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Silicon isotopes record dissolution and re-precipitation of pedogenic clay minerals in a podzolic soil chronosequence

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ABSTRACT

By providing the largest part of the reactive surface area of soils, secondary minerals play a major role in terrestrial biogeochemical processes. The understanding of the mechanisms governing neo(trans-)formation of pedogenic clay minerals in soils is therefore of the utmost importance to learn how soils evolve and impact the chemistry of elements in terrestrial environments. Soil-forming processes governing the evolution of secondary aluminosilicates in Podzols are however still not fully understood. The evolution of silicon (Si) isotope signature in the clay fraction of a podzolic soil chronosequence can provide new insight into these processes, enabling to trace the source of Si in secondary aluminosilicates during podzol-forming processes characterized by the mobilization, transport and precipitation of carbon, metals and Si. The Si isotope compositions in the clay fraction (comprised of primary and secondary minerals) document an increasing light ^{28}Si enrichment and depletion with soil age, respectively in illuvial B horizons and eluvial E horizon. The mass balance approach demonstrates that secondary minerals in the topsoil eluvial E horizons are isotopically heavier with δ^{30}Si values increasing from −0.39 to +0.64‰ in c.a. 200 years, while secondary minerals in the illuvial Bhs horizon are isotopically lighter (δ^{30}Si = −2.31‰), compared to the original "unweathered" secondary minerals in BC horizon (δ^{30}Si = −1.40‰). The evolution of Si isotope signatures is explained by the dissolution of pedogenic clay minerals in the topsoil, which is a source of light ^{28}Si for the re-precipitation of new clay minerals in the subsoil. This provides consistent evidence that in strong weathering environment such as encountered in Podzols, Si released from secondary minerals is partially used to form "tertiary clay minerals" over very short time scales (ca. 300 years). Our dataset demonstrates the usefulness to measure Si isotope signatures in the clay fraction to discern clay mineral changes (e.g., neoformation versus solid state transformation) during soil evolution. This offers new opportunity to better understand clay mineral genesis under environmental changes, and the short-term impact of the dissolution and re-precipitation of pedogenic clay minerals on soil fertility, soil carbon budget and elemental cycles in soil–plant systems.

1. Introduction

Soil is a precious but threatened resource (Banwart, 2011). In order to protect it for the future we need a better understanding of the soil-forming processes controlling the evolution of newly-formed minerals (secondary minerals). Soil formation progressively modifies parent rock material and controls the pathways of primary mineral weathering and secondary mineral synthesis in the clay fraction (Chadwick and Chorover, 2001). The secondary minerals consist of layer-type aluminosilicates (called pedogenic clay minerals) and Fe-, and Al-oxyhydroxides, both of which play a major role not only in soil fertility, but also in the transfer of elements and pollutants from land to ocean given their high surface reactivity (Sposito, 2008). Moreover, the capacity of charged mineral surfaces to form adsorption complexes can stabilize organic carbon (OC) in soils through the formation of organo-mineral associations, partly controlling global C budget (Parfitt et al., 1997; Torn et al., 1997).

The formation of secondary minerals and their evolution during pedogenesis have been studied for over a half century (Wilson, 1999). The proportion and the chemistry of minerals in the clay fraction change with soil evolution (Egli et al., 2002; Righi et al., 1999; Turpault et al., 2008). Some environmental changes (vegetation type, agricultural

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practices, land-use, climate and drainage) can amplify the modification of clay mineralogy on very short time-scales (10–1000 years) (Caner et al., 2010; Collignon et al., 2012; Cornu et al., 2012; Mareschal et al., 2013). These rapid clay modifications occur in chemically reactive soil micro-environments, i.e. the part of the soil influenced by roots and earthworms (Calvaruso et al., 2009; Jouquet et al., 2007), and can play a key role in geochemical balance of several minor and major elements in soils and sediments (Michalopoulos and Aller, 1995; Velde and Meunier, 2008). However, the origin of elements involved in clay neo(trans-)formation is still not well understood.

Podzol, the focus of this study, is a type of soil that covers more than 3% of the Earth's land surface. The low stock of weatherable minerals, the acidic conditions and complexing capacity of organic acids in the environment where Podzols developed are responsible for mobilization, transport and precipitation of carbon (C), metals (Fe, Al) and silicon (Si) in the soil profile (Lundström et al., 2000). A fully developed Podzol consists of a leached gray subsurface eluvial E horizon contrasting with the accumulation of elements in the dark illuvial B horizons. The topsoil is characterized by the production of organic acids that form soluble organo-metallic complexes enhancing weathering in the eluvial E horizon. This E horizon overlies the dark C-enriched Bh horizon and reddish Fe-, Si-, and Al-enriched Bhs/Bs horizons (Lundström et al., 2000). Given the very acidic conditions in Podzols, besides the weathering of primary minerals, secondary clay minerals can be dissolved in the podzolic weathering front (Ugolini and Dahlgren, 1987; Zabowski and Ugolini, 1992), which describes the soil depth where minerals dissolve faster than they form. A podzolic soil chronosequence, i.e. in which all soil-forming factors remain constant except time; represents an ideal natural system for the study of the effect of time on pedogenic clay minerals behavior in soils.

Stable Si isotopes fractionate during silicate weathering and the biogeochemical Si cycling (Opfergelt et al., 2010; Ziegler et al., 2005), and as such provide a means of tracing the bio-physico-chemical processes in terrestrial environments (Cornelis et al., 2011). In addition to its incorporation in the mineral structure during the formation of crystalline layer-type aluminosilicates, poorly-crystalline aluminosilicates and pedogenic opal, monosilicic acid (H_4SiO_4) released into soil solution can also be transferred into the biosphere to produce biogenic opal (phytoliths) or be adsorbed onto secondary Fe oxy-hydroxides. The incorporation of Si in mineral structures through neoformation of secondary pedogenic and biogenic precipitates and its adsorption onto the surfaces of Fe oxides are two processes favoring the retention of light ^{28}Si in soils and contributing to the enrichment of rivers in heavy ^{30}Si (Delstanche et al., 2009; Georg et al., 2007; Opfergelt et al., 2006; Ziegler et al., 2005). Clay minerals can also be unstable in organic and inorganic acidic environments where they dissolve (Sokolova, 2013; Zabowski and Ugolini, 1992), and enrich soil solutions (Cornelis et al., 2010) and rivers (Cardinal et al., 2010) in light ^{28}Si. The naturally occurring mass-dependent Si isotopic fractionation is induced by dissolution, precipitation and adsorption but not by complexation as chemical binding of Si to organic matter is negligible (Pokrovski and Schott, 1998). It has also been demonstrated that the Si isotopic compositions of secondary clay minerals relates to climatic gradient and its control on clay mineralogy (Opfergelt et al., 2012). However Si isotopes have never been used to better understand clay mineral modifications induced by soil-forming processes under identical geo-climatic conditions. The rapid modification of clay mineralogy in Podzol is well documented (Caner et al., 2010; Egli et al., 2002; Righi et al., 1999), but the fate of Si released in soil solution after clay modification has not yet been studied, even though it is of crucial importance for identifying the sources controlling the formation of pedogenic clay minerals in soils.

In this study, we aim to use Si isotope signatures of the clay fraction in a podzolic soil chronosequence for gaining better insights into the origin of Si in pedogenic clay minerals.

To achieve this goal, we analyzed Si isotopes, elemental (Ge/Si, Al/Si, Fe/Si) ratios and determined clay fraction mineralogy for an age sequence of four soil profiles undergoing podzolization (Cox Bay on Vancouver Island, Canada) (Fig. 1) and for a single Podzol pedon (Gaume, Belgium). The Cox Bay chronosequence offers an opportunity to study the variation of Si isotopic composition and elemental ratios of the clay fraction in the vertical pedogenic scale: E, Bh, Bhs, Bs, Bw and BC horizons, and in the horizontal time-dependent scale: duration of pedogenesis from 0 to 335 years. We used the Belgian Podzol as a "natural duplicate" in temperate climate to corroborate the processes documented in the soil samples from the Cox Bay podzolic soil chronosequence.

2. Materials and methods

2.1. Sample collection and location

We sampled a soil chronosequence undergoing podzolization in Cox Bay (CB), on the west coast of Vancouver Island (British Columbia, Canada). At the Cox Bay study site, three main vegetative associations are identified in the chronosequence. These correspond to Sitka spruce (*Picea sitchensis*) in the younger site (CB-120 years), and Sitka spruce (*P. sitchensis*) and salal (*Gaultheria shallon*) in the sites of 175 and 270 years (CB-175 and -270 years). The oldest site (CB-335 years) is characterized by Sitka spruce (*P. sitchensis*), Douglas fir (*Pseudotsuga menziesii*), salal (*G. shallon*) and western sword fern (*Polystichum munitum*). Heavy mean annual precipitation (3200 mm) coupled with frequent fogs and sea sprays ensure an abundance of moisture and nutrients year round in this maritime temperate climate (Cfb: without dry season and with warm summer; Peel et al., 2007). The Tofino Area Greywacke Unit is the source of the beach sand parent material, from which soils have developed in the age sequence (Singleton and Lavkulich, 1987). Sampling sites were located along a transect (0–94 m) perpendicular to the present shoreline (Fig. 1). Dendrochronology and geomorphology established surface duration of pedogenesis ranging from 0 to 335 years for the four selected pedons. Tree ages were determined counting the tree rings in the increment bores. Assuming that the beach built towards the ocean in a configuration parallel to the existing shoreline and that a linear deposition rate occurred with time between successive oldest trees, the rate of advance of the beach front was estimated to be 0.26 m per year. At this rate, the 13-m strip of sand containing tree seedlings would have accumulated in approximately 50 years (Singleton and Lavkulich, 1987). With soil development, there was progressive deepening and differentiation of genetic horizons during podzolization, resulting in soil classification (World Reference Base for Soil Resources — WRB) that ranged from Dystric Cambisol at the youngest sites (CB-120 years; CB-175 years) to a Placic Podzol at the oldest site (CB-335 years) (Fig. 1). The 335-year-old Podzol is characterized by the following soil horizon development: eluvial albic E horizon (strongly weathered horizon) → illuvial spodic Bh horizon (enriched in organic matter) → Bhs horizon (enriched in Fe oxyhydroxides and organic matter) → Bs horizon (enriched in poorly-crystalline aluminosilicates and Fe oxyhydroxides) → Bw horizon (development of color and structure without illuvial accumulation of materials) → BC horizon (weakly colored and structured; little affected by pedogenic processes).

The sampling area of the Podzol in Gaume (Belgium), ranging in altitude from 300 to 350 m above sea level, has an annual rainfall of 1100 mm and a mean annual temperature of 7.7 °C (Herbauts, 1982), and is also characterized by a maritime temperate climate (Cfb; Peel et al., 2007). The Podzol is located on the Lower Lias outcrop in South-east Belgium (Gaume). The bedrock (calcareous sandstone of Lower Lias age) is covered by a two-layered sheet: an autochthonous sandy layer, formed by the dissolution of the calcareous bedrock, is overlaid by a mixture of this sandy material with loessic silt-sized particles. The Belgian Podzol developed under heather (*Calluna vulgaris*) is characterized by a similar morphological profile as the Podzol in Cox Bay