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Oxidation state and coordination of iron in red pre-soils: first results from a Fe K-edge *XANES* study on regoliths from Santiago Island, Cape Verde

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Ferrihydrite is an iron (ferric) oxy-hydroxide characteristic of regoliths – that is, red pre-soils formed by loose weathered rock plus mineral debris with no organic content (humus); it is commonly designated as "2-line" or "6-line" on the basis of the broadened maxima observed in X-ray diffraction patterns, but the lack of known crystal structure only allows for reporting an approximate ideal formulation $5Fe_2O_3.9H_2O$ [1]. This nanomineral phase usually contains silica as a minor chemical component because it results from the alteration of iron-rich olivine (fayalite) and accordingly, it is also a precursor of smectite/nontronite in tropical soils [2].

Recent studies on synthetic ferrihydrite applying pair distribution function (PDF) methods [3] have disclosed the presence of icosahedral clusters similar to the well known Keggin's molecule and formed by twelve Fe^{3+} octahedra. Such clusters are supposedly centred by tetrahedral Fe^{3+} but this tetrahedral cation could well be silicon in natural ferrihydrite. In fact, a former Mössbauer study performed at low temperature [4] was inconclusive about the occurrence of tetrahedral iron.

X-ray absorption spectroscopy is particularly suitable for studying the formal valences of metal ions and their coordination environment: the near-edge features of X-ray absorption spectra (15-20 eV before the main K-edge crest) are related to $1s \rightarrow 3d$ (quadrupolar) and/or $1s \rightarrow 4p$ (dipolar) electronic transitions, thus providing information about the oxidation state and the coordination geometry of $3d$ transition metal

ions [5].

A Fe K-edge XANES study on regoliths from Cape Verde Islands was undertaken at the ESRF (European Synchrotron Radiation Facility in Grenoble/France) using the instrumental set-up of beamline ID21. The first results are reported and compared with well crystallized minerals - hematite and goethite, both containing octahedral Fe^{3+} in high-spin state. The hypothesis that some minor ferric iron stays in tetrahedral coordination was not entirely discarded as will be discussed.

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