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Morphology, mineralogy and geochemistry of natural Fe-(oxy)hydroxides in supergene ore deposits.

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Iron-(oxy)hydroxides (IOH) phases are ubiquitous in all Supergene Ore Deposits (SOD), where they are found regularly associated with economic ores. The most common IOH phase in this environment is goethite senso strictu due to its thermodynamic stability, followed by hematite, lepidocrocite, ferrihydrite and maghemite. Natural IOH are rarely chemically pure. In fact, a range of metal cations, isovalent or heterovalent to Fe3+, can be incorporated into their structure. Moreover, in many environments, it is common to find goethite intergrown and mixed with ferrihydrite, coating grain surfaces and mixed with hematite and minor maghemite. The aim of this study was to establish the geochemical, morphological and mineralogical variations of natural IOH collected from a diverse range of SOD, in order to asses which metals are routinely incorporated. The samples were taken from the oxidation zones of Ni-laterite deposits (Çaldağ and Karaçam, Turkey; Wingellina, Australia), supergene Zn-nonsulfides (Hakkari, Turkey; Jabali, Yemen) and from karst bauxites (Maiorano and Dragoni, Italy). The analyses were carried out at Natural History Museum (London, UK) using a range of analytical methods: XRD, SEM-EDS, EPMA, ICP-AES, LA-ICPMS. IOH samples from Ni-laterite and Zn-nonsulphide deposits mainly consist of goethite but also minor maghemite and hematite were identified, while bauxite-hosted specimens mainly consist of hematite with minor goethite. The detected IOH are rarely alone, as for the challenge to separate them from other minerals commonly occurring in supergene environments (i.e. quartz and clays). The textures and the morphology of IOH are quite different depending on the deposit of provenance. In Ni-laterite deposits the goethite commonly occurs as crusts associated with Mn-(oxy)hydroxides or quartz, botryoidal concretions within rock pores or in needle-like form. In some cases goethite can be pseudomorph on primary mineral phases (olivine or pyrite). In contrast, the IOH in bauxite deposits, consist of ooids with hematite cores surrounded by boehmite or by crusts of hematite associated with goethite. In all the selected samples Fe, Si and Al are the major elements hosted in IOH. The high Al content of the bauxite IOH reflects the presence of boehmite. EPMA analyses revealed that some amounts of Al and Si (up to a max. of ~ 3 wt%) is accommodated within goethite itself. The minor element contents change according to the deposit type: Cr, Ni and Co are elevated in goethite samples from Ni-laterite where EPMA shows Nivalues up to \sim 3 wt% and Co up to \sim 0.3 wt%; other elements detected include minor Mg and Mn. The IOH selected from Zn-nonsulphide deposits are enriched in Zn and Pb; some Pb is present as trace of cerussite, but EPMA analyses show that goethite itself can contain up to ~6 wt.% Zn and Pb. Titanium (from anatase) is a common minor element from IOH selected from bauxites. LA-ICPMS analyses successfully measured Sc, Ge, Ga and REE contents within IOH: the content of Sc, Ge and Ga appears to be negligible in most of the IOHs studied, whereas REE (up to \sim 1000 ppm) is found in IOH samples from bauxite deposits.