

XAS crystal-chemistry of Fe in mangrove sediments from New Caledonia. Implication for iron biogeochemical cycling

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Mangrove forests are the dominant intertidal ecosystem of tropical coastlines and play a fundamental role in the ecological balance of these areas. They strongly influence the transfer of trace metals between land and sea. In New Caledonia, mangroves act as a buffer zone between massive Fe lateritic deposits and a lagoon registered as an UNESCO World Heritage site. Mangroves are composed of different stands, each dominated by a botanical species. Mangrove zonation mainly results from difference in soil elevation, and length of tidal immersion, and induces different ecosystem productivity, and redox conditions {1}. As a consequence, it may be responsible for differences in sediment geochemistry, and thus differences in metal speciation and bioavailability {2}.

In the present study, we have determined the distribution and speciation of iron in mangrove sediments in relation with organic content, redox, salinity and botanical gradients. Chemical and mineralogical analyses of mangrove sediment core samples were complemented by direct speciation of Fe using EXAFS spectroscopy. The results obtained show that crystal-chemistry of Fe strongly follows the marked change in sediment redox conditions that range from oxic in surface horizons to anoxic in deep horizons. The Fe-bearing minerals (mainly goethite, with minor amounts of Fe-phyllsilicates) are major phases in the upwards horizons and are inherited from lateritic, then progressively disappear from the surface horizons towards deepest horizons where pyrite forms.

{1} Marchand (2012) *Chemical Geology* 300-301, 70-80. {2} Otero (2009) *Geoderma* 148, 318–335.

Back to basics: Boron isotopic fractionation in synthetic calcite and aragonite

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Boron isotopic fractionation in marine carbonates, such as foraminifera and corals, is dependent on the pH of the seawater in which they form, allowing boron isotopes to be used as a proxy of the ocean-pH. The pH-dependency of the boron isotopic composition in organic calcium carbonates has been confirmed in laboratory environment. This behavior of boron isotopes is classically explained by the incorporation of the borate ion from seawater, whose isotopic composition is a function of its abundance and hence of pH. Modern biologically-precipitated calcium carbonates however display widely spread boron isotopic compositions which can be partially explained by vital effects but do not fit the simple model of preferential incorporation of the borate ion.

In order to better understand the mechanisms responsible for boron isotopic fractionation in calcium carbonates, we precipitated, in laboratory, inorganic calcite, Mg-calcite and aragonite over a wide pH range and performed both isotopic and ¹¹B MAS NMR (Magic Angle Spinning Nuclear Magnetic Resonance) analyses on the solids. Results show that, although $\delta^{11}\text{B}$ rises with pH for all crystal types, calcite and Mg-calcite display a smaller fractionation (more marked for calcite) with respect to the precipitation solution and a much lesser sensitivity to solution pH than expected. NMR spectra show almost exclusively tetrahedral boron in aragonite but highly variable proportions of trigonal and tetrahedral boron in calcite. We therefore suggest that both borate ion and boric acid are incorporated in calcite and Mg-calcite and that boron is present in both crystalline and non-crystalline sites whereas in aragonite the borate ion is the dominant species, representing over 90% of the total boron. These results overall suggest that aragonite-based calibrations should be favoured in future paleo-pH reconstructions. Calcite-based calibrations require a rigorous characterization via NMR spectroscopy of boron speciation and site occupancy in the crystals.