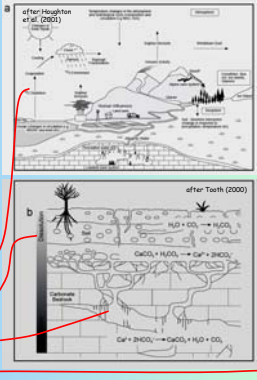




Introduction

Climatic and other environmental signals become encoded in speleothems by a number of distinct processes. These need to be thoroughly understood to make best use of the high-resolution information that is encoded in speleothems. The structure of this poster is in terms of five domains in which signals are generated and modified:

- Atmosphere
- Soil and upper Epikarst
- Lower karst and cave environment
- Crystal growth
- Diagenetic change



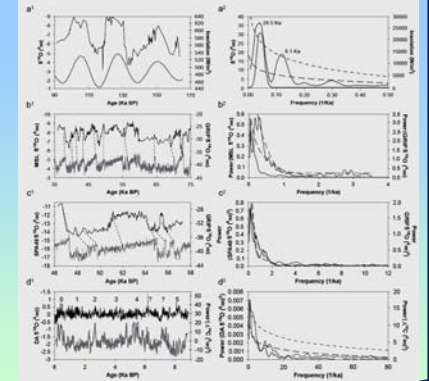
Diagrams from Fairchild et al., Earth-Sci. Rev., 2005

A. Atmospheric signals I

Many of the spectacular climate proxy records recently published from speleothems represent situations where the speleothem sensitively records changes in the climate system with only subordinate overprinting by terrestrial processes. For example, monsoonal and other climates where rainfall isotopic composition is sensitive to the amount and/or source of atmospheric precipitation yield oxygen isotope records reflecting reorganizations of the climate system.

The diagrams (Fairchild et al., Earth-Sci. Rev., 2005) compare published speleothem records (black) with forcing or other atmospheric proxies (grey). We have not processed the speleothem data, other than removing the long-term trend in d. Dongge cave D3, S China (Yuan et al., Science, 2004) illustrating similarity to precession signal (grey); power spectrum shows precession peak at 21 ka and harmonic at 8.5 ka related to non-linear response of isotopes to H₂O cave MSL, E China (Wang et al., Science, 2003) and e. Spangberg cave SP449 Austria (Spötl and Mangini, EPSL, 2002) compared in each case with Greenland GRIP isotopes and providing improved dates for Dansgaard-Oeschger oscillations of glacial climate.

d. Dongge cave BA (Wang et al., Science, 2005) with numbered excursions compared to North Atlantic ice-rafting events of Bond et al. (Science, 2001) and atmospheric $\Delta^{14}C$ record (Reimer et al., Radiocarbon, 2004). High-frequency variation is not significant, except after further processing, but cross-spectral analysis (diagram e) shows significant peaks: these at 59 and 216 years are also found by Wang et al. (2005) on highly-filtered data, and are similar to periods of variation of solar output.



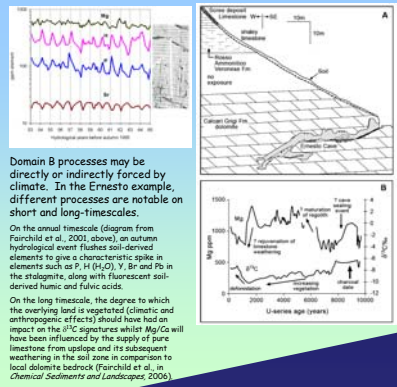
A major challenge for the future is to be able to interpret high-resolution changes reliably, which requires a consideration of the seasonal variations in sources and abundance of atmospheric moisture.

B. Soil and upper epikarst

Solutes acquired from vegetation, soil and bedrock can be preserved as $\delta^{13}C$ or trace element signatures in speleothems that display characteristic variation with time in response to climatic and other environmental changes

Some well-known examples:

- the inferred changing dominance of plants using C3 and C4 photosynthetic pathways leading to lighter and heavier ^{13}C signatures under more and less humid climates respectively in prairie-marginal environments (e.g. central USA, Dorale et al., Science, 1998)
- Inferred changes in CO₂ production in soils under varying T and humidity conditions in France (Genty et al., Nature, 2003); correlation of $\delta^{13}C$ with humid events (Bar-Matthews et al., GCA, 2003)
- Climatically-induced changes in aeolian supply of Sr deduced from $^{87}Sr/^{86}Sr$ signatures (Goede et al., EPSL, 1998)



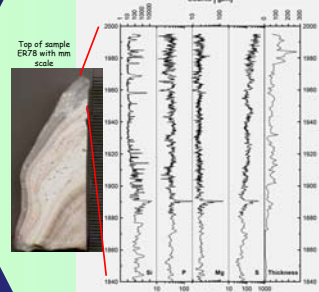
Domain B processes may be directly or indirectly forced by climate. In the Ernesto cave example, different processes are notable on short and long-timescales.

On the annual timescale (diagram from Fairchild et al., 2000, above), an autumn hydrological event flushes soil-derived elements to give a characteristic spike in elements such as P, H (H₂O), V, Br and Pb in the stalagmite, along with fluorescent soil-derived humic and fulvic acids.

On the long timescale, the degree to which the overlying land is vegetated (climatic and anthropogenic effects) should have had an impact on the $\delta^{13}C$ signatures whilst Mg/Ca will have been influenced by the supply of pure limestone from upflow and its subsequent weathering in the soil zone in comparison to local dolomite bedrock (Fairchild et al., in Chemical Sediments and Landscapes, 2006)

A. Atmospheric signals II

The twentieth century provided two strong atmospheric signals: temperature and S content, both of which are recorded as the first order changes in growth rate and S content respectively in speleothems from the Ernesto cave in NE Italy (Frisia et al., EPSL, 2003, 2005).



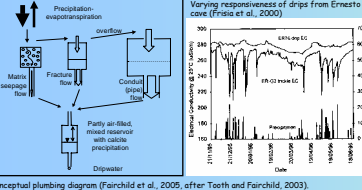
This soda straw stalactite shows the growth downward and shows annual bands that dramatically increased in thickness to around 0.2 mm as growth rate increased in the mid-20th century at the end of the Little Ice Age.

The S increase is a robust, first-order effect shown in duplicated traverses

Currently sulphate at the site is decreasing as a consequence of reduced atmospheric S emissions. This recovery was delayed, perhaps largely because of domain B processes - ecosystem storage at this wooded site on the side of the Val Sugana valley. Another modification of the signal is a strong seasonal fluctuation due to domain C processes - seasonal changes in the cave air CO₂ and system pH

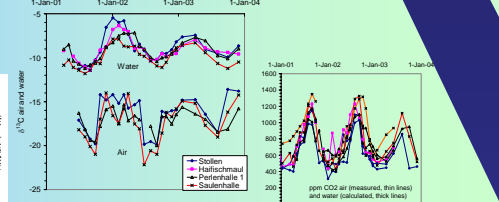
C. Karst aquifer and cave I

The drip hydrology and cave ventilation are now recognized as two crucial controls on speleothem growth and chemistry

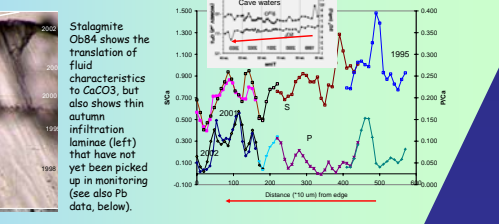


Each drip has a unique plumbing which results in large variations in their responsiveness to rainfall events, the degree to which the $\delta^{18}O$ of the water is well-mixed, and the susceptibility to degassing and carbonate precipitation along the flowline.

DMs data (below) from a Gibraltar stalagmite display large shifts in both isotopes when analyzed at sufficiently high resolution. The variation in $\delta^{18}O$ records seasonal variations in rainfall composition whereas $\delta^{13}C$ probably changes in cave humidity or CO₂ composition seasonally.



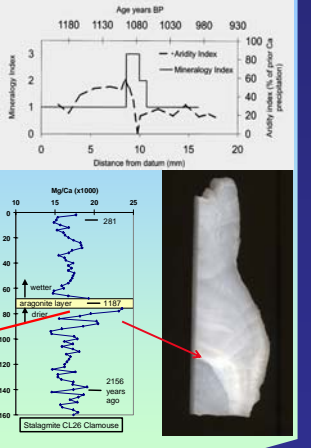
The Obir Cave in SE Austria (Spötl et al., 2005) demonstrates the effects of strong cave chimney-type ventilation. Forced winter air circulation leads to fall in cave air CO₂ and big increases in $\delta^{13}C$ and carbonate saturation. Similar, but less marked effects may characterize most caves. E.g. the Ernesto cave shows a strong seasonal variation in CO₂, but our recent measurements and modelling show that cave breathing (exchange with the external atmosphere) renews the cave air every 70-100 hours, implying that CO₂-rich soil/epikarst gas only reaches the cave in summer.



Ion probe analyses of Ob4 show strong seasonal changes in $\delta^{13}C$ (not illustrated) and S related to changes in cave air PCO₂ and a falling trend of S at the top of the stalagmite. P distribution reflects the different process of hydrological infiltration and P peaks coincide with visible laminae.

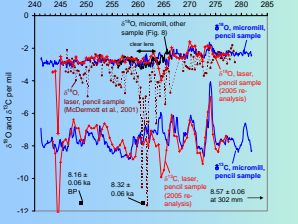
C. Karst aquifer and cave II

Caves that show strong variations in drip rate in relation to rainfall variations are susceptible to varying amounts of prior calcite precipitation that can be manifest in rising Mg/Ca and Sr/Ca in arid periods. McDonald et al. (GRL, 2002) showed a good example related to the 2002-3 El Niño event in SE Australia. Fairchild et al. (Chem. Geol., 2000) previously showed that dripwater the Clamouse cave in S France had characteristics to give rise these effects each summer. Ion microprobe analysis (McMillan et al., J. Quat. Sci., 2005) demonstrates strong Mg-Sr covariations over distances consistent with the annual timescale. An arid period 1100-1200 years BP is found in two stalagmites and culminates in an argonite layer. Similar aridity is found in the Sahel and central America at this time.



High-resolution isotope analyses

These data from Crag Cave (Ireland) stalagmite CC3 are from a segment originally thought to have a major 8.2 ka oxygen isotope anomaly (McDermott et al., 2001), now known to be caused by fractionation at a sample fracture. New analyses by three techniques give comparable results and show the lateral continuity of small fluctuations in isotopes. There is also evidence of possibly stochastic variation on the decimetric scale. (Fairchild et al., Earth-Sci. Rev., 2005)

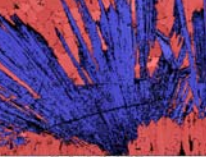


We need in the future reliably to distinguish atmospheric from cave and carbonate fractionation processes, and to be able to source and describe the atmospheric history of the rainfall through modelling. Suitable speleothems can give vital information on seasonal variations.

E. Secondary (diagenetic) change

Calcareous speleothems suffer little secondary change - fine chemical banding is well-preserved. Fluid inclusion oxygen should be more prone to alteration than other parameters. Primary argonite will ultimately change to calcite however, although the controls are unclear.

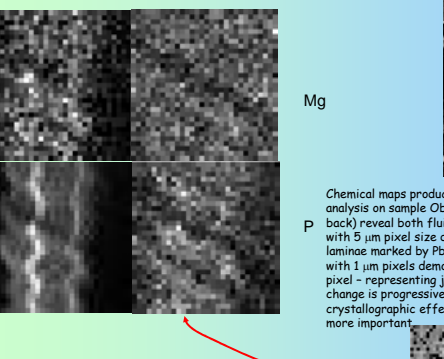
The technique of electron backscatter diffraction clearly resolves mineralogy (below = blue = argonite, red = calcite) and crystal orientation. The centres of the radiating argonite ray crystals from the Clamouse sample shown two panels back are shown to be unaltered.



D. Carbonate precipitation

Crystallographic controls on chemistry have been relatively neglected, but McDermott et al. (QSR, 1998) and Frisia et al. (J. Sed. Res., 2000) showed that fabrics were very variable from quasi-equilibrium, columnar textures (A, photo to right) to dendritic fabrics (B, see right) which are expected to show elevated $\delta^{13}C$ and $\delta^{18}O$ and trace element contents.

Mickler et al. (GCA, 2004) provided evidence from a Caribbean cave that there may be stochastic variation of up to 1 per mil in stable isotope signatures related to crystal precipitates nucleating from near identical waters at different times.



Chemical maps produced using synchrotron micro-XRF analysis on sample Ob4 from Obir cave (see two panels back) reveal both fluid and crystallographic controls. A map with 5 μ m pixel size displays several annual infiltration laminae marked by Pb enrichment (below). An enlarged area with 1 μ m pixels demonstrates that the Pb peaks are within a pixel - representing just a few days growth. The temporal change is progressively less marked in Zn, P and Mg, whereas crystallographic effects related to growth domains become more important.