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Cavity ring-down spectroscopy for the isotope ratio measurements of water from fluid inclusions in stalagmites

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Oxygen isotope record in stalagmites is useful to reconstruct past environmental changes. However, the interpretation of calcite isotope record is not straightforward because it is affected by various factors affect such as amount of precipitation and temperature. Water isotope composition of fluid inclusions, and oxygen isotope difference between water and host calcite, from stalagmite are potentially important proxies to estimate the paleo-temperature. Recently, infrared spectroscopy (IRIS) has been widely used for stable isotope ratio measurement of water. Unlike traditional isotope mass spectrometer (IRMS), the IRIS does not require pre-treatment processes (e.g., high-temperature furnace or equilibration device). A limitation of IRIS is that commercially available IRIS systems need large sample volume (1 - 2 micro litres) for liquid water measurement. In this study, we developed a custom-designed device suitable for precise measurement of smaller volume (0.05 to 0.20 microlitres) of water, and tested two extraction methods (thermal extraction and mechanical crushing). Oxygen and hydrogen isotope ratios of water were measured using cavity ring down spectroscopy (WS-CRDS Picarro L2130-i). Stalagmites samples were collected in several caves in Okinawa, Japan. Pieces of stalagmites (80-300mg) subsampled from homogeneous layers, and reproducibilities of the inclusion measurement were 0.2 permil for δ^{18}O and 1 permil for δD. The measured δ^{18}O and δD of inclusion water from recently grown stalagmites agrees with modern dripwaters, indicating that our extraction technique is useful to measure isotope ratios of past inclusion water.

Keywords: Stable isotope, Fluid inclusion, Speleothem, Stalagmite, Paleoclimate, CRDS