz in Precambrian chert, in which δ^{30}Si varied by 2.8‰ on the micrometer scale (Marin-Carbonne et al., 2012). However, such overprinting of isotope compositions is not ubiquitous on the bulk

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scale. Isotope fractionation was found to be absent during the formation of chert by the silicification of magadiite ($NaSi_7O_{13}(OH)_3 \cdot 3(H_2O)$) (Ziegler and Marin-Carbonne, 2012). Progress in synthesizing these disparate observations into a fundamental understanding of the underlying processes is hampered by our lack of knowledge of the isotope effects associated with diagenetic processes that convert amorphous opal into quartz.

Diagenesis of siliceous sediment means that the abundance of the crystalline SiO_2 polymorphs cristobalite and tridymite (opal-CT) and quartz increases with burial depth at the expense of amorphous silica (opal-A) where time and temperature exert the dominant control over the rate of diagenesis. The slow kinetics of these dissolution–reprecipitation processes explains why most chert deposits found are at least 20 Ma in age (Hesse, 1988). Besides time and temperature, the host sediment's chemical composition exerts a first-order control over rates of diagenesis. Such control is expressed in form of localized porcellanite beds (made up of opal-CT) and chert beds (made up of quartz) in unconsolidated siliceous sediment comprised predominantly of opal-A of the Monterrey Formation (Bramlette, 1946). Porcellanite layers as young as 430 ka were found in siliceous sediments of the Southern Ocean (Kerguelen Plateau: Schlich, 1989; Weaver and Wise, 1973; Maud Rise: Barker, 1988; Bohrmann et al., 1994) and Southwest Indian Ridge (Bohrmann et al., 1990, 1994) and were formed at temperatures of only 0 to 4 °C as inferred from their oxygen isotope composition (Botz and Bohrmann, 1991).

The phase transformation from opal-A to opal-CT does not require elevated temperature and can rather be explained by solubility changes of silica polymorphs (Williams et al., 1985). In early marine diagenesis opal-CT forms if the equilibrium solubility of silicon (setting pore water Si concentration with respect to the host sediment) exceeds that of opal-CT (ca. 25 ppm SiO_2 for cristobalite in aqueous solutions at 20 °C and standard pressure; Walther and Helgeson, 1977). At the seawater–sediment interface solutions are dominated by the low seawater Si concentrations (in the modern ocean between 0.6 and 10.8 ppm SiO_2; Tréguer et al., 1995) and are thus strongly undersaturated in Si. With increasing depth, Si concentrations increase gradually and attain equilibrium concentrations asymptotically at about 10 cm sediment depth, i.e. the 'asymptotic pore water concentration' (Van Cappellen and Qiu, 1997a, 1997b). These equilibrium solubilities depend on the composition of the sediment. Pure opal-A has an equilibrium solubility of ca. 60–130 ppm SiO_2 (Williams and Crerar, 1985; Williams et al., 1985). However, this value is significantly modified by pore water pH, the presence of carbonates and Mg-hydroxides in the sediment (Kastner et al., 1977), organic matter (Hinman, 1990), and Na, Mg, K, Al and Fe in solution (Hinman, 1998). Dissolved aluminum, promoted by the dissolution of detrital minerals at the water–sediment interface (Van Beusekom et al., 1997), has a particularly strong impact on the solubility of biogenic silica (Dixit et al., 2001). It has been found that the equilibrium solubility of siliceous sediment is reduced by the structural incorporation of Al into opal during biosynthesis (Dixit et al., 2001; Gehlen et al., 2002; Van Bennekom et al., 1991) and by the formation of authigenic aluminum silicates (Dixit et al., 2001; Van Cappellen and Qiu, 1997a). Aluminum silicates, i.e., poorly crystalline Al–Si phases containing various amounts of K, Fe, Mg and Cl (Michalopoulos et al., 2000) readily form in the sediment during early diagenesis and can form coatings on biogenic silica, e.g., diatom frustules (Michalopoulos and Aller, 2004; Rickert et al., 2002). In this case the solubility of biogenic silica is reduced and the asymptotic pore water Si concentration is lower than that of the biogenic silica (Hurd, 1973). Thus, during early diagenesis it is the geochemical environment that determines the timing of the phase transformations.

Stable silicon isotope ratios are likely to shift during these phase transformations. In the most simple terms the isotope composition of the pore water Si and the solids precipitated thereof can be affected by i) selective dissolution of silicon sources of variable isotope composition, ii) isotope fractionation during precipitation into solids that differ in their isotope fractionation factor, and iii) the mass balance between dissolution and precipitation. We are now in the position to unravel these effects as recent experimental work has shed light on the isotope fractionation accompanying Si precipitation with unprecedented detail. The precipitation of aluminum silicates is associated with a range of negative isotope fractionation factors ($\Delta^{30}Si_{solid/solution}$) of up to −4.5‰ (Oelze et al., 2015), while the adsorption onto gibbsite is associated with fractionation factors that range between −1.8 and −3.2‰ (Oelze et al., 2014). Both depend on the net solid formation or adsorption rate. In contrast, precipitation of Si from Al-free and low-Al solutions shows that silicon does not fractionate its isotopes upon precipitation, i.e. $\Delta^{30}Si_{solid/solution} = 0$ (Oelze et al., 2015). Furthermore, experimental studies show that preferential precipitation of light silicon isotopes occurs if chemical disequilibrium prevails, and that isotope fractionation is absent at equilibrium (Geilert et al., 2014; Roerdink et al., 2015). This view is supported by absence of Si isotope fractionation during chert formation (Ziegler et al., 2011).

To evaluate the fidelity of chert as a paleo-environmental archive we explored stable Si isotope fractionation accompanying early marine diagenesis. We sampled the youngest porcellanite found to date. Porcellanites (opal-CT) and the adjacent siliceous sediments (mainly opal-A) were sampled in piston cores from the Southwest Indian Ridge (PS2089-2, Pleistocene) and the Maud Rise (PS2070-1, Pliocene) (Bohrmann et al., 1994). The porcellanite found in these cores was preserved undisturbed in contact with its host sediment. We compared the Si isotope composition of the early diagenetic porcellanite with that of the precursor material. To determine the differential solubility of primary silica sources and to constrain their isotope composition we conducted sequential leaching experiments on bulk, unconsolidated siliceous sediments. To resolve the temporal evolution of opal-CT precipitation the porcellanite layers were investigated in detail by micro-scale silicon isotope analyses using UV femtosecond laser ablation ICP mass spectrometry (fs-MC-LA-ICP-MS). We model the effect that dissolution and precipitation processes have on pore water and porcellanite $\delta^{30}Si$ and Al/Si. Finally, we explore the implications for the use of Si isotopes to derive past biogeochemical fluxes from ancient chert.

2. Materials and methods

2.1. Samples

Two cores were recovered with a piston corer during *Polarstern* cruise ANT-IX/3 at the Southwest Indian Ridge (PS2089-2: Pleistocene; 53°11.3′S, 03°19.7′E; water depth 2618 m) and Maud Rise (PS2070-1: Pliocene; 65°06.3′5, 03°37′E; water depth 2611 m), respectively (Fig. 1). These sediments were deposited during Marine Isotope Stages 11 and 12 (ca. 470–360 ka BP: PS2089-2) and between ca. 4.7 and 3.6 Ma (PS2070-1) as deduced from diatom and radiolarian assemblages (Bohrmann et al., 1994). Both cores comprise very pure siliceous ooze, and contain porcellanite layers of a few centimeter thickness. Siliceous sediment was sampled from sediment depths between 7.3 and 5.4 m (PS2089-2), and 6.1 and 4.2 m (PS2070-1), respectively. Each sediment sample represents about one centimeter (Table S.1). We sampled the porcellanite layers that are intercalated with the siliceous ooze at depths of ca. 6.0 m (PS2089-2) and 4.7 m (PS2070-1). The Pliocene porcellanite layer in core PS2070-1 has a wide regional extent and covers large