

Manganese separations in superficial environments from Galicia (NW Spain)

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Manganese is the most abundant among the trace elements in the crust. Although it is a common component of soils and sediments, the study of Mn minerals in these environments has been rarely undertaken as, in addition to their chemical complexity, they commonly appear associated to the surface of other minerals, so that their identification by instrumental methods such as XRD is difficult. This study was aimed at the characterization of Mn precipitates in superficial environments from Galicia. Mn precipitates were clearly observed in a pseudogley soil over amphibolites, submitted to alternant oxic-anoxic conditions that favoured Mn translocation towards concretions, mixed with iron oxides, sometimes as remnants of weathered rock fragments. Fine irregular Mn-rich black concretions made up to 15% w/w of the 2Bcg horizon between 60-85 cm. Co was associated to Mn in the concretions, whereas Cu, Zn and Cr were not enriched in concretions compared to the soil. Psilomelane and pirolusite were identified by their distinctive reflections in XRD, whereas a peak at 3.98 Å can be attributed to ramsdellite or nsutite.

In sedimentary environments, Mn has been frequently observed as coatings on coarse grains or as fine particles dispersed in the matrix, over Fe deposits forming crusts in sandy Quaternary sediments, reflecting its greater mobility in superficial environments. Once translocated, Mn requires more oxidizing Eh conditions to precipitate in comparison with Fe, thus explaining its occurrence as coatings above the Fe precipitates, and closer to the more aerated sediment surface. The chemical characterization of Mn precipitates is difficult to achieve, as selective extractants designed to solubilize Fe fractions not always produce consistent results when applied to Mn precipitates. Thus, dithionite-citrate-bicarbonate, specifically designed to extract Fe crystalline components, solubilizes similar Mn concentrations in comparison with ammonium acid oxalate, specifically designed to extract Fe amorphous components, even in the presence of crystalline Mn oxides, whereas their solubility in HCl-hydroxylamine, aiming at solubilizing easily reducible Mn were quite variable. XRD characterization is also complicated by the coincidence of several reflection signals of Mn oxides. In spite of

these difficulties, Mn minerals have been identified in the precipitates: todorokite, lithiophorite, cryptomelane, and probably pyrolusite and psilomelane. Heavy metals such as Cu, Zn, Cr, and mostly Co, were associated to Mn precipitates.

A concentration procedure with 3% H₂O₂, aimed at separating Mn phases from Fe oxides and clay minerals was tested in soils and sediments [1]. The reaction of H₂O₂ with Mn components produces a bubbling entraining Mn rich particles. Nevertheless, the procedure is not effective in mica rich samples. A complementary densimetric separation using bromoform was recommended for the study of the >50 µm fraction.

References

- [1] Ross, S.J., Frazmeier, D.P., Roth, C.B., 1976. Mineralogy and chemistry of manganese oxides in some Indiana soils. *Soil Sci. Amer. Jour.* 40: 137-143.

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