

Modeling $\delta^{18}\text{O}$ in drip waters and recent speleothems: Implications for paleoclimate records in N Spain

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U-series dated, stable isotope series in speleothems are commonly studied in order to generate high resolution archives of climatic change. Despite the spectacular advances in identifying and dating major shifts in the climate system (e.g. glacial/interglacial transitions or D–O oscillations), the more subtle changes (as those that have occurred in the last millennia) cannot in many cases be interpreted unequivocally. This is due to the difficulty in separating the role of diverse atmospheric, soil, and karstic factors in the isotopic signal, a problem which is inherent to most mid-latitude caves.

With the aim of improving the interpretation of speleothem isotope records in three caves of N Spain (Cueva Mayor-Atapuerca, Kaite-Ojo Güareña, and Cueva del Cobre) a systematic multi-year study of oxygen isotopes in precipitation waters, cave waters of individual drip systems, and present-day speleothem precipitates is being carried out, with emphasis in the seasonal and interannual variations and their correlation with meteorological parameters. The study, completed with the calibration of recent speleothem records with the available meteorological series, suggests the interannual winter surface temperatures as the main factor in controlling changes of $\delta^{18}\text{O}$ in our recent speleothems. Other factors, such as precipitation amount and summer temperature seem to have a secondary role, although could notably contribute to changes in other proxies, as speleothem growth rate, elementary geochemistry, and $\delta^{13}\text{C}$.

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Structure and chemistry of Fe and Al aquatic colloids and their influence on P cycling in a tropical reservoir

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The biogeochemical cycling of nutrients and contaminants such as PO_4^{3-} and AsO_4^{3-} in lakes is largely controlled by the concentration and chemistry of Fe/Al colloids. However, the structure and chemistry of these phases is poorly understood. In addition, tropical lakes commonly experience long periods (>8 months) of hypolimnion anoxia, and thus the redox stability of colloids plays an important role in the nutrient and contaminant cycling in such systems.

Using a combination of conventional chemical analysis and synchrotron-based (both bulk and micro) XAS, XRD, and STXM techniques we characterized the size, composition, and mineralogy of inorganic and organic colloids collected from a eutrophic lake in Puerto Rico. We also focused on how these colloids modify the concentration and cycling of P.

Settling particulates were sampled at different depths and at different times throughout a year. Temperature at the epilimnion varied from 25.09°C to 30.6°C, while at the hypolimnion it ranged from 23.7°C to 25.9°C. Ranges of total P, Fe, and Mn in the hypolimnion were 0.01 – 0.22 mg/L, 0.06 – 2.39 mg/L, and nd – 2.07 mg/L, respectively, with the highest values coinciding with the most reducing environment (i.e., -180 mV).

The dominant mineral in the colloidal fraction at all depths is kaolinite, with a significant fraction of amorphous Al and Fe in particles in the size range of 80-200 nm. The spatial heterogeneity of Al was found to be highly dependent on the association of Al with Fe in the colloids. In addition, both Fe K-, and L-edge XANES spectroscopy indicate a systematic increase in the Fe^{2+} concentration with increasing depth and anoxia in the reservoir. The concentration of organic carbon in the colloidal fraction also decreased with depth. Phosphorus was found to be mainly bound to organic and Fe-oxide surfaces. A discussion of redox changes in the reservoir associated with summer anoxia, and its impact on colloid chemistry and P cycling will be discussed.