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. 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.

The main tasks of this study are the reconstruction of the environmental conditions during $CaCO_3$ formation and monitoring of ongoing precipitation of calcium carbonates and cement-water interaction in alkaline man-made environments. 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 $^{13}C_{calcite}$ values (down to -25 ‰, VPDB) as would be expected for the fixation of groundwater carbonate (typical $^{13}C_{calcite}$ values between -10 and -16 ‰, VPDB).

The evolution of Sr/Ca ratios in the alkaline drainage solutions and in the corresponding calcium carbonate precipitate 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 ($Mg(OH)_2$) under alkaline conditions. Low magnesium incorporation into the calcite structure is a strong indicator for carbonate precipitation from highly alkaline environments.

Several case studies demonstrate the potential applications of such multi proxy approaches for the understanding of the carbonate dynamics.

Influence of vegetation on chemical fluxes in a tropical watershed: Mule Hole, South India

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The experimental watershed of Mule Hole (4.3 km^2) is located in the sub-humid zone of a steep climatic gradient induced by the Western Ghâts in South India. It is covered by a dry deciduous forest whose evapo-transpiration accounts for almost 90% of the 1100mm annual rainfall [1]. The forest induces low groundwater recharge and maintains the groundwater disconnected from the stream: for this reason, Mule Hole constitutes an ideal site for estimating the influence of vegetation (throughfalls, forest fire ashes) on the chemical fluxes exported by a stream.

The chemical composition of rainfall, throughfalls, stream water and soil solutions are monitored since 2004. The composition of ash dissolution was characterized with batch experiments on ashes of the main tree leaves and grass species [2]. The contribution of vegetation components were calculated using End-Member Mixing Analysis (EMMA).

The signature of the ash end-member varies during the experiment according to (1) the vegetal species, i.e. high Ca, Mg, carbonate, K in leaves and high Si, K, Cl, OH in grass, (2) the dissolution kinetics of minerals present in ashes, in decreasing order salts (KCl, KOH), carbonates and amorphous silica. This latter factor influences the nutrient cycles: for instance, K mobility is enhanced by the instantaneous dissolution of salts whereas the slow dissolution of silica may allow efficient recycling within the soil profile.

The application of EMMA on the stream composition indicates that when forest fire occurs (in 2004) the chemical composition of the first storms of the humid season is >90% controlled by the vegetation component (mostly ashes) for K, Ca, Mg, Si, alkalinity and Cl. The relative contribution of the vegetation component decreases through the season as a result of (1) increase of soil solution contribution and (2) drop of ash contribution. The vegetation component still dominates during the first storms of 2005.

[1] Marechal *et al*. (2009) *J. Hydrol*. **364**, 272-284.
[2] Akerman *et al*. (2008) *Geochim. Cosmochim. Acta* **72**, A1-A40.