Applied Clay Science 118 (2015) 1–7

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Iron oxides in soils of different lithological origins in Ferriferous Quadrilateral (Minas Gerais, Brazil)

Amaury de Carvalho Filho [a], Alberto Vasconcellos Inda [b], Jessé Rodrigo Fink [b,*], Nilton Curi [c]

[a] Embrapa Solos, Jardim Botânico Street 1024, 22460-000 Rio de Janeiro, Brazil
[b] Department of Soils, Federal University of Rio Grande do Sul, Bento Gonçalves Avenue 7712, 91540-000, Porto Alegre, Rio Grande do Sul, Brazil
[c] Department of Soil Science, Federal University of Lavras, 37200-000 Lavras, Minas Gerais, Brazil

ARTICLE INFO

Article history:
Received 20 May 2015
Received in revised form 21 August 2015
Accepted 25 August 2015
Available online 5 September 2015

Keywords:
Parent material
Al-substitution
Pedoenvironmental
Soil mineralogy
X-ray diffraction spectroscopy

ABSTRACT

Different environmental conditions also lead to the formation of different pedogenic iron oxides, influencing soil chemistry. We examined the chemistry and mineralogical composition including various crystallographic parameters of pedogenic iron oxides of soils developed from itabirite, ferruginous dolomite, serpentinite and other parent materials. The low SiO_2 contents relative to Al_2O_3 and Fe_2O_3 suggest strong desilication by the effect of the environmental conditions for all soils. The main pedogenic iron oxides were hematite and goethite, followed by maghemite. The small crystal size of goethite resulted in an increased specific surface area; also, isomorphic substitution of aluminum in goethite differed with the parent material. The highest content of soil Fe_2O_3 from sulfuric acid digestion found here was 701 g kg^{-1}, which was the highest value registered in the world literature with this methodology, according to the author's knowledge. The Fe_d content in the soils was strongly influenced by the parent material, with hematite being the more abundant iron oxide. Al-substitution indicated that hematite formation occurred in a different pedoenviroment than for goehtite. These results suggest that the effects of parent material on soil properties are important for both well weathered soils and little-leached soils, determining their drainage, P adsorption and capacity of trace element accumulation.

1. Introduction

The Ferriferous Quadrilateral (FQ) encompasses an area of ca. 7000 km^2 in the central part of the state of Minas Gerais (southeastern Brazil) and has a high lithological diversity (Alkmim and Marshak, 1998) including iron ores (MME, 2011). Geology, mining and their environmental effects have been the subjects of much research in the FQ (Souza Diniz et al., 2014; Gomes et al., 2015). By contrast, rare studies on the spatial distribution and intrinsic characteristics of soils developed from different parent materials in FQ and their relationships with the biotic and abiotic components of the natural medium, aiming to contribute to the distinction, reconnaissance and sustainability of the regional environments, most of them degraded by mining activities, have been reported. Ferriferous soils in Brazil were characterized for the first time in the exploratory survey of soils of the FQ region conducted in the framework of the RADAMBRASIL project (MME, 1983) and by Curi (1983). These soils (particularly those developed from itabirite) usually have extremely high contents in iron oxides as determined by selective dissolution with sulfuric acid and the sodium dithionite–citrate–bicarbonate mixture (Curi and Franzmeier, 1987; Ker, 1997; Figueiredo et al., 2006; Costa et al., 2014). The clay fraction of ferriferous soils consists mainly of iron oxides [hematite (α-Fe_2O_3), goethite (α-FeOOH) and magnetite (γ-Fe_2O_3)], aluminum oxides [gibbsite ($Al(OH)_3$)] and titanium oxides [anatase and rutile (TiO_2)] (Figueiredo et al., 2006; Nitzsche et al., 2008; Schaefer et al., 2008; Costa et al., 2014).

Pedogenic iron oxides are formed (viz., transformation in the solid state and/or dissolution–neoformation) by alteration of primary minerals in the parent material or from secondary minerals. The formation and stability of these iron oxides are influenced by the diversity of pedogenetic environments under variable conditions of time, space, temperature, moisture, pH, Eh, organic matter content and ion release rate in solution (Schwertmann and Taylor, 1989; Kämpf and Curi, 2000; Bigham et al., 2002). Some intrinsic properties of minerals such as crystallinity, isomorphic substitution by aluminum (Al-substitution) and specific surface area also vary with pedoenvironmental factors such as weathering–leaching intensity, soil solution composition and drainage conditions (Motta and Kämpf, 1992; Schaefer et al., 2008; Costa et al., 2014).

The aim of this work was to characterize the chemistry and mineralogy of pedogenic iron oxides present in soils of the Ferriferous Quadrilateral, Minas Gerais (Brazil), establishing their relationship to the environmental factors, aiming to a better understanding of their effects on land use systems.

---

* Corresponding author.
E-mail address: fink1j@gmail.com (J.R. Fink).

http://dx.doi.org/10.1016/j.clay.2015.08.037
0169-1317/

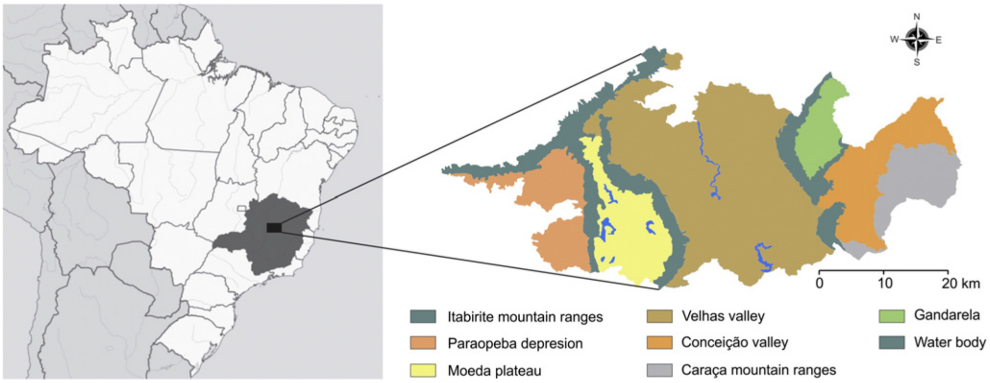

Fig. 1. Geographic location of Ferriferous Quadrilateral.

2. Material and methods

2.1. Soil selection, sampling and sample preparation

This work was conducted on soils from the Environmental Protection Area of the Metropolitan Region of Belo Horizonte—APA Sul RMBH, in Minas Gerais, Brazil (Fig. 1) and sampling was based on a survey report for the area (Shinzato and Carvalho Filho, 2005). The native vegetation is expressed by tropical fields on shallower soils and perennial/semiperennial forest on deeper soils. The altitude ranges from 950 to 1555 m and the predominant climate is Cwa, according to Köppen classification, with dry winter and rainy summer. Soils were selected in terms of Fe contents and parent materials, namely: itabirite, ferruginous dolomites (Moeda and Gandarela formations), serpentinite (Córrego dos Boiadeiros Complex) and various other materials including talus deposits, metaconglomerates, migmatites, gneiss and quartzite. A total of 18 soils were selected and classified into five groups according to parent material (Table 1).

Soil samples (500 g) of the diagonostic subsurface horizons were collected following the morphological description according to Santos et al. (2013). All samples were air-dried, ground and passed through a 2-mm mesh sieve to obtain "air-dried fine soil" (ADFS). A portion of ADFS (50 g) was dispersed in 1 mol L^{-1} NaOH and subjected to fast shaking at 12,000 rpm for 15 min on a shaker. The clay fraction was collected by sedimentation according to Stokes law, dialyzed and freeze-dried. The concentrated Fe oxide fraction was obtained by treating the clay fraction with a hot solution containing 5 mol L^{-1} NaOH (Kämpf and Schwertmann, 1982).

2.2. Chemical analyses

The ADFS fraction was subjected to selective dissolution by attack with sulfuric acid (Embrapa, 1997). The resulting extract was used to determine the contents (indices of total contents) of SiO_2, Al_2O_3, Fe_2O_3, TiO_2 and P_2O_5, which were used to calculate the indices $K_i = 1.7 \times \%SiO_2 / \%Al_2O_3$ and $K_r = 1.7 \times \%SiO_2 / (\%Al_2O_3 + 0.6325 \times \%Fe_2O_3)$. These indices indicate information on the development stage of soils: more weathered–leached soils show low indices. The Fe oxides (Fe_d) in the clay fraction were determined by selective dissolution with sodium dithionite–citrate–bicarbonate in four successive extractions at 80 °C (Mehra and Jackson, 1960). Iron oxides of low crystallinity (Fe_o) in another aliquot of the clay fraction were determined by selective dissolution with 0.2 mol L^{-1} ammonium oxalate at pH 3.0 in the absence of light in only one extraction (Schwertmann, 1964).

Table 1
Environmental characteristics and location of the studied soils in FQ.

Soil	Position in the landscape	Parent material	Location	Altitude, m
Itabirite soils				
P02	Mountain summit	Itabirite	Santa Bárbara, MG	1555
Ex06	Colluvial ramp	Itabirite	Itabirito, MG	1410
Ex04	Backslope	Itabirite	Nova Lima, MG	1300
Ferruginous dolomite soils (Moeda)				
P09	Summit	Ferruginous dolomite	Nova Lima, MG	1365
P04	Backslope	Ferruginous dolomite	Itabirito, MG	1360
Ex05	Footslope	Ferruginous/phyllite dolomite ferruginous/phyllite	Itabirito, MG	1290
Ferruginous dolomite soils (Gandarela)				
P01	Summit	Ferruginous dolomite	Santa Bárbara, MG	1270
P25	Footslope	Ferruginous dolomite	Santa Bárbara, MG	1160
P36	Coluvionar ramp	Ferruginous dolomite	Santa Bárbara, MG	1270
P37	Summit	Ferruginous dolomite	Santa Bárbara, MG	995
Ex03	Summit	Ferruginous dolomite/quartzite	Santa Bárbara, MG	1230
Serpentinite soils				
P33	Backslope	Serpentinite	Nova Lima, MG	1020
Ex09	Backslope	Serpentinite	Nova Lima, MG	1020
Ex02	Backslope	Serpentinite/metagabbro/steatites	Nova Lima, MG	1020
Ex10	Footslope	Serpentinite/metagabbro/steatites	Nova Lima, MG	1030
Soils from other materials (FQ)				
P16	Summit	Talus deposit/itabirite	Santa Bárbara, MG	1320
P21	Backslope	Metaconglomerate quartz-sericitic/gravels of ferriferous formation/metabasic rock	Santa Bárbara, MG	1300
P24	Summit	Migmatites/gneiss	Itabirito, MG	970