Some observations on the structural incorporation of trace elements in the structure of iron oxides

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Iron oxides are considered to be the most dominant adsorbent for trace metals in soils and sediments (Jenne, 1998; Singh, 2001). At lower concentrations, trace metals are mainly adsorbed by surface complexation reactions on to Fe oxides. However, in highly contaminated environments where trace metals are present at elevated concentrations (such as ASS or AMD) co-precipitation of trace metals with Fe^{3+} in the structure of Fe oxides may occur or even become a dominant process in controlling the solubility of metals. Co-precipitation of several trace metals including Cd, Co, Cr, Cu, Mn, Ni, Ti, V and Zn has been shown in the structure of synthetic goethites in single metal systems (Fitzpatrick *et al.*, 1978; Lim-Nunez and Gilkes, 1987; Cornell & Schwertmann, 1996; Singh *et al.*, 2002; Huynh *et al.*, 2003). Trace metals are also associated with Fe oxides in natural environments, but it is not always clear if these elements occur as separate phases or if isomorphous substitution for the Fe^{3+} in the structure of Fe oxides has occurred (Singh & Gilkes, 1992; Trolard *et al.*, 1995). Whether trace metals occur as discrete phases or as a solid solution in Fe oxides is extremely important in determining their aqueous solubility. Substitution of other cations in Fe oxides may influence the crystal habit, crystal size, crystallinity and chemical composition. These crystal properties are of great significance as they may modify the surface properties of Fe oxides and consequently affect the specific sorption of cations (e.g. Cd, Cu, Zn, Co, Cr) and anions (e.g. phosphate, molybdate, silicate). In the last few years my research group has investigated single and multiple metal cations (V, Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb) on the formation of goethite under industrial (Fe^{3+}, 70°C and highly alkaline pH) and environmental (Fe^{2+}, 25°C, slightly alkaline pH) relevant conditions. Similarly, akaganéite was synthesized in the presence of Mn, Zn, Cd and Pb by ageing mixtures of 0.1 M Fe and metal chloride solutions (at nominal metal concentration of 5 and 10 mol per cent) at 70°C and at 25±3°C, and aged for 14 days.

We discovered that the presence of multiple metals control the species of Fe oxides formed in a system, and the substitution of a particular metal varies depending on the presence of the other co-existing metals in the system. The maximum level of substitution of foreign metals in goethite in multiple-metal systems is different to their substitution limit observed in single metal experiments. The total metal substitution and changes in unit cell dimensions were not only influenced by ionic radii and charge balancing mechanisms, but also by the presence of co-metal(s) in the system. Our research demonstrated goethite's ability to incorporate multiple metal cations, however, it's formation is delayed and in some cases completely hindered, especially in Fe^{2+} formation pathway, by the

presence of some metals. X-ray absorption fine structure spectroscopy revealed that metals forming symmetrical octahedra are evenly distributed in the crystal and appear to enhance the incorporation of co-metals. Some key examples from these studies will be presented at the conference. The results are highly relevant to the management of contaminated systems, such as abandoned mine sites and acid sulfate soils, which often contain multiple metals along with Fe.

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