SHRIMP-SI ($^{18}O/^{16}O$) analyses of goethite: Technical aspects and applications to paleoenvironmental studies

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Stable isotope analysis of dated goethite from soils and weathering profiles permits retrieving continental paleoenvironmental conditions [1], potentially complementing the marine record in paleoclimatic reconstructions. The combination of geochronological analysis of supergene Fe-oxyhydroxides by the (U-Th)/He-^{4}He/^{3}He method with high-spatial resolution stable isotope ion-microprobe methods is a promising approach for probing the complex mineral assemblages in weathering profiles.

A major challenge in ion-microprobe analysis of goethite is the difficulty in finding pure and homogeneous material to produce suitable standards. Natural goethites often contain minor components (*e.g.*, Si, Al, Mn) that may alter their isotopic signatures. They often precipitate in colloform textures, where composition varies accross micrometer-scale growth bands. Even when homogeneous grains are identified, analytical difficulties associated with polishing heterogeneity, sample topography, crystal orientation, and surface irregularities (*e.g.*, porosity) may result in sample-induced apparent isotopic fractionation. After screening hundreds of candidates, we have found two potential goethite SHRIMP-SI standards (CAPAO-L4 and Roy-CY4) and independently callibrated their isotopic composition by the the laser fluoritnation method.

Preliminary results for supergene goethites from weathering profiles in the Carajás and Quadrilátero Ferrífero regions (Brazil) show a $\delta^{18}O$ *vs.* age trend, with goethites showing a progressively more negative isotopic signature from the Mid-Eocene to the Pleistoscene. Goethites displaying organic textures (pseudomorphic after bacteria colonies or fossilising filamentous microorganisms) yield more negative $\delta^{18}O$ values (-4 to -9‰) than coexisting goethites directly precipitated from aqueous solutions in empty cavities (4.9 to -2.8‰). The variation in $\delta^{18}O$ with precipitation mechanism confirms the need for high spatial resolution methods in order to use the isotopic composition of pedogenic phases in continental paleoclimatic reconstructions.

[1] Sjostrom *et al* (2004) *Quarternary Research*, 64-71