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Research paper

Influence of pedogenetic processes on the validity of kaolinite crystallinity indices: A case study of an Amazonian Ferralsol-Podzol soil system with white kaolin

Débora Ayumi Ishida[a], Antonio Carlos Vieira-Coelho[b], Adolpho José Melfi[a], Yves Lucas[c], João Paulo Brasiliano Camargo[d], Célia Regina Montes[e,*]

[a] *Instituto de Energia e Ambiente, IEE-USP, Universidade de São Paulo, Núcleo de Pesquisa em Geoquímica e Geofísica da Litosfera, NUPEGEL/USP, Av. Professor Luciano Gualberto, 1289, 05508-010 São Paulo, Brazil*
[b] *Escola Politécnica da USP, EP-USP, Universidade de São Paulo, Departamento de Engenharia Metalúrgica e de Materiais, NUPEGEL/USP, Av. Prof. Mello Moraes, 2463, 05508-900 São Paulo, Brazil*
[c] *Université de Toulon, BP20132, 83957 La Garde, France*
[d] *Universidade de São Paulo, NUPEGEL/USP, Av. Pádua Dias, 11, 13418-900 Piracicaba, SP, Brazil*
[e] *Centro de Energia Nuclear na Agricultura, CENA-USP, Universidade de São Paulo, NUPEGEL/USP, Av. Centenário, 303, 13416-903 Piracicaba, São Paulo, Brazil*

A R T I C L E I N F O

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A B S T R A C T

Structural defects of kaolinite could be associated with its genetic (weathering, pedogenetic, and hydrothermal) processes. Kaolinite crystallinity indices were evaluated in the context of pedogenetic processes associated with a representative Amazonian Ferralsol-Podzol soil system. This soil system, which is comprised of various types of kaolinitic materials and has a soil dynamics characterized by the progressive replacement of Ferralsols by Podzols, has been evaluated by Hinckley (**HI**), Aparicio-Galán-Ferrell (**AGFI**), Liètard (**R2**), and Amigó (**A_{001}**) "crystallinity indices" and the "expert system" of Plançon and Zacharie (**PZ**). The results indicate that the complexity of the kaolinite population, which is due to pedogenetic processes, makes it difficult to interpret the usual kaolinite crystallinity indices. In areas where kaolinites are formed under low aggressive conditions (higher pH and lower dissolved organic carbon, DOC) and in equilibrium with the soil solutions, low-defect phase becomes dominant and there is a good consistency between the "crystallinities" provided by each index. However, in areas where kaolinites are formed under highly aggressive conditions (lower pH and higher DOC), the proportion of low-defect phase decreases. This induces changes in the values of the indices, which do not have the same weight from one index to another.

1. Introduction

Although occurrences of kaolinite have reasonably similar chemical composition, they do not have a homogeneous crystalline structure that is close to the theoretical crystalline structure and is without defects. The crystalline structure of kaolinites is usually rather complex due to the high number of crystalline defects such as stacking faults (also called stacking defects). Since 1950, the low/high-defect characteristics of the crystalline structure of kaolinite (nature and evaluation of crystal defects) have been extensively studied (Murray, 1954; Murray and Lyons, 1955; Hinckley, 1962; Thiry, 1982; Cases et al., 1982; Brindley et al., 1986; Plançon et al., 1988; Giese, 1988; Plançon et al., 1989; Bookin et al., 1989; Plançon and Zacharie, 1990; Amigó et al., 1994; González et al., 1997; Galán et al., 1998; Aparicio and Galan, 1999; Vieira-Coelho and Souza Santos, 2001; Aparicio et al., 2006; Kogure et al., 2010; Sakharov et al., 2016).

Some authors associate stacking faults with kaolinite formation mechanisms. Thus, the analysis of structural order-disorder degrees could provide information about the physicochemical conditions prevailing during the formation of kaolinite crystals (Aparicio and Galan, 1999; Balan et al., 2014). Furthermore, stacking defects influence thermal stability (Ptáček et al., 2013) and other properties of kaolinite, such as surface properties, and may therefore interfere with industrial applications of kaolinite. Initial studies focused on the applications of kaolin in the paper industry (Murray and Lyons, 1955; Hinckley, 1962). These lead to the proposal of a "crystallinity index", called Hinckley Index (**HI**), calculated from the XRD patterns of kaolin.

Many studies use various "crystallinity indices" obtained through

* Corresponding author.
E-mail addresses: deboraishida@usp.br (D.A. Ishida), acvcoelh@usp.br (A.C. Vieira-Coelho), ajmelfi@usp.br (A.J. Melfi), yves.lucas@univ-tln.fr (Y. Lucas), crmlauar@usp.br (C.R. Montes).

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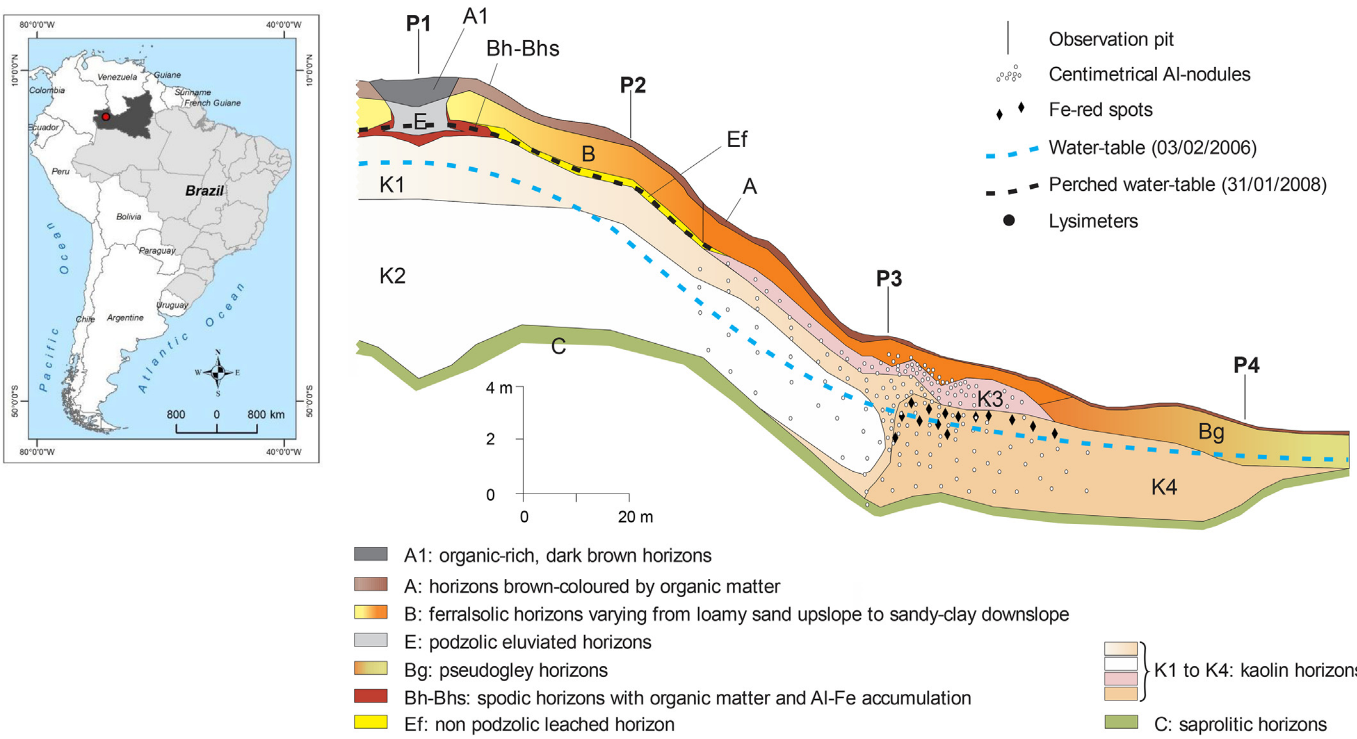

Fig. 1. Detailed view of the studied soil toposequence: P1 – Podzol, P2 – Ferralsol, P3 – Ferralsol, and P4 – Gleysol. Adapted from Ishida et al. (2014).

Table 1
Range of Hinckley (**HI**), Liètard (**R2**), Amigó (**A_{001}**), and Aparicio-Galán-Ferrell (**AGFI**) values for low-, medium-, and high-defect kaolinite.

Indices				
Structural order-disorder degree	HI	R2	A_{001}	AGFI
Low-defect kaolinite	0.90–1.15	> 1.20	< 0.30	1.25–1.60
Medium-defect kaolinite	0.50–0.90	0.70–1.20		0.90–1.25
High-defect kaolinite	< 0.50	< 0.70	> 0.40	< 0.90

the analysis of XRD curves for kaolinite characterization (Hughes and Brown, 1979; Tchoubar et al., 1982; Cases et al., 1982; Delgado et al., 1994; Galán et al., 1994; Aparicio and Galan, 1999; Melo et al., 2001; Varajão et al., 2001; Montes et al., 2002; Balan et al., 2005; Aparicio et al., 2004, 2006). However, to the best of our knowledge, no study has investigated “crystallinity indices” in the context of pedogenetic conditions associated with a soil transformation system to evaluate the ability of these indices to account for soil processes.

We evaluated crystallinity indices on a Ferralsol-Podzol soil system comprised of various types of kaolinitic materials. Ferralsol-Podzol soil systems are important since they are representative of the Amazonian area and are likely to be associated with kaolin deposits of high quality. The dynamics of these soil systems are characterized by the progressive replacement of Ferralsols by Podzols. Moreover, these soil systems are widespread throughout the Amazon area; > 18% of the Amazon area is covered by Ferralsol-Podzol soil systems and Podzols cover most of the Upper Rio Negro region (Dubroeucq and Volkoff, 1998; Montes et al., 2011). Thick, white clayey kaolinitic saprolite, which can be regarded as kaolin, has been observed beneath the Ferralsol-Podzol soil systems developed over sedimentary rocks in Manaus (Chauvel et al., 1987; Costa and Moraes, 1998) and over crystalline basement rocks in French Guiana (Veillon, 1990) and in the Upper Rio Negro area (Dubroeucq and Volkoff, 1998; Montes et al., 2011).

In this context, the specific objective of this study is to determine the crystallographic characteristics of kaolinites that are related to different pedogenetic processes by using “crystallinity indices” derived from XRD data. These indices were used to estimate structural order-disorder degrees that may be related with different generations of kaolinites. Therefore, kaolinites from a representative toposequence of a Ferralsol-Podzol soil system associated with white kaolin of high quality were studied by using the most widely cited indices derived from XRD data in the literature. This will allow the evaluation of the structural order-disorder degrees of kaolinites with a qualitative (Hinckley - **HI**, Aparicio-Galán-Ferrell - **AGFI**, Amigó - **A_{001}** and Liètard - **R2** indices) or quantitative (the “expert system” of Plançon and Zacharie - **PZ**) approach.

2. Materials

2.1. Location and characteristics of the soil toposequence

The studied soil toposequence (Fig. 1) represents a Ferralsol-Podzol soil system associated with white kaolin of high quality. It is located 26 km from São Gabriel da Cachoeira, Amazonas, Brazil, at 0°6′21″S and 66°54′22″W. It was formed from the granitic rocks. The samples were collected from four soil profiles: Podzol at the upper part (P1 profile), Ferralsols at the middle part (P2 and P3 profiles), and Gleysol at the lower part (P4 profile) of the toposequence. The soil in the upper part of the toposequence (Fig. 1) was well-drained Podzol. Further downslope, podzolic E horizons gave way to ferralsolic B horizons, which are colored by iron oxides and oxyhydroxides (hematite and goethite), that progressively changed from sandy to sandy-clay in the downslope direction. At the lower part of the toposequence, these B horizons had colored spots indicating the occurrence of waterlogging. In the top half of the soil toposequence, a pale yellow silty clay loam horizon (Ef) occurred below the B horizon. At depth, the thick kaolin K horizons extend downslope with progressive morphological and mineralogical changes. At the mid-slope, quartz grains remained at the upper part of the kaolin body and centimeter-scale gibbsite nodules were also apparent. These nodules became more abundant downslope, where Fe red spots were also observed. In the lower part of the toposequence, the B and K horizons became mottled and the water table had the typical odor of sulfides, indicating reducing conditions. Detailed