

Growth conditions of stalagmites derived from noble gas concentrations in fluid inclusions

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Stalagmites are increasingly used as climate archives to reconstruct past climate conditions over long time intervals and in wide ranges of continental regions. We analysed noble gases in 43 holocene samples from 2 tropical stalagmites (D1, P3) from Socotra Island, Yemen. Kr and Xe concentrations in many of the samples are explained as binary mixtures of noble gases from air-saturated fluid inclusion water and atmospheric noble gases released from air inclusions ('excess air'). After 2-component deconvolution, equilibrium concentrations of noble gases in the fluid inclusion water are calculated, from which in turn noble gas temperatures (NGTs) are deduced [1]. NGTs are assumed to reflect the ambient cave temperature at the time of the last gas exchange.

Many NGTs in D1 and P3 agree with the modern cave temperature (28°C). However, we observe relatively large NGT variations over short timescales, which cannot reflect actual cave temperature variations. We attribute these variations to changing conditions during air-water partitioning between inclusion water and the local cave atmosphere. An occasional enrichment in CO₂ around the stalagmite would lower the partial pressures of Kr and Xe and thus reduce their equilibrium concentrations in the inclusion water leading to spuriously high NGTs.

Our analyses also provide a record of the water content and allow to determine the amount of excess air in the samples. D1 shows a statistically significant regime shift at ~1.5 ka BP (see [2] for age model) both in the water content and in the amount of excess air. The regime shift coincides with the most negative excursion in the δ¹⁸O record of the calcite [2]. Thus, growth conditions of stalagmite D1 changed dramatically at this time, possibly in response to a reduced drip rate, which led to a major change in the amount of air and water inclusions incorporated in the stalagmite.

[1] Kipfer *et al.* (2002) *Rev. Mineral. Geochem.* **47**, 615–700.

[2] Fleitmann *et al.* (2007) *Quart. Sci. Rev.* **26**, 170–188.

Chromium isotopes in Saanich Inlet sediments and waters

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Saanich Inlet is a classic locality for study of anoxic sedimentation and sulfidic water column processes. Organic-rich sediments from the inlet are enriched in Cr relative to the detrital background. Water column sulfide develops in the summer months as a result of stratification and high primary productivity and restricted deep water renewal. Thus, Saanich Inlet provides an excellent opportunity to uncover the modern behaviour of Cr isotopes, which show promise as a tool for paleoenvironmental analysis with respect to redox cycling. Cr isotopes are fractionated through reduction of soluble Cr(VI) to relatively insoluble Cr(III), enriching the Cr(III) in the lighter Cr isotopes. This study will be the first to assess the fractionation between Cr in contemporaneous waters and sediments in an anoxic setting.

Preliminary results for total Cr in the water of Saanich Inlet (100 m depth) show a δ⁵³Cr of +0.30‰ (normalized to SRM 979), with a total Cr concentration of 0.11 μg/L. This is a lower concentration than open ocean seawater (North Atlantic Seawater; 0.26 μg/L), suggesting that there may be removal of Cr from the water column. At the time of collection (August 2010), the water column was sulfidic below ~80 m depth. Open ocean Cr [1] has a δ⁵³Cr of +0.45 to +0.71‰, which suggests that Cr in the sulfidic water column of Saanich Inlet is being reduced and removed to the sediments. The Cr leached from the organic component of Saanich sediments was -0.17‰, while bulk marine sediments average -0.03‰ [2]. This system does not conform to the results of groundwater and laboratory experiments performed by others, which yielded large fractionation factors of ~+3.5‰ and predicted sedimentary δ⁵³Cr values of ~-3‰. One possibility is that reduction goes to completion on only a small fraction of the available Cr, perhaps facilitated by water column particulates or processes operating at the sediment-water interface.

[1] Bonnand, Parkinson, James, Fehr, & Connelly (2010) PP11A-1428, Fall AGU. [2] Schoenberg, Zink, Staubwasser, & von Blanckenburg (2008) *Chem. Geol.* **249**, 294–306.