



Weathering of Permian sedimentary rocks and soil clay minerals transformations under subtropical climate, southern Brazil (Paraná State)

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ARTICLE INFO

Handling Editor: M. Vepraskas

Keywords:

Shales
Mixed-layered clays
Kaolinite-illite
Illite-smectite
XRD profile modeling
Mass balance
Paraná Basin

ABSTRACT

Mineral evolution in weathering zones is usually a complex process. Mixed-layered minerals (MLMs) can form as a result of progressive weathering advancement, promoting important geochemical changes in soils. In this contribution, four soil profiles located in Paraná State (southern Brazil) and formed from different fine-grained Permian sedimentary rocks (one siltstone, two Al-rich shales and one organic black shale) were characterized on mineralogical and geochemical bases. General physico-chemical/morphological characterization, XRD profile modeling of clay fractions, geochemical mass balance and weathering index calculations were performed to relate clay minerals transformation with the geochemical transformations in soils. MLMs dominate clay mineral suite, in progressive compositional ranges. The three soils developed from Al-rich shales (P1, P2 and P4) are dominated by several R0 K-I (kaolinite-illite) phases, and exhibit a trend of progressive kaolinitization towards surface soil horizons. The soil developed from Mg-rich organic black shale (P3), however, has R0 I-S (illite-smectite) as the dominant phase, and a progressive dominance of smectite in I-S phase prevails towards surface. These results suggest the prevalence of topotactic transformations (solid-state reactions) during the transition of one clay into another as weathering advances. In the three soils where kaolinitization of K-I phases prevails, geochemical mass balance calculations indicate massive losses of SiO₂, Al₂O₃ and alkalis, in addition to high values for weathering indices. Conversely, SiO₂ and MgO accumulate, and values for weathering indices are lower in the P3 soil profile. The agreement between the pathways of clay mineral transformations and the mass balance calculations and weathering indices suggests that transformations involving MLMs drive geochemical transformation in soils. The nature of clay suites, in turn, is highly dependent on the chemical compositions of fresh rocks, which determine how transformations involving clays proceed.

1. Introduction

Clay minerals are very active components in the rock-soil interface, controlling fundamental processes such as soil formation (Velde and Meunier, 2008), the uptake and release of major elements, (Caner et al., 2014; Waroszewski et al., 2016), the availability of nutrients (Barré et al., 2008; Simonson et al., 2009) and the mobility of toxic elements (Tashiro et al., 2018). Mineral transformations involving clays usually include the formation of mixed-layered minerals (MLMs), which is very sensitive to changes in environmental conditions (Wilson, 2004; Velde and Meunier, 2008; Hong et al., 2012, 2014).

MLMs are clay minerals whose stacking layer sequence along the Z

axis comprises two or more different layers, arranged in a regular or an irregular sequence. In soils and saprolites, irregularly stacked MLMs (R0 according to Jagodzinski's notation; see Moore and Reynolds, 1997) are usually present as a result of transitions between one clay mineral and another (Wilson, 2004; Ferrell et al., 2009). Illite-vermiculite (I-V), illite-smectite (I-S), kaolinite-smectite (K-S) (Hong et al., 2012; Ryan and Huertas, 2009, 2013; Vingiani et al., 2004; Bortoluzzi et al., 2007, 2008; Waroszewski et al., 2016) and kaolinite-illite (Hubert et al., 2009, 2012; Viennet et al., 2015) can result from mineral transformations in these zones. Three-components MLMs, such as mixtures including illite, chlorite, kaolinite and hydroxy-interlayered minerals (HIMs) have also been described in recent works (Hubert et al., 2012;

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Dumon et al., 2014; Viennet et al., 2015), and interpreted as transient products of weathering advancement. The detection and crystal-chemical description of MLMs in the soil-rock interface can therefore improve the comprehension of the role of clays during the weathering and soil formation processes.

In soils formed from fine-grained sedimentary rocks, such processes assume an important geochemical role (Hong et al., 2012, 2014), since these minerals are very abundant, from fresh rock/saprolite layers to upper soil horizons. In the southern region of Brazil, there are abundant fine-grained sedimentary rocks whose mineral assemblages are rich in clay minerals formed in a wide variety of environmental conditions (Formoso et al., 1995; Holz et al., 2010). In addition, the subtropical climate (with cooler temperatures and well-distributed rainfall) contrasts with climatic conditions prevailing in other Brazilian regions (higher temperatures and a wide variation in the rainfall distribution), which usually promotes very intense weathering and prevalence of kaolinite and iron oxides as residual alteration products in the clay fraction of soils (Melo et al., 2001). Under subtropical conditions, the formation of MLMs as transitory weathering products may dominate mineral reactions in soils (Bortoluzzi et al., 2007, 2008) and, thus, a detailed study of mineral assemblages can elucidate the role of clays as drivers of the geochemical pathways.

In this work, we assume that the transformations of clay minerals are major controls on the geochemical evolution of soils developed in environmental settings of the southern Brazilian region. Considering this hypothesis, the aims of this work are: 1) to characterize the clay minerals of < 2 μm fraction of poorly developed soils formed from fine-grained Permian rocks, in order to detect the existence of MLMs and; 2) to relate the formation of MLMs with different weathering pathways in four different fine-grained sedimentary rocks, using mass balance calculations and weathering indices.

2. Materials and methods

2.1. Geological settings

The study area is located inside the Paraná Basin, an intracratonic basin on the South American platform, where Paleozoic/Mesozoic rocks form a complex mixture of sedimentary and volcanic deposition sequences. These rocks spread across an extensive area in the southeastern and southern Brazilian regions and in parts of the Paraguay, Argentina and Uruguay (~1,700,000 km²). Paleozoic sedimentary rocks filled the Paraná Basin from Ordovician (~400 M.y.) to Jurassic/Early Cretaceous periods (140 M.y.) in a wide variety of tectonic and environmental conditions (Amaral, 1967; Matos et al., 2001; Holz et al., 2010; Chahud and Petri, 2013). In the state of Paraná (Fig. 1), where this study was carried out, the stratigraphic succession of Paleozoic sedimentary rocks is well exposed in the central/southern area of the state, and comprises ~25% of the total state area (~50,000 km²) (Mineropar, 2001). For further details on the petrology and fossil content of Paleozoic sedimentary sequence in the Paraná Basin, see the descriptions in Holz et al. (2010).

In the region of Irati and São Mateus Cities, the stratigraphic sequence of Permian sedimentary rocks includes the Palermo, Irati and Serra Alta Formations. They are composed of fine-grained siliciclastic sediments, deposited mainly in shallow marine waters, under different conditions for water circulation and O₂ contents. These differences caused variations in clay/silt contents, rock mineral assemblages and organic matter accumulation. The Palermo Formation (Early Permian) is dominated by light to dark-gray mudrocks, siltstones and fine-grained sandstones. Poorly developed soils occur in high-slope areas, such as Cambisols and Regosols. The studied soil profile related to this parent material is designated P1 and formed above an outcrop of weathered light-gray siltstone.

In the upper transition zone of the Palermo Formation lies the Irati Formation (Mineropar, 2001). This geologic formation extends over a

broad area of Paraná Basin in Brazil (Amaral, 1967; Anjos et al., 2010; Chahud and Petri, 2013) and contains several fine-grained rock facies, including oil-bearing black shales and distinct fossiliferous layers (Holz et al., 2010). In the cities of Irati and São Mateus do Sul, the dark-gray and black shales/mudrocks are exposed in zones of high-slope relief. The soils associated with these parent materials are mainly Leptosols, Regosols and Cambisols. The soil profiles developed from Irati Formation rocks in this study are designated P2 (sampled in Irati, from black shale weathering profile) and P3 (sampled in São Mateus do Sul, from an organic matter-rich black shale weathering profile).

The Serra Alta Formation, overlying the Irati Formation, is characterized by gray, dark gray and black shales with low organic matter contents (Warren et al., 2015; Mineropar, 2001; Holz et al., 2010). In the study region, laminated dark gray mudrocks prevail, occupying high-slope areas where poorly developed soils are usually found. The studied soil formed over this parent material (a laminated gray mudrock) corresponds to the P4 profile.

2.2. Study site and sampling procedures

Four poorly developed soils were sampled in the referred region, in the cities of Irati and São Mateus do Sul, midwestern region of Paraná State, Brazil (Fig. 1). The climate is classified as Cfa according to the Köppen-Geiger classification and characterized by yearly rainfall rates of 1476 mm, very well distributed during the year, with a maximum average temperatures of 22 °C and a minimum of 13 °C. All soil profiles are positioned in high-slope areas (declivity ~20–30%). The soils were morphologically described and sampled at four exposed weathering profiles. The distinction between soil/saprolite and fresh rocks was based on bulk density and the absence of weathering features in the materials described as fresh rocks (Buol et al., 2011; Juilleret et al., 2016). The fresh rock of the P1 profile could not be accessed and bottom samples thus correspond to Cr2 horizons. Soil and rock samples were manually collected and stored in plastic bags for laboratory analyses. The soils were classified according to the WRB-FAO system (IUSS-WRB, 2014) using morphological, physical and chemical parameters.

2.3. Chemical and physical analyses

Soil samples were dried at 45 °C for two days, ground and sieved (2 mm) to produce the fine earth necessary to perform physical, chemical and mineralogical analyses. Gravels and coarser parts were not considered. The granulometry of < 2 mm samples was investigated by the pipette method, after dispersion in 0.1 M NaOH solution and shaking for 16 h. Coarse (2000–200 μm sized) and fine sand fractions (200–53 μm sized) contents were determined after sieving. Silt (53–2 μm) and clay (< 2 μm) fractions were determined after decantation procedures according to Stoke's Law. The bulk densities of soil/saprolite and rock samples were determined by the paraffin method (Embrapa, 1997). Up to four aggregates (3–7 cm) per sample were sunk into warm paraffin (~50 °C) and the mass and volume of individual soil aggregates/rock fragments + paraffin were determined (by water displacement, in a beaker). Next, the paraffin was removed and its mass/volume was determined individually. The difference between the two measurements provided the bulk density of soil/rock samples (in g cm⁻³).

The base cations P, Al³⁺ and H⁺ present in the exchangeable complex were determined according to the following methods: Ca²⁺, Mg²⁺, Al³⁺ and H⁺ were extracted in KCl 1 mol L⁻¹ solutions. The Ca²⁺ and Mg²⁺ contents were determined using atomic absorption spectrophotometry (AAS). The Al³⁺ and H⁺ contents were determined by titration in 0.025 M NaOH 0.025 solution; K⁺ and Na⁺ were extracted in acid Mehlich solution (H₂SO₄ + HCl) and determined by flame spectrophotometry; P was extracted in a Mehlich solution and determined by colorimetry. The organic carbon (C_{org}) was determined by titration in FeSO₄ after wet oxidation in K₂Cr₂O₇ solution (Walkley-Black method; Walkley et al., 1934).

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