

Isotopic re-equilibration of fluid inclusions in natural speleothem by artificial heating

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Isotopic compositions of inclusion water in speleothems are promising new climatic proxies. Oxygen isotope ratio of water ($\delta^{18}\text{O}$) may provide direct estimate for past temperature changes. Several studies, however, used hydrogen isotope ratio of water (δD) because the $\delta^{18}\text{O}$ may be affected by re-equilibration between water and host calcite. Thus, precise knowledge about magnitude and reaction rate of the re-equilibration has a fundamental importance for paleoclimate studies using speleothems.

To evaluate the re-equilibration effect, we measured isotope composition of fluid inclusions in natural stalagmites, which had been heated in laboratory before isotope measurement. Several (3-5) subsamples were cut from the same depth of stalagmites. Then, each sub-sample was heated at different interval (0 – 80 hours) under continuous evacuation using a turbomolecular pump. The experiments were conducted under three different temperatures (25, 70, and 105°C). The $\delta^{18}\text{O}$ and δD values of fluid inclusions in a sub-sample was measured using a semi-automated system, which was modified based on cavity ring-down spectroscopy technique (Uemura et al., 2016).

Under the 105°C heating, the inclusion $\delta^{18}\text{O}$ value of a layer shows a small increase from the initial to ca.30 hours heating, and then after that it appears to stay flat. This preliminary result suggests that a limited amount of calcite reacts with inclusion water, and ca. 5% of fluid inclusion water may be re-equilibrated with surrounding host calcite at the 105°C. The magnitude of re-equilibration effect is not significant for estimating glacial-interglacial temperature changes but measurable. On the other hand, the $\delta^{18}\text{O}$ value shows no trend under the room temperature experiment. The δD value shows no trend at any experimental conditions, suggesting that loss of inclusion water during long-time evacuation does not cause the $\delta^{18}\text{O}$ enrichment.

Uemura, R. et al. (2016) Precise oxygen and hydrogen isotopic determination of speleothem inclusion water in nanoliter quantities using cavity ring-down spectroscopic techniques, *Geochimica et Cosmochimica Acta*, 172, 159-176, doi:10.1016/j.gca.2015.09.017