



The silicon isotope composition of the upper continental crust

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Abstract

The upper continental crust (UCC) is the major source of silicon (Si) to the oceans and yet its isotopic composition is not well constrained. In an effort to investigate the degree of heterogeneity and provide a robust estimate for the average Si isotopic composition of the UCC, a representative selection of well-characterised, continentally-derived clastic sediments have been analysed using high-precision MC-ICPMS.

Analyses of loess samples define a narrow range of Si isotopic compositions ($\delta^{30}\text{Si} = -0.28\text{‰}$ to -0.15‰). This is thought to reflect the primary igneous mineralogy and predominance of mechanical weathering in the formation of such samples. The average loess $\delta^{30}\text{Si}$ is $-0.22 \pm 0.07\text{‰}$ (2 s.d.), identical to average granite and felsic igneous compositions. Therefore, minor chemical weathering does not resolvably affect bulk rock $\delta^{30}\text{Si}$, and loess is a good proxy for the Si isotopic composition of unweathered, crystalline, continental crust.

The Si isotopic compositions of shales display much more variability ($\delta^{30}\text{Si} = -0.82\text{‰}$ to 0.00‰). Shale Si isotope compositions do not correlate well with canonical proxies for chemical weathering, such as CIA values, but do correlate negatively with insoluble element concentrations and Al/Si ratios. This implies that more intensive or prolonged chemical weathering of a sedimentary source, with attendant desilicification, is required before resolvable negative Si isotopic fractionation occurs. Shale $\delta^{30}\text{Si}$ values that are more positive than those of felsic igneous rocks most likely indicate the presence of marine-derived silica in such samples.

Using the data gathered in this study, combined with already published granite Si isotope analyses, a weighted average composition of $\delta^{30}\text{Si} = -0.25 \pm 0.16\text{‰}$ (2 s.d.) for the UCC has been calculated.

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1. INTRODUCTION

Silicon (Si) is the second most common element in the Earth's crust (Wedepohl, 1995; Rudnick and Gao, 2003), and the upper continental crust (UCC) is the major source of primary silica to the oceans; around 85% of marine silica is derived from the continents (Tréguer et al., 1995). The (supracrustal) Si cycle is also intrinsically linked with the carbon cycle because it is a major nutrient for planktonic

diatoms which represent ~40% of marine primary productivity (e.g. Tréguer et al., 1995; De La Rocha et al., 1998). These organisms with silica skeletons sequester carbon and hence mediate atmospheric CO₂ through burial (Ragueneau et al., 2000). In addition, weathering of silicate minerals through reaction with carbonic acid (dissolved in meteoric water) also provides a sink for atmospheric CO₂ (Walker et al., 1981). As stable isotope fractionation can provide information about sources and rates in such cycles, the Si isotope system is of obvious relevance to the aforementioned processes.

Over the last decade there have been a number of studies investigating Si isotopes in biological and weathering processes. These have demonstrated that isotopic fractionation

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is generated as a result of biological utilisation by marine organisms (De La Rocha et al., 1998; Hendry et al., 2010) or vegetation (Ding et al., 2005; Opfergelt et al., 2008; Bern et al., 2010), low-temperature weathering (Ziegler et al., 2005a,b; Georg et al., 2009a; Opfergelt et al., 2009, 2010, 2011, 2012; Bern et al., 2010; Steinhöfel et al., 2011) and precipitation of secondary silica (Basile-Doelsch et al., 2005). Precipitation of secondary minerals tends to enrich the product in the lighter isotopes of Si; compared to unweathered igneous rocks ($\sim -0.4 < \delta^{30}\text{Si} < -0.1\text{‰}$; e.g., Fitoussi et al., 2009; Savage et al., 2010, 2011, 2012), large negative mineral enrichments of $\delta^{30}\text{Si} \approx -6.0\text{‰}$ to -3.0‰ have been deduced (e.g., Basile-Doelsch et al., 2005; Ziegler et al., 2005a,b) – resulting in a fluid with a relatively heavy isotopic composition (De la Rocha et al., 2000; Ding et al., 2004; Georg et al., 2006a, 2009b; Cardinal et al., 2010). This appears to be as a result of dynamic equilibrium between dissolution and re-precipitation of Si, whereby the degree of isotopic fractionation is much greater during the formation of secondary phases than during dissolution (e.g. Ziegler et al., 2005a). There has, however, been no systematic study of the overall Si isotopic composition of, and the degree of isotopic heterogeneity within, the continental crust. Ultimately, all Si utilised in the above environments is sourced from the continents and so characterising this source is essential.

The widely-cited studies of Douthitt (1982) and Ding et al. (1996) were the first to hint at the isotopic composition of the continental crust but, since then, very little progress has been made. In both studies it was demonstrated that evolved (high-Si) igneous rocks tended to be enriched in the heavier isotopes of Si and were more isotopically variable when compared to basalts and mantle lithologies. Such observations have since been reappraised using modern analytical techniques, but are still broadly accepted (Savage et al., 2011, 2012). The aforementioned earlier studies also suggested that chemically derived sedimentary material (e.g., siltstone, shale) is, in general, isotopically lighter, whereas the Si isotopic composition of mechanically derived sediment (e.g., sandstone) is comparable to that of igneous rocks (again, these observations have been corroborated by more recent weathering studies, see above). However, both of these studies were aimed at cataloguing the natural variation of Si isotopes, and no attempt was made to provide an average isotopic composition for the UCC.

This research uses a well-characterised set of shale and loess samples, as well as the data for granitoid material previously acquired (Savage et al., 2012) to characterise the UCC. The degree of Si isotopic heterogeneity in the UCC is also constrained.

2. SAMPLES

2.1. Loess

Loess is aeolian sediment that covers approximately 10% of the world's land surface and is deposited during cold-dry climatic phases (Taylor et al., 1983; Pye, 1995). It is composed mainly of quartz, feldspar, sheet silicates and/or calcite depending on regional geology, and is

derived predominantly from deserts and/or glacial milling (Taylor et al., 1983). Mechanical sedimentary derivation from glacial milling has limited the extent of chemical weathering that has affected loess, although most loess has experienced at least one cycle of chemical alteration (Gallet et al., 1998). Because loess samples large areas of crust, it has been used by many to constrain the average composition of the upper continental crust (e.g., Taylor et al., 1983; Barth et al., 2000; Hu and Gao, 2008). We have analysed 13 Pleistocene loess samples, sourced from China, New Zealand, Germany, Hungary and the USA, which have previously been studied for major and trace elements (Taylor et al., 1983; Gallet et al., 1998; Barth et al., 2000; Hu and Gao, 2008) and Li and Mg stable isotopes (Teng et al., 2004; Li et al., 2010). The major element composition of loess is somewhat variable, with each suite reflecting the diverse regional geology of its source region, e.g., Si-rich loess from the Banks Peninsula is derived from Mesozoic greywackes from the Southern Alps, whereas European loess is more carbonate-rich, reflecting its derivation from Alpine terrains. The Iowa and Kansas loess is thought to derive from the Rocky Mountains; by contrast, much Chinese loess is non-glacial, deriving instead from a desert environment (Taylor et al., 1983).

Degree of chemical weathering of a sediment is often established using the Chemical Index of Alteration (CIA; Nesbitt and Young, 1982) which is defined as $\text{CIA} = \text{molar Al}_2\text{O}_3 / [\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}]$. In this equation, CaO^* refers to the CaO present only in silicates, not in apatite and carbonate, and is corrected using molar P_2O_5 and Na_2O quantities (see McLennan, 1993). The loess samples analysed in this study have CIA values between 57 and 65, which is slightly elevated when compared to unweathered igneous rocks ($\text{CIA} \sim 50$; Nesbitt and Young, 1982), but lower than shales (see later), consistent with the suggestion of Gallet et al. (1998) that most loess has experienced minor chemical weathering.

2.2. Shales

Shales are fine-grained sedimentary rocks composed mainly of clay minerals, detrital quartz, and variable amounts of carbonate, which are deposited in low energy environments. They are derived from erosion over large areas and so, like loess, are often used as representative samples of the upper continental crust (e.g., Haskin and Haskin, 1966; Nance and Taylor, 1976; Gromet et al., 1984; Taylor and McLennan, 1985; Barth et al., 2000). Shale petrogenesis is more complicated than loess, involving both mechanical and chemical weathering, as well as variable amounts of diagenesis and metamorphism, resulting in higher CIA values than loess. Despite this, shales show little variation in their insoluble element ratios (Taylor and McLennan, 1985) and so provide good estimates for these in the upper crust. Also, whereas loess is normally confined to the Pleistocene, shales are present in the geological record throughout most of Earth's history.

Thirty eight samples, taken from Australia, Canada and the USA were analysed for Si isotopes. Twenty two shales were analysed from the Post-Archaean Australian Shale

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