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STUDY OF MANGANESE ORE FROM MATO GROSSO DO SUL, BRAZIL

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ABSTRACT

Manganese ore coming from Corumbá, Mato Grosso do Sul, Brazil was investigated to ascertain its mineral composition. Chemical analysis, X-ray diffraction along with energy dispersive analysis allowed establishing that the mineral is a mixture of Mn2+Mn3+2 and Mn4+O2 oxides, hausmannite and pyrolusite which are present as major and minor phases respectively. It is assumed that the mineral also contains neotocite, a manganese-iron silicate (Mn+20.75, Fe2+0.25) SiO3 H2O that is present in the amorphous state and cannot be detected by X-ray technique.

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INTRODUCTION

Manganese is the 10th most abundant element in the Earth's crust. Most of its industrial use is in steel making with a much lesser amount going into the production of batteries. This element is commonly found substituted in small amounts in iron minerals. The basic electronic configuration of manganese is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$. Its ions can have up to 10 oxidation states (Greenwood and Earshaw, 1998), of which in the conditions of the Earth's crust are realized only four—Mn^{2+} (d^5), Mn^{3+} (d^4), Mn^{4+} (d^3), and Mn^{7+} (d^0). These states give rise to a number of complex manganese oxide minerals, however the latter do not always have iron counterparts. Despite the accumulation of a vast array of data on the geology of manganese deposits and particularly pertaining to the chemical composition of manganese rocks and ores, many questions of manganese ore-genesis remain only partially answered (Kuleshov V, 2017). The manganese and iron deposits of the Morro do Urucum are located in the vicinity of 19°.20' S., 57°40' W., or about 25 kilometers south of the city of Corumbá, Mato Grosso do Sul state, Brazil, near the Brazilian border with Bolivia (Van N Dorr, 1945). Its geology and genesis have been characterized in detail by the German researchers calculating the geological manganese reserves as 608 million tons (Urban *et al.*, 1992). A recent investigation has presented a study on the chemical and mineralogical constitution, the distribution of the porosity and the thermo gravimetric behavior of the Urucum Morro samples. In particular, the authors suggested that the prevalence mineral phases are cryptomelane KMn_8O_{16} (>40%), pyrolusite MnO_2 (<20%), braunite $Mn(Mn_2O_3)MnSiO_3$ (<10%) and goetite FeOOH (<3%) (Faria *et al.*, 2013).

Although the general conclusions of this research work are unobjectionable, it seems doubtful that X-ray diffractogram containing only 23 reflections would have permitted to positively identifying 4 individual crystalline phases, including goetite; the latter with the content beyond the possibilities of discovery by the technique employed. Moreover, as the results of chemical analysis given in the paper did not show any reasonable amounts of potassium, the declared presence of the cryptomelane phase (>40%) logically becomes dubious. On the other hand, iron content (~14%) is too high to be accounted

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for <3% of goetite present. Thus it is possible, in our opinion, that a more convincing set of compounds than that proposed by the aforementioned authors may be suggested. The purpose of this communication is to revert to the study of the Urucum Morro ore samples offering a different and more realistic composition of its mineral constituents.

MATERIALS AND METHODS

The starting material, lamp ore from the Urucum mine was homogenized and quartered for spectroscopic and mineralogical characterization. Crystalline phases were investigated using X-ray diffraction method. Powder patterns were registered with a Siemens Kristalloflex diffract meter (Ni-filtered CuKα radiation) provided with a graphite monochromator, 2θ range of 4–70◦. The identification was carried out using a set of search-match computer programs Crystallographica and X´pert linked to the International Center for Structural Data (ISCD), Pensylvania, USA. Energy dispersive analysis (EDAX) was performed using a Princeton Gamma Tech PGT instrument provided with SiLi detector.

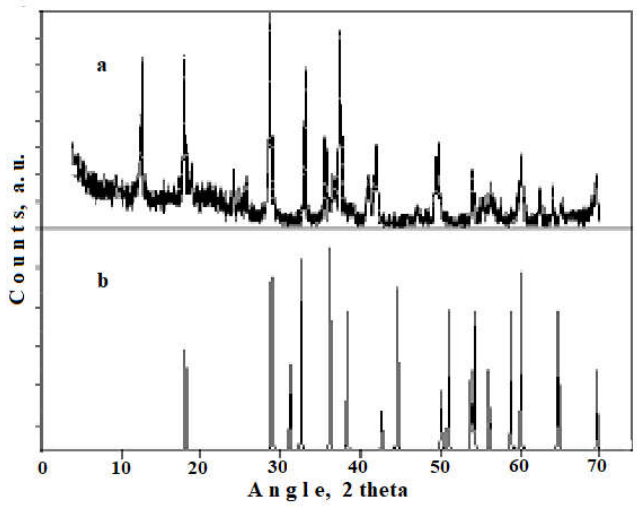

Fig. 1. X-ray identification of. a - mineral sample; b – literature data for hausmannite (ICSD file 68174)

RESULTS AND DISCUSSION

The results of chemical analysis gave the following results (wt.%): Mn – 39.55; Fe – 11.45; P – 0.054; SiO_2 19.98; Al_2O_3 – 1.82; Na_2O – 1.487; K_2O – 0.003; CaO – 0.524; MgO – 1.059; TiO_2 – 0.157. In parallel trials, the data dispersion did not exceed 2 - 3%. It is obvious however that by themselves these figures are not sufficient to identify the mineral composition of the samples beyond reasonable doubts. Elemental analysis of the samples performed by the dispersive energy X-ray spectroscopy (EDXS) showed the presence of oxygen, manganese, iron and silicon. The absence of potassium lines is an additional confirmation that KMn_8O_{16} is not part of the mineral sample. The X-ray diffraction pattern of the mineral sample is shown in Figure1a. The comparison with the hausmannite diffract gram given in Figure 1b allows us to conclude that most of the reflections belong to this mineral.

The rest corresponds to the pyrolusite diffraction pattern except for one reflection that could not be identified. It is obvious that the X-ray technique does not allow neither to establish or to reject the presence of minerals which commonly exist in the amorphous state. In the first place it can be neotocite (neotokite or neotokit), manganese-iron hydrated silicate $(Mn^{2+}_{0.75}, Fe^{2+}_{0.25})SiO_3\ H_2O$ found for example in Lovozero Massif (Russia) and other locations (Perov, 2000, Webmineral, 2018, Mineralienatlas, 2018). This possibility makes it possible to reconcile the results of chemical analysis with the X-ray data, thus accounting for the presence of silicon and iron compounds undetected by this last technique. Besides, since manganese and iron ionic radii are very close (0.66 and 0.63Å, respectively) further substitution of iron for manganese in neotocite cannot be excluded, as this occurs in hausmannite (Baron *et al*). Evidently, future investigations are needed to confirm this hypothesis.

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