

Application of LA-MC-ICP-MS for analysis of Sr isotope ratios in speleothems

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Speleothems are well established climate archives. In order to reconstruct past climate variability, several geochemical proxies, such as $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ as well as trace elements are available. Since several factors influence each individual proxy, robust interpretation is often hampered. This calls for multi-proxy approaches involving additional isotope systems that can help to delineate the role of different sources of water within the epikarst and changes in soil composition. Sr isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) have been shown to provide useful information about water residence time and water mixing in the host rock. Furthermore, Sr isotopes are not fractionated during calcite precipitation, implying that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the speleothem provides a direct record of the drip water. While most speleothem studies applying Sr isotopes used the TIMS methodology, LA-MC-ICP-MS has been utilized for several other archives, such as otoliths and teeth. This method provides the advantage of faster data acquisition, higher spatial resolution, larger sample throughput and the absence of chemical treatment prior to analysis. Here we present the first LA-MC-ICP-MS Sr isotope data for speleothems. The analytical uncertainty of our LA-MC-ICP-MS Sr data is in a similar range as for other carbonate materials. The results of different ablation techniques (i.e. line scan and spots) are reproducible within error, implying that the application of this technique on speleothems is possible. In addition, several comparative measurements of different carbonate reference materials (i.e. MACS-3, JcT-1, JcP-1), such as tests with standard bracketing and comparison of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with nanosecond laser ablation system and a state-of-the-art femtosecond laser ablation system, show the robustness of the method. We applied the method to samples from Morocco (Grotte de Piste) and India (Mawmluh Cave). Our results show only very small changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of both speleothems. However, one speleothem from Mawmluh Cave shows a slight increase of $^{87}\text{Sr}/^{86}\text{Sr}$ within the error, which is reproducible with line scans and spots.