Si cycling and isotope fractionation: Implications on weathering and soil formation processes in a typical subtropical area

Jin-Ling Yang, Gan-Lin Zhang[*]

State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China
University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

ABSTRACT

The translocation of silicon (Si) is closely related to soil evolution. However, how to trace the transformation and migration paths of Si and further understand its effects on soil formation and evolution remains as a challenge in geochemistry and soil science. Here we studied the Si isotope (δ^{30}Si) values and physical, chemical and mineralogical properties of rock, soil, plant and water in representative small watersheds in the south of Anhui province, subtropical China. The aims are to illustrate weathering and soil formation processes by tracing the fractionation of Si isotope among those ecosystem components as well as soil components and plant organs. Results show that the δ^{30}Si values of bulk soil and clay are significantly related to many soil development indicators, such as total, free and amorphous Al oxides, as well as active Fe oxides, clay, silt and sand contents, Al/Si molar ratio and chemical index of alteration (CIA). These indicators evidence the relationships between Si isotope changes and mineral weathering and soil development degree. Biological resilication (accumulation of Si) by plant does not lower soil δ^{30}Si because further fractionation occurs among plant organs, and soil phytoliths have significantly higher δ^{30}Si than soil clay and silt particles. However, soil desilication (loss of Si) lowers soil δ^{30}Si because much ^{30}Si is transported to streams in runoff. The consistently positive δ^{30}Si values of water and their relationships with Si concentrations and discharge suggest that dissolved Si (DSi) in stream water mainly comes from weathering of primary minerals; the contribution of dissolution of secondary minerals, quartz and phytolith is minor. Differential δ^{30}Si values in clay, silt, sand, rock and water are the result of soil formation processes which directly evidence a dominate neoformation pathway of secondary clay minerals in this area. This study can help to further understand mechanisms and processes of Si translocation during soil evolution and, extend the application of Si translocation in soil genesis studies.

1. Introduction

Silicon (Si) is one of important elements in the Earth's crust (Iler, 1979) and the skeleton of most soils (McKeague and Cline, 1963; Sommer et al., 2006). It is increasingly recognized that silicate weathering releases dissolved Si (DSi) (Sommer et al., 2006; Huang et al., 2012) that is precipitated with secondary silicates, taken up by vegetation, returned to the soil through decomposition, and discharged to the hydrologic network (Gérard et al., 2008; White et al., 2012). During these processes, soils are gradually formed and developed. Therefore, Si translocation not only plays an important role in plant growth and contributing to ocean Si sources (Tréguer et al., 1995; Derry et al., 2005; Hammerschmidt, 2005; Gérard et al., 2008), but is also a critical process in soil genesis (Brimhall et al., 1991; Lucas et al., 1993;

Alexandre et al., 1997; Sommer et al., 2006).

Silicate weathering releases Si, which is the basis of soil formation from silicate parent materials (Huang et al., 2012). The formation of clay is accompanied by Si releasing, translocation and transformation, which is very important to soil development and function. Therefore, the content, distribution and translocation of Si in the soil are related to soil mineral component, physical and chemical properties (Jenny, 1941; Brimhall et al., 1991; Street-Perrott and Barker, 2008). Early in the 20th century, the total analysis of silicon-aluminum-iron (Si-Al-Fe) and Si-Al ratios in clay minerals were considered as important indicators to be used in soil classification (Jenny, 1941). Later on other indicators, such as the 'A', $((SiO_2 + CaO + K_2O + Na_2O)/(Al_2O_3 + SiO_2 + CaO + K_2O + Na_2O))$ (Krongberg and Nesbitt, 1981; Gugenberger et al., 1998), 'R', (SiO_2/Al_2O_3) and 'PI', $((SiO_2) \times 100/$

$(SiO_2 + TiO_2 + Fe_2O_3 + Al_2O_3))$ (Ruxton, 1968; Topal, 2002) were developed to characterize the soil desilication process, i.e. Si loss from soil. However, these indicators are static and only show the situation at the time of sampling, and do not by themselves provide insight into sources, processes and mechanisms of Si translocation. Furthermore, amount of research on Si as an element is much less than that for other major elements in soil, such as Fe and Al. This is likely because Si (compound) is much less active than other elements, and Si in nature exists as tetrahedral SiO_4 groups with no variation of valence. Therefore, there is a strong need to introduce new methods to advance research on Si translocation and transformation in the soil.

From the middle and late in the last century, the fractionation of Si isotopes in nature has been recognized (Douthitt, 1982; Ding et al., 1996, 2008). In nature, there are three Si stable isotopes: ^{28}Si, ^{29}Si and ^{30}Si with relative abundances of 92.223%, 4.685% and 3.092%, respectively (De Laeter et al., 2003). Si isotope value ($\delta^{30}Si$), a relative ratio of ^{30}Si to ^{28}Si in sample standardized by international standard, is often used to trace the biogeochemical pathways of Si as it moves from its continental sources to its sink in ocean sediments (De La Rocha et al., 2000; Ding et al., 2004; Ziegler et al., 2005a; Georg et al., 2009; Bern et al., 2010). Furthermore, soil Si isotopes have been shown to be related to weathering intensity (Ziegler et al., 2005a; Bern et al., 2010; Pogge von Strandmann et al., 2012). Some studies showed that soil evolution could affect the Si isotope values of water in the watershed and downstream (Ding et al., 2004; Ziegler et al., 2005a). Therefore, Si isotope value should be a useful indicator to trace Si translocation and transformation during soil genesis and evolution.

South of Anhui, China, locates in the subtropical area with monsoon climate and high vegetation coverage. The lithology in this area is mainly granite. Si cycling is very active in this region due to abundant heat and rainwater, ample silicate minerals and vigorous plant growth. This area provides an excellent natural laboratory to explore the Si isotope fractionation and its implications for the dynamic processes of mineral weathering and soil formation under a robust Si cycling environment. The aims of this study are: (1) to understand the fractionation of Si isotopes among rock, soil, water and plants in granitic watersheds; (2) to trace the Si pathways of translocation and identify water Si sources in the watersheds and (3) to further understand soil formation process and mechanisms related to Si cycling in subtropical areas.

2. Materials and methods

2.1. Site description

This study was carried out in three adjacent small watersheds (F, FA1 and FA2), located in the southern part of Anhui Province in subtropical China, centered on 30°33′ N, 118°02′ E (Fig. 1). The geomorphology is a low hill area with altitude ranging from 100 m to 575 m above sea level (Fig. 1). The area is characterized by a subtropical monsoon climate with nearly half of the rainfall occurring in summer, and only about 10% in winter. The mean annual temperature is 16.5 °C. The mean annual precipitation is 1585 mm. The bedrock is granite formed in Early Cretaceous (135–120 Ma) (Wu et al., 2012). The F watershed is an undisturbed forest area mainly with coniferous trees, including Masson pine (*Pinus massoniana Lamb.*) and Chinese fir (*Cunninghamia lanceolata* (*Lamb.*) *Hook*). A small quantity of mixed broad-leaved arbor, mainly chestnut (*Castanea mollissima*), some shrubs, including *Symplocos caudate*, *Loropetalum chinense* and *Camellia sinensis*, and some moso bamboo (*Phyllostachys pubescens*). FA1 and FA2 are both forest-agriculture watersheds with 18% and 24% of cultivated paddy, respectively. The vegetation of forest in FA1 and FA2 is similar to that of F watershed.

2.2. Monitoring and sampling program

Representative soil samples were collected in each watershed at the hilltop, hillside and footslope. The soils in the forest of three watersheds were classified as Lithic Udorthents (Entisols) (profiles FP1, FP2, and FP3, only with A and C horizons) and Lithic Dystrudepts (Inceptisols) (profiles FP4, FP5, FP6 and FP7, with A, Bw and C horizons) according to Soil Taxonomy (Soil Survey Staff, 1999). The soils in the paddy in FA1 and FA2 watersheds were classified as Typic Epiaquepts (Inceptisols) (profiles AP1 and AP2, both with Ap, Br and Cr horizons) (Soil Survey Staff, 1999). A total of 32 samples were collected, including six saprolites underlying profiles FP1-FP6. These saprolites are weakly weathered with preservation of rock structure. Profiles of FP7, AP1 and AP2 are developed from colluvial footslope deposits, the others are from in situ residuum. Fresh granite rock was also sampled in each watershed.

The Masson pine, Chinese fir, maso bamboo, chestnut as main broad-leaved arbor, various shrub, grass and rice were sampled in triplicate. The leaves and trunks of woody plants were collected, respectively. Rice roots, straw and grains were sampled in autumn before harvest. The details of sampling plants have been introduced in Yang and Zhang (2018).

Stream water samples were manually collected at the outlet of each watershed every three months during three monitoring years, i.e., in each of the four seasons, to determine their $\delta^{30}Si$ values. Rainfall, air temperature, solar radiation, relative humidity and wind speed were measured by a Weather Station in the study area. Rainwater samples were collected by an automatic sensing wet/dry deposition collector, installed in watershed F. Stream flow volume was detected by a sensor measuring water level, installed in the outlet of each watershed. The groundwater was not monitored because no groundwater was considered to exist and a previous estimation of water balance in this area had shown negligible contribution of groundwater to the stream in the outlets of watersheds for the impervious granitic bedrock (Yang et al., 2013).

2.3. Chemical analysis

The concentrations of DSi in rain and stream water were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Total analysis for element contents in soils and rocks were determined by ICP-AES after digestion with HF, HNO_3 and HCl in a closed Teflon vessel (USDA-NRCS, 2004). Soil free Al was extracted by dithionite-citrate-bicarbonate (DCB) and determined by atomic absorption. Amorphous Al and active Fe oxides were extracted by oxalic acid and ammonium oxalate extraction and determined by atomic absorption (USDA-NRCS, 2004). The mineralogical composition of the parent rock, soil (< 2 mm) and clay (< 2 μm) samples was identified by X-ray diffraction (XRD) (German D8 ADVANCE) (USDA-NRCS, 2004). Soil particle size distribution was determined by laser diffraction (Zhang and Gong, 2012).

Sand, silt and clay fraction contents in 26 bulk soil samples, except six saprolite samples, were separated by wet sieve and decantation methods after removal of organic matter by oxidation with 30% H_2O_2 and dispersion using sodium hexametaphosphate (Kelly, 1990). Phytoliths in soil were extracted from the silt fraction by densimetric separation using a zinc bromide ($ZnBr_2$) solution with a specific gravity of 2.3 g cm^{-3} (Kelly, 1990; Alexandre et al., 1997).

2.4. Silicon isotope analysis

Si isotope values were determined for the parent rock, bulk soil (< 2 mm), sand (0.05–2 mm), silt (0.002–0.05 mm), clay (< 0.002 mm), phytolith, plant and water samples. The soil and rock samples were fused by alkaline fusion ($LiBO_2$) in a covered Pt crucible at 1000 °C and dissolved in 10% HNO_3 (Abraham et al., 2008). Silicon