δ^{56}Fe variations in Fe-Ti oxides of IODP Hole 1256D (East Pacific Rise)

W. Dziony*, I. Horn, J. Koepke and F. Holtz

Institute of Mineralogy, Leibniz University of Hannover,
Germany (*correspondence:
w.dziony@mineralogie.uni.hannover.de)

The formation of the oceanic crust is one of the main fundamental processes building our planet. Representing the first completely drilled section of the upper oceanic crust the basalts and gabbros recovered from IODP Hole 1256D (Eastern Pacific) provides us with the good opportunity to improve our understanding of the formation and evolution of the crust.

Currently Fe isotope ratios are investigated in oxides and sulphides from basalts and gabbros in order to gain basic knowledge of the Fe isotope cycle in the ocean crust. The open question is whether these isotopic signatures can be used as a proxy of hydrothermal alteration.

In this approach a deep UV-femtosecond laser ablation system coupled to a MC-ICP-MS is used. This method allows us to determine iron isotope ratios *in situ* at high spatial resolution with a precision of ±0.1‰ (2σ) for the δ^{56}Fe ratio ($\delta^{56}\text{Fe} = (^{56}\text{Fe}/^{54}\text{Fe}_{\text{sample}}/^{56}\text{Fe}/^{54}\text{Fe}_{\text{IRMM-14}}-1)*1000$). Additionally it has been shown that a high degree of matrix-independency has been reached using this technique allowing a single metallic standard to be used for the analysis of a large variety of matrices.

Evenso igneous rocks show little variations in their whole rock δ^{56}Fe values, within the investigated samples large variations in δ^{56}Fe are observed on the micron scale for both, magnetite and ilmenite. $\Delta^{56}\text{Fe}_{\text{magnetite-ilmenite}}$ values ($\delta^{56}\text{Fe}_{\text{magnetite}}$ - $\delta^{56}\text{Fe}_{\text{ilmenite}}$) of coexisting pairs of magnetite and ilmenite are in agreement with the general trend of temperature-dependent fractionation. However, a shift towards higher Δ^{56}Fe values compared to the predicted values implies that isotopic equilibrium has not been reached. These observations can be explained by the influence of hydrothermal alteration, since all investigated samples show petrographic evidence typically for hydrothermal alteration. It has been shown that Cl-bearing supercritical fluids can contain considerably amounts of bi-valent Fe. Such solutions of Fe^{2+} tend to favor mobilization of isotopically light iron. Assuming that magnetite is more sensitive to exsolution of iron than ilmenite in the presence of a Cl-bearing fluids, an increase in the δ^{56}Fe value of magnetite is observed which in turn also increases the Δ^{56}Fe magnetite-ilmentite. Variations of up to 0.4‰ in δ^{56}Fe within a single grain of magnetite illustrates that isotopic alteration can be extremely localized.

'Clumped isotope' thermometry in bioapatite

R. Eagle[1]*, E. Schauble[2], A. Tripati[1,2], T. Tütken[3], H. Fricke[4], R. Hulbert[5] and J. Eiler[1]

[1]Geological and Planetary Sciences Division, California Institute of Technology, Pasadena, CA 91125 (*correspondence: robeagle@caltech.edu)
[2]Department of Earth and Space Sciences, UCLA, Los Angeles, CA, 90095
[3]Steinmann Institut für Geologie Mineralogie und Paläontologie, Universität Bonn, 53115 Bonn, Germany
[4]Department of Geology, Colorado College, Colorado Springs, CO 80903
[5]Florida Museum of Natural History, University of Florida, Gainesville, FL 32611

The stable isotope compositions of biologically precipitated apatite in bone, teeth, and scales are widely used to reconstruct past climate and to obtain information on the diet, behavior, and physiology of extinct organisms. Apatite is an attractive target for paleoclimate studies because biogenic and inorganic apatites are frequently preserved in the geologic record, including in locations where carbonates are not found. Here we report the application of a new type of geochemical measurement to bioapatite, a 'clumped isotope' paleothermometer, based on the thermodynamically driven preference for ^{13}C and ^{18}O to bond with each other within carbonate ions in the bioapatite crystal lattice. This effect is dependent on temperature but, unlike conventional stable isotope paleothermometers, is independent from the isotopic composition of water from which the mineral formed. We show that the abundance anomaly, relative to a stochastic distribution, of ^{13}C-^{18}O bonds in the carbonate component of tooth bioapatite from modern specimens decreases with increasing body temperature of the animal, following a relationship between isotope 'clumping' and temperature that is statistically indistinguishable from inorganic calcite. This result is in agreement with a theoretical model of isotopic ordering in carbonate ion groups in apatite and calcite. This thermometer constrains body temperatures of bioapatite-producing organisms with an accuracy of 1-2°C. Analyses of fossilized tooth enamel of both Pleistocene and Miocene age yielded temperatures within error of those derived from similar modern taxa. In addition to the study of paleoclimate, the clumped isotope analysis of bioapatite also represents a new approach in the study of the thermophysiology of extinct species, allowing the first direct measurement of their body temperatures. Our initial application of this thermometer has been to measure the body temperatures of Mesozoic dinosaurs to shed light on the 'cold-blooded' versus 'warm-blooded' dinosaur debate.