



## Isotopic signatures of carbon, oxygen and strontium of historical mortar and plaster in Styria

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Historical buildings are constructed of geo-materials, mortar, and plaster of various compositions. The chemical and isotopic composition of mortar and plaster comprises information about the historical environment with respect to the provenance of the materials, processing, and weathering. Moreover, isotopic data may provide additional information about the ancient composition of carbon dioxide and water. The present study is focused on the mineralogical, chemical and isotopic composition of dated and well-characterized carbonate mortar and plaster of roman, medieval, and early modern (pre-industrial) times in Styria (Austria).

Mortars and plasters were sampled from historical buildings in the area of Flavia Solva, Frauenberg, Deutschlandsberg, Seggauberg, Kleinstübing, Niederhofen, Södingberg, and Graz. Sampling was conducted from the exterior to interior mortar layer, wherever applicable. The sampled materials mostly consist of a  $\text{CaCO}_3$  (calcite) cement with aggregates of quartz and additional silicates like clay minerals. In principle, the analyzed Sr/Ca and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios reflect the composition of the natural deposits used for manufacturing of lime mortar. The respective values depend on the environment of formation and on the mineralogical composition (e.g. calcite or aragonite) of the primary limestone.

However, the distribution of  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios in the carbonate mortars and plasters indicates a more complicated situation as isotopic compositions comprise a

wide range of  $\delta^{13}\text{C}_{\text{CaCO}_3}$ (PDB) from -24 to -1, and of  $\delta^{18}\text{O}_{\text{CaCO}_3}$ (PDB) from -24 to  $-3\text{‰}$ . The stable carbon and oxygen isotope distributions in the carbonate cement displays an almost linear correlation. In general calcite is continuously isotopically “heavier” from the exterior to 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 individual cement.

In principle isotope distributions depend on the composition of the gaseous  $\text{CO}_2$  and aqueous  $\text{OH}^-$  according to the overall reaction



during the formation of carbonate cement. Reaction 1 is accompanied by a kinetic isotope fractionation due to the hydroxylation of gaseous  $\text{CO}_2$  (Dietzel, 2000), resulting in an enrichment of  $^{12}\text{C}$  versus  $^{13}\text{C}$  in the precipitated  $\text{CaCO}_3$ . If gaseous  $\text{CO}_2$  is delivered from the present Earth’s atmosphere ( $\delta^{13}\text{C}_{\text{CO}_2(\text{atm})} = -7\text{‰}$ ) a  $\delta^{13}\text{C}_{\text{CaCO}_3}$  value of about  $-25\text{‰}$  is obtained. Evolution of oxygen isotopes is more complex and yield  $\delta^{18}\text{O}_{\text{CaCO}_3}$  values of about  $-20\text{‰}$  for calcite precipitated according to reaction 1 (Dietzel et al., 1992). Upon setting of the cement, the diffusion of gaseous  $\text{CO}_2$  and subsequent reaction to  $\text{CaCO}_3$  leads to a continuous enrichment of  $^{13}\text{C}$  and  $^{18}\text{O}$  (versus  $^{12}\text{C}$  and  $^{16}\text{O}$ , respectively) of  $\text{CO}_2$  within the gas phase along the cement setting path. Accordingly, precipitated calcite is isotopically “lighter” at the exterior mortar layer.

The results show that analyses of carbon and oxygen isotopic compositions permit to follow the historic cementation process and to detect potential variations of the composition of the atmospheric  $\text{CO}_2$  and liquid ( $\text{H}_2\text{O}$ ). Variations may be caused by natural or anthropogenic impacts, e.g. evaporation of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  of anthropogenic origin, respectively. From another point of view, secondary processes like interaction with isotopically “light”  $\text{CO}_2$  from combustion 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.

## References

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