

Geochemical and isotopic composition of historical mortar and plaster in Styria, Austria

Barbara Kosendar¹, Martin Dietzel¹, Albrecht Leis², Bettina Wiegand³,
Bernhard Schrettle⁴, Karl Stingl⁵, Ralf Benischke²

¹Institute of Engineering Geology and Applied Mineralogy, Graz University of
Technology, Rechbauerstrasse 12, A-8010 Graz. e-mail: kosednar@egam.tu-graz.ac.at

²Institute of Water Resources Management, Hydrogeology and Geophysics, Joanneum
Research Graz, Elisabethstraße 16 / II, A-8010 Graz.

³Department of Geological and Environmental Sciences, Stanford University, CA 94305-
2115, USA

⁴Am Bach 2, A-8501 Graz

⁵Bahnhofstraße 16, A-8054 Graz

Historical buildings are constructed of geo-materials, mortar, and plaster of various compositions. Mortar and plaster are man-made materials. Thus, the chemical and isotopic composition comprises information about the historical environment with respect to the provenance of the materials, processing, and specific applications. 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 CaCO₃ (calcite) cement with aggregates of quartz and additional silicates like clay minerals. The analyzed Sr/Ca and ⁸⁷Sr/⁸⁶Sr ratios of the cement are between 0.00030 and 0.0023, and 0.7093 and 0.7104, respectively. These 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 -24.2 to -0.8, and of $\delta^{18}\text{O}_{\text{CaCO}_3}$ (PDB) from -23.9 to -2.6‰. 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 of the individual cement.

In principle isotope distributions depend on the composition of the gaseous CO_2 and aqueous 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 CO_2 (Dietzel, 2000), resulting in an enrichment of ^{12}C versus ^{13}C in the precipitated CaCO_3 . If gaseous 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‰ is obtained. Evolution of oxygen isotopes is more complex and yield $\delta^{18}\text{O}_{\text{CaCO}_3}$ values of about -20 ‰ for calcite precipitated according to reaction 1 (Dietzel et al., 1992). Upon setting of the cement, the diffusion of gaseous CO_2 and subsequent reaction to CaCO_3 leads to a continuous enrichment of ^{13}C and ^{18}O (versus ^{12}C and ^{16}O , respectively) of 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 CO_2 and liquid (H_2O). Variations may be caused by natural or anthropogenic impacts, e.g. evaporation of H_2O and burning of coal, respectively. From another point of view, secondary processes like interaction with isotopically “light” soil- CO_2 or re-crystallization of carbonate cements in the presence of H_2O from various origins may be deciphered.

References

- Dietzel, M., 2000. Measurements on stable carbon isotopes in calcite sinters on concrete, *Cement-Lime-Gypsum-International* 53 (9), 544-548.
- Dietzel M., Usdowski, E., Hoefs, J., 1992. Chemical and $^{13}\text{C}/^{12}\text{C}$ - and $^{18}\text{O}/^{16}\text{O}$ -isotope evolution of alkaline drainage waters and the precipitation of calcite. *Applied Geochem.* 7, 177-184.