

Hydrological variations inferred from colloiddally-transported and pH-dependent trace elements in stalagmites

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Speleothem records allow for time-resolved atmospheric paleoclimate reconstructions through stable isotope analysis (C, O) and U-Th dating, but also partition a variety of trace elements. These trace elements are predominantly sourced from host carbonate rocks, and their concentrations and transport processes reflect local hydrological and chemical variations. Here, we proxy the degree of dissolution of bedrock-hosted pyrite by measuring trace element concentrations in stalagmites from Porrúa, Asturias, Spain. In particular, we examine S, P and As content using a tandem inductively-coupled plasma mass spectrometer (ICP-QQQ). The collision reaction cell in the ICP-QQQ allows for removal of isobaric interferences on these masses from C, N, O and Ar interferences, dramatically decreasing the limits of detection. In addition, we examine transition metals and chalcophile elements through a combination of ICP-QQQ and laser ablation (LA)-ICP-QQQ to obtain the highest possible spatial resolution.

Transition metals and chalcophile element are enriched in pyrite, also have variable rates of transport depending on their affinities for organic ligands and colloids in overlying soils. Rare earth elements (including Y) typically have low concentrations in pyrite, but show strong preference for colloidal binding, allowing us to examine pyrite dissolution-independent variations in colloidal transport. Finally, because colloidal transport is influenced by soil pH, we qualitatively proxy the soil acidity through seasonal variations of the hydrogen phosphite ion (HPO_4^{2-}) in the stalagmite.