HIGH RESOLUTION STABLE ISOTOPE ANALYSIS
OF A TASMANIAN SPELEOTHEM

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(with eight text-figures)


High resolution oxygen and carbon isotope analyses of part of a uniform diameter stalagmite from a cave in northern Tasmania have been used to study the climatic transition from stadial to interstadial conditions during the early Last Glacial (109-95 ka). A significant change in oxygen isotope values suggests that temperature warmed rapidly by approximately 2°-3°C between 100 and 97 ka. A decrease in carbon isotope values between 101 and 98 ka indicates that moisture availability was increasing slightly in advance of rising temperature.

Key Words: Speleothem, stable isotope analysis, climatic change, Last Glacial, Tasmania, Australia.

INTRODUCTION

The aim of this study was to produce a high resolution record of the stable isotope composition (δ18O/δ16O and δ13C/δ12C) of the basal 600 mm of a 1420 mm tall, uniform diameter calcite stalagmite (LT) from Little Trimmer Cave in the Mole Creek karst region, northern Tasmania (146°14'4"E, 41°34'21"S). The site is at an altitude of 460 m (fig. 1). A low resolution study had been done previously (Goede et al. 1986) but did not include interpretation of the basal 400 mm because of doubts that deposition had occurred under conditions of isotopic equilibrium. These doubts have been resolved by the present study (Desmarchelier 1994).

Uniform diameter stalagmites, when examined in longitudinal section, consist of a central core where vertical accretion takes place on a subhorizontal surface, producing a sequence of convex upward layers surrounded by a narrow mantle formed by discontinuous deposition on a near-vertical outer surface (Goede 1994). Sampling was done at 5 mm intervals along the centre of the axis, using a dental drill with a 1.6 mm bit. In addition, in order to confirm conditions of isotopic equilibrium, seven samples were drilled from each of eight growth layers (Hendy & Wilson 1968) but, following Talma & Vogel (1992), sampling was restricted to the upper subhorizontal portion of each growth layer. Advances in sensitivity and automation of stable isotope mass spectrometers since the previous study of Goede et al. (1986) have enabled us to analyse a large number of samples with a much higher degree of measurement precision, while using much smaller quantities of calcite.

GEOCHRONOLOGY

Age determination of the speleothem (LT) is based on alpha particle analysis of seven samples spaced along its length. Four of these fall within the lowest 400 mm (fig. 2). Full analytical details are provided in Goede et al. (1986). The time scale used has been determined by linear regression analysis of heights above base against radiometric age estimates of all seven samples (r = 0.98). This technique minimises the random error involved in individual age determinations (Goede & Harmon 1983). The regression line indicates a growth rate of approximately 43 mm/ka. Samples at 5 mm intervals represent time intervals of approximately 116 years.

NATURE OF STABLE ISOTOPES

Measurement of variations in the isotopic ratios of δ18O/δ16O and δ13C/δ12C allows investigation of aspects of environmental conditions. Measurements are expressed as per mil (‰) using the delta (δ) notation relative to the PDB (Peedee Belemnite) standard. The following subscripts are used throughout the text: w - water, c - calcite, p - precipitation and sw - seawater.
$^{18}$O/$^{16}$O ratios can be used as indicators of palaeotemperatures provided that certain criteria are met (Handy 1971, Talma & Vogel 1992). They are:

1. The carbonate precipitate must have formed in isotopic equilibrium with the dripwater;
2. The oxygen isotope content of the drip water must be estimated;
3. No diagenetic alteration of the calcite must have occurred;
4. The deposit must be datable.

Conditions conducive to isotopic equilibrium are near-constant temperature conditions, humidity close to 100%, and little or no air movement. Such conditions are most likely to be found well away from cave entrances. Deposition of calcium carbonate under isotopic equilibrium conditions will occur only where there is a continuous supply of carbonate-saturated seepage water with a partial pressure of CO$_2$ greater than that of the cave atmosphere.

Handy & Wilson (1968) suggested the following tests to confirm the existence of isotopic equilibrium:

1. Paired measurements of $\delta^{18}$O and $\delta^{13}$C taken from the centre of the core along the vertical axis should show an absence of strong positive correlation.
2. Paired measurements of $\delta^{18}$O and $\delta^{13}$C taken from a sequence of at least seven samples along an individual growth layer from the centre of the core outwards should not show a trend towards isotopically heavier values. This test should be done for a number of growth layers.

Harmon et al. (1978) have proposed that the variations in oxygen isotope values in speleothems deposited under conditions of isotopic equilibrium are controlled by the three major factors noted below:

1. Changes occur in the temperature of the depositional environment of the cave. The cave temperature usually approximates to the mean annual surface temperature and will respond to any fluctuations in the latter if climatic conditions change.
2. Changes in the isotopic composition of seawater occur due to the accumulation of $^{18}$O-depleted glacial ice on land. They affect the isotopic composition of precipitation by a similar amount.
3. Changes in the isotopic composition of precipitation are also caused by temperature and humidity changes at sites of evaporation and precipitation, as well as possible changes in the geographical location of moisture source areas.

Goede et al. (1986) discussed these factors, noting that factors (1) and (2) cause secondary calcite deposited during cold periods to become enriched in $^{18}$O, whereas factor (3) has the opposite effect. Harmon et al. (1978) noted that the majority of stalagmites examined by them showed a negative relationship between $\delta^{18}$O values of calcite and palaeotemperatures. In contrast, stalagmites from Vancouver Island, Norway and Tasmania, all areas subject to a temperate maritime west coast climate, show a positive relationship between $\delta^{18}$O values of calcite and palaeotemperatures (Gascoyne et al. 1980, 1981, Goede et al. 1986, 1990, Lauritzen et al. 1990). This indicates that, in these areas, factor (3) is dominant in determining the isotopic ratio of speleothem calcite.

FIG. 2 — Longitudinal section of basal 600 mm of LT stalagmite examined in this study. Median positions of uranium series dates are indicated along the estimated age scale. Concave upward lines represent prominent growth horizons. Large and medium-size circles indicate sampling by Goede et al. (1986). Small circles indicate high resolution sampling for this study. Sets of samples were taken along growth lines to establish deposition under conditions of isotopic equilibrium.
Seasonal variation in the isotopic composition of precipitation will not affect seepage waters because soil water is homogenised, causing cave drip water to maintain a near-constant isotopic composition. Goede & Hitchman (1984) and Goede et al. (1986, 1990) have shown that, in Tasmania, the isotopic composition at present is best related to the weighted mean value of winter precipitation. This implies that summer precipitation in Tasmania does not contribute significantly to the supply of seepage water. Therefore, the δ¹⁸O values of contemporary Tasmanian speleothems reflect predominantly changes in winter temperatures rather than mean annual temperatures (Goede 1994). This may not always have been true in the past under conditions of wetter and cooler summers.

Variations in δ¹³C values in speleothems, unlike δ¹⁸O values, are not related to palaeotemperature. Values are either unrelated or only weakly correlated with the oxygen isotope values. Secular variations in carbon isotope values indicate that they contain palaeoenvironmental information but, until recently, interpretation has been contentious. In recent years, research relevant to this problem has been done not only on speleothems (Brooke et al. 1990, Dorale et al. 1992, Talma & Vogel 1992) but has also included studies of soil carbonates (Cerling et al. 1989, Quade & Cerling 1990, Quade, Cerling & Bowman 1989a, b) as well as sub-aqueous wall crust in a karst spring (Coplen et al. 1994).

The relevant literature is discussed by Goede et al. (in press), who conclude that, in temperate environments, changes in δ¹³C over time reflect predominantly temporal changes in plant activity, with a minor influence due to natural changes in the isotopic composition of CO₂, at least until the beginning of the industrial revolution (Baskaran & Krishnamurthy 1993, Marino et al. 1992). Carbon isotope values are also affected slightly by the composition of the limestone, but this effect is assumed to remain constant during the growth period of a stalagmite. In cool temperate climates, such as are found in Tasmania, plant activity is likely to be controlled by temporal variations in summer insolation and moisture availability.

TESTS FOR ISOTOPIC EQUILIBRIUM

The first test suggested by Hendy & Wilson (1968) involves the degree of positive correlation between δ¹⁸O and δ¹³C values of samples taken along the longitudinal axis. A weak but statistically significant negative correlation was found (r = -0.40, n = 119, p < 0.001), confirming deposition under conditions of isotopic equilibrium (fig. 3).

The second test involves examination of sets of seven samples from each of eight growth layers. The position of the samples is illustrated in figure 2. These sets show no significant correlation between paired δ¹⁸O and δ¹³C values, with one exception where the changes are relatively small. Overall the evidence is strongly in favour of deposition under isotopic equilibrium conditions.

PREVIOUS ANALYSIS

The stalagmite was analysed previously by Goede et al. (1986) who used a 5 mm masonry drill to sample at intervals of 45 mm. Three growth layers were also sampled to establish deposition under equilibrium conditions. The basal 400 mm was not interpreted as a palaeotemperature record, because of doubts about equilibrium deposition. The results of isotopic analyses done in the previous study are given in figure 4. The present-day isotopic composition of speleothem material was determined by multiple analyses of calcite removed from two plastic funnels used to collect dripwater during 1979. The values obtained were δ¹⁸O = -3.75 and δ¹³C = -12.21‰ PDB.

In an earlier paper dealing with the LT stalagmite, palaeotemperature estimates were obtained by measuring δD values of fluid inclusions (Goede et al. 1986). The relationship between δD and δ¹⁸O established by monthly sampling for one year near the cave entrance was used to estimate corresponding values of δ¹⁸O at the time of deposition of the stalagmite. These values, in turn, were used to calculate palaeotemperatures. The problem with this approach is that it does not give a unique outcome, since the intercept

![FIG. 3 — Scattergram of 119 δ¹⁸O and δ¹³C values of samples taken from the long axis of the LT stalagmite. The regression line is shown.](image)

![FIG. 4 — Temporal variations in the values of δ¹⁸O and δ¹³C obtained by interval sampling of the whole of the Little Trimmer stalagmite in an earlier study (Goede et al. 1986).](image)
in the relationship between $\delta D_w$ and $\delta^{18}O_w$, known as the deuterium excess ($d_e$), is known to have varied over time. In Antarctica, values of $d_e$ have been found to range from 8.3 to 4 over the last glacial-interglacial hemicycle ( Jouzel et al. 1982). In Tasmania the deuterium excess is unlikely to have remained constant over time, but the amount of variation is not known.

A different approach, first suggested by Gascoyne et al. (1980, 1981), is used here. It is particularly appropriate for areas where the oxygen isotope composition of calcite has a positive relationship with temperature ($d\delta^{18}O/dT > 0$). It relies on the supposition that the value of $\delta^{18}O_c$ changes in response to three factors:

1. Changes in cave temperature: at $10^\circ C$, the fractionation effect for $\delta^{18}O_c = -0.24\%$/$^\circ C$ (Epstein et al. 1951).
2. Changes in isotopic composition of precipitation due to changes in the isotopic composition of seawater resulting from variations in the amount of glacial ice on land. Shackleton & Opdyke (1973) estimated that, under full glacial conditions, the value for seawater was 1.20% higher than at present. To calculate the effect for a $1^\circ C$ change in temperature requires an estimate of the amount of temperature lowering in the area during the last glacial maximum. Hannan (1989) used the extent of glacial ice in the Mersey Valley, close to the cave site, to estimate a lowering of mean annual temperature of 6.2$^\circ C$. This suggests a change in the oxygen isotope composition of $-0.2\%$ for a $1^\circ C$ rise in temperature.

3. In some areas, there is a strong positive relationship between the oxygen isotope composition of precipitation and temperature. Gascoyne et al. (1980) suggested that this is due to a change in temperature gradient between the site of evaporation and the site of precipitation. Recent work suggests that the reasons are more complex (Grooves 1993, Roziński et al. 1995). The magnitude of this factor has been determined as 0.7$^\circ C$ per 1000 km for oceanic precipitation sites (Dansgaard 1964, Lauitzen et al. 1990).

Gascoyne et al. (1980, 1981) summarised the relationship as follows:

$$\Delta \delta^{18}O_c = d\Delta_{c-w}/dT + \Delta \delta^{18}O_{sw} + (d\delta^{18}O_p/dT)\Delta T \quad (1)$$

For a $1^\circ C$ lowering in temperature, $\Delta \delta^{18}O_c = -2.6\%$.

Since the present-day oxygen isotope composition of calcite is known, temperature at time $T_i$ can be estimated from the following expression:

$$T_i = 9.5 + (\delta^{18}O_c + 3.75)/0.26 \quad (2)$$

This expression has been used to calculate the palaeo-temperature estimates shown in figure 5.

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**FIG. 5** — Five-year running mean of temperature deviation from the present mean annual temperature of 9.5°C for the LT isotope record compared with the temperature difference record for Vostok where present mean annual temperature is $-55.5^\circ C$ (Lorius et al. 1985).
DISCUSSION AND RESULTS

Oxygen Isotope Record

The δ¹⁸O values and the five-year running means have been plotted against the estimate age in figure 6. The most significant change occurs between 100 ka and 97 ka, where values rise from ~5.4% to ~4.8% corresponding to a warming of approximately 2°C. In figure 5 departures from the present mean annual temperature of 9.5°C are shown. They have been calculated using equation 2 (above). In the same diagram, the smoothed temperature record from the Vostok ice core is also shown (Jouzel et al. 1987).

Figures 5 and 6 suggest that warming, equivalent in time to the transition between marine isotope stages 5d and 5c, occurred in two steps. A similar pattern can also be seen in the Vostok record where a similar stepped temperature rise occurred at approximately the same time. The 3000-year timeshift required to match the two sets of records is easily explained by the limitations of dating. The Vostok record shows a greater temperature rise (4°C) during the transition from 5d to 5c compared with the LT record (2°C). However, following the rise, temperature estimates for the amount of temperature lowering during stage 5c are very similar.

The Vostok record is dominated by a 100 ka glacial–interglacial oscillation with a temperature amplitude of about 6°C (Lorius et al. 1985, Jouzel et al. 1987). The stages in the Vostok record are identified by capital letters, commencing with A for the Holocene epoch. Vostok stage E is an interstadial, characterised by two well-defined temperature maxima at approximately 100 and 81 ka, as well as some minor oscillations. The earlier maximum appears to match the maximum at 97 ka in the LT record. A slight difference in timing is to be expected, due to limitations in the accuracy of dating in both records. The recent development of uranium series mass spectrometry (TIMS) dating and its successful application to speleothems means that dating precision can be improved substantially (Lundberg & Ford 1994).

Carbon Isotope Record

The δ¹³C isotope record is shown in figure 7. There is a fluctuating upward trend from 109 ka until a maximum value of ~6.0‰ is reached at 101 ka. Between 101 and 98 ka values fall rapidly to ~9.0‰. A slight upward trend follows until the record terminates at 95 ka.

It has been argued that, in cool, temperate climates, carbon isotope variations may be interpreted largely in terms of variations in plant activity, with more negative values indicating higher levels of activity (Goede et al. in press). Change in the atmospheric composition of atmospheric CO₂, due to secular variation, can be expected to have made a minor contribution — at least in pre-industrial times.

In the Tasmanian environment, plant activity is seasonal and strongly influenced by available moisture, which can be expected to be at least partly modulated by variations in summer insolation. Some evidence has already been detected that variations in δ¹³C in speleothems from Tasmania and eastern Victoria are affected by summer insolation. Goede (1994) published a speleothem record from the Florentine Valley in south central Tasmania, covering a period from 98 to 55 ka. The carbon isotope record shows two prominent peaks of isotopically heavy carbon at approximately 95 and 75 ka and troughs of isotopically light values at 85 and 60 ka. Mid-month insolation data for December at 30°S (Berger & Loutre 1991) show radiation maxima at 95 ka (531 W/m²) and 72 ka (510 W/m²) and radiation minima at 84 ka (462 W/m²) and 61 ka (472 W/m²). A short isotopic record (13.4 to 10.6 ka) from Buchan, eastern Victoria, shows a trough of isotopically light carbon isotope values at 11.2 ka closely following a December insolation minimum at 12.5 ka (474 W/m²) (Goede et al. in press).

Summer insolation minima coincide with winter insolation maxima with a change of similar percentage magnitude. It appears that, in southeastern Australia, conditions for maximum plant productivity coincide with conditions of minimum summer radiation which are also times of minimum seasonal variation. The radiation curve of Berger & Loutre (1991) for the time period examined in this study is of particular interest, because the summer insolation minimum that occurred at 106 ka (mid-month December value of 449 W/m²) is the lowest of any values calculated for the Late Pleistocene and Holocene.

FIG. 6 — Oxygen isotope data plotted against age together with the five-year running mean.

FIG. 7 — Carbon isotope data plotted against age together with the five-year running mean.
In order to test the hypothesis that strongly negative values of δ¹³C tend to coincide with summer radiation minima, the δ¹³C values for the LT stalagmite have been plotted on the same time scale as the solar radiation curve for 30°S (fig. 8). Agreement between the two curves is poor, but this may be due to the limited accuracy and precision of the early alpha spectrometry dates on which the age scale is based (Goede et al. 1986). Until such time as more precise mass spectrometric uranium series dates can be obtained, the hypothesis cannot be adequately tested.

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REFERENCES


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