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Trace gas content in air inclusions in speleothems as new paleoenvironmental archive?

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In a companion abstract (Scheidegger et al. 2007) we report a pilot study to extract paleoclimate information from noble gases dissolved in water-bearing inclusions in speleothems. Here, we report the first attempt to use also the air trapped in the water-free inclusions from the same speleothemes for paleoenvironment reconstructions.

Based on microscopy inspection we concentrated on a stalagmite from Socotra (Yemen). We clearly could optically distinguish air from water inclusions. The assessed amount of air inclusions is about 3% by volume. Samples of 1-2cm^3 of a recent (< 50y) and an old ($\sim$2000y) section of the stalagmite were crushed under vacuum in a copper tube. The released gases (being predominantely from air inclusions) were analysed by dynamic mass spectrometry. Fractional abundances of the major gas components – N_2, O_2 and Ar – were found to be atmospheric within the experimental precision of a few percent. However, CO_2 was clearly in excess by 2-10 times relative to atmospheric composition. Similarly, methane concentrations (200-600ppm) exceeded atmospheric values by 2 to 3 orders of magnitude. In addition, part of the samples were even enriched in N_2O.

Hence all major atmospheric greenhouse gases – CO_2, CH_4 and N_2O – could be determined and quantified in air inclusions of speleothems. Further, we analysed

the isotopic composition of the CO_2 of the trapped air by a GC-MS technique commonly used for trace gas analysis in ice cores. In a recent sample a δ^{13}C value of –39.4 $\permil$ V-PDB and a δ^{18}O value of –7.5 $\permil$ V-PDB were observed, whereas an

old sample showed a δ^{13}C value of –28 ‰ V-PDB and δ^{18}O of –6 ‰ V-PDB. The observed light isotopic compositions point either towards a biogenic carbon dioxide source or an oxidation of methane with low δ^{13}C to CO_2. The CO_2 results suggest that air inclusions in stalagmite crystals can be used to assess the characteristics of the overlying soil (e.g. productivity, humidity etc.) and its evolution in time.

In summary, this pilot study is a first convincing step to assess the suitability of air inclusions in speleothems as another high quality archive to reconstruct past local environmental conditions.

Ref: Scheidegger et al. (EGU Vienna 2007, this conference) Microscopical speleothem calcite investigations proofing the existence of two different types of fluid inclusions.