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Si precipitation during weathering in different Icelandic Andosols

Clymans W[a,]*, Lehtinen T[b], Gísladóttir G[b,e], Lair GJ[c,f], Barão L[d], Ragnarsdóttir KV[e], Struyf E[d], Conley DJ[a]

[a]Department of Geology, Lund University, Sölvegatan 12, SE-22362 Lund, Sweden
[b]Faculty of Life and Environmental Sciences, University of Iceland, Sturlugata 7, IS-101 Reykjavík, Iceland
[c]Institute of Soil Research, University of Natural Resources and Life Sciences (BOKU), Peter Jordan Strasse 82a, AT-1190 Vienna, Austria
[d]Department of Biology, Ecosystem Management, Antwerp University, Universiteitsplein 1, BE-2610 Wilrijk, Belgium
[e]Institute of Earth Sciences, University of Iceland, Sturluguta 7, IS-101 Reykjavík
[f]Institute of Ecology, University of Innsbruck, Sternwartestrasse 15, AT-6020 Innsbruck, Austria

Abstract

Basaltic weathering from volcanic islands plays a critical role in the climate feedback loop. Geochemical and climate models require information on the rate of secondary mineral formation. We provide direct evidence for precipitation of amorphous Si in organic rich and acidic Histic Andosols compared to preferential allophane formation in organic poor and less acidic Haplic Andosols. Similar results have been obtained from the pioneering work by Opfergelt et al[1] using Si isotope composition. Additionally, enhanced allophane precipitation in Haplic Andosols, independent of long-term soil property changes, highlight the potential role of land use and management on secondary mineral formation.

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Keywords: Silicon, Allophane formation, Land Management, Weathering, Andosols

1. Introduction

The weathering of silicate rocks drives CO_2 consumption on the continents and biological C sequestration in oceans generating a climatic feedback[2]. Basaltic rocks and volcanic ashes constitute of easily weatherable silicate

* Corresponding author. Tel.: +46-4622-27888; fax: +46-464622-24830.
E-mail address: wim.clymans@geol.lu.se

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minerals[3]. About 30-35% of the atmospheric CO_2 consumption has been attributed to continental Si weathering of basalt[4,5], out of which ca. 25% stems from weathering of volcanic islands[6,7]. Driven by rapid weathering processes, basaltic islands such as Iceland, play a key role in the delivery of Si to the oceans[8]. Consequently, the rate of weathering as well as formation of secondary minerals is a key parameter in present day geochemical and climate modeling[9].

Opfergelt et al.[1] examined the controls on mineral formation along a weathering gradient in Icelandic Andosols, using the Si isotope composition of allophanes. They suggested successive processes of mineral formation in the more weathered and organic rich soils. Initially lighter Si isotopes are incorporated during amorphous Si precipitation followed by allophane formation and the incorporation of residual heavier Si isotopes. The amorphous Si can precipitate because Al is complexed with organic compounds in these organic rich soils. A low Si isotopic signature for allophanes in less weathered and organic poor soils confirms the secondary formation of short-range ordered minerals to be the major sink for Al and Si. In both instances Al availability controls the fate of dissolved Si. Unfortunately, the evidence for amorphous Si precipitation was lacking from their study to confirm the hypothesis[1].

The rate of chemical weathering is not only controlled by lithology and hydrology. In addition, climate[10], physical erosion[11], land use and management[12.13], chemical affinity[14,15], microbial activity[16] and plant-induced effects on soil formation processes[17] influence elemental release of minerals. Different soil management practices like fertilization or liming may enhance or decelerate chemical weathering of rock material at different timescales. However, agricultural effects are often omitted from geochemical models.

We investigate the content of amorphous Si precipitation on two different types of Icelandic Andosols on non-and managed grasslands to examine the fate of weathered Si. Our results support the use of Si isotope composition to record mineral formation processes under different environmental conditions.

2. Methods

Two typical Icelandic soil types were selected in SW Iceland: Histic Andosol (HiA) and Haplic Andosol (HaA) (WRB classification). The soil types represent two opposing ends of a spectrum in terms of the status of basaltic weathering with the organic rich HiA more depleted in weatherable minerals than the low organic HaA soils[1]. Each soil type was sampled from 0-0.1m and 0.1-0.2m depth with a soil corer, under three differently managed grassland systems: unimproved grassland (grass) and improved grasslands (organically (org) and conventionally (con)). Each analyzed sample represents one out of three random sites sampled within a field, and composed of 10-15 subsamples taken at each site (1m radius). Lethinen et al.[18] give full details on the management history for each site. Briefly, the improved grasslands sites differ in crop rotation and in the application of inorganic and organic fertilizers over the past 15-17 years. Organic farms follow Icelandic regulations[19], implying no use of inorganic fertilizers. Harvest for forage production occurs bi-annually on the improved grassland sites, while unimproved grassland sites were never harvested. However, grazing by sheep occurs during autumn at the HaA grassland. Finally, unimproved sites have not been ploughed while improved sites were ploughed latest to 0.2m depth less than 20yrs ago.

Soil pH was measured in water with a 1:2.5 solid to solution ratio[20]. Total soil organic carbon content (SOC) was quantified by dry combustion using an elemental analyzer (CENA1500). Alkaline extractable Si and Al (Si_a, Al_a) were measured continuously colorimetrically (Skalar) during a heated 0.5 NaOH (85°C) dissolution experiment[21]. Alkaline extractions are known to dissolve amorphous Si precipitates of both biogenic and non-biogenic in nature, short-range ordered minerals (e.g. allophanes), and to release absorbed Si from Al and Fe (hydr-)oxides surfaces[22]. The Si and Al release rate combined with Si:Al ratio are used to identify their sources[21,23]. Non-crystalline Al and Si were determined by standard ammonium-oxalate-extraction (Al_o, Si_o)[24]. Oxalate extraction is selective for allophanic constituents and release of humus bound Al without dissolving amorphous and crystalline silica[25]. Allophane content was estimated by multiplying Si_o by 6[26], based on an average Al:Si ratio of 1.5 as suggested by Parfitt[26]. Organically bound Al forms were extracted with sodium pyrophosphate (Al_p)[27]. Al_p is used in conjunction with Al_o to correct for Al-humus complexes when calculating allophanic Al:Si ratios ((Al_o-Al_p)/Si_o).