Annual trace element records in speleothems from Grotta di Ernesto, NE Italy

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Speleothems in caves are considered to have potential as high resolution terrestrial palaeoclimatic records because stalagmites are able to provide palaeoclimatic proxy time series (such as oxygen isotopes, C isotopes and trace elements). This potential has been further augmented by existence of visible and/or UV banding caused by presence of impurities in stalagmites, which may provide annual chronological control (Baker *et al.*, 1993). In addition, trace element variations in speleothems are measurable using micro analytical techniques (Roberts *et al.*, 1998), such as secondary ion mass spectrometry (SIMS), and are likely to provide detailed records of cave water chemistry from which they precipitated.

A stalagmite (~380 mm high) collected from Grotta di Ernesto, NE Italy has clear bands in some parts and has been dated using U-series technique. Comparison of dates interval with continues bands defined by impurities indicate that these bands are likely to be annual. In addition, weak ultraviolet luminescent bands also exist in this stalagmite and they, in general, overlap with visible bands.

In contrast, natural soda straw stalactites often display periodic visible bands, typically 0.05–0.5 mm wide, comparable with likely linear annual extension rates of the structures. Such bands are found to represent thickenings of the walls of the structures at growth steps. However, soda straw stalactites from Grotta di Ernesto, NE Italy display both growth step and thin inclusion rich bands (3–5 μm), the latter being similar to those in stalagmites. On the thin section, inclusion rich layers appear to preserve tip shapes and positions during its extension. In general, the growth steps and impurity layers correspond well although the growth steps are subject to later overgrowth.

Trace elements, Mg, Sr, P, Si and Fe, together with Ca have been measured in 10 μm steps for 1 mm at 5 mm from the top on the stalagmite, and ~ 4.65 mm at the tip on the stalactite, using a SIMS at Edinburgh. Although there are a few spikes of Si indicating silicate inclusions, which may affect some trace element contents, such as Mg, most part of the samples are unaffected. The stalagmite and stalactite have similar trace element contents a few hundred ppm Mg, 40–120 ppm P, and about ~30 ppm Sr, respectively.

Mg/Ca, Sr/Ca and P/Ca ratios profiles from the soda straw stalactite are shown in Fig. 1 and all the ratios exhibit oscillations (those affected by silicate inclusions have been omitted). Both stalagmite and stalactite show a broad negative correlation between P/Ca and Sr/Ca ratios, i.e. peaks of P/Ca and Mg/Ca generally match troughs of Sr/Ca profile. In addition, it appears that P peaks encompass the impurity layers in the stalagmite and stalactite. However, Mg/Ca ratio appears to correlate with P/Ca in the stalactite data, although there is no consistent co-variation observed in the stalagmite data.

Fairchild *et al.* (1998) demonstrated that trace element ratios are variable in cave waters and they may correspond to reaction time between water and bedrocks. They argued that reaction time tends to be shorter in wet seasons than in dry seasons, and therefore, corresponding hydrology balance. Speleothems are likely to record chemical variation in cave water from which they were precipitated, however, other parameters can affect trace element partitioning during calcite precipitation and alter signals. Although partition coefficient of Mg into calcite has been demonstrated to be temperature dependent (Burton and Walter, 1991), the Ernesto cave has a constant present temperature. In contrast, Sr partitioning into calcite may be controlled by precipitation rates (Tesoriero and Pankow, 1996), and P is very strong inhibitor for growth of calcite (Meyer, 1984). This appears to be consistent with the broad negative correlation between P/Ca and Sr/Ca profiles. Although form of P existing in the speleothems is not clear, on the basis of available experiment data on orthsphophate (Meyer, 1984), calculations show that measured variation of P in the Ernesto speleothems can change precipitation rate significantly. This variation of precipitation rates is able to cause ~40% change of Sr partition coefficient

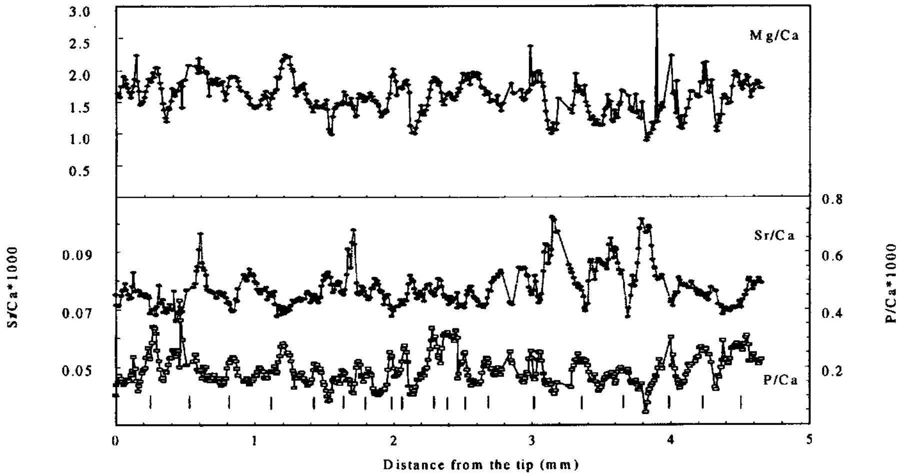

FIG. 1. Showing trace element variations and spatial relationship between the variation and the inclusion rich layers in the soda straw stalactite. Small bars indicate inclusion rich layers in the thin section.

at a certain precipitation rate (Tesoriero and Pankow, 1996), which is comparable to the size of Sr variation observed in the Ernesto speleothems. This demonstrates that better knowledge of precipitation control on trace element partitioning is required to link trace element variations recorded in speleothems to cave water chemistry, and then to high resolution palaeoclimatic proxy.

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