Silicon cycle in weathering sequences of volcanic soils in Cameroon using δ^{30}Si and Ge/Si

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In soils, silicon released by mineral weathering can be incorporated into secondary clays, adsorbed onto iron or aluminum oxides, or taken up by plants. These processes may significantly impact the Si isotopic signature and Ge/Si ratio of Si dissolved phase exported to water streams. Here we test these proxies, and report on detailed δ^{30}Si of sand (>50µm), silt (2-50µm), clay (<2µm), and amorphous Si (ASi) fractions and Ge/Si ratios of clay fractions from basaltic ash soils differing in weathering stage. The δ^{30}Si values were measured by MC-ICP-MS Nu Plasma in medium resolution, operating in dry plasma with Mg doping: δ^{30}Si vs NBS28 ± 0.12‰ (± 2□$_{SD}$), while Ge/Si ratios were determined after Ge measurements by HR-ICP-MS and Si by ICP-AES.

Compared to fresh basaltic ash (δ^{30}Si = -0.38‰; Ge/Si = 2.21µmol/mol), clay fractions displayed a gradient from -1.19‰ to -2.37‰ (δ^{30}Si) and from 4.10 to 5.25µmol/mol (Ge/Si) from young (Y) to old (O) volcanic soil (vs), confirming the trend of lighter isotopic compositions and Ge enrichment with increasing weathering. Sand and silt fractions displayed Si isotopic signatures close to fresh ash (-0.33‰) or heavier (+0.18‰) due to dust quartz contribution evaluated by isotopic balance. Relatively to Ovs, clay fractions in Yvs were isotopically heavy and Ge-depleted in surface horizons, denoting a heavier Si source for clay neoformation therein. ASi fractions were generally isotopically close the fresh ash. However, relatively to Yvs, ASi fractions in Ovs were isotopically heavy in surface horizons, within the range of plant phytoliths. Combined with phytolith content in surface, this supports a biogenic Si input in surface horizons. In addition to Si provided by volcanic glass weathering, clays may have been partially impacted by this input. Isotopic balance calculations indicate that (i) bulk soil signatures were determined by Si proportions in mineral fractions rather than dissolved Si from irrigation water or Si adsorbed onto iron oxides, (ii) Si adsorbed onto Fe-oxides was mainly impacted by biogenic Si and irrigation water. Combining δ^{30}Si and Ge/Si ratio is promising to identify major processes impacting the Si cycle in soil.

Sorption characteristics of oxyanions during and after allophane precipitation

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Allophane naturally exists as aluminosilicate hydrate commonly present in volcanic ash soil, pumice deposits and stream sediments. It has great retention capacity for anions over a wide range of pH (4-8) because of its high surface area and variable charge characteristics. However, the retention by adsorption due to electrostatic interaction with the variable charge would be unstable in terms of long term stability. Therefore, it is crucial to understand the mechanism of oxyanion incorporation during allophane formation because it has soil/geochemical implication for predicting their mobility in earth's surface environment.

The reactivity of Cr(VI) and As(V) on synthetic allophane like particles were investigated during and after allophane precipitation in batch experiments. Solutions containing $AlCl_3$ and Na_4SiO_4 (with Si/Al ratio of 1.0 and 0.67) and oxyanions (Cr(VI) and As(V)) (10 ppm) were mixed and adjusted to near neutral pH with 1M NaOH. The mineral suspensions were shaken for 1 hr and incubated at 80 C for 5 d. The precipitates were collected by centrifugation at 15000 rpm for 30 mins and the supernatant were analysed for residual oxyanion concentration using ICP-AES. Chemical extraction of freeze dried samples was carried out using TAO and Na_2HPO_4 solutions and were analysed for Si, Al, Cr and As concentration. ATR-FTIR analyses were conducted to investigate the sorption of Cr and As onto allophane.

The adsorption experiments indicated that more Cr and As uptake on allophane with initial Si/Al ratio of 0.67 and after precipitation respectively. The final Si/Al ratio of the samples were around 0.52 and 0.79 for Cr and around 0.5 for As. The ATR-FTIR spectroscopy of paste and freeze dried samples showed that Cr and As were surface sorbed after allophane precipitation while coprecipitated Cr and As are presumed to be in tetrahedral coordination by substituing for Si in the tetrahedral layer of the allophane structure. The structurally fixed Cr and As are more resistant to release than surface sorbed Cr and As.