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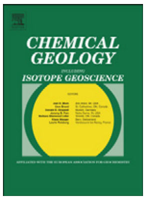

Research papers

# Micrometer silicon isotope diagnostics of soils by UV femtosecond laser ablation

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ABSTRACT

This study presents the first Si isotope data of the principle Si pools in soils determined by a UV femtosecond laser ablation system coupled to a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS). This method reveals accurate and precise Si isotope data on bulk materials, and at high spatial resolution, on the mineral scale. The following Si pools have been investigated: a) the Si source to soils on all major silicate minerals on thin sections from bedrock fragments in the soil profiles; b) bulk soils (particle size <2 mm) after fusion to glass beads with an iridium-strip heater or pressed into powder pellets; c) separated clay fractions as pressed powder pellets and e) separated phytoliths as pressed powder pellets. Multiple analyses of three rock standards, BHVO-2, AGV-1 and RGM-1 as fused glass beads and as pressed powder pellets, reveal $\delta^{30}$Si values within the expected range of igneous rocks. The MPI-DING reference glass KL2-G exhibits the same Si isotope composition after remelting by an iridium-strip heater showing that this technique does not alter the isotope composition of the glass.

We used this approach to investigated two immature Cambisols developed on sandstone and paragneiss in the Black Forest (Germany), respectively. Bulk soils show a largely uniform Si isotope signature for different horizons and locations, which is close to those of primary quartz and feldspar with $\delta^{30}$Si values around −0.4‰. Soil clay formation is associated with limited Si mobility, which preserves initial Si isotope signatures of parental minerals. An exception is the organic horizon of the paragneiss catchment where intense weathering leads to a high mobility of Si and significant negative isotope signatures as low as to −1.00‰ in bulk soils. Biogenic opal in the form of phytoliths, exhibits negative Si isotope signatures of about −0.4‰. These results demonstrate that UV femtosecond laser ablation MC-ICP-MS provides a tool to characterize the Si isotope signature of the principle Si pools left behind after weathering and Si transport have altered soils. These results can now serve as a fingerprint of the residual solids that can be used to explain the isotope composition of dissolved Si in soil solutions and river water, which is mostly enriched in the heavy isotopes.

## 1. Introduction

The formation of soils represents an important part of the global biogeochemical cycle because chemical weathering of silicates consumes atmospheric $CO_2$ and drives the flux of continental Si to the oceans, where Si enables primary production of silica-secreting organisms (e.g. Tréguer and Pondaven, 2000; Sommer et al., 2006). Recent studies have shown that abiotic and biotic processes in soils involving the release or precipitation of Si are associated with significant stable Si isotope fractionation. Igneous rocks reveal minimal variation, with an average $\delta^{30}$Si of −0.3‰ (Ding et al., 1996; Ziegler et al., 2005a,b; Georg et al., 2007). Secondary clay minerals formed by weathering processes incorporate preferentially light Si isotopes and show a wide range in $\delta^{30}$Si from −2.9 to 1.5‰, where lower values dominate as compared to igneous rocks (Ding et al., 1996; De La Rocha et al., 2000; Ziegler et al., 2005a,b; Opfergelt et al., 2008; Georg et al., 2009; Bern et al., 2010; Opfergelt et al., 2010). A study of a soil chronosequence on the Hawaiian Islands shows a progressive development to more negative isotope signatures with soil age as an increasing fraction of Si accumulates in neoformed clay minerals (Ziegler et al., 2005a). Plants utilize preferentially light Si isotopes from solutes and reveal the largest variability in $\delta^{30}$Si which ranges from −2.3 to 6.1‰ (Ding et al., 1996, 2005; Opfergelt et al., 2006a,b; Engström et al., 2008; Hodson et al., 2008; Opfergelt et al., 2008; Sun et al., 2008; Ding et al., 2008a,b; Köster et al., 2009; Bern et al., 2010; Opfergelt et al., 2010).

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The preferential uptake of light Si isotopes into soil clays and by organisms leads to predominately positive Si isotope signatures in continental surface waters with $\delta^{30}$Si values between −0.1 and 3.4‰ (De La Rocha et al., 2000; Ding et al., 2004; Alleman et al., 2005; Ziegler et al., 2005a; Georg et al., 2006, 2007; Delstanche et al., 2009; Georg et al., 2009; Cardinal et al., 2010; Engström et al., 2010; Opfergelt et al., 2010). Rivers in the Swiss Alps show seasonal changes in $\delta^{30}$Si, which are attributed to temporal variations in the relative contributions of soil water, groundwater and superficial runoff (Georg et al., 2006). Hence the stable Si composition of surface water represents a fingerprint of the processes that contribute to the release of Si from unweathered rock and the geochemical, mineralogic, and biologic transformations that were involved in this Si cycle. But while in most previous studies much emphasis was placed on the investigations of the fluids, bulk soil and bulk plant material, systematic investigation of the pools within the solid residue is still rare and mostly incomplete. Such study is essential to identify the mechanisms driving the isotope fractionation during transfer of Si into fluids. This deficit was due to the lack of suitable microanalytical tools that enabled detecting Si isotope variations at the micrometer scale.

In this study, we present the first results on Si isotope ratios in both bulk soil and its constituents determined by UV femtosecond laser ablation (UV fs LA) coupled to a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS). This approach provides the opportunity to carry out stable isotope analyses at high (micrometer-scale) spatial resolution and for bulk sample materials to cover all principle Si pools in soils while maintaining precision and accuracy.

## 2. Environmental setting and sample materials

For this study, we investigated two Haplic Cambisols (humic, dystric) (WRB, 2006) developed on periglacial debris of sandstone and paragneiss, respectively, in the Black Forest, Germany. The soils are located in well-investigated catchments within the cool, perhumid Black Forest, SW Germany (e.g. Sommer et al., 2001; Fiedler et al., 2002). The sandstone catchment “Seebach” is located about 40 km northeast of Freiburg in the Northern Black Forest at an altitude of 750 m above sea level. The bedrock is Triassic sandstone (“Unterer Buntsandstein”), which consists mainly of quartz and K-feldspar of variable proportions with intercalated silty to clayey layers dominated by illite (e.g. Sommer et al., 2001). The investigated paragneiss catchment “Wildmooswald” is located about 20 km east of Freiburg within the Southern Black Forest at an altitude of 1099 m above sea level. The Palaeozoic paragneiss originated from graywackes consists of 10–20% quartz, 50–60% feldspars (mainly plagioclase), 10–20% biotite and 10–20% hornblende (Wimmenauer and Schreiner, 1999). For both locations, the mean annual temperature is about 6 °C, precipitation occurs throughout the whole year with mean annual amounts of 1600 mm $y^{-1}$ in the paragneiss catchment (discharge = 900 mm $y^{-1}$) and 1935 mm $y^{-1}$ in the sandstone catchment (discharge = 1344 mm $y^{-1}$), respectively. The vegetation has been strongly influenced by anthropogenic impact since the 12th century and is dominated by Norway spruce (*Picea abies* L.-Karst.) in both catchments.

Soil formation in both areas is an ongoing process since at least 10 ka beginning after deglaciation of the Black Forest (e.g. Sommer et al., 2001; Fiedler et al., 2002). Soil formation processes in these catchments are accompanied by limited Si mobility. Therefore, soil clays should have largely preserved the Si isotope signature of the initial minerals. These properties make these areas ideally suited to test our analytical approaches, including clay separation techniques and isotope analysis. In the sandstone catchment, we estimate that only about 10% of the clay minerals within the soil have been formed during Holocene weathering, whereas the majority is inherited illite from clay-rich layers in the sandstone or derived from it. Illite, mixed layered illite/vermiculite intergrades and vermiculite dominate the clay fraction (Table 1). Vermiculite forms from illite by the release of $K^+$, hence the effect on Si isotope fractionation should be negligible. Kaolinite, whose formation can be associated with large isotope fractionation (e.g. Ziegler et al., 2005b), is a minor constituent in the clay fraction and is therefore likely not resolvable.

In the paragneiss catchment, the soil clay assemblage in the investigated horizon is mainly composed of vermiculite, Al-hydroxy interlayered vermiculite and some kaolinite (see Table 1). Biotite weathering transforms biotite to vermiculite. At pH conditions of normal rainfall, this reaction is accompanied by loss of mainly $K^+$ and $Mg^{2+}$ leaving the original silicate structure largely unmodified (e.g. Acker and Bricker, 1992; Wilson, 2004). Acidic conditions ($pH<4$) enhance the disruption of the mineral lattice, which leads to an increased release of Si among other elements. However the clay mineral assemblage suggests that this process is of minor importance in this soil horizon. Al-hydroxy interlayered vermiculite forms commonly in acidic soil environments by introduction of Al-hydroxy polymers either derived directly from decomposition processes within the mineral structure or indirectly from weathering of other aluminous minerals such as feldspars (e.g. Wilson, 2004). It is likely that neither of the involved processes mobilizes large fractions of Si and therefore the expected isotope fractionation should be small. Kaolinite can be derived from plagioclase or biotite weathering by major element loss including Si, Na, K, Mg and Ca (e.g. Wilson, 2004), which can induce large isotope fractionation up to 2‰ in $\delta^{30}$Si (Ziegler et al., 2005b). However kaolinite makes up only about 20% of the clay fraction.

Soil samples were collected from morphogenetic horizons in both Cambisols. Their major characteristics are presented in Table 2. To examine the parent material to these soils, which is mostly allochtonous debris contained in the periglacial slope deposits, we chose least weathered rock fragments incorporated in the soil profiles. Microscopic analyses reveal a mineral composition of about 50% quartz, 40% feldspar and 10% biotite in the paragneiss sample investigated and approximately 50% quartz and 50% K-feldspar in the sandstone sample, respectively. Further, an intercalated silty–clayey layer was sampled from a sandstone outcrop close to the investigated soil profile in the sandstone catchment. Sampling was carried out in 2007.

## 3. Methods

### 3.1. Soil analyses

Bulk soil samples were air dried, gently crushed and sieved at 2 mm to obtain the fine earth fraction (particle size < 2 mm). Soil pH was determined electrometrically in 0.01 M $CaCl_2$ (soil: solution = 1:2.5). The total carbon content was determined by

**Table 1**
Semiquantitative estimates (relative percentage) of the mineralogical composition of the total clay from the Bw horizons and the clay sample originated from a sandstone outcrop.

| Horizon | Kaolinite [%] | Illite (I) [%] | Vermiculite (Vm) [%] | Mixed layers (I/Vm) [%] | Al-hydroxy interlayered vermiculite [%] | Chlorite [%] |
|---|---|---|---|---|---|---|
| 2Bw (sandstone, Seebach) | 15 | 19 | 28 | 32 | 0 | 6 |
| Bw (paragneiss, Wildmooswald) | 22 | 8 | 28 | 0 | 34 | 8 |
| Clay from sandstone | 0 | 100 | 0 | 0 | 0 | 0 |