Si stable isotopes in the Earth’s surface: A review

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Abstract

Silicon (Si) is the second most abundant element on Earth after oxygen. Only few studies have attempted to use stable isotopes of Si as proxies for understanding the Si cycle and its variations in the past. By using three different methods (IRMS, MC–ICP–MS and SIMS), the overall measurements show that the isotopic composition ($\delta^{30}\text{Si}$) of terrestrial samples ranges from $-5.7\%$ to $+3.4\%$. Dissolved Si in rivers and seawater is $^{30}\text{Si}$-enriched ($-0.8\%<\delta^{30}\text{Si}<+3.4\%$) compared to Si in endogeneous rocks ($-1.1\%<\delta^{30}\text{Si}<+0.7\%$). This global enrichment is counterbalanced by the Si-bearing phases (biogenic silica, clays, quartz) where Si is, in average, $^{30}\text{Si}$-depleted ($-5.7\%<\delta^{30}\text{Si}<+2.6\%$). These values are the result of fractionation which have been measured or estimated from $0.3\%$ to $3.8\%$. The fractionation is modeled by two types of approaches: the Rayleigh distillation model (closed system) and the steady-state model (open system). These models have been used in the most recent studies to explain the observed $^{30}\text{Si}$ variations in continental environments and in the sub-Antarctic Ocean.

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1. Introduction

Silicon (Si) is the second most abundant element on earth after oxygen. It is involved in surface environments in several essential biogeochemical transfers: in seawater, dissolved Si represents one of the main nutrient for phytoplankton (Ragueneau et al., 2000); in soil solutions, dissolved Si is absorbed in large amounts by terrestrial vegetation (Alexandre et al., 1997); weathering of silicates removes CO$_2$ from the atmosphere (Berner, 1997). However, despite the importance of Si on Earth surface, the biogeochemical cycle of Si is neither well known nor quantified.

In a global simplified view of its cycle, Si can be considered as being distributed in two main pools: a “primary” Si pool (Si$_I$), which represents Si contained in igneous rocks of the continental and oceanic crusts and a “secondary” Si pool (Si$_II$) which represents Si that leaves Si$_I$ by weathering. The Si$_II$ pool includes both dissolved Si (as silicilic acid, Si(OH)$_4$, in continental and seawaters) and Si-bearing phases (formed by geochemical or biochemical precipitation of Si in various terrestrial and marine environments). The distribution of Si in these pools may have changed during the geological times as well as during climatic cycles. Only a few studies have attempted to use stable isotopes of Si as proxies for understanding the present biogeochemical Si cycle and its variations in the past. We present here a short review of these studies.
2. Comparison of the analytical methods (IRMS, MC–ICP–MS, SIMS)

Silicon has three stable isotopes: $^{28}\text{Si}$ (the most abundant), $^{29}\text{Si}$ and $^{30}\text{Si}$. The $^{30}\text{Si}/^{28}\text{Si}$ ratio is usually reported with the $\delta^{30}\text{Si}$ notation, in permil variations relative to the $^{30}\text{Si}/^{28}\text{Si}$ ratios of the NBS28 quartz standard (Coplen et al., 2002):

$$\delta^{30}\text{Si} = \left( \frac{^{30}\text{Si}_{\text{sample}}}{^{30}\text{Si}_{\text{NBS28}}} - 1 \right) \times 1000.$$ 

The $^{29}\text{Si}/^{28}\text{Si}$ ratio is sometimes reported (Cardinal et al., 2003, 2005; Carignan et al., 2004).

Three methods have been used for measuring silicon stable isotopes in terrestrial samples: IRMS (isotope ratio mass spectrometry), MC–ICP–MS (multi-collection induced coupled plasma mass spectrometry), and SIMS (secondary ions mass spectrometry). By IRMS, any kind of bulk sample (total rock, soil, water...) can be analyzed. The $\delta^{30}\text{Si}$ is measured with a good precision ($\pm 0.2\%$ (2σ)) which has been recently improved ($\pm 0.1\%$ (2σ)) (Ding et al., 2004). This method, however, is highly dangerous due to the use of hazardous gasses. The MC–ICP–MS method allows, as IRMS, the analysis of any kind of bulk sample. In the recent published works (De La Rocha, 2002; Cardinal et al., 2003, 2005), only measurements of the masses $^{28}\text{Si}$ and $^{29}\text{Si}$ are reliable, but a new generation of MC–ICP–MS seems to reach a sufficient resolving power to fully separate $^{14}\text{N}^{16}\text{O}$ and $^{30}\text{Si}$ (Carignan et al., 2004). In terms of precision of MC–ICP–MS, Cardinal et al. (2003) reached a very good precision on $\delta^{29}\text{Si}$ ($\pm 0.08\%$ (2σ)). Contrary to the previous methods, SIMS does not perform analyses on bulk samples, but on in situ individual grains larger than ~50 μm in diameter. It is possible to measure different types of grains that constitute a single rock (Basile-Doelsch et al., 2005), whereas IRMS and MC–ICP–MS would only give a mean value. However, water samples cannot be analyzed in term of analytical precision, SIMS measurements are less precise ($\pm 0.75\%$ (2σ)) (Basile-Doelsch et al., 2005). In terms of accuracy, the comparison of the three methods is more delicate since no standard with a certified value exists. The Rose Quartz is the most cited reference with a non-certified value of $-0.3\%$.

In the future, effort thus should be done (1) to provide a reference material, (2) to better assess the homogeneity of the isotopic composition of NBS28 (Coplen et al., 2002; Carignan et al., 2004) and (3) to report all the data with the same isotopic ratio.

3. Isotopic composition of Earth samples

The different reservoirs of Si are presented on Fig. 1. The $\text{Si}_{\text{I}}$ reservoir formed by endogeneous rocks has a $\delta^{30}\text{Si}$ ranging from $-1.1\%$ to $+0.7\%$, with a mean value of $-0.3\%$ (Douthitt, 1982; Ding et al., 1996) (see Coplen et al., 2002 for a review of $\delta^{30}\text{Si}$ according to the types of rocks).

The dissolved $\text{Si}_{\text{II}}$ is distributed in several pools. In river waters, it is $\text{Si}_{\text{II}}$-enriched and the $\delta^{30}\text{Si}$ ranges from $-0.4\%$e to $+3.4\%$e (De La Rocha et al., 2000; Ding et al., 2004), with a mean value of $+1.1\%$e (Basile-Doelsch et al., 2005). The dissolved $\text{Si}_{\text{II}}$ in a soil solution ranges from $-0.8\%$e to $+1.7\%$e (Ziegler et al., 2002a) and the dissolved $\text{Si}_{\text{II}}$ of groundwaters has never been measured. However, quartz formed at the watertable may indicate that this pool is depleted in $^{30}\text{Si}$ (Basile-Doelsch et al., 2005). In seawater as in river waters, the dissolved $\text{Si}_{\text{II}}$ is $^{30}\text{Si}$-enriched and ranges from $+0.6\%$e to $+3.1\%$e (De La Rocha et al., 2000; Varela et al., 2004; Cardinal et al., 2005).

For $\text{Si}_{\text{II}}$ precipitated in solid phases, the biogenic silica of diatoms is the most documented with a $\delta^{30}\text{Si}$ ranging from $-0.3\%$ to $+2.6\%$ (De La Rocha et al., 1998; Varela et al., 2004). This pool represents by far the most important sink of Si in oceans. However, the most $^{30}\text{Si}$-depleted biogenic silica has been measured in sponges with a $\delta^{30}\text{Si}$ of $-3.7\%$ (Douthitt, 1982; De La Rocha, 2003). In continents, biogenic silica of phytooliths ranges from $-1.7\%$ to $+2.5\%$ (Douthitt, 1982; Ding et al., 1996; Ziegler et al., 2002b). The other phases of precipitated $\text{Si}_{\text{II}}$ are secondary minerals (1) formed in soils (mainly clays) and (2) precipitated in silcretes (mainly quartz). Clays are slightly $^{30}\text{Si}$-depleted, with a $\delta^{30}\text{Si}$ ranging from $-2.3\%$ to $+0.1\%$ (Ding et al., 1996; De La Rocha et al., 2000; Ziegler et al., 2002b). Quartz of silcretes represent the most $^{30}\text{Si}$-depleted pool yet measured, with a $\delta^{30}\text{Si}$ ranging from $-5.7\%$e to $-1.6\%$e (Basile-Doelsch et al., 2005).

In conclusion, even if many more analyses have to be done for each reservoir, the existing data show that dissolved $\text{Si}_{\text{I}}$ is $^{30}\text{Si}$-enriched ($-0.8\%$e$<\delta^{30}\text{Si}$e$+3.4\%$e) compared to $\text{Si}_{\text{I}}$ ($-1.1\%$e$<\delta^{30}\text{Si}$e$+0.7\%$e), whereas $\text{Si}_{\text{II}}$ in the precipitated phases is in average $^{30}\text{Si}$-depleted ($-5.7\%$e$<\delta^{30}\text{Si}$e$+2.6\%$e) compared to $\text{Si}_{\text{I}}$.

4. Isotopic fractionation: lab experiments, natural samples and models

The isotopic variations described above are explained by the principle of kinetic isotopic fractionation, according to which dissolved $^{28}\text{Si(OH)}_{4}$ tends...
to precipitate preferentially, leaving the residual solution enriched in $^{30}$Si(OH)$_4$ (Ding et al., 1996).

The orders of magnitude of Si isotopes fractionation are reported for chemical or biochemical precipitations of Si in water of known $\delta^{30}$Si. Chemical precipitation experiments show that silica and clay are $-0.3\%$o to $-3.8\%$o more negative than the final water (Ding et al., 1996; Ziegler et al., 2002a); pedogenic and groundwater silicifications (Basile-Doelsch et al., 2005); groundwater (Ziegler et al., 2002b; Basile-Doelsch et al., 2005); river water (De La Rocha et al., 2000; Ding et al., 2004); suspended particulate material (Ding et al., 2004); leaving marine diatoms (Varela et al., 2004); leaving sponges (Douthitt, 1982; De La Rocha, 2002); seawater (De La Rocha et al., 2000; Varela et al., 2004; Cardinal et al., 2005); diatoms in sediments (De La Rocha et al., 1998); sponges in sediments (De La Rocha, 2003); detrital quartz in sediments (Basile-Doelsch et al., 2005); quartz in diageneric cements (Basile-Doelsch et al., 2005).

Fig. 1. Biogeochemical cycle of Si in continental and marine environments. D: dissolution; P: precipitation; T: transport; E: epigenesis; Up: uptake; De: death. $\delta^{30}$Si ranges are from: endogeneous rocks (Douthitt, 1982) and this work; soil solution (Ziegler et al., 2002a); phytoliths (Douthitt, 1982; Ding et al., 1996; Ziegler et al., 2002b); neoformed clays (Ding et al., 1996; De La Rocha et al., 2000; Ziegler et al., 2002b); pedogenic and groundwater silicifications (Basile-Doelsch et al., 2005); groundwater (Ziegler et al., 2002b; Basile-Doelsch et al., 2005); river water (De La Rocha et al., 2000; Ding et al., 2004); suspended particulate material (Ding et al., 2004); leaving marine diatoms (Varela et al., 2004); leaving sponges (Douthitt, 1982; De La Rocha, 2002); seawater (De La Rocha et al., 2000; Varela et al., 2004; Cardinal et al., 2005); diatoms in sediments (De La Rocha et al., 1998); sponges in sediments (De La Rocha, 2003); detrital quartz in sediments (Basile-Doelsch et al., 2005); quartz in diageneric cements (Basile-Doelsch et al., 2005).
Si(OH)₄) and the Si incorporated in Si-bearing product equals the gross Si(OH)₄ input (Sigman et al., 1999). This model, initially developed for nitrate fractionation (Sigman et al., 1999), has been recently applied to explain the biological fractionation of Si isotopes in ocean waters (Varela et al., 2004; Cardinal et al., 2005).

5. Using Si isotopes in Earth science

The above cited studies on Si stable isotopes probably represent the very beginning of the works on the Si cycle in Earth’s surface environments. For examples, in continental environments, Ding et al. (2004) used Si isotopes to explore the Si cycle at the scale of a river system, the Yangtze River. They show that the δ³⁰Si in solution decreases from the upper to lower reaches, in the large range of +0.7‰ to +3.4‰. This study, together with the one of De La Rocha et al. (2000), also shows that river waters form a reservoir with a mean isotopic value of +1.1‰. It is enriched in ³⁰Si with respect to the igneous rocks reservoir which has a mean isotopic value of −0.3‰. In order to produce a “positive” dissolved reservoir from a “negative” rock reservoir, a major fractionation must occur during weathering. This results in the formation of continental ³⁰Si-depleted reservoirs. It has been recently shown by Basile-Doelsch et al. (2005) that the pool formed by quartz cements of silcretes forms, for millions of years, as well as along vertical water column profiles (Varela et al., 2004; Cardinal et al., 2005). Another continental pool in the terrestrial silicon cycle. Nature 433, 399–402.

6. Conclusion

The existing data on Si isotopes show that dissolved SiII is ³⁰Si-enriched (−0.8‰<δ³⁰Si<+3.4‰) compared to SII of endogeneous rocks (−1.1‰<δ³⁰Si<+0.7‰). This global enrichment is counterbalanced by the precipitated phases (formed by geochemical or biochemical precipitation of Si in various terrestrial and marine environments) where SiII is in average ³⁰Si-depleted (−5.7‰<δ³⁰Si<+2.6‰) compared to SII. The fractionations, which vary from −0.3‰ to −3.8‰, are modelled either by the Rayleigh distillation model (closed system) or by the steady-state model (open system). The use of isotopic Si budgets, which add a quantitative constraint in the Si cycle of the studied system, have recently opened a new field of research in continental as well as in marine geosciences, for present and past environments. This research should be stimulated in the future by the emerging and non-hazardous techniques (MC–ICP–MS and SIMS), but collaborating efforts between laboratories should be done for analytical calibration and homogeneity of measurements.

References


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