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Climatic and hydrological control on trace element variations in a speleothem from the Chauvet Cave, France

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An ICPMS quantitative analysis of Ca, Mg, Ba, Sr, U, Mn, Y and 14 Rare Earth Elements (REE) has been performed on a speleothem from the Chauvet cave (south-east of France). The Chau-stm-6 stalagmite that grew from 33 ky to 11.5 ky before present had been previously dated by U-Th series method and the published d13C and d18O profile is used as a paleoclimatic benchmark.
Chau-stm-6 recorded that major element Ca ratios (Mg, Ba, Sr), U and REY (REE + Y) responded to early deglaciation (15 ky). Their concentrations show relative variations of 40% to 75%. Ba and Sr profiles are significantly correlated (r = 0.85) and show a two-step increase during early deglaciation. Mg and U are weakly correlated and display a decreasing trend from 15 ky to 11.5 ky. REY concentrations decrease during early deglaciation (15 ky to 14.5 ky). The clear onset of Younger Dryas as recorded by both d13C and d18O profiles is not well marked by any of these trace elements though the averaged Sr concentration is slightly lower in the more recent part of the profile. Sr and Ba increase is best explained by the tenfold rise of the growth rate rather than changes in water residence time in the karst which would also increase Mg. The incongruent dissolution of dolomite upstream is invalidated by the absence of reported dolomite in the Chauvet karst system.
No correlation was found between REY and Mn (an element strongly bound with colloidal and particular phases in water), suggesting that REY were mainly dissolved (and likely to be complexed) in groundwater. Due to the poorly developed soil above the cave, REY are thought to come mainly from the dissolution of the limestone bedrock. Bedrock samples display a rather flat pattern, only slightly depleted in LREE (light REE) and with a weak cerium (Ce) anomaly (0.6 to 1). In comparison Chau-stm-6 patterns show a marked depletion in LREE and a more pronounced Ce anomaly (0.3 to 0.75). This shale-normalized pattern is construed as coming from REY fractionation during mobilization or transport of the elements in seepage water rather than from the mixing of several REY sources. Preferential removal of LREE may come from their stronger affinity with particles and from a weaker carbonate complexation.
The different climatic and environmental conditions don't seem to have affected REY fractionation – LREE/HREE (light REE on heavy REE) remained quite constant, although the ratio peaks or fall sharply at the climatic transitions. This could be the result of brief periods of intense leaching of colloids or particles.
A weak anticorrelation was found between the Y/REE ratio and Ce anomaly. Moreover glacial conditions correspond to a high Y/REE-low Ce pattern whereas milder climate correspond to the opposite situation. The probable higher concentration of particles during the warmer period could explain both the better transport of REE relative to Y that has a slower particle-reactivity and larger scavenging of all REE that smoothes Ce anomaly. pH and Eh could also control the selective removal of Ce. Again no significant difference between Bolling-Allerod and Younger Dryas samples could be observed on REY patterns.
This study is one of the first steps towards the use of REY as paleohydrologic and paleoclimatic proxies in continental environments.