Fate of Ni in local reduced environments developed on lateritic Ni ores from New Caledonia

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In New Caledonia, the weathering of ultramafic rocks in a tropical climate produced extremely thick laterites (≤ 80m), particularly enriched in metals such as Ni. The main weathering pathway involved the formation of large amounts of goethite (α-FeOOH), and X ray absorption spectroscopy (XAS) showed that the major proportion of Ni is incorporated into the structure of this Fe(III)-oxyhydroxide [1].

However, as previously reported in New Caledonia, reducing conditions can occur locally in the lateritic formations, due to the development of dolines and the accumulation of organic matter [2]. Samples from a lateritic profile characterized by X ray diffraction and ICP-AES showed the occurrence of siderite ($FeCO_3$) in a 4 meters thick horizon, suggesting the local reduction of Fe(III)-oxides into Fe(II)-carbonate. SEM-EDS analysis indicates significant amounts of Ni associated with siderite (~ 0.80 wt% NiO).

The speciation of Ni in this weathering context was then investigated by XAS in the solid phase, at the scale of the whole profile, and by comparison with synthetic analogues. XAS showed that Ni is mainly incorporated into the siderite structure in the reduced horizon, and is in goethite in the unreduced laterite above. This result helps understanding the trace metals behavior in altered lateritic weathering contexts, and shows the importance of local Ni trapping in reduced iron phases.

[1] Dublet *et al*.. (2012) *GCA* **95**, 119–133 [2] Podwojewski and Bourdon (1996) *C.R. Acad. Sci. Paris*, **322**, series II a, 453-459

Long-time alteration of iron slags inferred from paleometallurgical heaps

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Moulière is a large forest (area of 6800 ha) and is located on a plateau between the valleys of the Vienne and the Clain rivers (Vienne, France). Exploration by Abbé de la Croix in the nineteenth century and the work of the ONF (Office National des Forêts) have revealed the presence of numerous slag heaps. These heap associated with the iron metallurgy fall into several areas of the forest sector and outside. They are identifiable on the ground because they form mounds 0.5 to 2 m high and they are usually invaded by typical vegetation (holly - *Ruscus aculeatus* - and hawthorn). The age of these mounds is not known, but more than 10 ironworks were in operation at the time of the reformation of forests by Colbert in 1667. The establishment of the ironworks in the Forest of Moulière is related to the facility offered for logging to operate low blast furnaces. The iron ore is probably also of local origin. Whereas no significant outcrop has been actually observed, an iron-bearing sandy layer is discontinuously present in the forest underground.

A study of the mineralogical and chemical slags was carried out by optical microscopy, scanning electron microscopy (SEM) and Raman microspectroscopy in order to make a characterization, in particular for the presence of an alteration layer. Indeed, the slag storage sites offer the opportunity to study the long-term behavior of vitrified materials subjected to weathering periods of time (several centuries) well above the experimental approach.

High density slags present various dimensions from centimetric to decimetric blocks, rounded surface, sometimes within a matrix strongly the existence vacuole. They are black or red-orange. The samples exhibit a mineralogy consisting mainly of silicates (olivine (Fe_2SiO_4), quartz, feldspar) and oxides (hematite (Fe_2O_3), titanium oxide) in the periphery of the vacuoles or in forming droplets. This great disparity of mineralogical and chemical composition conditions the chemical durability of this material. Experimental studies are conducted to study the behavior of such slags.

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