

Mn-oxides from Serra da Mina deposit: mineralogy and paragenetic sequence of crystallization

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INTRODUCTION

Chemical equilibria and the relative stability of Fe-Mn phases are the main governing factors behind the mineralogical characteristics and elemental distribution of iron and manganese in supergene enrichment deposits. In the present work, we focus on the textural, mineralogical and chemical investigation of mineral associations, typical of the enriched zone of the vein-hosted Fe-Mn deposit of Serra da Mina, SW Portugal, by means of micro-Raman spectroscopy and electron microprobe analysis (EMPA). The coupling of such methods enabled both the identification of the main mineralogical components and their corresponding paragenetic sequence of crystallization.

GEOLOGICAL BACKGROUND

The Serra da Mina deposit outcrops in the westernmost part of the Iberian Pyrite Belt, within the Cercal-Odemira sector, and alongside other Fe and Mn mineralizations. According to previous surveys (Santos, 2020), the primary mineralization of this vein-hosted deposit consists of intergrown hematite and goethite, with minor amounts of pyrolusite, quartz and galena. Posterior tectonic events lead to a chemical remobilization of the latter associations, with the consequent formation of a secondary paragenesis of goethite, hematite, pyrolusite, cryptomelane, manganomelane, and quartz. The continuous chemical weathering of such mineralizations yielded intergrowths of goethite, pyrolusite, cryptomelane, coronadite, ramsdellite, manganomelane, quartz, and barite. The sample presently discussed originated from the latter ore zone, and contains all its typical paragenetic associations.

RESULTS AND DISCUSSION

The results obtained from EMPA and Raman spectroscopic analysis revealed the presence of tabular goethite, $(\text{Fe}^{3+}_{1.30}, \text{Zn}^{2+}_{0.02})_{\Sigma=1.32} \text{O}_{1+x}\text{OH}_{1-2x}$, anhedral and drusy ramsdellite, $(\text{Mn}^{4+}_{0.80}, \text{Fe}^{3+}_{0.009}, \text{Al}^{3+}_{0.006})_{\Sigma=0.82}(\text{O}, \text{OH})_2$, cryptomelane, $(\text{K}^{+}_{0.44}, \text{Na}^{+}_{0.14}, \text{Ba}^{2+}_{0.03}, \text{Ca}^{2+}_{0.02}, \text{Mg}^{2+}_{0.006}, \text{Zn}^{2+}_{0.06})_{\Sigma=0.70}(\text{Mn}^{\text{total}}_{6.84}, \text{Al}^{3+}_{0.05}, \text{Fe}^{3+}_{0.17})_{\Sigma=7.06}(\text{O}, \text{OH})_{16}n\text{H}_2\text{O}$, and prismatic chalcophanite in geodes, $(\text{Zn}^{2+}_{0.6}, \text{Fe}^{2+}_{0.1}, \text{Mn}^{2+}_{0.4})_{\Sigma=1.11}\text{Mn}_3^{4+}\text{O}_7\cdot 2.82\text{H}_2\text{O}$. Manganite, MnOOH , was identified by petrographic and Raman spectroscopic means. The observed textural relationships indicate that manganite is production of the reaction between MnO_2 and Fe^{2+} , which also entails a decrease in pH , according to the following equation:

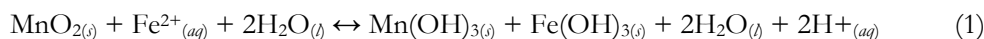


Fig. 1 displays the associations of drusy and prismatic Mn-oxide phases, growing in fractures and voids. The occurrence of ramsdellite lining fractures suggests an increase in Eh conditions, following the precipitation of manganite, since the former includes manganese in 4+ state exclusively. Our results reveal that a layer of drusy cryptomelane is also grown on top of ramsdellite, inwards towards the centre of fractures, forming cavities containing geodes of acicular chalcophanite crystals. Taking into consideration the oxidation state of Mn in the structure of each phase, these textures clearly suggest a progression from initially oxidative conditions, conducive

to the precipitation of Mn^{4+}O_2 , to a more reductive environment, favouring the crystallization of cryptomelane ($\text{Mn}^{3+}/\text{Mn}^{4+} = 0.16$).

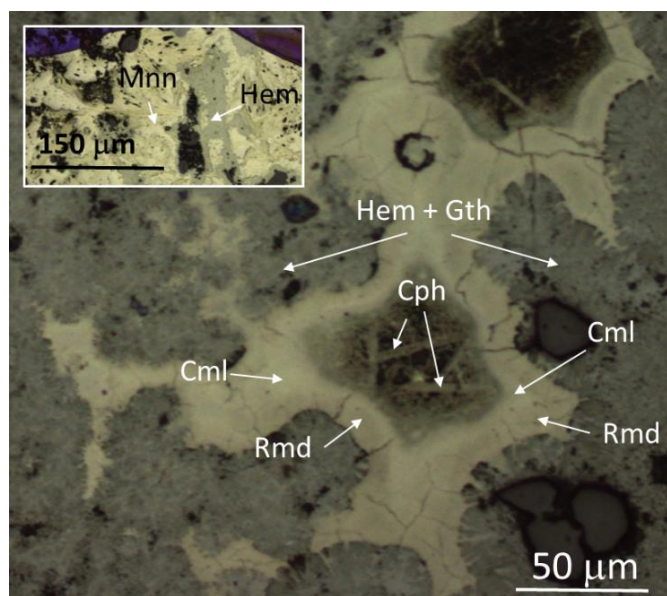


Fig 1. Plane-polarized reflected light micrograph of intergrown Mn and Fe-bearing oxides from the weathered zone of the Serra da Mina deposit. Rmd = Ramsdellite, Cml = Cryptomelane, Cph = Chalcophanite, Mnn = Manganite, Hem = Hematite, Gth = Goethite.

The growth of chalcophanite as prismatic, acicular crystals in geodes, suggests nucleation and growth from a static solution, within a confined space. The depletion of Mn in the aqueous solution, due to the previous formation of hollandite-group phases (ramsdellite and cryptomelane), may have favoured the precipitation of a Mn oxide poorer in manganese, such as chalcophanite. The ratio of Mn to tunnel-site cations is 7:1 in hollandite group oxides, dropping to 3:1 when considering the same ratio, but with respect to interlayer cations in layered Mn oxides, like chalcophanite.

REFERENCES

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