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Halloysite versus gibbsite: Silicon cycling as a pedogenetic process in two lowland neotropical rain forest soils of La Selva, Costa Rica

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Abstract

Halloysite and gibbsite, although known to require quite different conditions for their formation, commonly occur together in the same horizon in oxisols derived from andesitic parent materials in tropical Costa Rica. We selected two soils of similar parent material, but of different ages and soil moisture regimes to identify possible clues to the coexistence of these two minerals. We employed selective dissolution procedures, X-ray fluorescence analysis and X-ray diffraction on field moist and air dry bulk soil samples to investigate how mineralogy changes with depth. We further separated the size fraction <2 μm by means of sedimentation after organic matter and iron oxide removal to obtain more specific information on the phyllosilicate mineralogy of the clay size fraction.

We found both soils to be depleted of primary minerals and pedogenesis to have progressed to advanced weathering stages particularly in the subsoils. Gibbsite XRD signal intensities were linearly and significantly related to weathering indices, corroborating the residual nature of gibbsite as an endproduct of weathering processes. The Si-bearing quartz and kaolinite-group minerals were enriched in the topsoils, indicating (i) their independence from a primary mineral Si source and (ii) the existence of a mechanism capable of protecting them against the continuous tropical weathering pressure. As we found no indications for retrospective additions of soil material through mass movement or aeolian additions, we believe a vegetation dependent, biological pumping mechanism to be the most plausible explanation for the presence of silica bearing minerals in the La Selva topsoils.

The vertical distribution of 1.0 nm halloysite and its accumulation in the lower reaches of the wetter alluvial soil suggest that this metastable mineral forms as a result of Si enrichment where the residence time of the pore water is long enough to allow for Si concentrations to exceed the halloysite precipitation threshold. Taken together, our evidence indicates gibbsite in the La Selva soils to be the endproduct of intense tropical weathering, while the presence of hydrated halloysite seems to have mainly kinetic reasons and is most probably coupled to the contemporary soil moisture regime.

Keywords: Halloysite; Gibbsite; Allophane; X-ray diffraction; Silicon cycling; Tropical soils; Rain forest

1. Introduction

Halloysite formation has been linked to conditions where Si in soil solution is high, either as a result of (i) poor drainage or (ii) summer moisture deficit or (iii) of spatially confined transformations within microenvironments containing feldspar and pumice pseudomorphs (Parfitt and Wilson, 1985; Quantin et al., 1988; Ziegler et al., 2003). Gibbsite, on the contrary, is a silicon free mineral [$Al(OH)_3$] and the endproduct of alumino-silicate weathering in soils. Thus, the presence of both halloysite and gibbsite in the same soil horizon, although often observed, presents a challenge to the pedologist: while halloysite formation is attributed to conditions of high silicon concentration in the soil solution (>10 mg l^{-1}; Lowe, 1995), gibbsite formation is related to silica poor conditions (<0.5 mg l^{-1};

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Scheffer and Schachtschabel, 2002). Halloysite can therefore be seen as a result of Si enrichment while gibbsite forms as a consequence of desilication. It follows that, depending on the prevailing composition of the soil solution, one of the two minerals should always be thermodynamically unstable, rendering their prolonged coexistence unlikely.

Bates (1962) presented evidence of a sequential feldspar–halloysite–gibbsite transition in an andesite weathering sequence in Hawaii. Jongmans et al. (1994) also showed that differences on a microscale in weathering environment, especially in the deeper parts of the profile may lead to the simultaneous formation of halloysite and gibbsite. Nieuwenhuyse (1996) attributed the simultaneous presence of these minerals to different conditions to which the soil may have been exposed at different times. He hypothesized that halloysite may have formed during drier climatic conditions, while gibbsite formed under more humid conditions. Ziegler et al. (2003) demonstrated that halloysite had been forming throughout the lifetime of their soils in an arid zone basalt weathering sequence containing gibbsite. According to their findings, halloysite formation resulted from (i) silica release from the parent material during intense, short wet periods, and subsequent (ii) silica enrichment in the soil solution resulting from subsequent prolonged extremely dry seasons.

A more pedological approach to the problem led Calvert et al. (1980a,b) to propose that the typical upward decrease in gibbsite contents observed in Ultisols might be the result of resilication of gibbsite to halloysite, which then would eventually transform into kaolinite. This idea has recently been revived in a number of publications (Furian et al., 1999; Furian et al., 2002; Islam et al., 2002) and seems to coincide with assumptions of a biological silicon cycling mechanism operating in tropical forest ecosystems (Lucas et al., 1993; Alexandre et al., 1997; Lucas, 2001). Similar to the reasoning of Ziegler et al. (2003), but looking at a different environmental setting, Kautz and Ryan (2003) suggested that halloysite transformations under the udic moisture regime prevailing at La Selva are controlled by kinetic factors. Their data do not immediately suggest an ongoing halloysite–gibbsite transformation or a desilication scheme. However, Kautz and Ryan (2003) focused on the 1.0 to 0.7 nm halloysite transition using B-horizon samples from different soil age groups and geomorphic positions, which is why the work presented here deliberately looks at the depth dependence and thus a more pedogenetic aspect of halloysite and gibbsite coexistence in the highly weathered tropical soils of La Selva.

Compared to halloysite, gibbsite is clearly the mineral that should be more thermodynamically stable under the pedogenetic conditions in a residual tropical rainforest soil. Pedogenetic theory of highly weathered tropical soils demands that silicon be lost with progressing pedogenesis while Fe and Al-oxides (=gibbsite) accumulate over time. Given high percolation and a long time span for soil development, a silicon bearing mineral can only be present if (i) it has been retrospectively added to the soil by some geomorphological process (erosion/deposition, aeolian deposition) or if (ii) there are point sources like isolated primary mineral containing rock fragments supplying the Si needed to raise concentrations above the threshold required for mineral formation. Such a silicon source can result from the presence of primary minerals like plagioclase feldspar (Bates, 1962) but may be confined to microenvironments (Jongmans et al., 1994). However, (iii) lateral redistribution of dissolved silicon within the landscape may be a source for elevated concentrations in the lower horizons of soils with a stagnant moisture regime (Sommer et al., 2006), while (iv) vertical Si cycling through vegetation has been linked to the stability of kaolinite in strongly weathered topsoils (Lucas, 2001).

Our central assumption was that the processes responsible for the coexistence of gibbsite with halloysite and other Si-bearing minerals can be deduced from the depth functions of the minerals in soil profiles of different age and different moisture regime. Information from selective dissolution procedures and from total elemental analysis (X-ray fluorescence) was obtained to support the inference drawn.

2. Area description and methods

2.1. Site

The study site was the La Selva Biological Station of the Organization for Tropical Studies (OTS) in the Atlantic lowlands of the Republic of Costa Rica, Central America. The forest is classified as Tropical Wet Forest in the Holdridge System (Hartshorn and Hammel, 1994), with an average rainfall of 4000 mm and a mean temperature of 26 °C (Sanford et al., 1994). A comprehensive account of the site is available (McDade et al., 1994). Andesitic lava flows have formed La Selva's land surface (Alvarado, 1990). At the higher elevations within the reserve, the flows have weathered slowly to form the so-called 'residual' soils. At lower elevations, the lava flows were later covered by alluvial and colluvial deposits of volcanic origin. Soils formed on stream-deposited volcanic sediments are termed 'old alluvium' by La Selva convention (Sollins et al., 1994).

2.2. Sampling

We selected soils representative of the 'old alluvium' and the 'residual' soil types (Carbono plots A4 and L6, respectively; Clark and Clark, 2000; Veldkamp et al., 2003; Schwendenmann and Veldkamp, 2005). Elevation is 40–45 m above sea level at A4 and 103–114 m at L6. The soils were sampled by uniform depth increments because the objective was to compare mineral inventories and to achieve a high resolution of changes in mineralogy with depth. The alluvial A4 was sampled down to 3 m, where rounded, saprolithic gravel was encountered. The residual L6 was sampled down to a depth of 4 m. As there was reason to expect the presence of short range order materials and hydrated halloysite (Werner, 1984), field moist samples were stored in air-tight plastic containers to prevent dehydration.

2.3. Basic soil analysis

Bulk density was determined by taking undisturbed soil samples (300 cm^3), which were subsequently dried at 105 °C