

## Solid state concepts to understand catalysis using nanoscale metallic particles

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New advances in theoretical background and recent experimental results concerning nanometer scale metallic clusters are presented. We will begin by a presentation of the advantages and the limitations of synchrotron radiation techniques to characterize nanometer scale entities. Then, through a review of recent papers, we try to make a link between metallic surfaces and nanometer scale monometallic clusters in the case of the interaction with a small molecule, namely NO.

## Iron Isotope Constraints on Fe Cycling and Mass Balance in the Oxygenated Earth

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The origin of mass-dependent variations in Fe isotope compositions that occur in nature is poorly understood. Igneous rocks have a homogenous Fe isotope composition,  $\pm 0.05$  ‰ in  $^{56}\text{Fe}/^{54}\text{Fe}$  (46 samples analysed). The constant Fe isotope composition of igneous rocks provides an ideal baseline for evaluating Fe isotope variations with respect to a bulk earth composition and we define Fe isotope variations as:

$$\delta^{56}\text{Fe} \text{ ‰} = \left( \frac{^{56}\text{Fe}/^{54}\text{Fe}_{\text{sample}}}{^{56}\text{Fe}/^{54}\text{Fe}_{\text{Igneous Rocks}}} - 1 \right) * 1000.$$

Using this baseline, the  $\delta^{56}\text{Fe}$  value of the IRMM-014 Fe isotope standard is  $-0.09$  ‰. In contrast to the homogenous Fe isotope composition of igneous rocks, chemically precipitated sediments have a wide range of  $\delta^{56}\text{Fe}$  values from  $-2.5$  to  $+1.1$  ‰. The origins of the Fe isotope variations in chemically precipitated sediments may be caused by inter mineral fractionation and/or a reflection of variable Fe isotope compositions of the fluid that precipitated the sediment.

The Fe isotope composition of Proterozoic to modern clastic sedimentary rocks and aerosols defines a range in  $^{56}\text{Fe}/^{54}\text{Fe}$  isotope ratios that are only slightly more variable than that of the range of Fe isotope compositions measured in terrestrial igneous rocks (82 samples analysed), indicating that chemical weathering, sedimentary transport, and diagenesis played only a minor role in producing Fe isotope variations in environments where Fe redox conditions have been controlled by current levels of atmospheric oxygen. These analyses of clastic sediments serve to define the particulate riverine and atmospheric Fe loads that reach oceans to have a  $\delta^{56}\text{Fe}$  value of 0 ‰. In contrast, the Fe isotope composition of hot fluids ( $>300^\circ\text{C}$ ) from mid ocean ridge (MOR) spreading centres define a narrow range in Fe isotope compositions that is shifted to lower values by 0.2 to 0.5 ‰ in  $^{56}\text{Fe}/^{54}\text{Fe}$  ratios as compared to igneous rocks (7 analyses). These new data allow a conceptual model for the Fe isotope composition of the oxic oceans that predicts large ranges in Fe isotope composition under conditions of changing aerosol and MOR Fe fluxes, such as during periods of major worldwide glaciation over the last 800 million years. Additionally, this model predicts that currently, southern ocean basins should have low  $\delta^{56}\text{Fe}$  values as compared to northern ocean basins. The inferred difference in Fe isotope compositions between northern and southern oceans is a result of the high atmospheric dust component that is generated at northern latitudes.