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Noble gas concentrations in stalagmite fluid inclusions as a potential proxy for past cave temperatures

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Dissolved atmospheric noble gas concentrations in water can be used to determine the environmental conditions that prevailed at the time of the last gas exchange with the atmosphere, because the solubilites of noble gases are a well-defined function of the temperature and the salinity of the water. Accordingly, noble gas concentrations in fluid inclusions in stalagmites are a potential proxy for the cave temperature. In stalagmite research, independent and direct cave temperature proxies are still rare, but very important for the interpretation of the stable isotopic composition of the calcite. As the cave temperature is a good measure of the annual mean temperature outside the cave, noble gas concentrations in stalagmite fluid inclusions may also allow to directly reconstruct paleotemperatures.

We developed a method to precisely determine noble gas concentrations (analytical error of 2-4%) in small amounts of water (1mg) extracted from stalagmite samples. It includes an extraction technique to separate water inclusions from air inclusions, which are also abundant in stalagmites and mask the temperature dependent noble gas signature of the water inclusions. To achieve such a separation, the samples are pre-crushed to a defined grain size to remove inter-crystalline air inclusions, before water and noble gases are extracted by heating. The pre-crushing occurs in a glove box filled with pure He to avoid any contamination by adsorption of atmospheric gases on the freshly produced surfaces of the calcite. The liberated water mass is determined by measuring its pressure in a known volume kept at a constant temperature of 40°C to prevent water condensation.

The determined noble gas concentrations in modern stalagmite samples show that air and water inclusions are sufficiently separated with our extraction technique, resulting in low “excess air” amounts. The measured Kr and Xe concentrations are clearly different in samples from stalagmites that were deposited at a cave temperature of 27°C and of 13°C respectively. Both results are important steps towards the determination of noble gas temperatures (NGTs) in fluid inclusions in stalagmites. However, we also found an excess in Ar, which most likely adsorbed on the samples during pre-crushing in the glove box. Therefore, we plan to further purify the air in the glove box by connecting a liquid N2 cold trap to the glove box. The noble gas concentrations of all heavy noble gases are then expected to be composed air and air saturated water only, allowing to determine NGTs using standard least squares fitting methods.