Development of a method for sequential extraction of Si-pools from soils

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Abstract

For the first time, a method for sequential extraction of silicon (Si) from soils has been developed. This new method enables investigating different Si pools in soils and thus represents an important contribution to improve our understanding of biogeochemical Si-processes and global Si-cycling. The method fractionates and analyses various Si-pools, from the most mobile to immobile phases in soils. The sequential extraction allows differentiation of soluble and biogenic as well as pedogenic amorphous and crystalline silicon, so that the different Si-pools can be analysed. Firstly, the most mobile phase is separated by extraction with $CaCl_2$, followed by extraction of the adsorbed Si-fraction with acetic acid. Thereafter, the fraction of silicon occluded in sesquioxides is isolated by treatment with ammonium oxalate in the light. Oxidation with hydrogen peroxide releases silicon bound in organic matter. Bio-opals (mainly phytoliths) are separated with sodium polytungstate, while minerogenic (chemically precipitated) amorphous silica is extracted with sodium hydroxide. The total silica content is determined by fusion with lithium borate and subsequent dissolving in nitric acid. Si contents in the extracts are measured by ICP-OES. The share of crystalline silicates is calculated.

The new method was applied to a soil catena in the Black Forest in SW-Germany. The results of the sequential extraction indicate that most of the Si (98- 99%) is bound in primary and secondary silicates. Up to 1% of Si originates from the abiotic amorphous phase or from organic matter.

Key Words

Sequential extraction, amorphous silica, bio-opal

Introduction

Silicon (Si) is the second most abundant element in the earth's crust after oxygen. More than 1/4 (26.3%) of the earth's crust's mass is silicon (Holleman and Wiberg, 2007). This element has central functions for biogeochemical processes, as a nutrient for marine and terrestrial biota, in buffering soil acidification and in the regulation of atmospheric carbon dioxide (Derry *et al.,* 2005). Silicon plays multiple roles in plant life and crop performance (Epstein, 2001). Nevertheless, the silicon turnover in soils – an important compartment within the global silicon cycle – has received little attention so far. There is no specific information about the silicon pools and dynamics, in the following sequence: ***rock weathering → soil → hydrosphere and biosphere***. However, without such information the modelling of global Si-cycles is impossible. The lack of knowledge to the basic magnitudes of the Si-release is partly due to the fact, that no technique for quantitative extraction is available for the Si-Pools in soils in the sense of a chemical fractionating extraction method (Sauer *et al*., 2006).

A large variety of silicon fractions may occur in soils. Soil particles can adsorb dissolved silicic acid from the soil solution. Silica can also be included in sesquioxides or bound to organic matter. Amorphous silica exists in the form of biogenic (e.g. phytoliths) and minerogenic opal (e.g. silica cutans). Moreover, Si in the form of dissolved silicic acid is retained in the soil solution. Finally, many primary and secondary crystalline silicates (e.g. quartz, feldspar, micas, clay minerals) are generally found in soils. While the knowledge about crystalline minerals is advanced, the quantification of other Si fractions such as Si in amorphous silica is not thoroughly discussed in the literature.

The existing methods for extracting amorphous silica are in general extractions at high temperature with e.g. sodium carbonate (DeMaster, 1981), sodium hydroxide (e.g. Foster, 1953; Koning *et al*., 2002), Tiron (Biermans and Baert, 1997). The results obtained by these methods depend on the efficiency of the extracting agent. The problem thereby is that clay minerals are extremely sensitive and easily attacked by the chemical agents. Hence, the contribution of mineral-Si to the amounts of Si measured in amorphous silica extraction needs to be considered, and the extraction results need to be corrected for this portion of Si. Such correction is common in marine sedimentology but not in soil science. The extrapolation method from DeMaster, (1981) (Figure 1) used in marine sedimentology is a better approach than the simple extractions that are commonly used in soil science. The technique is based on the observation that under these extraction conditions (high pH, 80-85°C) most biogenic silica dissolves completely within the first 2 h of the extraction, while alumino-silicates release Si at constant rate over the whole extraction time, which allows for the determination of biogenic silica by extrapolation the Si release through time back to the intercept to correct mineral dissolution (Sauer *et al.*, 2006). In this work, quantitative chemical extractions that are commonly used in soil and aquatic sciences for extracting silicon from different soil fractions have been tested and improved.

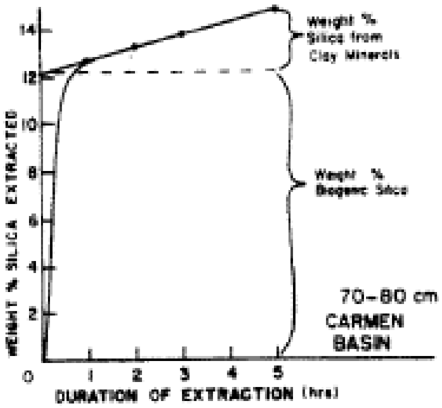

Figure 1. Weight percent silica extracted from a sediment sample versus time (from DeMaster 1981).

Methods

Soils

Samples were taken in the northern part of the Black Forest in SW Germany (8°E and 48°N). The vegetation in this area is dominated by fir and spruce, and the underlying parent rock is Lower Triassic sandstone. The humid-temperate climate is characterised by a mean annual precipitation of 1935 mm and a mean air temperature of 6.5°C (Sommer *et al.,* 2002). The soils along the catena (Figure 2) include a Podzol with abundant eluvial horizon (pedon 1), a Podzol with abundant illuvial horizon (pedon 2) and a Cambisol (pedon 3).

Figure 2. Location of the pedons in the northern part of the Black Forest in SW Germany. From Google Earth (2009).

The pedons were described in the field and sampled horizon-wise. The soil samples were air-dried and passed through a 2-mm sieve. The mineralogical composition of the clay fraction (< 2µm) was determined by X-ray diffraction analysis with Cu-Kα radiation (Siemens D 500-Diffractometer). Percentages of clay minerals were calculated by use of the software Diffrac AT 3.3. Particle size distribution of the soil samples was determined by wet sieving (sand fractions) and pipette method (silt and clay) (Schlichting *et al.* 1995).

Sequential extraction

The most mobile phase was separated by extraction with 0.01M $CaCl_2$ 1:5 soil suspensions were put on a horizontal shaker for 24h. They were shaken only for 1 minute per hour in order to accelerate the extraction but at the same time to avoid Si abrasion from mineral grains. The next extraction step was modified from Snyder (2001) for determination of the adsorbed Si-fraction: 1:10 soil suspensions with 0.01M acetic acid were horizontally shaken for 24h (1 minute per hour). The Si-fraction, occluded in sesquioxides, was extracted by a method described by Schwertmann (1964), using oxalate solution (17.56 g $(COOH)_2$ $2H_2O$ + 28.4 g $(COONH_4)_2$ H_2O) in the light. Subsequently, the samples were treated with H_2O_2 in a water bath at 85°C, until the soil colour had turned to grey. Afterwards the samples were divided in two aliquots.

One aliquot was used for bio opal separation according to the method of Madella et al. (1997). The samples were dispersed overnight with NH_3 and wet-sieved through a 63-µm sieve to exclude the sand fraction. The bio opals (in the fine fractions) were separated with sodium polytungstate (Na_6 ($H_2W_{12}O_{40}$) H_2O), ρ= 2.3 g cm^{-3}. The silicon from bio opal was extracted with 0.2M sodium hydroxide, shaking the samples permanently horizontally for 24 h.

The second aliquot of each sample was analysed for minerogenic amorphous silica. The samples were extracted with 0.2M sodium hydroxide (soil to solution ratio 1:400) at room temperature in three time steps (5h, 24h and 48h), thus modifying the method of DeMaster (1981). To calculate the amounts of Si from amorphous silica, Si-concentrations were plotted against extraction time. The obtained extraction curves were extrapolated to the y-axis (Fig.1), yielding the amounts of Si from total amorphous silica (biogenic + minerogenic). The amounts of Si from minerogenic amorphous silica were obtained by subtracting Si from biogenic silica.

The total Si in the soil samples was determined by fusion of soil samples 200 mg di-lithium-tetraborate and 800 mg lithium-metaborate and subsequent dissolving in 0.5 M nitric acid (DIN ISO 14869-2, 2003).

All extracts were centrifuged at 3000 rpm, filtered with paper filter and analysed for Si with ICP-OES at the wavelengths 250.690, 251.611 and 288.158 nm. The samples were washed with distilled water after each step of the extraction procedure.

After analysing all fractions, the balance of silicon in the samples could be established:

Si_t= Si_{mo} + Si_{ad}+ Si_{occ}+ Si_{org}+ Si_{ba}+ Si_{ma}+ Si_{min},

where Si_t is total silicon in the sample, Si_{mo} is silicon from the mobile phase, Si_{ad} is silicon from adsorbed silica, Si_{occ} is silicon occluded in sesquioxides, Si_{org} is silicon bound to organic substances, Si_{ba} is silicon from biogenic amorphous silica, Si_{ma} is silicon from minerogenic amorphous silica, Si_{min} is silicon from primary and secondary silicates.

Results

The clay fractions of the soils are characterised by a mixture of kaolinite, illite, vermiculite, secondary chlorite and illite-vermiculite mixed layer clay minerals. Large quantities of secondary chlorites are found in the eluvial horizons of all pedons and in the illuvial horizon of pedon 2. The clay fraction increases downslope within the catena.

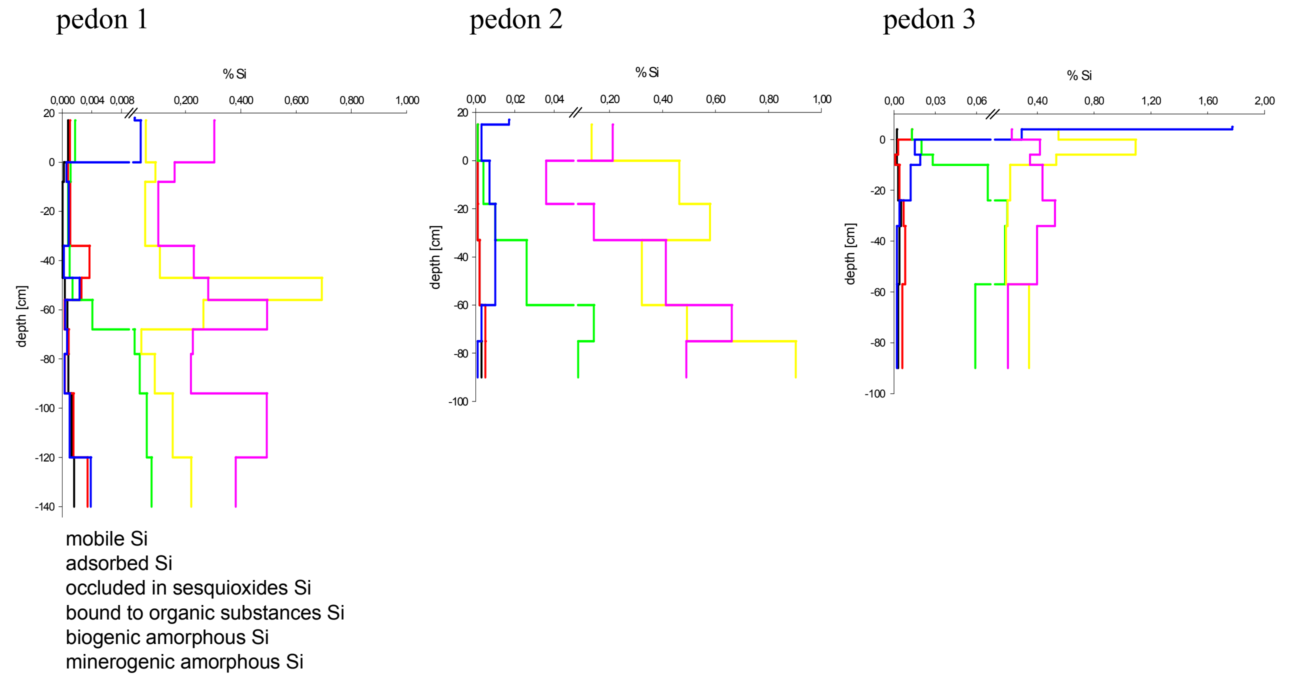

Figure 3. Depth functions of Si (wt. %) in different fractions after sequential extraction.

As shown in Figure 3, silicon extracted by the sequential extraction method makes up maximal 1-2% of the total silicon content, whereas 98-99% of silicon in the soils is in primary and secondary silicates. The amounts of Si in the mobile and adsorbed fractions are very small in all three soil profiles (always < 0.01%). The amounts of Si occluded in sesquioxides are very small in the upper horizons of all pedons and increase with depth. The highest amounts of this fraction are found in the Cambisol.

High amounts of biogenic amorphous Si occur in the upper horizons, especially in the Cambisol. Si extracted by H_2O_2 and NaOH (silicon bound to organic matter and silicon from minerogenic amorphous silica, respectively) constitute the largest fraction of extractable Si in almost all samples, with the only exception being the O-horizon of the Cambisol (in which Si from bio opal is the predominant extractable Si fraction).

Conclusion

A sequential extraction method for determination of different Si fractions in soils was developed and tested on soils on sandstone in the Black Forest, SW-Germany. Using the extraction solutions and conditions (temperatures, extraction times, soil:solution ratios) described above, silicon can be sequentially extracted from different Si-pools in soils. Silicon from minerogenic amorphous silica and organically bound silicon make up the highest proportion of extractable silicon in the soils analysed in this study. However it comprises only up to 1-2% of total Si. The majority of silicon in the investigated soils is in secondary and primary silicates. The method needs to be applied to more soils with different parent materials in order to obtain an overview about typical ranges in the proportions of the different Si fractions in soils.

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