Manganese Oxides in Iron Ore Province Soils, Brazil and Their Relations with Trace Elements

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ABSTRACT

The mineralogy of manganese (Mn) oxides is highly variable and complex, since the number of minerals is large and the knowledge of their structures imprecise. In view of the scarcity of specific papers on Mn oxides in Brazilian soils and their unusually high contents in some soils of one of the Iron Ore Province (IOP) of Minas Gerais State, this study aimed to characterize the chemistry and mineralogy of these oxides in the soils of this region, stratifying them according to the parent material and their relations with trace elements (TE). The study was conducted in a representative area of the IOP, in an area of environmental protection of Belo Horizonte city (APA Sul RMBH), with 1,625.32 km^2. Soils with high Mn contents of three distinct parent materials were sampled and characterized: itabirites, ferruginous dolomites and serpentinites, as well as some soils derived from other parent materials within the IOP. Some IOP soils have extraordinarily high Mn contents in the fine earth fraction, mainly soils derived from the ferruginous dolomites of the Gandarela Formation (Mn up to 69 g kg^{-1}). Diverse manganese oxides were identified by X-ray diffraction (XRD) and high-resolution imaging and electron diffraction (MEV) without concentration pretreatments, especially: todorokite, lithiophorite and pyrolusite with Ni and Cr associated in the soils clay fraction. The influence of the parent material on the chemistry and mineralogy of Mn oxides was stronger than the weathering degree of Mn-rich soils.

INTRODUCTION

Iron-manganese (Fe-Mn) oxides shown commonly in soils nodules are well-known to act like scavengers of trace elements (TEs) such as Co, Ni, Zn and Pb [1]. These nodules are rich in Fe and Mn oxides, being in tropical soils hematite and goethite the most common Fe-oxide forms and birnessite and lithioforite the more widespread forms of Mn oxides in nodules [2].

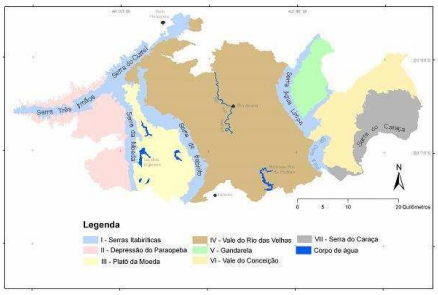
In Brazil, dolomitic rocks of the Iron Ore Province (IOP) had showed extraordinarily high Mn contents in the fine fraction without concentration pretreatments, specially soils derived from the ferruginous dolomites of the Gandarela formation (45%) [3]. Therefore, a better knowledge of the chemical and mineralogical constitution of this soils is of great environmental relevance.

OBJECTIVE

To characterize the chemistry and mineralogy of Fe-Mn oxides in IOP soils to improved the knowledge about anomalously high values of Mn in the area and, to verified the association of trace elements (Co, Ni, Zn and Pb) in the Fe-Mn mineral phases.

MATERIALS AND METHODS

Soils selected from rocks with high Mn contents of the (IOP) of Minas Gerais state, Brazil: Itabirite and ferruginous dolomites from Moeda and Gandarela Formations [1].



Chemical Mn extraction :
- Bulk fraction: Sulphuric acid attack and triacid extraction
- Clay fraction: sequential extractions with dithionite-citrate-bicarbonate (DCB) and one extraction using ammonium oxalate acid
- Mn analyses by flame AAS

Mineralogy of the clay fraction: DRX and MEV-EDS

RESULTS

Table 1. Mn content by sulphuric acid attack and by triacid extraction in the bulk fraction and from sequential extractions with DCB (Mn_d) and one extraction by ammonium oxalate acid (Mn_o) in the clay fraction of the soils.

Soil	depth	Sulfuric acid attack	Triacid Attack	Mn_d		Mn_o	Mn_o / Mn_d
		(Mn)	(Mn)	First extraction	Total (of 3 extractions)		
		TFSA		Clay fraction			
		g kg^{-1}					
Soils of itabirites							
P02 - BCc	183-230	0.45	0.24	0.85	1.01	0.05	0.1
Ex06 -B	50-70	11.08	4.00	25.07	25.47	9.92	0.4
Soils of ferruginous dolomites (Moeda Formation)							
FC4 - Cc	92-175	7.70	9.50	22.82	26.27	9.08	0.4
Ex08 - Cc	171-200	25.00	73.00	75.23	81.23	8.32	0.1
Soils of ferruginous dolomites (Gandarela Formation)							
FC1 – Bc1	32-98	21.50	23.40	35.46	40.63	15.37	0.4
P37 – Bi1	42-71	35.88	69.00	81.33	84.03	33.72	0.4
P37 – Bi3	123-160	20.33	36.00	46.62	50.81	23.15	0.5

- Soils from ferruginous dolomites (Fm Gandarela): first report of extraordinarily high Mn contents in Brazilian soils.
- Variable Mn content due to solubilization and nodules.
- High Mn_o/Mn_d ratio – predominance of low cristallinity Mn forms

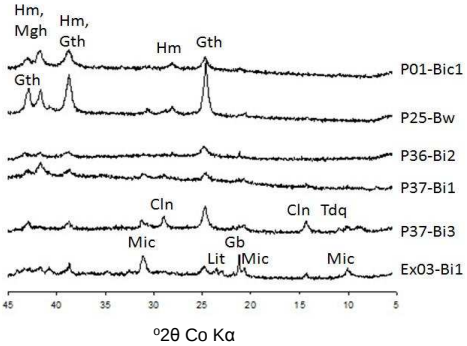


Figure 1. XRD patterns - oriented clay of soils from ferruginous dolomite of the Gandarela formation (Hm: hematite, Mgh: maghemite, Gth: goethite, Cln: kaolinite, Tdq: todorokite, Mic: mica, Lit: lithioforite, Gb: gibbsite)

RESULTS

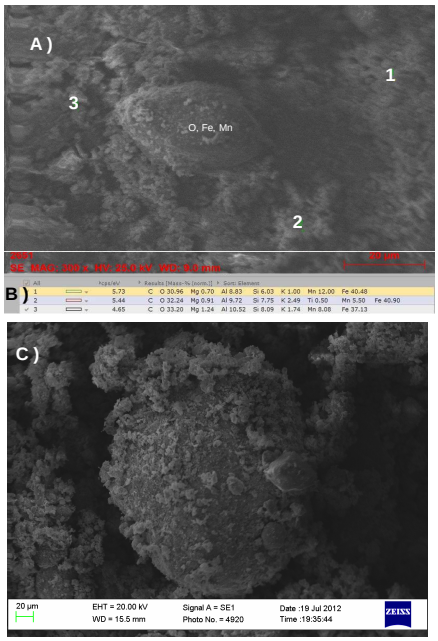


Figure 2. A) MEV-EDS image SE and B) microanalise of Fe-Mn nodules in the clay fraction of the P37A soil. C) Nodular habit Fe-Mn oxides in the sample. (Photos by Olívia Graziela Gelioli do Carmo)

- XRD results were corroborated by MEV-EDS. O, Fe, Mn, Mg, Al, Si, K and Ti reinforce the mineral assembly in soils of the Gandarela formation: i.e., Hm, Gth, Mgh, as the main Fe-oxides as well as minerals of the clay fraction (Cln, Gb, Mic.)
- The amorphous structure of Fe-Mn nodules confirm the low cristallinity supported by the high Mn_o/Mn_d ratio, suggesting the presence of nodular Tdq (O,Mn,K,Mg,Al), as well as Bixbyita $(Mn^{3+},Fe^{3+})_2O_3$, a new phase not identified by XRD. None of them presented detectable contents of TEs by MEV-EDS.

CONCLUSION

MEV-EDS confirmed the low cristallinity of the Fe-Mn oxides and the predominance of nodular phases. The elemental composition suggests a new phase of a Mn-Fe-oxide, and a low content or absence of TEs. The influence of the parent material on the chemistry and mineralogy of Mn oxides was stronger than the weathering degree of the Mn-rich soils.

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