Annual to sub-annual resolution of multiple trace-element trends in speleothems

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Abstract: This study aims to establish evidence for the widespread existence of preserved high-resolution trace element variations in speleothems that may have climatic significance. Ion microprobe analysis of speleothems reveals that annual to sub-annual variations in element chemistry exist at five, shallow western European cave sites (Crag Cave, County Kerry and Ballynaminqu, County Waterford, Ireland; Uamh an Tartair, Sutherland, Scotland; Grotte Pere-Noël, Belgium; Grotta di Ernesto, NE Italy) with widely varying climatic, geomorphic and geological settings. The variations are not restricted to species (Mg, Sr and Ba) known to substitute directly for Ca in the calcite lattice, but include H, F, Na and P. Phosphorus (as phosphate) displays the greatest variability and may have the most significance as a proxy for the seasonal temperature cycle because of its role as a nutrient element. The technique allows estimation of growth rate of speleothems at any interval of interest, which is one of several possible uses in palaeoclimatology.

Keywords: speleothem, carbonates, geochemistry, phosphates, palaeoclimate.

There is a need for improved palaeoclimatic records at both high spatial and high temporal resolution in order to test our concepts of past climatic change in populated regions and aid projections of future change. This need has led to a rapidly increasing analysis of continental archives including speleothems. The most common type of speleothems studied for palaeoclimate are cylindrical stalagmites, which accrete predominantly vertically from CaCO3 precipitated from drip water. Stalagmite drips are often supplied by tubular (soda straw) stalactites that grow mainly by linear extension at their tip. A third form of precipitates is crusts, formed by water flowing over a surface and which can develop into thick flowstones. Climate proxies studied in speleothems include growth rate (e.g. Genty & Quinif 1996; Qin et al. 1999; Proctor et al. 2000), stable isotopes (e.g. McDermott et al. 1999; Lauritzen & Lundberg 1999; Bar-Matthews et al. 1999), Sr isotopes (e.g. Banner et al. 1996; Goede et al. 1998; Verheyden et al. 2000) and trace elements (e.g. Ayalon et al. 1999; Hellstrom & McCulloch 2000). Whereas most proxies reflect averages on the decadal to centennial scale, microanalysis of trace elements (along with the study of visible or UV-fluorescent laminae) yields information at the annual to sub-annual level and hence has the potential to recover the changing nature of seasonality through time. Two microanalytical studies on calcite speleothems (Roberts et al. 1998; Huang et al. 2001) and one on aragonitic speleothems (Finch et al. 2001) employing secondary ionization mass spectrometry (SIMS) on an ion microprobe have shown that such records exist, but their generality has yet to be established. Here we present outline descriptions of five examples to illustrate that such annual trace element variations are a normal, rather than an exceptional feature in shallow cave sites, and that several other trace elements, of contrasting geochemical character, show similar behaviour. The geochemical determination of an annual pulse allows the determination of growth rates, which is especially significant since many speleothems lack annual laminations (Baker et al. 1993). It may also prove possible in individual cases to quantitatively calibrate the trace elements for palaeoclimatic variables such as rainfall.

Study sites and materials

The study sites span a range of geographic, climatic, geological and pedological settings. Ballynaminqu (County Waterford, SE Ireland) has a brown forest soil and underlies a wooded isolated hill made of Carboniferous limestone. The climate is mild (mean temperature 9.4 °C), with 1200 mm annual rainfall and a summer soil moisture deficit. Uamh an (cave of) Tartair (8.6 °C, Sutherland, NW Scotland, Roberts et al. 1998; Proctor et al. 2000) contrasts in that the soil is a thin moorland peat overlying Cambro-Ordovician dolomites and limestones; precipitation is high (2000 mm annually) throughout the year, and there is winter snow cover. Grotta d’Ernesto (NE Italian Alps, McDermott et al. 1999; Fairchild et al. 2000; Huang et al. 2001) is developed in Jurassic dolomites and limestones overlain by a brown forest soil in woodland, but is significantly cooler than the other sites with a mean temperature of 6.6 °C. It has typically two months of winter snow cover and a summer soil moisture deficit despite an average 1300 mm annual rainfall. Grotte Pere-Noël (SE Belgium; Genty & Quinif 1996; Genty & Dellandre 1998; Verheyden et al. 2000) lies under woodland with a brown forest soil on Devonian limestones and dolomite. Whereas the other caves are all around 10–15 m below the surface, Pere-Noël lies at a depth of 70 m, but this is compensated for by rapid percolation of water.
along near-vertical bedding planes. Mean annual rainfall and temperature are 800 mm and 9.2 °C, and there is a pronounced summer soil moisture deficit. Finally, Crag Cave (County Kerry, Ireland) lies under grazing land on the western Atlantic seaboard (annual precipitation 1500 mm, mean temperature 10.4 °C), and is developed in Carboniferous limestone and dolomite. It is distinctive in that soils are developed on a 2 m cover of waterlogged till overlying bedrock that ensures a more consistent supply of drip waters in the cave.

The purpose of this paper is to establish some generalities about the quality and significance of high-resolution trace element variations in speleothems, not to make an exhaustive treatment of each site. Water chemical data are important for palaeohydrological interpretations (Fairchild et al. 2000), but in this case we restrict the discussion to available water data from close to the studied speleothems. Trace element data are presented from several types of calcitic speleothem, all forming from drip waters: stalagmites (Ballynamintra, Tartair and Ernesto), a soda straw stalactite (Crag) and a crust that formed on an aluminium cave monitoring installation (Pere-Noël). Frisia et al. (2000) stressed the importance of documenting the crystal fabrics of speleothems, because of the relationship of certain fabrics with disequilibrium growth and hence modified geochemistry. We argue that all the speleothems studied here formed close to equilibrium conditions from solutions with low supersaturation values (Frisia et al. 2000) since they are either, columnar or fibrous, or have unit extinction and rhombohedral crystal terminations (Fig. 1). This is corroborated by water chemical data where available (Tooth 2000; Huang et al. 2001).

In each case, we infer the growth rate of speleothems in relation to the time scale of trace element variation and argue for the dominance of annuality. Growth rates of speleothems can be determined in various ways including those of direct observation, especially at those disturbed sites where distinct time markers can be identified, and have also been predicted theoretically (Buhmann & Dreybrodt 1985; Baker et al. 1998). In temperate environments, linear extension rates of stalagmites are typically in the range 20–300 µm per year, and can potentially be predicted to within a factor of two from a knowledge of cave temperature, cave air PCO₂ and the Ca content of drip water. Direct evidence of growth rate can be supplied by annual lamination, visible optically in thin section or by UV-fluorescence or both (Baker et al. 1993; Genty et al. 1997; Roberts et al. 1998; Huang et al. 2001). However, in hydrologically sensitive settings, as well as regions with particular climate seasonality (e.g. the two wet seasons observed in many sub tropical climates), sub-annual responses can be detected (Shopov et al. 1994; Baker et al. 1999). Therefore it is prudent to argue, rather than assume, an annual origin of fine lamination.

**Laboratory methods**

We used the SIMS technique because of the combination of high spatial resolution, high precision and low detection limits for many elements and have optimized techniques for study of zoned calcites as described below. Strontium and magnesium are the elements of first choice because of their ubiquity in
sedimentary carbonates and controls on their incorporation in calcite have been extensively studied (Huang & Fairchild, 2001), and the recent discovery of annual variations in P made this also a key target (Huang et al. 2001). Other elements studied are those that proved to be both detectable and to display high-resolution variation. Of elements known to be present in bulk analyses of pure carbonates, we omitted Ba (cf. Roberts et al. 1998) because of its similar properties to Sr and lower abundance. As only positive secondary ions were measured the low positive ion yields of S and Cl precluded effective measurement of these species. Fe and Mn were also not analyzed since the speleothems studied formed in oxic environments and so were not expected to incorporate significant amounts of these elements except in separate mineral phases. Instead, Si served to indicate non-carbonate impurities.

Sample preparation is of the utmost importance, with a polished compact surface being required to optimize spatial resolution and minimize contamination. Fragile or porous samples were first embedded in Epothin™ resin that showed no tendency to volatilize in the ion probe instrument. Samples were sawn with a thin-blade to minimize sample damage and loss of material and polished (final 0.3 µm alumina) to a final constant thickness of around 150 µm for both analysis and optimal examination of micromorphology in transmitted light.

The CAMECA ims-4f ion probe instrument in Edinburgh University was employed. Elements were measured as positive secondary ions created by impact of a primary negative ion (O\(^-\)) beam from a duoplasmatron source (Hinton 1995). During the analysis the beam typically removes material down to a depth of 2–5 µm. Ions were measured with an electron multiplier at masses 1(H), 19(F), 23(Na), 26(Mg), 30(Si), 31(P), 44(Ca) and 88(Sr). Each mass corresponds to a stable isotope and the choice of mass is dictated by isotopic abundance, secondary ionization efficiency and molecular ion overlap. The isotope 44(Ca) was measured as the 40(Ca) signal was too high for the electron multiplier detector.

Si values were used to monitor silicate inclusions and surface contamination. The only inter-ion interference calculated to be significant (Huang & Fairchild 2001; Huang et al. 2001) was 44(Ca)\(^+\) on the 88(Sr)\(^+\) peak which corresponds to c. 1.4 ppm total Sr (at 75 eV energy offset) or c. 6.4 ppm (at zero energy offset), but this has not been corrected for in this paper.

Analyses were carried out using the step scan mode in which the sample was automatically moved a set distance (in the range 1–12 µm) between analytical points, beneath a 20 nA primary beam with a diameter of around 30 µm. Each analytical cycle took typically 45–60 seconds to complete. Two different combinations of conditions were used. Where spatial resolution of the order of 10 µm was adequate, a collimating aperture (‘field aperture’) for secondary ions of 10 µm was used. Under these conditions count rates were sufficient to permit a high energy (75 ± 20 eV offset) to be used. This mode of operation significantly reduces overall count rates but ensures greater suppression of molecular interferences and generally improves overall stability. Where scans were stepped at less than 10 µm, the 1 µm field aperture was used with zero energy offset in order to gain the maximum secondary ion beam intensity. No interference problems were found in the calcite matrix as a result of the lack of an energy filter (zero offset) when using the 1 µm field aperture, and the effective resolution was estimated to be around 2–4 µm (allowing for some secondary ion focussing aberrations). Analysis of P was however adversely affected by the combined use of the 1 µm aperture and low energy recording because P has a relatively poor ionization efficiency at low secondary ion energy. Hence, lowering of the energy offset is insufficient to compensate for the fact that the area imaged was around 100 times smaller with the 1 µm field aperture. This can be compensated for by longer counting times. For example for a sample with 10 ppm P, and using a 10 µm field aperture, a 5 s counting time was sufficient to amass 150 counts, yielding a 1-s counting precision (Long 1995) of ±8%. Using the 1 µm field aperture, counts dropped to 1 per second, but by using a 25 s counting time, a 1 s.d. precision of ±20 relative % was obtained.

Detection limits are constrained by the presence of molecular ions or surface contamination rather than by the detection system.

Near-surface contamination must be ablated before correct analytical data are obtained and so the sample is ablated at each spot before analysis. Because the beam is much wider (c. 30 µm) than the steps, much ablation occurs automatically in advance of the analysis, but an additional period of ablation of 10 s (10–12 µm steps) or 2–4 s (2 µm steps) at each point was used. Checks were made by repeating analyses along the same analytical track and most elements showed no change. However, for typical conditions as used in this paper, it was found that H and Na tended to decrease on the return track by a relatively constant amount (50–100 ppm) and hence the spatial variation displayed by Na and H was enhanced. H is particularly susceptible to background contamination, although this was minimized by the use of a liquid N\(_2\) cold-finger trap, resulting in a vacuum of typically <1.3 × 10\(^{-5}\) Torr measured in the specimen chamber by a residual gas analyzer. The quantitative values obtained for Na and H are thus specific to the analytical conditions used.

The ion microprobe measures ion ratios with high precision, and all the species reported here were measured as ratios to Ca (subsequently converted to equivalent ppm element in calcite). OKA calcite (Mg=618 ppm and Sr=10300 ppm, Roberts et al. 1998) was used to calibrate the elemental results for Mg and Sr and gave raw ratios (Mg/Ca and Sr/Ca) that varied by less than 2% over several months. The precision (1 s.d.) of different points analysed in step scans on this standard was around 2% for Mg (3 s count time) and 1% for Sr (10 s count time) with a 2 s count time for Ca.

Other elements were calibrated using an apatite from Durango with 17.6% P, 0.17% Na, 0.027% H, 0.20% Si and 3.4% F. The results obtained could be systematically offset, by up to a few tens of per cent in relative terms, from their true values because the ionization efficiency of these elements may vary in a carbonate as compared with a phosphate matrix. This is not a problem in the present study for which precision is the key parameter and if carbonate standards for these elements subsequently become available, results can be adjusted in retrospect. Also the Na ionization efficiency was found to be very similar to that of NBS-610 glass. The 1 s.d. precision of different points during step scans on the apatite standard were typically 1% for P (3 to 10 second count time), 2% for Na (2 s count time), 5% for Si (3 s count time), 10% for H (2 s count time) and 2% for F (10 s count time).

The new data

**B499-4 (Ballynaminta, SE Ireland)**

This stalagmite displays a fibrous mosaic of composite crystals several mm long in growth direction, by 50–200 µm wide...
Prominent flat internal laminae, dark and pseudo-paleochroic in plane polarized light, are present in its upper 14 mm. Figure 2 indicates that Si is commonly detectable in dark laminae, attributed to dispersed micron-sized silicate particles, indicative of increased hydrological flushing in wet periods. The dark laminae are UV-fluorescent, which is probably generated by scattering due to inclusions, although a contribution from organic matter cannot be ruled out. The laminae occur in bundles, typically 30–200 µm in thickness, whereas individual laminae, only visible at high magnification, average 14 µm in thickness (range 5–30 µm). There are currently no geochemical data on the water drip that fed the studied stalagmite, although seasonality is indicated by the observation that the drip ceases in the summer.

Preliminary interpretation of carbonate radiocarbon dates (D. Genty pers. comm. 2000) suggest ages of between 2 and 4 ka for the 2–13 mm interval, and hence that the uppermost dark layer predominantly represents a hiatus. The growth rate implied from radiocarbon analyses (15 µm per year, assuming constant proportion of dead carbon) is equivalent to the mean spacing of the finest dark laminae, which are therefore interpreted as annual.

Trace elements display some long-term trends superimposed on a high-frequency variation which is most pronounced for P (Fig. 2). The long-term trends might be related to climatic or hydrological factors and are outside the scope of this paper. P increases into each dark lamina or lamina-cluster (Figs 2 and 3), but there is no simple linear correlation overall. Mg tends to be antipathetic to P on the scale of individual peaks whereas Sr peaks can coincide with either peaks or troughs in P. Five repeat parallel scans, spaced over a lateral distance of 0.6 mm, were carried out in the interval 3.25–3.45 mm below the top of the stalagmite, and yielded quantitatively similar results. Figure 3 illustrates that H, Na and F tend to follow P. Since all analyses with silicate interference have been removed, the correlation of elements with visible laminae in Figures 2 and 3 is presumed to represent elemental species dispersed as sub-microscopic solid inclusions or individual ions or molecules in the calcite crystals. Figure 4 illustrates a 1 µm step scan in order to provide maximum spatial resolution, but there is an irreducible registration error of the order of 5–10 µm between the analyses and both optical and UV images. Nevertheless a correlation of the spacing of the finest laminae, visible either in UV or optically, with P-enriched laminae, can be inferred from Figure 4.

SU96-7 (Tartair, NW Scotland)

Roberts et al. (1998) described annual chemical variation coincident with UV-fluorescing laminae in a stalagmite from close to the entrance of this cave. There was a consistent
pattern of antipathetic variation of Mg with Sr and Ba. We analysed the top 5.5 mm of a different stalagmite, SU96-7, from the cave interior. This displays, parallel to the growth direction, fibrous composite crystals (6 mm long, and 50–100 µm wide) with feathery boundaries and smooth, flat growth zones (Fig. 1b). UV-fluorescent laminae (often also visible optically, and 20–60 µm in thickness) were demonstrated to be annual (autumnal) by Proctor et al. (2000), who have used their thickness variation as a proxy for rainfall over the last millennium.

Figure 5 illustrates chemical analyses of a representative portion of the speleothem whose UV-fluorescent image is also shown. In addition to longer-term variations, there are high-frequency cycles comparable with the spacing of some both visible and UV-fluorescent annual laminae. Duplicate parallel scans show consistency for both Mg and Sr. The levels of P, Na and H vary between scans, but annual peaks are still developed, and are in the same spatial position. In the interval 2.5–3.02 mm, there are 14 coincident peaks in Sr, H and Na, and a further four clear peaks in H beyond this. This compares with 18 luminescent bands developed in the same interval (Fig. 5). There are a similar number of P peaks, but they are slightly offset from those of Sr, H and Na. The chemical peaks are still present in a part of the stalagmite (2.5–2.8 mm below top) where laminae are less distinct and more inclusions were observed in plane polarized light. Mg shows variation significantly above analytical noise, but at high and inconsistent temporal frequencies.

Dripwater chemistry varies significantly spatially in the cave chamber: Ca (30–70 mg/L), Mg (15–40 mg/L), Sr (1–12 mg/L), Na (3–30 mg/L) and individual drips show 50% of this variation over time, but there are insufficient data to define seasonal trends.
Figure 6 illustrates analyses of laminae that formed 53–65 hydrological years before autumn 1995. The annual cyclicity is obvious for Sr, (and inversely for) H and P, with subtle year-to-year variations in the precise form of peaks and troughs in relation to the visible laminae. Mg displays more intricate variation as well as an overall tendency to vary sympathetically with H and P.

PN26 (Pere-Noël, Belgium)

This cave site is marked by a distinct summer water deficit, which leads many drip sites to dry up. Locally, a fast perennial drip has been monitored for electrical conductivity (EC) over several years and Genty & Deflandre (1998) found a tendency for it to reduce in EC in late summer and rise in late autumn. Since drip rate and EC are positively correlated, Fairchild et al. (2000) have interpreted this relationship to reflect prior calcite precipitation in the aquifer above the drip during the period of reduced EC. Typical drip chemistry is Ca 125 mg l\(^{-1}\), Mg 16 mg l\(^{-1}\), Sr 0.13 mg l\(^{-1}\) and Na 2.5 mg l\(^{-1}\) for much of the year. A calcite coating (PN26) of part of the aluminium apparatus at this location was collected in 1995, 4 years after installation. The coating consists of polycrystalline 100–250 µm calcite crystals (Fig. 1d) each with unit extinction, rhombohedral terminations, and local growth zones. It varies in thickness from 0.5 to 1.5 mm laterally.

A chemical profile across the coating is illustrated in Figure 7. Sr, Na and F display small variations that do not correlate consistently with the other elements or each other. However, H and P display mostly correlated variation, but inverse to Mg: there are a series of four or five distinct Mg peaks and P troughs.

The hydrological characteristics of the feeding drip are consistent with a significant component of flow derived from aquifer storage and the different pattern from previous examples, in particular in the behaviour of P, is notable. Each Mg peak/P trough is consistent with an annual event, possibly an episode of prior calcite precipitation (Fairchild et al. 2000), associated with removal of much Ca and nearly all P from solution, leading to high Mg/Ca in drip water and in the resultant speleothem.

Soda straw stalactite R (Crag cave)

The straw stalactite was active when collected in August 1997 and results are presented for the last few years of its growth. The straw displays sub-horizontal bands, which represent periodic thickenings of its inner wall, spaced at around 0.6 mm. Each band corresponds to a macrostep of stacked rhombohedral crystallites, all in optical continuity, on the inner surface of the straw (Fig. 1e) and we interpret these as annual. The linear extension rate of soda straw stalactites is known to be somewhat faster than that of underlying stalagmites (we have observed mm-scale annual growth of marked soda straws elsewhere in Crag cave since 1995) and Moore (1962) attributed similar bands to an annual fluctuation of cave conditions. The annual interpretation has recently been corroborated elsewhere, in a rare case where a banded soda straw also displays internal visible laminae, similar to laminae in nearby stalagmites known to be annual, and with the same spacing (Huang et al. 2001).

Figure 8 illustrates the analysed cross-section as seen in reflected and transmitted light. In the figure the outer surface of the straw is at the bottom and growth was towards the right (originally vertically downward). A series of five thickened intervals (bands), representing growth steps facing towards the growth tip, are found over a 3.5 mm interval. In addition, the soda straw progressively doubles in thickness within around 1 mm of its tip, indicating that it continues to grow inwards.
whilst within two years growth of the tip. Hence the outer half of the structure forms by essentially linear downward growth extension at the tip (around 0.6 mm per year), whilst the inner portion represents overgrowth sideways into the interior (around 0.1 mm in a year), in the first mm behind the tip. Thus the highest resolution and simplest growth profile over time are found in the outer half of the structure.

Figure 8 illustrates a composite elemental trace of several SIMS scans sub-parallel to the outer surface of the straw. P displays much more extreme relative variation than Mg and Sr. Overall, Sr tends to increase towards the growth tip, but there is no overall trend for the other elements. There is a coherent set of correlations with Mg, Na and P positively correlated with each other and Sr negatively correlated to them (Fig. 9). Limited F data are available and they correlate strongly with P; H is bimodal but shows no other obvious variation. There is a difference between the patterns of analyses closer to the outer and inner surfaces in that both Sr and Na are lower for a given Mg value in the inner analyses. This is interpreted later as reflecting growth rate. Also Mg and P data tend to be displaced towards higher values in the inner analyses, although the overall data trends are the same.

Hydrochemical measurements of the drip over a 13-day period in August 1997 showed a constant drip rate of 12 drips/minute and a Mg/Ca (weight) ratio of 0.037 (Ca=114 mg l\(^{-1}\)). In January 1999 the drip rate was only one per 5 minutes and the Mg/Ca increased to 0.049 (Ca=130 mg l\(^{-1}\)). Between these two sampling periods, the drip thus showed the negative relationship between aqueous Mg/Ca and drip rate found at some other sites at Crag Cave (Tooth 2000), and which is consistent with theory (Fairchild et al. 2000). By comparison with other drip sites at Crag cave which displayed falling discharges during the monitoring period in August 1997, the constant short-term discharge and constant hydrochemistry of the drip feeding ‘Crag R’ implies a predominant stored component of aquifer water. Nevertheless, Figure 8 illustrates that an intricate chemical variation is captured over a period of several years, with individual events as short as a few weeks in duration. The position of each thickened interval overlaps with a shift from relatively high to relatively lower Mg and higher Sr, which could represent an overall annual cyclicity. P is affected to a greater degree than Mg by repeated high-magnitude, short-term events which tend to be asymmetric (sharp fall and slower rise e.g. at 0.5, 1, 2 and 3.3 mm). They resemble the form of increased hydrological flow events (compare for example with Frisia et al. 2000, fig. 9 which illustrates falls in conductivity resulting from infiltration following major rainfall events at Grotta di Ernesto).

The growth rate of the straw may depend on seasonal variations in CO\(_2\) supply to the cave through dripwater, influencing the saturation state of the solution. In this Atlantic climatic situation with year-round rainfall such factors could yield a stronger seasonal signal (expressed as thickness variations of the straw wall) than the hydrological events that may control Mg and P.

**Significance of elemental variations**

The annual to sub-annual variations that have been described are displayed by four groups of elements.

1. Mg and Sr, whose partitioning into calcite is known to be systematic and describable in terms of a partition coefficient (K\(_X\)) where X refers to Mg or Sr. X/C\(_{\text{aq}}\)=K\(_X\) (X/C\(_{\text{calcite}}\)) where X/C\(_{\text{calcite}}\) is the ratio of X to Ca in water and X/C\(_{\text{calcite}}\) is the ratio in calcite. Mg and Sr partition coefficients are the subject of a large literature. These elements are also known to commonly display zonation in calcite.

2. Na, whose partitioning behaviour has been found to be erratic, and for whom there is little previous evidence of systematic zonation behaviour.
Decadal or shorter time scales is therefore that it re
straws). Hence, the simplest explanation of Mg variation on
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with other evidence of variation in solution composition with
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ff


magnitude of prior calcite precipitation along the flow path or, where
dolomite is present, because of enhanced dolomite dissolution
(Fairchild et al. 2000). Although such a pattern is shown by
some Ernesto drips, the variation in dripwater chemistry was
small during the monitoring period of the drip that fed ER77.
However, this is consistent with the small variation in the
stalagnite during the earlier part of the period shown in
Figure 6. Clearer evidence of the hydrological control of
Mg/Ca is shown by our data from Crag site R and by the
tendency for lower Mg in the inclusion- and P-rich infiltration
laminae at Ballynaminta.

**Magnesium**

Magnesium is the best understood of this set of trace elements,
since Mg simply substitutes for Ca in the calcite lattice (Mucci
& Morse 1990) and Mg content is directly proportional to
solution Mg/Ca. Huang & Fairchild (2001) present new experi-
mental data in karst-analogue experiments and compare with
previous studies. They conclude that growth rate and solution
PCO₂ are unimportant under such conditions, and that tem-
perature is the main variable affecting partitioning, provided
that samples are analyzed on a spatial scale larger than that
corresponding to any crystallographic heterogeneities such as
those described by Paquette & Reeder (1990, 1995).

In our case, the speleothems grew under isothermal
conditions and the spatial patterning of the variation coincides
with other evidence of variation in solution composition with
time (lamination in speleothems, wall thickening in soda
straws). Hence, the simplest explanation of Mg variation on
decadal or shorter time scales is therefore that it reflects
parallel variations in solution Mg/Ca. In turn, these are likely
to reflect the changing hydrological regime, with solution
Mg/Ca tending to be lower under high flow conditions because
of prior calcite precipitation along the flow path or, where

(3) P, whose incorporation (as phosphate) has been studied
experimentally only at relatively high phosphate concen-
trations.

(4) H and F, which are best known from magnesian calcites
and which have not, to our knowledge, been studied previously
by microanalysis in calcite.

We seek to show below that the factors governing the
incorporation of these elements differ from one another, and
hence that their analysis as a suite is potentially a powerful
approach.

**Strontium**

In cave environments with low Na and Mg/Ca and constant
temperature, the key variable (in addition to varying solution
Sr/Ca) affecting partitioning is likely to be growth rate, or
more specifically crystallographic changes that influence Sr
incorporation at higher growth rates (Huang & Fairchild
2001). Pingitore & Eastman (1986) hypothesized that the low
values of the Sr partition coefficient in high-Na solutions was
due to competition for non-lattice (defect) sites. We suggest
that whereas Sr is confined to Ca lattice sites where incorpor-
at is likely for additional Sr incorporated at
interstitial location is likely for additional Sr incorporated at
higher growth rates (e.g. Lorenz 1981). Direct evidence for the
influence of growth rate is given by the data of Figure 9
which show lower Sr for a given Mg content in the more
slowly-growing inner parts of the straw from solutions relatively high in Mg/Ca.

Fig. 9. Cross-plots of analytical data from the soda straw stalactite depicted in Fig. 8, contrasting analyses from step scans closer to the outer
surface with those closer to the inner surface. Statistically significant correlations (99.9% confidence level) exist in each case. Regression lines are
similar in the P versus Mg plot, but both Mg and P show a range to higher values for ‘inner’ analyses. In the Sr versus Mg plot, the regression
lines show a consistent difference of around 6 ppm in Sr, ‘outer’ data being higher than inner data. In the Na versus Mg plot, the regression line
for ‘outer data’ is 10 (low Mg values) to 100 (high Mg values) ppm higher in Na than for ‘inner’ data. These data are interpreted as reflecting
relatively slow growth in the inner part of the straw from solutions relatively high in Mg/Ca.

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We seek to show below that the factors governing the
incorporation of these elements differ from one another, and
hence that their analysis as a suite is potentially a powerful
approach.

Magnesium is the best understood of this set of trace elements,
since Mg simply substitutes for Ca in the calcite lattice (Mucci
& Morse 1990) and Mg content is directly proportional to
solution Mg/Ca. Huang & Fairchild (2001) present new experi-
mental data in karst-analogue experiments and compare with
previous studies. They conclude that growth rate and solution
PCO₂ are unimportant under such conditions, and that tem-
perature is the main variable affecting partitioning, provided
that samples are analyzed on a spatial scale larger than that
corresponding to any crystallographic heterogeneities such as
those described by Paquette & Reeder (1990, 1995).

In our case, the speleothems grew under isothermal
conditions and the spatial patterning of the variation coincides
with other evidence of variation in solution composition with
time (lamination in speleothems, wall thickening in soda
straws). Hence, the simplest explanation of Mg variation on
decadal or shorter time scales is therefore that it reflects
parallel variations in solution Mg/Ca. In turn, these are likely
to reflect the changing hydrological regime, with solution
Mg/Ca tending to be lower under high flow conditions because
of prior calcite precipitation along the flow path or, where
dolomite is present, because of enhanced dolomite dissolution
(Fairchild et al. 2000). Although such a pattern is shown by
some Ernesto drips, the variation in dripwater chemistry was
small during the monitoring period of the drip that fed ER77.
However, this is consistent with the small variation in the
stalagnite during the earlier part of the period shown in
Figure 6. Clearer evidence of the hydrological control of
Mg/Ca is shown by our data from Crag site R and by the
tendency for lower Mg in the inclusion- and P-rich infiltration
laminae at Ballynaminta.
probably applied to Ernesto stalagmite ER77 also, but the tendency for strong change in dripr water chemistry at Tartair implies that solution composition may be the dominant control in that case. Monitoring of specific drips would be needed to resolve this issue in individual cases.

**Sodium**

Total Na in calcites can show a correlation with aqueous Na content or salinity (Ishikawa & Ichikuni 1984), although much of the Na encountered in previous studies may be located within fluid inclusions. There is no evidence that we have analysed any such inclusions (which would be quickly volatilized) and so our Na records, once surface contamination is removed, are baseline values representing Na dispersed sub-microscopically through the crystal. Huang & Fairchild (2001) presented ion probe Na data from calcites grown under controlled, karst-analogue conditions using solutions with 80–90 ppm Na. Typical mean values in calcite were around 300 ppm, but a range of a factor of two was found in experiments with identical conditions. In our caves, Na values in calcite were typically 50–200 ppm regardless of whether aqueous Na was around the 20 or 1 mg l\(^{-1}\) level. This indicates that SIMS Na in speleothem calcite does not record variations in aqueous Na content. This conclusion is also demanded by the observation that Na changes significantly with time over an annual cycle in speleothem calcite, whereas in our cave waters it changes little with time (Fairchild et al. 2000; Tooth 2000; Baker et al. 2001). It should also be noted that our step-scan procedure in this paper yielded lower values on return scans and hence the Na values are not quantitatively reproducible, although the high-resolution aspects of the patterns of variation with time are reproducible.

The relative sense of change of Na can be explained by the observation of Busenberg & Plummer (1985) who showed that Na is incorporated at lattice defect sites and hence more is incorporated at higher growth rates. Direct evidence for this is again provided by the data of Figure 9, which shows a tendency for lower Na incorporation for a given Mg concentration in the more slow-growing inner part of the Crag soda straw. However, competition for defect sites, and hence the Na concentrations in the more slow-growing inner part of the Crag soda straw, should also play a role in the absolute Na concentration, particularly when comparing calcites from different caves.

**Phosphorus**

Phosphate is one of the strongest adsorbents onto defect sites on the calcite surface (Meyer 1984). House & Donaldson (1986) grew calcite crystals at growth rates ranging from over 100 to less than 1 lattice layers per minute under conditions where the adsorption sites were saturated by relatively high aqueous phosphate concentrations in the range 1.5 to 9.3 µM 1\(^{-1}\) phosphate. Around 2% of the adsorbed phosphate was incorporated into the calcite (some thousands of ppm). Under such conditions, no zonation in P would be found. The much lower levels and the zonation encountered in our studied speleothems compared with the experiments of House & Donaldson (1986) suggest that there was insufficient P available to saturate the adsorption sites. Hence P incorporation may be sensitive to factors such as phosphate concentration in solution and rate of supply of dripr waters. Sparse available data from non-agricultural catchments suggest that the values of both of these parameters may increase during the autumn in pulses of infiltrating water (Heathwaite 1997). Hence, Huang et al. (2001) argued that both P concentration and drip rate could play a role in the annual autumnal increase in P in Ernesto stalagmite ER76 (and also showed that potential organic sources of P were insufficient by orders of magnitude to explain observed concentrations). A control on P incorporation by rate of supply of inorganic P, rather than by defects produced during faster growth, is inferred from the lack of correlation of P and Sr in this case.

The lack of published data on aqueous phosphate concentrations in cave waters and the nature of the coprecipitation behaviour at low concentrations (Huang et al. 2001) hamper our interpretations of P. However, our interpretations are consistent with unpublished results on aqueous dripr water phosphate (Borsato et al. 2000) from caves in the Trentino province (in which Ernesto lies) indicating typical total P contents of from 3 to 8 µg l\(^{-1}\), rising to 30–50 µg l\(^{-1}\) during infiltration events. It is also clear that growing calcite crystals can very effectively scavenge phosphate from water by adsorption and hence that its incorporation behaviour is very different from the species previously considered. It is noteworthy that the log-scale variation in P within each of the five samples, largely expressed annually, is greater than any of the other trace elements.

In the Ballynamintra speleothem, the coincidence of phosphate-rich laminae with silicilastic inclusions indicates that P is positively tracking infiltration events in this case. At Ernesto, the ER77 data agree with previous work on ER76 pointing to the role of seasonal infiltration events. At Tartair, seasonal influence on P may also have been important, but this is offset in timing from the peaks of other trace element records in this case. In the Crag soda straw, there is a negative correlation of P with inferred infiltration events. This could reflect, in this case, a relatively large concentration of phosphate in the aquifer, in relation to that in rapidly infiltrating water. Finally, the Pere-Noel speleothem derives from a steadily-discharging stored water source insensitive to individual infiltration events: here P decreases were argued to be related to prior calcite precipitation, which could have scavenged P from solution leading to the observed decreases.

**Hydrogen**

H shows a tendency to correlate with Na and P, but its interpretation is limited by lack of understanding of the form in which it is present. The H/P ratios are too high and variable for HPO\(_4^{2-}\) ions to be the dominant source of H. A possible alternative source of H\(^+\) ions in the ion probe would be organic species, although H is present at relatively high concentrations (up to 1000 ppm) in clear calcites lacking any evidence of organic inclusions. The most likely alternative is as OH-ions or molecular water dispersed through the lattice. Mackenzie et al. (1983) used infra-red absorption data to demonstrate the presence of large amounts of molecular water in biogenic magnesian calcites and Busenberg & Plummer (1985) demonstrated up to 100 ppm of H as OH- groups by alkalinity determinations on similar materials. Surface adsorption of hydroxyl (Pokrovsky et al. 2000) as well as molecular water onto inorganic calcite is now well known. Despite the lack of a theoretical understanding on the incorporation of such species into calcite, H as analysed on the ion probe clearly can be
a useful element in demonstrating annual cyclicity in speleothems.

**Fluorine**

F should be present as the fluoride (F\(^-\)) ion and observation and experiment (summarized by Mucci & Morse 1990 and Rude & Aller 1991) indicate that significant amounts can be incorporated in calcite. However these cited works focused only on marine systems. More generally F- might be expected to occur at defect sites where it could compensate charge imbalances caused by incorporation of orthophosphate (PO\(_4^{3-}\)) or singly charged cations such as sodium. Indeed, there is often a correlation of F with Na and P that may reflect the varying presence of growth defects. Since the ion probe is unable to analyze Cl efficiently, study of fluoride may serve as a proxy for the behaviour of other halides.

**High-resolution records of trace elements in speleothems**

This study demonstrates the quality of high-resolution trace element data, potentially of palaeoclimatic significance, encoded in calcitic speleothems, and the varying forms in which it can be expressed, depending on the geological-hydrological-climatic setting. It is now clear that trace element (Sr, Mg, H, F, P, Na) variations commonly display an annual cyclicity, in addition to sub-annual and longer-term variations. Corroboration of the annual length cycle by diʃerential decay of vegetation. More research is particularly needed for P, the element that displays greatest geometric range of values. Being a nutrient element, it has a link to the annual temperature cycle via the growth and decay of vegetation. More field data on aqueous phosphate concentrations as well as experiments on its incorporation in calcite at low concentrations are required to make predictions of its behaviour.

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