

Redox behavior of nanoscale Fe oxides: Stable isotope investigations

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Iron oxides are ubiquitous. They are present in the soil beneath your feet, the rust on your car, the hard-drive in your computer, and the rocks on Earth and Mars. Essentially anywhere that iron is exposed to oxygen, iron oxides form. These tiny, often nanoscale, particles are responsible for most of the red, yellow, green, and black color you observe around you and they profoundly influence the quality of our water, air, and soil through the biologically-driven redox cycling between ferric (Fe^{III}) and ferrous iron (Fe^{II}). We are using stable Fe isotopes in conjunction with ⁵⁷Fe Mössbauer spectroscopy to study redox reactions between ferrous Fe and Fe oxides.

Our results show that sorbed Fe (II) is oxidized by Fe (III) in Fe oxides, such as goethite, hematite, ferrihydrite, and magnetite and that Fe (II)-Fe (III) electron transfer initiates and propagates extensive mixing between the Fe oxide and aqueous Fe (II) [1]. We propose that a redox-driven conveyor belt is established where remote sorption and dissolution sites are linked via electrical conduction through the bulk crystal, as was recently demonstrated for hematite [2]. For goethite we observed complete mixing between structural Fe and aqueous Fe over a period of thirty days, whereas for magnetite only partial mixing is observed. This general finding has substantial implications for understanding heavy metal sequestration and release, and reduction of soil and groundwater contaminants.

[1] Handler *et al.* (2009) *ES&T* **43**, 1102–1107. [2] Yanina & Rosso (2008) *Science* **320**, 218–222.

Palaeoecological considerations in Oligocene vertebrates of Western Europe—C and O stable isotope compositions

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Tooth enamel of 44 terrestrial mammals (horses, rhinoceroses, entelodons, anthracotheres) and bones of 17 aquatic reptiles (turtles, crocodiles) from five Oligocene localities of the Swiss Molasse Basin and Aquitaine Basin (France) have been analysed for their carbon and oxygen stable isotope compositions. The chosen localities are biostratigraphically well dated by small mammals and distributed through the Oligocene: Villebramar (Rupelian, Palaeogene mammal zone MP22, ~32 Ma) in Western France, and Beuchille and Poillat (Rupelian, MP23-24, ~30 Ma), Bumbach (Chattien, MP25, ~28 Ma), and Rickenbach (Chattian, MP29, ~24 Ma) in Switzerland.

The mean $\delta^{13}\text{C}$ values are very similar for all the species in each of the localities with values lower than -8‰. This supports a diet for the analysed species that is based on C₃-plants only (such as today's trees, shrubs, and humid cool-season grasses), confirming an absence of C₄-plants (today's dry warm-season grasses) during the Oligocene in Western Europe. Despite these apparently homogeneous values some niche partitioning can be detected among the different taxa though, suggesting preservation of primary carbon isotope compositions.

The aquatic reptiles in the sampled localities have systematically lower $\delta^{18}\text{O}_{\text{PO}_4}$ values compared to the terrestrial mammals, in support of their freshwater aquatic habitat. Considering only the terrestrial mammals, the specimens from Villebramar have higher mean $\delta^{18}\text{O}_{\text{PO}_4}$ values (20.3±2.1‰) compared to those of the Swiss localities (e.g. Rickenbach $\delta^{18}\text{O}_{\text{PO}_4}$ values averaging 17.6±1.1‰). This suggests slightly colder conditions in Switzerland up to the Late Oligocene. [SNF project 126420]