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Trace element variations and layer thickness analysis of recent laminated stalagmites from Asturias, Northern Spain

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As speleothems become more popular as paleoclimatic archives, trace element variations are being explored as a complement to stable isotope variations. In this study, we examine trace element variations in actively growing stalagmites from three caves in Asturias, Northern Spain, where cave formation is common throughout the nondolomitic limestones of the Carboniferous Barcaliente Formation. Our caves follow a traverse from seaside to highlands and constitute a variety of land uses from undisturbed native forest to pasture and developed areas. In each cave we sampled small (10-20 cm) actively growing stalagmites. Stalagmites were slabbed and drilled along their main growth axis every 0.5 mm –to 1 mm. XRD confirms calcitic mineralogy. Powder was dissolved and analyzed for a suite of elements, including metals and sulfur, using simultaneous ICP-AES. Samples from the karst host rock were also analyzed at each site to test for homogeneity throughout the formation.

The drilled stalagmites were then imaged using a high-resolution scanner. Two caves yielded annually laminated stalagmites with annual couplets varying between 0.1 mm and 2 mm thick. The longest record we sampled contains 350 such couplets, although there are many caves in the Barcaliente Formation with larger, more slowly growing stalagmites suitable for longer paleoclimatic reconstructions. An age model was derived from layer counting and further age control is provided by U/Th dating and by

correlation of a clay layer with a major floor in one of the stalagmites.

Ba/Ca and S/Ca ratios covary in many stalagmites and show multidecadal variation which may be linked with vegetation influence on element mobility. In the highest resolution, fasted growing, laminated stalagmites peak Ba and S ratios in the last 5-7 years are twofold higher than levels from 1970-2000. In the longest laminated record we observe a comparable twofold increase in the molar S/Ca and Ba/Ca ratio during a 15-year period in the 1820s-1840s. This 19^{th} century peak also corresponds to 50% increase in Sr/Ca ratios. Where multiple laminated stalagmites were recovered from the same cave, permitting tight age correlation, similar time series trends are identified for most element/Ca ratios. Laminae thickness also shows evidence of multidecadal variation. Modern lamina thickness is greatest in the cave dripwaters with the highest Ca concentration. We will correlate these elemental records with a new calibrated instrumental precipitation record covering the past 50 years and with records of land use changes at the developed and agricultural sites over the past several centuries.