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Multi proxy approach for the formation of calcium carbonates in alkaline man-made environments

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The formation of calcium carbonates, e.g. in drainage systems of tunnels, may be induced by degassing of CO_2-rich groundwater which enters the building. However, the dissolution of portlandite ($Ca(OH)_2$) from cements or the shotcrete of the tunnel wall bears an additional and immense potential for the formation of carbonates from alkaline solutions. Variations in trace element incorporation and distribution of the stable isotopes of carbon and oxygen in the precipitated calcium carbonates may represent powerful tools to identify individual mechanisms for carbonate formation.

As portlandite dissolves, highly alkaline solutions are obtained. In this case, precipitation of calcium carbonate can be related to the absorption of CO_2 from the atmosphere. Isotopic analyses of the calcite show that fixation of CO_2 from the Earth's atmosphere leads to significantly lighter $\delta^{13}C_{calcite}$ values (down to -25 $^{o}/_{oo}$, VPDB) as expected for the fixation of groundwater carbonate (typical $\delta^{13}C_{calcite}$ values between -10 and -16$^{o}/_{oo}$, VPDB).

The evolution of Sr/Ca ratios in the alkaline drainage solutions and in the corresponding calcium carbonate precipitation provides insight into the dissolution process at the concrete with respect to the amount of primarily dissolved portlandite from the cement. Moreover, an inverse relationship between Mg/Ca and Sr/Ca ratios is observed due to the liberation of aqueous strontium by the dissolution of portlandite and the formation of brucite ($Mg(OH)_2$) at alkaline conditions. Less incorporation of magnesium in the calcite structure is a strong indicator for carbonate precipitation from highly alkaline environments.

Applications of such multi proxy approaches are discussed with case studies. Main tasks are the reconstruction of the environmental conditions during primary $CaCO_3$ formation and monitoring of ongoing precipitation of calcium carbonates and cement-water interaction in alkaline man-made environments.