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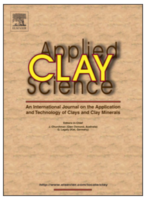

Research paper

The mangrove reactor: Fast clay transformation and potassium sink

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ABSTRACT

Most known clay mineral reactions are slow. Clay formation by weathering is recognized as faster (hundreds of thousands to few million years) than clay reverse weathering (few to tens My), even if the latter takes place in deep diagenetic conditions at temperatures above 100 °C. Identifying hot spots of fast clay retrograde reactions acting as effective potassium sinks would contribute to eliminating the present imbalance of the potassium budget towards release into the oceans. We have identified and modeled the reaction *kaolinite + Fe + cations → Fe-illite* occurring in Brazilian mangroves, which takes place through kaolinite-smectite and illite-smectite intermediates. The reaction is very fast, transforming 72–154 $g\ m^{-2}\ y^{-1}$ of kaolinite into Fe-illite, or 16–38% of the newly sedimented kaolinite each year. This kaolinite-to-illite transformation is 10s–100s times faster than kaolinite formation by weathering. Extrapolation of the calculated potassium consumption to mangrove forests worldwide produces $0.6–3 \times 10^{12}\ g\ y^{-1}$, or 1–6% of the yearly potassium riverine input into the oceans.

1. Introduction

The discovery of rapid-precipitating clay containing Al, Fe, Mg, and K in Amazon sediments about 20 years ago (Michalopoulos and Aller, 1995) reopened the possibility that marine sedimentary environments play a significant role in the control of the ocean chemistry. The several well-documented clay reactions known to take place in connection with detrital shelled organisms in shallow to relatively shallow marine sediments, such as glauconite (Baldermann et al., 2013) or berthierine (Ku and Walter, 2003) formation, appear to be too slow and/or local to be of global significance. Recently, however, Baldermann et al. (2015) have shown that green clays are also efficiently formed in the deep ocean and they argue that this fact adds a large expanse of the areas where clay formation may take place and render this reaction globally relevant. Also, gathering information indicates that Fe-Mg-K-rich clays form in marine sediments with high sedimentation rates within contexts wider than those of decaying shell organisms (Aller, 2014). Such information also argues for a globally significant effect of these reactions on ocean chemistry (Burdige, 2006; Emerson and Hedges, 2008).

Ocean shelf sediments have been found to simply reflect the character of the continental input modified by differential sedimentation due to particle size, flocculation and ocean currents (Chamley, 1989; Burdige, 2006; Emerson and Hedges, 2008), with the long-held view of insignificant reactivity of clay minerals in ocean shelves (Chamley, 1989). This frame of mind was fostered by the slow reaction rates of clays in burial diagenesis processes, reactions which have been extensively studied because of their widespread occurrence and their important control on the physical and chemical conditions of these environments (Cuadros, 2006). However, consideration of these and other typical clay mineral reactions suggests that the slow reaction rates are a combination of clay stability and the slow supply of cations that are incorporated into the new clay phases. Some of such cations need first to be released from other mineral phases, typically silicates (Si, Al, Mg, Na and, to a lesser extent Fe, Ca). There is, however, evidence that faster clay reactions can be produced in systems where the chemistry of reacting fluids is very far from equilibrium with clay minerals. The fluid chemistry needs to be kept relatively constant during the reaction to maintain the far-from-equilibrium conditions, implying either a large pool of the reacting cations or their steady input to avoid their quick depletion. An example of such systems is hypersaline lakes, where specific conditions of sediment composition and hydrology generate suits of Mg- and Fe-rich smectite, illite and chlorite, as well as talc (Chamley, 1989; Bristow and Milliken, 2011), some of which mineral phases require either high temperature (>60 °C) or long periods of time (hundreds of thousands to millions of years) or both to be formed in other geological settings. The relative rapidity of these reactions is demonstrated by mineralogical and chemical changes observed in the ancient Olduvai lake, Tanzania, where recent sediments underwent a series of transformations between the Pliocene and early Pleistocene.

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Volcanic glass deposited in fresh water first produced montmorillonite, which was then transformed by the effect of increased water salinity into increasingly magnesian illite-smectite (Deocampo et al., 2009).

According to the above, geochemically significant clay reactions in sedimentary environments would require (1) a steady input of reacting clay or other silicate phase, (2) a stable source of reacting cations in sufficient concentration to destabilize this clay/silicate phase and drive the reaction forward at a relatively rapid pace, and (3) that these conditions take place in a significantly large area worldwide. Mangrove forests are good candidates to fulfil the three conditions because sedimentation rate is high (typically ≥ 1 mm y^{-1}; Ellison, 2008), deposited sediments have a large clay content, seawater contributes an inexhaustible source of reacting elements, intense biological activity generates far-from-equilibrium chemical conditions, and they occur in tropical and subtropical coasts across the globe. Mangrove soils from three Brazilian locations, Bragança (BR), Santa Cruz (SC) and Cananéia (CN) were mineralogically and chemically studied to investigate the clay mineral reactions taking place and their rates. The results indicate that, in mangrove forests, there is a rapid transformation of kaolinite into Fe-illite that may have global geochemical significance.

2. Methods

2.1. Environmental settings

The BR mangrove, within the Bragança Peninsula, in Pará State, consists of great mud planes (~250 km^2) generated by a macrotidal regime (average amplitude of 3.5 m; Lima da Costa et al., 2004) and is placed between the 1–2 m high cliffs of the coastal plateau to the south and a barrier-dune-beach ridge to the north (Cohen et al., 2005). The SC mangrove, ~20 km south-east of Aracruz, Espírito Santo State, has a microtidal regime (<2 m amplitude) and Quaternary sandy plains of relatively small size. The mangrove ecosystem between Aracruz and Santa Cruz covers approximately 12 km^2 and contains the Piraquê-Açu and Piraquê-Mirim River estuaries. The sampling site is in the Piraquê-Mirim River estuary, ~7 km from the river mouth. CN, São Paulo State, in the island of Pai Matos, is a well developed sandy coastal plain in a microtidal regime (tidal amplitude of 0.82 m) of semidiurnal periodicity. Pai Matos island is located in a complex estuary system surrounded by mangroves with an overall area of 110 km^2. The system is connected to the Atlantic Ocean by the inlets/estuaries of the Cananéia (to the south) and Icapara (to the north) rivers (Ferreira et al., 2007a). Two sampling sites were used in each locality, with the following coordinates: BR1 −0.965417, −46.73544; BR2 −0.828122, −46.61012; SC1 −19.94848, −40.18465; SC2 −19.94973, −40.17543; CN1 −24.99763, −47.90677; CN2 −24.99500, −47.90522. Further information and satellite views of the sites are available from Andrade et al. (2014).

2.2. Sample collection and preparation

The samples were collected as described previously (Andrade et al., 2014). They were extracted from the soil using an auger-type wetland soil sampler. Immediately after extraction the core was divided into 10 cm intervals (5 cm at the very top) and pH and Eh were measured (Andrade et al., 2014). The samples were kept frozen until laboratory treatment. Because the aim of the study was to investigate the clays in the soils, the samples were treated with H_2O_2 (30% v/v) to eliminate organic matter, and with dithionite-citrate-bicarbonate to eliminate Fe oxides (Mehra and Jackson, 1960). The oxide- and organic-free soil fraction can be analyzed for clay mineralogy with much greater accuracy. Size separation was carried out by sedimentation (0.2–2 μm) and centrifugation (<0.2 μm). All subsequent analyses were carried out on these two fine fractions of the mangrove soils.

2.3. TEM and microanalysis

TEM-EDS analysis was performed with a Philips CM-200 at 160 kV on ultra-dispersed soil aliquots placed on Cu grids with a C film. Live counting time for the analyses was 40 s. Analyses were performed with a beam diameter of 55 nm from point analysis to areas with sides of 200 nm. Before analysis, individual grains were tested for contamination using electron diffraction. Chemical data were calibrated with silicate standards and transformed into structural formulas (Moore and Reynolds, 1997). The average error in individual TEM-EDS point analyses was <10% (for the added elemental errors), as obtained from several analyses in different points of a same grain of the silicate standards.

2.4. Mössbauer spectroscopy

For Mössbauer analysis finely ground samples were pressed between two Lucite plates (16 mm diameter, 0.503 mL internal volume), at 10 mg Fe/cm^2. Spectra were acquired at 295 K with a conventional constant-acceleration spectrometer (Driving Unit from Halder GmbH, model MR351), using a source of ~25 mCi ^{57}Co in Rh. Collection time was 24 h to achieve a good statistical counting, with a linear velocity scale defined by the spectrum of the 25 μm Fe metallic foil used for calibration. Data were folded before fitting about the channel value that produced the minimum least squares sum difference between the two halves of the spectrum. Spectra were fitted with two Lorentzian doublets using the “Fesites” program, where isomer shifts (IS) and quadrupole splittings (QS) of the doublets were allowed to vary, and the widths of the four peaks were coupled to vary in pairs. Errors are ± 0.01 mm/s for IS and QS, and ± 1% absolute on doublet areas. Additional spectra were collected at 4.2 K, which confirmed that the only Fe-containing phases detected in the samples were the clay minerals.

2.5. X-ray diffraction and pattern modeling

The mineralogical analysis was carried out on oriented mounts to emphasize the 00l peaks of the clays. They were prepared by placing 1 mL of the sample-water dispersion (10 mg mL^{-1}) on a glass slide and let it dry. The oriented mounts were treated with ethylene-glycol (24 h at 60 °C) to expand smectite layers and facilitate the analysis (Moore and Reynolds, 1997). X-ray diffraction (XRD) analysis was performed with a Shimadzu XRD 6000, using graphite monochromator and CuKα radiation. The modeling of the XRD patterns was carried out with the software CLAYSim® from MDI, which uses the NEWMOD® code. This program allows calculation of the 00l peak series of mixed-layer clay phases with two layer types. Input parameters are the mixed-layer clay phases, their chemical composition, the relative proportion of each phase, and their X-ray coherent scattering domain distributions (Moore and Reynolds, 1997). Typical uncertainty values were 4% for each clay phase.

2.6. Reaction kinetics model

The reaction from kaolinite to Fe-illite takes place through intermediate mixed-layer kaolinite-smectite (Kao-Sm) and illite-smectite (I-Sm) (see below). Our model attempts to establish the rates of reaction of the several intermediate phases relative to the rate of kaolinite input into the mangroves, all of which together shape the relative proportions of the several phases present (kaolinite, Kao-Sm, I-Sm and Fe-illite). Because the mangroves are receiving a constant input of reagents (kaolinite and Fe oxides from the sediment; Si, Mg, Na and K from seawater), which do not become depleted during the reaction, we used the simplest kinetic model of zero order. In other words, because the system is open and recharging all the reagents constantly (far from equilibrium conditions), it is not necessary to investigate and use the real kinetic equation of kaolinite transformation into Fe-