



$^{13}\text{C}/^{12}\text{C}$ - and $^{18}\text{O}/^{16}\text{O}$ -Signatures of Historical Carbonate Mortar and Plaster – Field Study and Experiment

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Carbonate mortar and plaster of roman, mediaeval, and early modern buildings were sampled in Styria (Austria). The cement consists of calcite wherein aggregates like quartz, feldspar, mica, calcite, and dolomite are embedded. The cement to aggregate ratios typically lay in the range from 0.3 to 0.6.

The $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{18}\text{O}_{\text{CaCO}_3}$ values of the historical carbonate cements comprise a wide range from -28 to 0 ‰ and from -26 to 3 ‰ (PDB), respectively. Obviously, such signatures represent not the primary limestone used for burning. Isotope signatures are due to slaking and especially to setting of the cement. In principle, calcite cements are isotopically lighter at the exterior versus the interior mortar layer of a mortar fugue. For the ideal mortar fugue the ratio of stable oxygen to carbon isotope signatures is 0.605.

In order to evaluate the mechanisms for calcite formation from the uptake of gaseous CO_2 into such alkaline environments gaseous CO_2 is absorbed into sequentially linked vessels containing nearly saturated $\text{Ca}(\text{OH})_2$ solutions. Absorption and hydroxylation of CO_2 result in the formation of calcite. In general, the total amount of precipitated calcite decreases as the partial pressure of CO_2 is reduced by CO_2 consumption. The evolution of isotope signatures of the precipitated calcite can be followed by a $\delta^{18}\text{O}_{\text{CaCO}_3}/\delta^{13}\text{C}_{\text{CaCO}_3}$ ratio of 0.672, which correlates well to the relationship for the ideal mortar fugue of historical mortar.

The experimental results indicate that the $^{13}\text{C}/^{12}\text{C}$ - and $^{18}\text{O}/^{16}\text{O}$ -signatures of the calcite reflect the setting behaviour of carbonate mortar. Initially CO_2 from the atmosphere is fixed within the calcite, which is accompanied with kinetic carbon isotope fractionation of $\Delta^{13}\text{C}_{\text{CaCO}_3-\text{CO}_2} \approx -17 \text{ ‰}$ and an oxygen isotope fractionation of $\Delta^{18}\text{O}_{\text{CaCO}_3-\text{CO}_2} \approx -9 \text{ ‰}$. As calcite formation continued the remaining gaseous CO_2 is subsequently enriched in ^{13}C and ^{18}O . This caused isotopic heavier calcite along the cement setting path. However, progress of ^{13}C and ^{18}O enrichment is limited by the decrease of the CO_2 partial pressure in the remaining gas phase.

Consequently, deviations from such ideal behaviour of stable isotopes may reflect the following processes: 1. Evaporation of H_2O , where heavy isotopes preferentially remained in the liquid . 2. Interaction with isotopically light CO_2 from the soil atmosphere and the combustion of fossil fuel, respectively. 3. Relicts of the primary unburned limestone or occurrence of carbonate aggregates. 4. Re-crystallization and isotopic re-equilibration in particular at moderate pH. 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 ^{14}C dating a promising pre-selection of suitable samples can be done by exclusively using carbonate cement or especially lime pops with low $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{18}\text{O}_{\text{CaCO}_3}$ values close to -26 ± 2 and $-25 \pm 2 \text{ ‰}$, respectively. Such signatures confirmed that the CO_2 for CaCO_3 precipitation is gained directly from the Earth's atmosphere. Considering individual time spans for complete settlement of the historical carbonate binder a minimal processing date can be obtained.