



## Historical Carbonate Mortar and Plaster - Isotopic and chemical signatures

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The main focus of this study is to investigate the mineralogical, chemical and isotopic composition of historic carbonate binders and local limestone deposits. Mortar and plaster samples of roman, medieval and pre-industrial buildings were sampled in Styria/Austria (Eisenerz, Thörl, Kleinstübing, Niederhofen, Graz, Flavia Solva, Kainach, Deutschlandsberg, Kapfenstein) as well as samples from chalk-pits, marble and dolomite quarries close to the corresponding historical buildings. In several samples the historic age gained from archaeological aspects was confirmed by  $^{14}\text{C}$  dating. The respective mortars and plasters mostly consist of  $\text{CaCO}_3$  (calcite) as cement with aggregates of calcite, dolomite, quartz, and other silicates like clay minerals or mica. The chemical composition was analyzed by ICP-OES, ICP-MS, IC, and XRF. Further aspects such as microstructure and pore space were analyzed with SEM.

The isotopic composition of stable isotopes of carbon, oxygen, and strontium were measured by mass spectrometry. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the cement are between 0.7091 and 0.7115, whereas Sr/Ca ratios do not exceed 0.003. In principle, these ratios reflect the composition of the natural deposits used for manufacturing of lime mortar. The  $^{87}\text{Sr}/^{86}\text{Sr}$  values depend on the geologic environment and mineralogical composition of the primary limestone.

Burning and setting experiments were conducted in laboratory to investigate the behaviour of REE and the strontium isotopes. Burning has a negligible influence on Sr/Ca,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and REE distribution, and rather minor effects may be caused by aggregate leaching during  $\text{CaCO}_3$  setting. However, in several cases Sr/Ca and

$^{87}\text{Sr}/^{86}\text{Sr}$  signatures can be used as a kind of fingerprint.

The  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  composition of the carbonate cement comprise a wide range of  $\delta^{13}\text{C}_{\text{CaCO}_3}$  (PDB) from -24 to  $-1\text{‰}$ , and of  $\delta^{18}\text{O}_{\text{CaCO}_3}$  (PDB) from -24 to  $-3\text{‰}$ . The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  distribution shows an almost linear correlation. In general, calcite is isotopically lighter at the exterior versus the interior mortar layer. The 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.

The  $^{13}\text{C}/^{12}\text{C}$  distribution depends on kinetic fractionation due to hydroxylation of gaseous  $\text{CO}_2$ , resulting in an enrichment of  $^{12}\text{C}$  versus  $^{13}\text{C}$  in the precipitated  $\text{CaCO}_3$ . Upon setting of the cement, the diffusion of gaseous  $\text{CO}_2$  leads to a continuous enrichment of  $^{13}\text{C}$  and  $^{18}\text{O}$  of  $\text{CO}_2$  within the gas phase along the cement setting path. This is confirmed by laboratory sequential precipitation experiments. Accordingly, precipitated calcite is isotopically heavier at the interior mortar layer. Variations may be caused by natural or anthropogenic impacts, e.g. evaporation of  $\text{H}_2\text{O}$  during the setting or  $\text{CO}_2$  from anthropogenic origin. On the other side,  $\text{CO}_2$  from burning of fossil fuels and soils or re-crystallization of carbonate cements in the presence of  $\text{H}_2\text{O}$  from various origins may be deciphered.