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Physicochemical surface properties of different biogenic silicon structures: Results from spectroscopic and microscopic analyses of protistic and phytogenic silica

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ABSTRACT

The significance of biogenic silicon (BSi) for Si cycling in terrestrial biogeosystems has been acknowledged since decades. Its importance originates from the fact that BSi generally is more soluble than silicate minerals and thus i) controls Si fluxes from terrestrial to aquatic ecosystems and ii) plays an important role as source of readily- or plant-available Si (i.e., H_4SiO_4) in soils. In this context, physicochemical surface properties of BSi structures determine their dissolution kinetics. We applied transmission Fourier transform infrared (FTIR) spectroscopy, diffuse reflectance infrared Fourier transform (DRIFT) microscopy, and confocal laser scanning microscopy (CLSM) to investigate physicochemical surface properties of different biogenic silica structures. Using these techniques we were able to detect differences on a molecular level (FTIR, DRIFT) and in surface roughness parameters (CLSM) between BSi synthesized by protists (testate amoebae, diatoms) and BSi synthesized by plants (phytoliths) as well as between fresh (extracted from plants) and aged (extracted from soils) phytoliths. While fresh phytoliths showed organic impurities that can be assigned to occluded organic matter, aged phytoliths showed additional impurities of mineral origin. This is due to the fact that the used non-destructive gravimetric extraction of phytoliths is unsuitable for a distinct differentiation between biogenic silica (phytoliths) and non-biogenic (minerogenic or microcrystalline) Si forms in general. We recommend DRIFT microscopy for analyses of phytoliths extracted from soils because this technique allows measurements of selected, single siliceous phytoliths (as well as other BSi structures). Surface roughness parameters of aged phytoliths decreased compared to the ones of fresh phytoliths indicating a decrease of specific surface areas available for dissolution processes. Physicochemical surface properties will help us to better understand the BSi status (BSi quality and quantity) of soils with implications for Si availability in soils and thus Si cycling in terrestrial biogeosystems.

1. Introduction

Various prokaryotes and eukaryotes are evolutionary adapted to use monomeric silicic acid (H_4SiO_4) for the synthesis of hydrated amorphous silica ($SiO_2{\cdot}nH_2O$), a process called biosilicification (Ehrlich et al., 2010). In terrestrial biogeosystems synthesized structures of biogenic silicon (BSi) represent different BSi pools depending on their origin, and thus microbial (bacteria, fungi), phytogenic (plants), protistic (diatoms, testate amoebae), and zoogenic (sponges) BSi pools can be found (Puppe et al., 2015; Sommer et al., 2006). On a global scale, fluxes of dissolved Si from terrestrial to aquatic ecosystems influence the reproduction of marine diatoms, which in turn have an important effect on climate change due to their ability to fix large quantities of carbon dioxide via photosynthesis, since up to 54% of the biomass in the oceans is represented by diatoms (Tréguer and De La Rocha, 2013; Tréguer and Pondaven, 2000). These Si fluxes are controlled by BSi pools to a great extent (Dürr et al., 2011; Sommer et al., 2006; Struyf and Conley, 2012) because BSi is more soluble compared to silicate minerals (e.g., Fraysse et al., 2006a, b, 2009).

Due to its higher solubility BSi also plays an important role as source of readily- or plant-available Si (i.e., H_4SiO_4) in soils (Sommer et al., 2006), a factor that is of special importance in agricultural biogeosystems (Haynes, 2014, 2017). Si is considered as a quasi-essential element for higher plants because various beneficial effects of Si accumulation in plants have been revealed, i.e., increased plant growth and resistance against abiotic and biotic stresses (e.g., Epstein, 2009). For the understanding of influences of BSi pools on Si fluxes and plant-available Si fractions in soils, information on physicochemical surface properties of BSi structures are crucial as they are a key factor of BSi dissolution kinetics (e.g., Bartoli, 1985; Cornelis and Delvaux, 2016). Fraysse et al.

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(2006a, b, 2009) conducted laboratory experiments and showed that i) surface properties (herein electrophoretic mobilities and surface charge) of phytoliths of different plant and tree species generally seem to be similar resulting in similar dissolution kinetics and ii) that surface properties of fresh and aged phytoliths differ. In this context, the specific surface areas of fresh and aged bamboo phytoliths indicated large differences ascribed to dissolution processes over a period of several centuries (Fraysse et al., 2006a). Sommer et al. (2013) quantified phytoliths with differently pronounced signs of dissolution in soils of a forested biogeosystem. They found a decrease of phytoliths showing no signs of dissolution, a simultaneous increase of phytoliths showing signs of dissolution with soil depth, and the phytogenic Si pool to be related to the fluxes of water-soluble Si. From their findings they concluded dissolution of phytoliths as the most important driver of exports of dissolved Si from this study site. While these studies focus on phytoliths, only scarce information is available on physicochemical surface properties of BSi structures synthesized by soil-inhabiting unicellular organisms (protists) like testate amoebae or diatoms. Puppe et al. (2017) used confocal laser scanning microscopy (CLSM) for the comparison of surface-area-to-volume ratios (A/V ratios) of various BSi structures as an indicator for their resistibility against dissolution as higher A/V ratios indicate a bigger surface area available for dissolution processes. They found A/V ratios of BSi structures synthesized by protists, i.e., testate amoeba shells and pennate diatom frustules to differ from the ratios of phytoliths.

Fourier transform infrared (FTIR) spectroscopy in the mid-infrared range (wave lengths of 2.5 to 25 μm) represents a widely used technique in soil sciences to qualify organic and mineral matter in terms of its functional groups (e.g., Parikh et al., 2014). Several studies have shown the potential of FTIR spectroscopy for BSi quantification as well as the detection of qualitative differences between fresh and aged BSi structures in general (Liu et al., 2013; Loucaides et al., 2010). While transmission FTIR is usable only for homogenized and diluted samples, the diffuse reflectance infrared Fourier transform (DRIFT) technique can also be applied to analyze intact samples, e.g., soil surfaces (Leue et al., 2017). Coupling a DRIFT spectrometer with a microscope (DRIFT microscopy) allows using infrared spectroscopy even on a μm-scale (e.g., Rosén et al., 2010). In contrast to transmission FTIR, DRIFT microscopy as well as CLSM represent non-destructive methods, which allow measurements directly at intact BSi structures and offer the potential to use the same samples for further investigations.

The aim of our study was to assess the suitability of spectroscopic (transmission FTIR, DRIFT microscopy) and microscopic (CLSM) techniques to detect i) short-term changes in physicochemical surface properties of phytoliths (fresh vs. aged phytoliths) and ii) differences in physicochemical surface properties of different BSi structures, i.e., protistic and phytogenic BSi. We hypothesized i) physicochemical surface properties to be dependent on BSi origin (protistic vs. phytogenic BSi) and ii) age related differences in physicochemical surface properties to occur relatively fast (already after some years). To test our hypotheses we took soil and plant samples in an artificial catchment (Chicken Creek), that was created in 2005 and has been left to an unrestricted and unmanaged succession to investigate the initial stages of ecosystem development (Gerwin et al., 2010). This study site allowed us to analyze relatively young (about 10 years) soil and plant samples by a combination of transmission FTIR, DRIFT microscopy, and CLSM. Information on physicochemical surface properties of different BSi structures will help us to better understand their dissolution kinetics, thus their specific role in Si cycles of terrestrial biogeosystems.

2. Material and methods

2.1. Site description and sampling

Plant and soil samples for BSi analyses were taken in the artificial catchment Chicken Creek (*Hühnerwasser*) (51°36′18″ N, 14°15′58″ E), which was constructed in a post-mining landscape located in the active mining area Welzow-South (lignite open-cast mining, 150 km southeast of Berlin) in the state of Brandenburg, NE Germany. Details on site construction can be found in Kendzia et al. (2008), Russell et al. (2010), and Gerwin et al. (2010). Climate at Chicken Creek is characterized by a mean annual air temperature of 9.6 °C and a mean annual precipitation of 568 mm. Analyses subsequent to catchment completion (2005) indicated that the primary mineral component in all particle size fractions was quartz (only small amounts of K-feldspar, plagioclase) (Puppe et al., 2017). Chicken Creek represents a study site with defined initial conditions and offers the rare opportunity to monitor ecosystem development processes from the very beginning (e.g., Elmer et al., 2013; Gerwin et al., 2011) and several studies regarding BSi pool dynamics have been conducted at this site (Puppe et al., 2014, 2016, 2017).

Aboveground plant materials of *Brachypodium sylvaticum* (falsebrome, Poaceae family), *Calamagrostis epigejos* (bushgrass, Poaceae), *Equisetum arvense* (common horsetail, Equisetaceae), *Festuca rubra* (red fescue, Poaceae), and *Phragmites australis* (common reed, Poaceae) were collected each in an area of about 0.04 m^2 (20 cm × 20 cm) in 2013. Soil samples (undisturbed; without plant materials and litter) were taken in 2015 at the same spots (dominances of the corresponding plant species were unchanged) using a core cutter (diameter 3.4 cm, depth 5 cm) and transferred into plastic bags. As these spots were densely covered by plant materials and litter of the respective dominating plant species, we assumed the subjacent soil to contain phytolith assemblages dominated by phytoliths of the corresponding plant species with negligible quantities of other phytoliths. For a detection of potential differences in physicochemical surface properties of phytoliths from these different assemblages, we differentiated between aged phytoliths of the corresponding spots (i.e., *B. sylvaticum*, *C. epigejos*, *E. arvense*, *F. rubra*, and *P. australis* spots) for our analyses.

2.2. Sample preparation

The collected plant material was washed with distilled water to remove adhering soil minerals and oven-dried at 45 °C for 48 h. Soil samples were air dried and sieved and only the fine earth fraction (< 2 mm) was used for phytolith analyses. In general, phytoliths represented 14–69% of total BSi (= phytogenic BSi + zoogenic BSi + protistic BSi) in soils at Chicken Creek in 2015 (Puppe et al., 2017). Phytoliths from plant (fresh phytoliths) as well as soil samples (aged phytoliths) were extracted following the procedures described in Puppe et al. (2017). In brief, fresh phytoliths were extracted as follows: (1) plant material was washed with distilled water and oven-dried at 45 °C for 48 h, (2) organic matter (OM) was removed by burning the samples in a muffle furnace at 450 °C for 12 h, (3) OM was oxidized using H_2O_2 (30 vol%) for 12 h, (4) the obtained material was filtered (Teflon filter, mesh size 5 μm). Aged phytoliths were extracted as follows: (1) 10 g of dry soil material (< 2 mm) was weighed, (2) OM was oxidized using H_2O_2 (30 vol%), HNO_3 (65 vol%), and $HClO_4$ (70 vol%) at 80 °C until reaction subsides, (3) carbonates and iron oxides were dissolved by boiling the sample in HCl (10 vol%) for 30 min, (4) the < 2 μm granulometric fraction was removed by dispersion of the remaining solid phase with a sodium hexametaphosphate solution (2 vol%, 6–12 h), (5) samples were centrifuged (1000 rpm, 2–3 min) and decanted, (6) phytoliths were separated by shaking with 30 mL of sodium polytungstate ($Na_6(H_2W_{12}O_{40})\cdot H_2O$) with a density of 2.3 g cm^{-3} and subsequent centrifugation (3000 rpm, 10 min), (7) the supernatant was carefully pipetted and filtered (5 μm Teflon filters, repeated three times), (8) the filter residue was washed with distilled water, bulked, dried at 105 °C, and weighed. Fresh and aged phytoliths were transferred to clean object slides or a gold-coated metal plate for CLSM and DRIFT microscopy, respectively. For transmission FTIR, 0.5 mg of fresh and aged phytoliths were diluted in potassium bromide (KBr; Merck) to obtain 100 mg in total. As reference substance for transmission FTIR quartz powder with a particle size < 20 μm was

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