

Relationship between oxygen isotopes in rainfall, cave percolation waters and speleothem calcite at Waitomo, New Zealand

Paul W. Williams and Anthony Fowler

*School of Geography & Environmental Science, University of Auckland,
PB 92019, Auckland, New Zealand*

e-mail: *p.williams@auckland.ac.nz a.fowler@auckland.ac.nz*

Abstract

The relationship between the $\delta^{18}\text{O}$ values of rainfall, vadose percolation water, and speleothem calcite was investigated in a cave at Waitomo. Water samples were obtained approximately monthly for two years from a storage rain gauge on the surface and from stored seepage from three stalactites underground. Rain water $\delta^{18}\text{O}_{\text{SMOW}}$ values varied considerably throughout the observation period, with a precipitation-weighted mean of -5.3‰ . Seasonal variability was evident, with winter values being more negative than summer values. Cave seepage waters had a mean of about -5‰ and showed very little variability and no discernible annual variation. This is explained by thorough mixing in the soil and subcutaneous zone stores. Given the average cave temperature (12.8°C) and the $\delta^{18}\text{O}_{\text{SMOW}}$ value determined for seepage water, the $\delta^{18}\text{O}_{\text{PDB}}$ value of calcite that is actively depositing in isotopic equilibrium on speleothems at Waitomo should fall in the range of -4.1 to -4.6‰ . Observed δ -values of modern speleothem calcites overlap the positive end of this range of theoretical values, indicating that some growing speleothems are not in isotopic equilibrium with seepage waters, but are experiencing either evaporation or kinetic fractionation.

Introduction

Crystalline deposits found in caves, such as stalactites, stalagmites and flowstones, are collectively known as speleothems (Hill and Forti, 1997). They are usually formed of calcite (CaCO_3) chemically precipitated from seepage water that has percolated through overlying limestone beds. Oxygen isotopes in speleothem calcite can be used to estimate the temperature at the time of deposition, because the $^{18}\text{O}/^{16}\text{O}$ in calcite during its precipitation is temperature dependent (Hendy and Wilson, 1968; Hendy, 1971; Gascoyne, 1992). The temperature within the interior of a cave varies very little over

the year and is very close to the external mean annual air temperature of its locality (Wigley and Brown, 1976). If the external temperature changes over time, the cave temperature will adjust accordingly, which will result in oxygen isotope ratio changes of the calcite as the speleothem grows. Thus the $\delta^{18}\text{O}$ values of a stalagmite reflect temperature changes as it grew, provided this growth occurred under conditions of isotopic equilibrium (Hendy, 1971; Gascoyne, 1992; Lauritzen and Lundberg, 1999), which are common in the interior of caves away from the effects of evaporation.

Goede *et al.* (1982) found cave drips in Tasmania to show apparently random, non-seasonal variation in $\delta^{18}\text{O}$ values, the arithmetic mean being close to the weighted mean $\delta^{18}\text{O}$ value of rain water. Yonge *et al.* (1985) reached similar conclusions from a study of a wide range of sites across North America. They found the stable isotope composition of cave drip waters to be essentially invariant over the year, the water evidently being homogenized during passage through the soil and the epikarst (the top-most weathered zone of limestone beneath the soil, also known as the subcutaneous zone). Although they considered the possibility that transpiration might result in the selective loss of that part of the meteoric water deposited during the period of most active plant growth, causing the isotopic composition of seepage water to be displaced towards winter values, the percolation waters in the caves were found to have values close to the weighted mean annual precipitation in the locality. Yonge *et al.* (1985) suggested that the mixing time scale may be important in determining the extent to which any seasonal signals are transmitted, because if it is of the order of a year or more, the seasonal transpiration cycle will have no effect on δ -variability, with values remaining approximately constant throughout the year.

More recent work has shown $\delta^{18}\text{O}$ values of percolation waters to vary slightly from place to place, even in the same cave (Chapman *et al.*, 1992; Dennis *et al.*, 2001), probably because of different storage, mixing and flow-through rates in various parts of the soil and epikarst. Thus sampling from more than one site in a cave is required to obtain a reasonable estimate.

It is evident that the mean $\delta^{18}\text{O}$ value of seepage waters should approximate the mean $\delta^{18}\text{O}$ value of rain water. However, determination of an appropriate value for percolation waters in caves is problematic because of their relative inaccessibility. Since many more measurements are taken from precipitation waters than from cave seepage waters, the mean annual $\delta^{18}\text{O}_p$ (p = precipitation) value of rain can be expected to provide a reasonable estimate for the $\delta^{18}\text{O}_w$ (w = percolation water) value of seepage water, provided the rain water samples are obtained near the cave. Where rain water samples are not available, representative samples must be taken from cave seepage drips. This also assumes that no significant sub-surface processes occur that might alter the relationship.

The principal station in the North Island for which long records of stable isotopes in rain water are available is Kaitaia, which is 390 km from the cave research site at Waitomo (Figure 1). Thus to understand the relationships at Waitomo among $\delta^{18}\text{O}$ values in rain water, cave seepage water, and modern speleothem calcite it is necessary to make measurements at Waitomo. Such information is required to calculate and interpret palaeo-cave temperatures. For these reasons, this research set out to establish the relationship between the oxygen isotope composition of rain water and cave seepage water at Waitomo, and then the relationship between the oxygen isotope composition of seepage water and newly deposited speleothem calcite.

Research design

The Waitomo region was selected as the principal site for cave-based measurements because its caves are accessible and have proven suitable for isotopic work (Hendy and Wilson, 1968; Hendy, 1971). The approach adopted was to measure the $\delta^{18}\text{O}$ value of rainfall and to compare it to the value of percolation water from stalactite drips in an underlying cave. Measurements were taken for two years from water accumulated during approximately monthly sampling intervals.

In order to identify what statistical relationships could be expected in the short-term isotopic record from rainfall at Waitomo ($38^{\circ} 16' \text{ S}$), the long-term record of oxygen isotopes in rainfall at Kaitaia ($35^{\circ} 07' \text{ S}$) was examined. Kaitaia is important as the principal New Zealand meteorological station that contributes isotopic data to the Global Network for Isotopes in Precipitation, its data having been screened for quality and analysed by Taylor (1990). It is an open station near the coast at about 80 m above sea level compared to the site near Waitomo, which is 35 km inland and about 40 m higher.

Daily rainfall is recorded formally at Waitomo rainfall station (C85213), about 3 km distant and 70 m lower in elevation than the rain water sampling site (referred to as Ruakuri), which was established in an open field about 650 m from the sampling site in Aranui Cave, but at a similar altitude to the surface above the cave (Figure 1). A previous study by Parsonson (1995) had found no significant difference between monthly rainfall totals at Waitomo and Ruakuri. Therefore the Waitomo station records were used to estimate accumulated rainfall totals between sampling intervals. Aranui Cave is located between the two sites and so the surface above the cave can be considered to receive approximately the same mean annual rainfall as Waitomo (1618 mm). Since the ground surface above Aranui Cave is covered by unmodified natural podocarp-hardwood forest, annual evapotranspiration losses above the cave will be at least 650 mm, judging from a water balance estimate for the Waitomo catchment (Hawke, 1982).

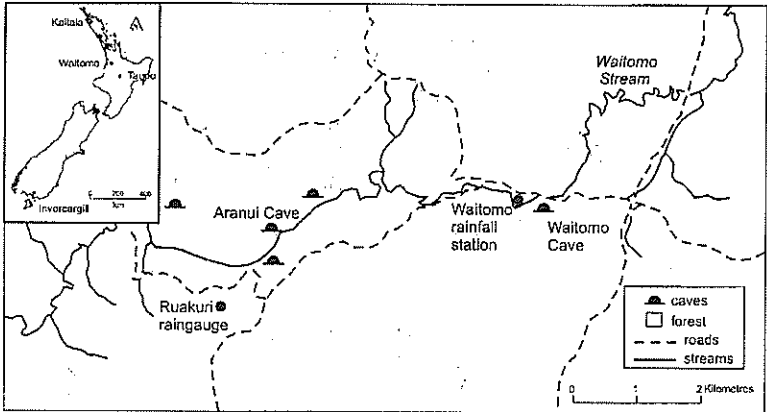


Figure 1 – Location of Waitomo and Aranui Cave. The inset shows other sites mentioned in the text.

Percolation water samples were obtained from Aranui Cave, which is well decorated with stalactites and stalagmites and is a tourist cave, although visitor numbers are relatively small and lights are extinguished between visits. It is located about 60 m above the Waitomo stream (Figure 2). The cave is part of an abandoned stream passage and is approximately horizontal. It has only one narrow entrance and is blocked by rockfall and speleothem deposition at its inner end; thus limiting air circulation and minimizing evaporation. The cave is permanently wet as a consequence of continuous percolation, although there is marked seasonal variability in the number of seepage points and drip rates. The cave atmosphere should thus be at or close to 100% relative humidity all year, although no measurements have been made to confirm this.

Three percolation sites were established in the cave to cover a spectrum of fast, medium and slow rates of flow. In order to minimize the possible influence of evaporation, sites were located in the innermost recesses of the cave, beyond the limit of tourist access (Figure 2). The bedrock above the sites is entirely limestone, but may in places be overlain by thin patches of incompletely eroded but weathered mudstone. Soils are up to 2 m thick and developed on volcanic ash parent materials.

Percolation sites A and B were at the end of the northeastern arm of the cave, approximately 60 m vertically below the surface. Site A was a fast drip, with water seeping from a ceiling fissure over a stalactite. Site B was a slower drip from an adjacent fissure, also flowing over a stalactite, and was situated within about two metres of site A. Site C was at the end of the

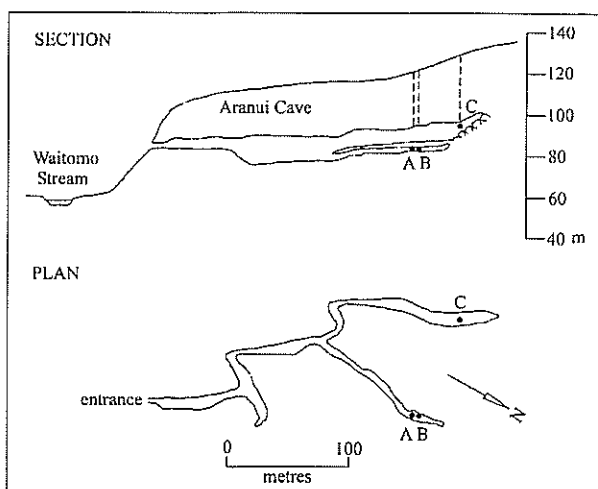


Figure 2 – Aranui Cave and the location of seepage water sampling sites A, B and C.

northwestern arm of the cave, approximately 40 m below the surface. It was a very slow drip, with water emerging from within the end of a hollow straw stalactite a few millimetres in diameter. The hydrology of the seepage sites sampled thus differed: sites A and B involved water flowing over speleothem surfaces, whereas site C comprised water emerging from a capillary passage through the interior of a straw.

Cave temperature estimates were based primarily on measurements made in Ruakuri Cave (located beneath the raingauge site) and Gardners Gut Cave, which is a little further up the valley. Ruakuri was formerly a tourist cave, but has not been used for that purpose for about 10 years, so cave temperatures can be considered natural. Gardners Gut is a wild cave. Subterranean rock wall temperature had been determined in Ruakuri Cave by de Freitas (1999) from spot measurements using an infrared radiometer. These averaged 12.8° C and were found to correspond exactly to the mean of a 5 month period of continuous air temperature measurement at the same site from July to December 1998. In Gardners Gut Cave in June 2001, spot measurements by the author using the same infrared radiometer showed a range of values from 10.5–11.9° C; whereas in Aranui Cave readings ranged from 12.2–13.4° C. Hence it is probable that tourist activity in Aranui has slightly elevated the temperature. The natural temperature of caves in the area clearly varies from place to place within a cave as well as over different seasons. A value of 12.8° C was adopted as representative of natural interior cave temperatures in the region. For comparison, the average surface air temperature from a 71-year record at Ruakura meteorological station, 60 km to the NNE and at a slightly lower altitude, is 13.4° C.

Methods

Water samples were stored at 4°C prior to analysis. Stable isotope determinations were made at the NZ Institute of Geological and Nuclear Sciences. Changes in the oxygen isotope ratio are reported in delta units (Stewart and Taylor, 1981; Coplen, 1994; Kendall and Caldwell, 1998), which are parts per thousand (per mil) deviations of the isotopic ratio from a standard; thus

$$\delta \text{ (in ‰)} = ((R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}) \cdot 1000 \quad (1)$$

where R is the ratio of the heavy to light isotope. The standard for oxygen isotopes in water is Vienna Standard Mean Ocean Water (V-SMOW) and for calcite is a fossil belemnite V-PDB. Delta $^{18}\text{O}_{\text{VPDB}}$ values are reported to two decimal places with an error of ± 0.02 and $\delta^{18}\text{O}_{\text{VSMOW}}$ values are reported to two decimal places with an error of ± 0.1 . Friedman and O'Neil (1977) provide expressions that show the relationship between the two:

$$\delta_{\text{SMOW}} = 1.03086 \delta_{\text{PDB}} + 30.86 \quad (2)$$

$$\delta_{\text{PDB}} = 0.97006 \delta_{\text{SMOW}} - 29.94 \quad (3)$$

It is possible to estimate the temperature (T) of the cave at the time when the speleothem was deposited from the $\delta^{18}\text{O}_c$ (c = calcite), relative to PDB, and $\delta^{18}\text{O}_w$, relative to SMOW, by using equations based on O'Neil *et al.* (1969). Hays and Grossman (1991) developed the expression

$$T \text{ (°C)} = 15.7 - 4.36 (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w) + 0.12 (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w)^2 \quad (4)$$

and Genty *et al.* (2002) the alternative expression

$$T \text{ (°K)} = [2780 / \{\ln [(1+10^{-3} * \delta^{18}\text{O}_c) / (1 + 10^{-3} * \delta^{18}\text{O}_w)] + 0.00289\}]^{-2} \quad (5)$$

where $\delta^{18}\text{O}_c$ and $\delta^{18}\text{O}_w$ are with respect to PDB and SMOW respectively.

Rain water samples were collected in a standard raingauge that was countersunk into the soil to reduce exposure and damage from grazing stock (though some losses still occurred). Medical quality liquid paraffin was added to the gauge to provide a surface seal to prevent evaporation of the accumulated water.

Percolation water from the cave was sampled in two ways. At the two sites (A and B) where water tricked over stalactite surfaces, water was captured in funnels and led by flexible plastic hoses into large plastic bottles. The screw top bottle caps were pierced for the hoses to reach the base of the containers, allowing air to escape as the vessels filled. At site C water drops emerged from the interior of a hollow straw stalactite. This was captured by sliding a small diameter flexible plastic hose over the end of the straw and leading it through a pierced cap into a small narrow-necked plastic bottle.

Possible overflow (which only occurred at site A) was therefore permitted, while still restricting air circulation and inhibiting evaporation.

The electrical conductivity of seepage waters at 25°C was measured in the laboratory.

Oxygen isotopic composition of rain waters

In their investigations of the stable isotopic composition (hydrogen and oxygen) of New Zealand rain waters, surface and ground waters, Stewart and Taylor (1981), Stewart (1983, 1987) and Taylor (1990) found the usual linear relationship described by the meteoric water line (Craig, 1961) to apply, although with minor adjustment to the coefficients. For Kaitaia, monthly average isotopic measurements from rain waters have been published for the period 1963 to 1991, although with some breaks in the record (Taylor, 1990). The average $\delta^{18}\text{O}_p$ value of annual means for 17 years is -4.45‰ , although the means of individual years vary within a range of -3.74 to -5.42‰ . If weighted for the amount of precipitation, the average $\delta^{18}\text{O}_p$ value for the 17 years is somewhat lighter at -4.85‰ .

The positive correlation between $\delta^{18}\text{O}_p$ and condensation temperature identified by Dansgaard (1964) appears to hold at Kaitaia, with values being less negative in summer. Despite the scatter, the relationship illustrated in Figure 3 is significant at the 0.01 level. The annual pattern of $\delta^{18}\text{O}_p$ values shows a seasonal variation, with the winter six months (April-September) averaging -5.51‰ compared to -4.19‰ in the summer half of the year, a seasonal difference of 1.32‰ (Figure 4). A volume effect is also evident, with $\delta^{18}\text{O}_p$ values at Kaitaia varying inversely with rainfall amount (Figure 5a). Individual monthly values span a range from less than -1‰ to almost -10‰ . The most negative values can probably be accounted for by high altitude condensation in thunderstorms, which involves both low temperatures and large volumes of rain, and the least negative values by enrichment caused by evaporation of water droplets in the atmosphere during lighter summer rains. In Tasmania, Goede *et al.* (1982) noted the rainfall effect to be especially noticeable in summer, although this is not the case at Kaitaia (Figure 5b). There are significant inverse relationships of average monthly $\delta^{18}\text{O}_p$ values to rainfall in intervals dominated by La Niña or El Niño conditions at Kaitaia (Figure 5c), but the slopes of the regressions are not significantly different.

At Ruakuri rain water samples were collected at approximately monthly intervals between June 1998 and June 2000. The arithmetic average $\delta^{18}\text{O}_p$ value was -5.38‰ and the precipitation-weighted mean was -5.32‰ , which is within analytical error of the former. From this limited sample, therefore, Ruakuri rain appears to be 0.47‰ more negative than rain at Kaitaia. This

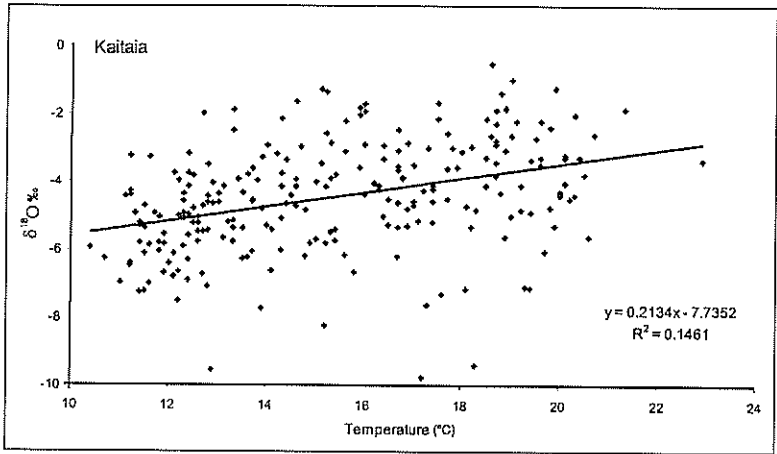


Figure 3 – Relationship of mean monthly $\delta^{18}\text{O}_{\text{VSMOW}}$ values of rain water to mean monthly surface temperature at Kaitaia (1963-1991).

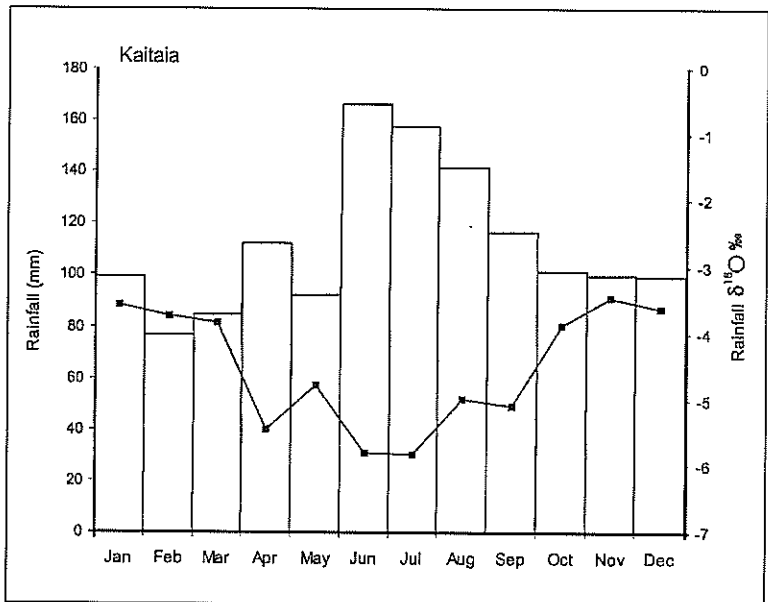


Figure 4 – Annual variation of mean monthly rainfall amount and mean monthly $\delta^{18}\text{O}_{\text{VSMOW}}$ values of rain water at Kaitaia (1963-1991). Note the strong correlation between $\delta^{18}\text{O}_{\text{VSMOW}}$ values and season, with more negative δ -values in winter months.

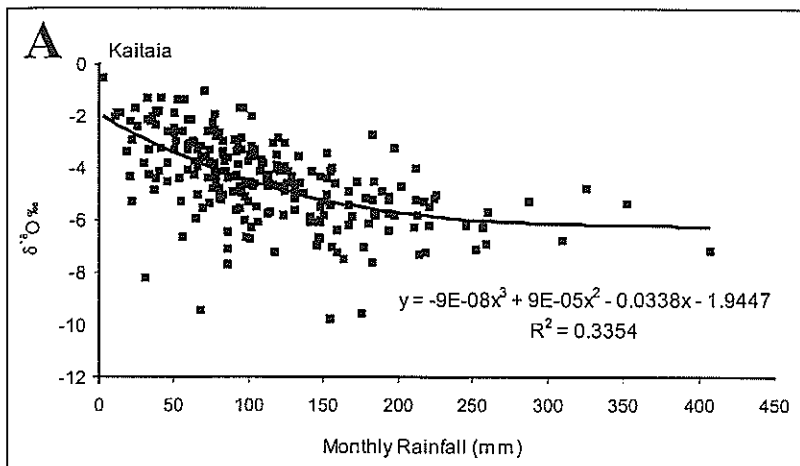


Figure 5A – Relationship of mean monthly $\delta^{18}\text{O}_{\text{VSMOW}}$ values of rain water to total monthly rainfall at Kaitaia (1963-1991).

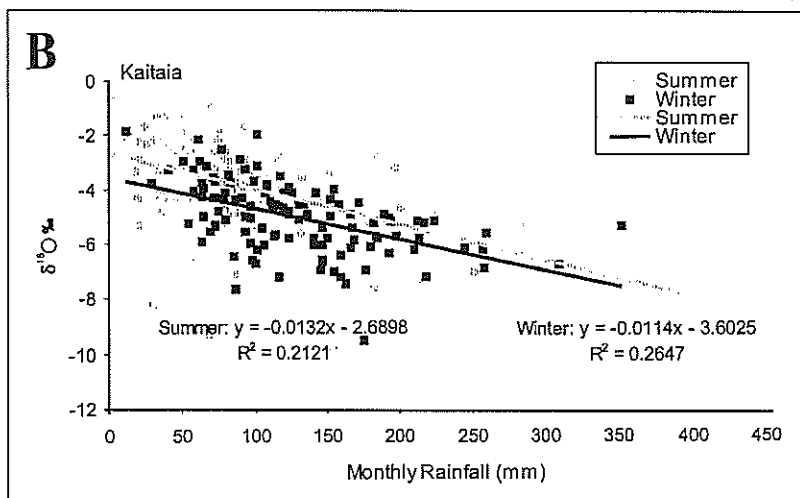


Figure 5B – Relationship of mean $\delta^{18}\text{O}_{\text{VSMOW}}$ values of rain water for 'summer' and 'winter' months to total monthly rainfall for the same six-monthly periods. In both winter and summer δ -values are more negative as rainfall increases.

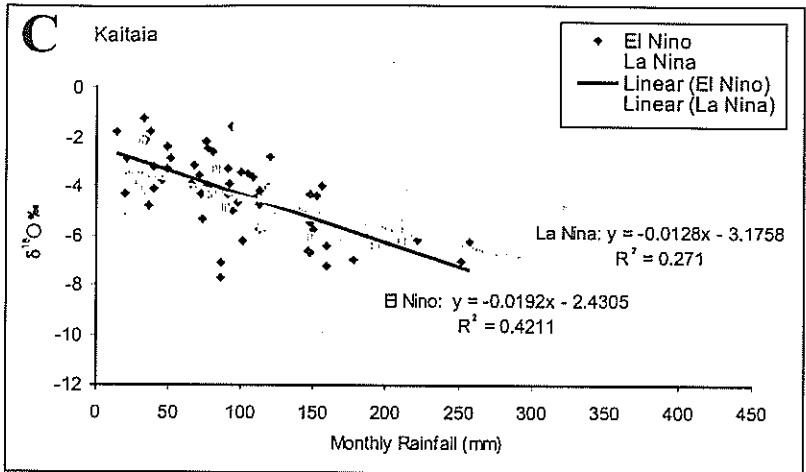


Figure 5C – Relationship of mean $\delta^{18}\text{O}_{\text{VSMOW}}$ values of rain water and rainfall amounts for months dominated by El Niño and La Niña conditions. Both relationships are statistically significant at the 0.01% level.

difference is consistent with a latitudinal effect; rain water has progressively more negative average $\delta^{18}\text{O}$ values in New Zealand stations with increasing latitude (Taylor, 1990). A comparison of mean $\delta^{18}\text{O}_p$ values at Kaitaia and Invercargill (data from Taylor, 1990) indicates a gradient along the length of New Zealand of 0.19‰ per degree latitude, which implies that rainfall at Waitomo should be 0.58‰ more negative than at Kaitaia. The short-term record at Waitomo may thus slightly over-estimate the long-term average.

The oxygen isotope composition of the rainfall at Ruakuri can be seen from Figure 6 to be highly variable throughout the period of observation, although seasonal variation is still discernable from mean values. The precipitation-weighted $\delta^{18}\text{O}_p$ values for April to September average -6.42‰ , compared to -4.22‰ for October to March: a seasonal difference of 2.2‰ . Seasonality is also clearly evident in the 10-year record at Taupo (Taylor, 1990), which is about 100 km southeast of Ruakuri and at 290 m higher elevation. However, at Ruakuri the effect of varying rainfall (Figure 7a) is not as evident as at Kaitaia (Figure 4), even if analysed on a seasonal basis (Figure 7b). This could be either because the same relationship does not exist or because the sample size of only 22 determinations is insufficient to reveal it. The latter may be the case because the weak relationship shown in Figure 7a is an inverse one.

It can be concluded, therefore, that the Ruakuri $\delta^{18}\text{O}_p$ values fall within the range observed at Kaitaia and are consistent with rain water in the winter

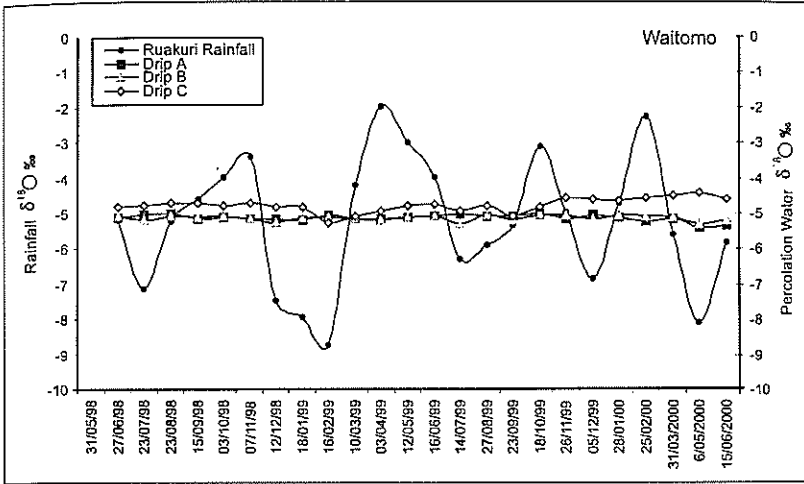


Figure 6 – Stable isotope composition of rainfall and percolation waters at Waitomo, as indicated by rain water from the Ruakuri rain gauge site and percolation waters from three seepage points in Aranui Cave. The $\delta^{18}\text{O}_{\text{VSMOW}}$ value of percolation waters is very close to the average rainfall value.

half of the year being more negative than that which falls in summer. Nevertheless, the statistical relationships found at Kaitaia are not revealed strongly in the Ruakuri data, perhaps because of the very much smaller sample size.

Oxygen isotope values in percolation waters

Percolation water samples were taken from the three seepage sites in Aranui Cave on the same day as rain water samples were collected from Ruakuri rain gauge. The rock through which the percolation occurs is a thinly bedded pure Oligocene limestone with a $\delta^{18}\text{O}_{\text{PDB}}$ value of -3‰ (Williams *et al.*, 1999). The thick soil above the cave regulates the rate of infiltration into the underlying limestone, with ponding after heavy rain showing that its infiltration capacity is less than that of bare karstified rock, where ponding never occurs except in very small solution cups.

The volume of seepage water that accumulated between sampling intervals was measured, although the 25 litre vessel used for accumulating seepage from drip A usually overflowed, and average daily seepage rates during sampling intervals were calculated. Over the two-year observation period, the average seepage rate of Drip B was 38 ml/day, with a range of 25–54 ml/day; and for Drip C was 2 ml/day, varying from 0.3–4.3 ml/day. Occasional daily to weekly observations showed that the average seepage

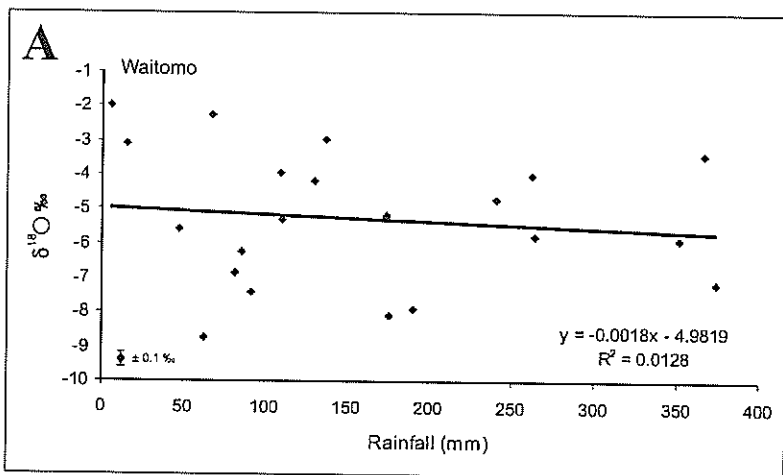


Figure 7A – Relationship of $\delta^{18}\text{O}_{\text{VSMOW}}$ value of rain water at the Ruakuri raingauge site to rainfall amount for the same (approximately monthly) intervals at Waitomo. The relationship is not statistically significant.

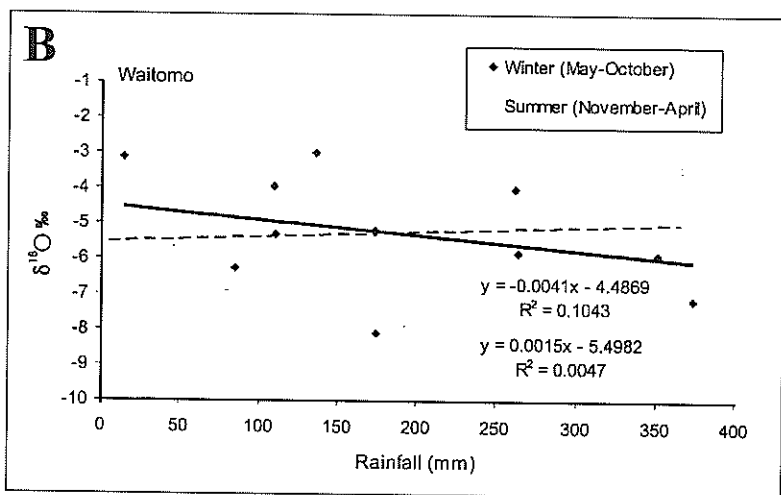


Figure 7B – Relationship of seasonal $\delta^{18}\text{O}_{\text{VSMOW}}$ values of rain water at the Ruakuri site to seasonal rainfall amount at Waitomo. The relationships are not statistically significant.

rate of Drip A sometimes exceeded 3 litres/day, and two spot measurements indicated Drip A to yield 127–225 ml/hour when Drip B yielded 1.3–2.6 ml/hour. Short-term measurements therefore reinforced the point that seepage rates vary over several orders of magnitude between sites.

Continuous measurement of Drip A over a 5 month period from summer to early winter by Parsonson (1995) revealed the percolation rate to vary considerably and to show a lag of 3 to 5 weeks with respect to rainfall (Figure 8a), although the reasons for the variability of the lag have not been determined. The monthly relationship for Drips B and C over the two year sampling period is shown in Figure 8b. The forcing mechanism that causes drip rate to respond to precipitation events is assumed to be a pressure pulse effect associated with recharge during rain that forces out 'old' water already in transit (Williams, 1993); the pressure wave in the Aranui Cave limestones travels at about 2 m/day. This contrasts with the actual flow-through time of the water, which is much longer. The δ -value of water being 'pulsed out' could thus relate to the recharge of water from storms that occurred some months previously. In principle, one way of measuring the flow-through time would be to match the δ -value pattern of rainfall with that of seepage water, but in practice the recharge is so well mixed in the epikarst that a clear signal is not transmitted through the zone.

The oxygen isotope composition of percolation waters from Aranui Cave is presented in Figure 6. Three earlier samples of Drip A taken between May and June 1995 had $\delta^{18}\text{O}_{\text{SMOW}}$ values of -5.06 to -5.17‰ , which is within the range shown here. Drips A and B have arithmetic mean values of -5.12‰ and -5.13‰ respectively, which are mutually indistinguishable given the $\pm 0.1\text{‰}$ precision of measurements. However, their electrical conductivity values are quite different, with Drip A having an average conductivity of $398\ \mu\text{S}$ compared to $313\ \mu\text{S}$ for Drip B. This indicates that although they have a similar source of meteoric water, they have different histories of transit and dissolution through the rock. The much faster flowing Drip A had a significantly wider range of δ -values than Drip B, with -4.99 to -5.39‰ compared to -5.07 to -5.29‰ respectively. By contrast, Drip C (from the interior canal of a straw) was more positive, with an arithmetic mean $\delta^{18}\text{O}_{\text{SMOW}}$ value of -4.77‰ , and it displayed a greater range of variability, from -4.42 to -5.25‰ . Its conductivity was also much lower, averaging $280\ \mu\text{S}$, which by comparison to Drips A and B suggests a dissolutional history closer to a sequential than a coincident system (Ford and Williams, 1989).

If $\delta^{18}\text{O}$ values are weighted by seepage volume, the values for Drips A, B and C are statistically indistinguishable from their arithmetic mean values. The mean $\delta^{18}\text{O}_{\text{SMOW}}$ value of the three drips is -5.0‰ , which is only slightly more positive than the weighted mean annual Ruakuri rain water value of

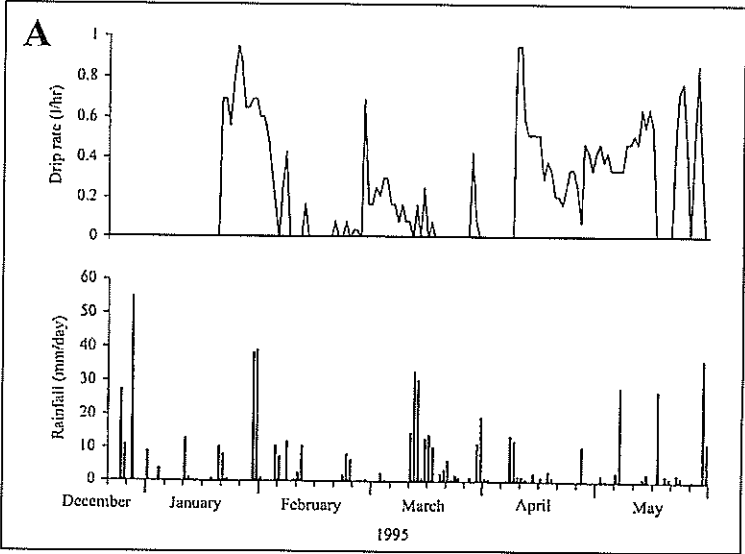


Figure 8A – Relationship of daily rainfall at Ruakuri near Waitomo to seepage water discharge rate at site A in Aranui Cave. The rainfall record starts on 24 December, 1994, and the percolation record on 19 January, 1995. The records suggest that drip rate variations lag rainfall by 3 to 5 weeks (from Parsonson, 1995).

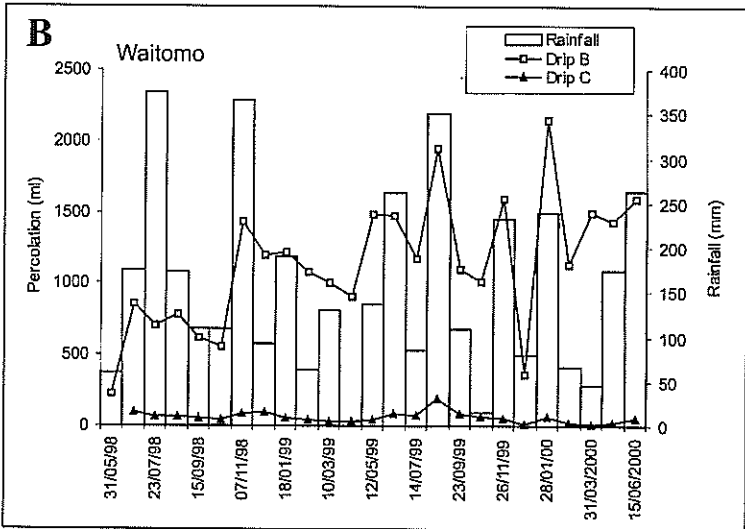


Figure 8B – Relationship of approximately monthly rainfall total to percolation rates of drips B and C in Aranui Cave.

-5.32 ‰ and lies between its six-monthly seasonal means of -4.22 ‰ in summer and -6.42 ‰ in winter. Seepage values in the cave are therefore very close to average rainfall values. They may err slightly on the side of summer recharge over the observation period, although given the effect of epikarstic mixing and flow-through lag, the percolation waters sampled would have had a significant component of water that recharged the area before rainfall sampling began. One might have expected that most summer rain would not contribute to recharge, because of evapotranspiration losses, and that seepage water might thus more closely reflect winter δ -values. But even summer rainfall can have strongly negative values, especially the heavy rain that would make the largest contribution to recharge.

It is difficult to assess with precision the δ -value that is most representative of cave seepage as a whole. It is possible that a larger volume of recharge penetrates via a few rapid seepage pathways than through the very much larger number of very slow seepage routes, but there is insufficient evidence to calculate a seepage-weighted value for the entire cave. Nevertheless, from the above evidence, a $\delta^{18}\text{O}_w$ value in the range of -4.8 to -5.2‰ is reasonable, with -5‰ the best estimate (Figure 6).

Relationship between oxygen isotope values in percolation water and oxygen isotope values in speleothem calcite

Inserting into equation (4) cave temperatures of 12.6 to 13°C and $\delta^{18}\text{O}_{\text{SMOW}}$ values of -4.8 to -5.2‰, actively depositing speleothems at Waitomo in thermodynamic equilibrium with seepage water should have $\delta^{18}\text{O}_{\text{PDB}}$ values in the range of -4.1 to -4.6‰, but with a present day mean of about -4.35‰ $\delta^{18}\text{O}_{\text{PDB}}$. Assuming a cave temperature of 12.8°C, the same $\delta^{18}\text{O}_{\text{SMOW}}$ values in equation (5) suggest a present day mean in the range of -4.1 to -4.5‰, averaging about -4.29‰ $\delta^{18}\text{O}_{\text{PDB}}$. Hendy (1969) estimated an equilibrium $\delta^{18}\text{O}_{\text{PDB}}$ value of -3.7‰, although he used an earlier version of the equation and a cave temperature of 12.5°C. Measurements of $\delta^{18}\text{O}_{\text{PDB}}$ from the tips of growing stalagmites and straws in the district were reported by Williams *et al.* (1999) in the range of -3.3 to -4.1‰. These have since been confirmed by other measurements (Williams *et al.*, 2002). Three new determinations of actively precipitating calcite in Aranui had $\delta^{18}\text{O}_{\text{PDB}}$ values of -2.69 to -3.34‰. The less negative values are almost certainly indicative of non-equilibrium deposition caused either by evaporation or kinetic fractionation (Hendy, 1971).

Given the uncertainties in determining both the most representative $\delta^{18}\text{O}_w$ value and the most representative cave temperature, coupled with experimental error and our current understanding of oxygen isotope fractionation (Kim and O'Neil, 1997), some latitude must apply to

interpretation of $\delta^{18}\text{O}_{\text{PDB}}$ values from speleothems. However, speleothem calcite deposited in thermodynamic equilibrium with seepage water in the Waitomo region would be expected to have $\delta^{18}\text{O}_{\text{PDB}}$ values of about $-4.3 \pm 0.25\text{‰}$.

Conclusions and discussion

Rain water at Waitomo has $\delta^{18}\text{O}$ values that vary considerably throughout the year (Figure 6), although six-monthly means reveal a seasonal distinction, with summer rains (-4.2‰) being slightly more enriched in ^{18}O than winter rains (-6.4‰). By contrast, water percolating into Aranui Cave shows no discernible seasonal variability in δ -values (Figure 6) and has an arithmetic mean of -5.0‰ , which is close to the weighted mean value of rainfall of -5.3‰ . This supports the findings of Goede *et al.* (1982) in Tasmania and Yonge *et al.* (1985) in North America on the general relationship of the δ -values of cave seepage waters and rainfall.

Individual seepage points in Aranui Cave showed minor differences over the two year observation period in $\delta^{18}\text{O}_{\text{SMOW}}$ values, which ranged from -4.4‰ to -5.4‰ . However, since only three seepage sites were monitored, more extreme values could be encountered elsewhere. For comparison, five seasonally monitored sites in GB Cave in England were reported by Dennis *et al.* (2001) to have average values of -7.9‰ to -9.1‰ , which is a slightly greater range. Thus the representative $\delta^{18}\text{O}_{\text{w}}$ value for any given cave is best reported as a range of average values for individual percolation points around an overall mean. For Aranui Cave, a reasonable assessment is -4.8‰ to -5.2‰ , averaging -5.0‰ .

The $\delta^{18}\text{O}_{\text{w}}$ values from Aranui Cave seepage waters and $\delta^{18}\text{O}_{\text{c}}$ values of deposition on speleothems in the Waitomo region imply that if deposition occurs under thermodynamic equilibrium at today's temperature ($12.8 \pm 0.2^\circ\text{C}$), then calcite $\delta^{18}\text{O}_{\text{PDB}}$ values will fall in the range of -4.1‰ to -4.6‰ with a central tendency towards -4.3‰ . Such values are at the negative end of the spectrum of $\delta^{18}\text{O}_{\text{PDB}}$ values reported by Williams *et al.* (1999) for caves in the Waitomo region, which suggests that some actively depositing speleothems are not in isotopic equilibrium with seepage waters.

Acknowledgements

Peter Crossley is thanked for assistance in the field and laboratory, Darren King for cartography, and Victoria Smith for analytical work in the early stages of the research. We are especially grateful to Kevin Faure, who made many suggestions that improved the manuscript.

References

- Coplen, T.B. 1994: Reporting of stable hydrogen, carbon and oxygen abundances. *Pure and Applied Chemistry* 66: 2423-2444.
- Chapman, J.B.; Ingraham, N.L.; Hess, J.W. 1992: Isotopic investigation of infiltration and unsaturated zone flow processes at Carlsbad Cavern, New Mexico. *Journal of Hydrology (Netherlands)* 133: 343-363.
- Craig, H. 1961: Isotopic variations in meteoric waters. *Science* 133: 1702-1703.
- Dansgaard, W. 1964: Stable isotopes in precipitation. *Tellus* 16: 436-468.
- Dennis, P.F.; Rowe, P.J.; Atkinson, T.C. 2001: The recovery and isotopic measurement of water from fluid inclusions in speleothems. *Geochimica et Cosmochimica Acta* 65 (6): 871-884.
- de Freitas, C. 1999: Atmospheric conditions in the cave, in Williams, P.W. (compiler) *The Current State of the Ruakuri Cave Environment*. Unpublished Report, Department of Geography, University of Auckland: 10-14.
- Ford, D.C.; Williams, P.W. 1989: *Karst Geomorphology and Hydrology*. London. Unwin Hyman, 601p.
- Friedman, I. and O'Neil, J.R. 1977: Compilation of stable isotope fractionation factors of geochemical interest. In M. Fleischer (ed.) *Data of Geochemistry* (sixth edition), Chapter KK.
- Gascoyne, M. 1992: Palaeoclimate determination from cave calcite deposits. *Quaternary Science Reviews* 11: 609-632.
- Genty, D., Plagnes, V., Causse, C., Cattani, O., Stievenard, M., Falourd, S., Blamart, D., Ouahdi, R., and Van-Exter, S. 2002: Fossil water in large stalagmite voids as a tool for paleoprecipitation stable isotope reconstitution and paleotemperature calculation. *Chemical Geology* 184: 83-95.
- Goede, A.; Green, D.C.; Harmon, R.S. 1982: Isotopic composition of precipitation, cave drips and actively forming speleothems at three Tasmanian cave sites. *Helictite* 20: 17-29.
- Hawke, D.V. 1982: *Fluvial processes in the upper Waitomo catchment*. Unpublished PhD thesis, University of Auckland.
- Hays, P.D.; Grossman, E.L. 1991: Oxygen isotopes in meteoric calcite cements as indicators of continental paleoclimate. *Geology* 19: 441-444.
- Hendy, C.H. 1969: The isotopic geochemistry of speleothems and its application to the study of past climates. Unpublished PhD thesis, Victoria University, Wellington.
- Hendy, C.H. 1971: The isotopic geochemistry of speleothems- I. The calculation of the effects of different modes of formation on the isotopic composition of speleothems and their applicability as palaeoclimatic indicators. *Geochimica et Cosmochimica Acta* 35: 801-824.
- Hendy, C.H.; Wilson, A.T. 1968: Palaeoclimatic data from speleothems. *Nature* 216: 48-51.
- Hill, C.; Forti, P. (eds) 1997: *Cave Minerals of the World*. National Speleological Society, Huntsville, Alabama, 2nd edition. 463 p.

- Kendall, C.; Caldwell, E.A. 1998: Fundamentals of isotope geochemistry. In Kendall, C.; McDonnell, J.J. (eds), *Isotope Tracers in Catchment Hydrology*. Elsevier, Amsterdam: 51-86.
- Kim, S.-T.; O'Neil, J.R. 1997: Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochimica et Cosmochimica Acta* 61 (16): 3461-3475.
- Lauritzen, S.-E.; Lundberg, J. 1999: Speleothems and climate: a special issue of *The Holocene*. *The Holocene* 9 (6): 643-647.
- O'Neil, J.R.; Clayton, R.N.; Mayeda, T.K. 1969: Oxygen isotope fractionation in divalent metal carbonates. *Journal of Chemical Physics* 51: 5547-5558.
- Parsonson, M.J. 1995: Percolation processes in the unsaturated zone, Waitomo, New Zealand. Unpublished MSc thesis, University of Auckland.
- Stewart, M.K., Cox, M.A., James, M.R. and Lyon, G.L. 1983: Deuterium in New Zealand rivers and streams. New Zealand Institute of Nuclear Sciences INS-R-320, 29 p.
- Stewart, M.K. 1987: Distribution of D and ^{18}O in New Zealand rainfall and the isotopic identification of groundwater recharge sources. *Proceedings Groundwater Chemistry Workshop*, Auckland Regional Water Board Publication 41: 123-138.
- Stewart, M.K.; Taylor, C.B. 1981: Environmental isotopes in New Zealand hydrology. 1 Introduction: the role of oxygen-18, deuterium, and tritium in hydrology. *New Zealand Journal of Science* 24: 295-311.
- Stewart, M.K., Cox, M.A., James, M.R., Lyon, G.L. 1983: Deuterium in New Zealand rivers and streams. *New Zealand Institute of Nuclear Sciences* INS-R-320, 29p.
- Taylor, C.B. 1990: Stable isotope compositions of monthly precipitation samples collected in New Zealand and Rarotonga. *New Zealand Department of Scientific and Industrial Research*, Physical Sciences Report 3, ISSN1170-4438.
- Wigley, T.M.L., and Brown, M.C. 1976: The physics of caves. In *The Science of Speleology*, T. Ford & C.H.D. Cullingford (eds). London, Academic Press: 329-58.
- Williams, P.W. 1993: Climatological and geological factors controlling the development of polygonal karst. *Zeitschrift für Geomorphologie Suppl.-Bd 93*: 159-173.
- Williams, P.W.; Marshall, A.; Ford, D.C.; Jenkinson, A.V. 1999: Palaeoclimate interpretation of stable isotope data from Holocene speleothems of the Waitomo district, North Island, New Zealand. *The Holocene* 9(6): 649-657.
- Williams, P.W.; King, D.N.T.; Zhang, J.-X.; Collerson, K.D. 2002: Speleothem master chronologies and Holocene palaeotemperature interpretation from the North Island of New Zealand. *The Holocene* (in review).
- Yonge, C.J.; Ford, D.C.; Gray, J.; Schwarcz, H.P. 1985: Stable isotope studies of cave seepage water. *Chemical Geology* 58: 97-105.

**Manuscript received: 3 July 2001; accepted for publication:
18 February 2002.**