

## Historical carbonate mortar and plaster – Proxies for ancient environments

B. KOSEDNAR-LEGENSTEIN<sup>1</sup>, M. DIETZEL<sup>1</sup>, A. LEIS<sup>2</sup>,  
K. STINGL<sup>1</sup>, B. WIEGAND<sup>3</sup> AND M. BAUMGARTNER<sup>1</sup>

<sup>1</sup>Institute of Applied Geosciences, Graz, Austria  
(martin.dietzel@tugraz.at)

<sup>2</sup>Institute of Water Resources Management, Hydrogeology and Geophysics, Joanneum Research Graz, Austria

<sup>3</sup>Dept. of Geological and Environmental Sciences, Stanford University, USA

Main focus of this study lays on mineralogical, chemical and isotopic composition of carbonate binders of historic roman, medieval and pre-industrial buildings as well as local limestone deposits (Styria, Austria). The respective mortars and plasters mostly consist of calcite as cement with aggregates of calcite, dolomite, quartz, and other silicates like clay minerals or mica.

E.g. <sup>87</sup>Sr/<sup>86</sup>Sr, Sr/Ca, and Mg/Ca ratios of the cement may reflect the composition of the natural deposits used for manufacturing of lime mortar. Values depend on the geologic environment and mineralogical composition of the primary limestone.

<sup>13</sup>C/<sup>12</sup>C and <sup>18</sup>O/<sup>16</sup>O composition of the carbonate cement comprise a wide range and for an ideal case  $\delta^{13}\text{C}$  vs.  $\delta^{18}\text{O}$  shows an almost linear correlation. In general, calcite is isotopically lighter at the exterior versus the interior mortar layer. Range and systematic correlation of the data reflect isotopic fractionation effects upon setting of the cement and during the history (e.g. re-crystallization and weathering) of the cement. From another point of view isotope signatures can be used as a proxy for calcite formation conditions.

As one may use historical carbonate binder for <sup>14</sup>C dating a promising pre-selection of suitable samples can be done by exclusively using carbonate cement or especially lime pops with specific  $\delta^{13}\text{C}_{\text{CaCO}_3}$  and  $\delta^{18}\text{O}_{\text{CaCO}_3}$  values.

## Fe isotopic composition in sulphides from hydrothermal deposits at the Arctic mid-ocean ridge

JAN KOSLER AND ROLF B. PEDERSEN

Department of Earth Science, University of Bergen, Allegaten 41, Bergen, N-5007 Norway. (jan.kosler@geo.uib.no)

Hydrothermal vents represent an important source of iron for the deep ocean water. Their iron isotopic composition has been reported as constant relative to Fe residence time in the ocean but also as highly variable with respect to the sampling sites. It has been proposed that sedimentary record of Fe isotopic composition can be used locally to study the past fluxes of Fe but such study is limited by our poor understanding of Fe isotopic fractionation in the hydrothermal systems.

On average, the hydrothermal vent fluids have a slightly lighter ( $\sim -0.5\%$   $\delta^{56}\text{Fe}$ ; Sharma *et al.*, 2001) iron isotopic composition compared to the oceanic crust ( $\sim 0\%$   $\delta^{56}\text{Fe}$ ; Rouxel *et al.*, 2003), suggesting that seafloor hydrothermal systems fractionate iron isotopes. The isotopically light hydrothermal emanations of Fe<sup>2+</sup> become progressively lighter through subsequent oxidation and precipitation processes within the water column (Severmann *et al.*, 2004). The isotopic fractionation of Fe between the fluids and the precipitated sulphides is not yet fully understood but it varies with redox conditions, progress of the reaction and reaction rates.

We have studied isotopic composition of Fe in sulphides associated with newly-described hydrothermal systems along the Mohs Ridge in Norwegian-Greenland Sea. Pyrite from a tectonic breccia recovered from deep parts of the upflow zone is isotopically heavier compared to the pyrite from chimney fragments and sulphide precipitates on the sea floor. The studied pyrite precipitated at ca. 300-330 °C, i.e. at temperatures similar to many black smoker fluids, and higher than can be tolerated by thermophile bacteria. It also formed before the redox conditions were significantly changed by interaction of the Fe-bearing fluids with the deep sea water. The heavy iron isotopic composition in the pyrite from the tectonic breccia suggests that a significant fractionation may take place in the deeper parts of the upflow zone, and that this could explain the shift towards lighter iron seen in many vent fluids. The enrichment of heavy iron in pyrite from the deeper part of the upflow zone is probably related to factors other than the fluid temperature.

### References

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