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# The age and hydrological history of Blue Lake, South Australia

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## Abstract

Three sediment cores from the Blue Lake, a groundwater fed lake of volcanic origin in South Australia, have been investigated using a range of chemical and isotopic parameters. The <sup>14</sup>C activity of both the inorganic and organic carbon fractions of the sediment decreases monotonically with depth. The rate of change with depth is greater for near-surface samples with an apparent hiatus in sedimentation rate at about 7000 yr B.P. Estimates of age for the precipitated authigenic carbonate, after correction for dilution with dead carbon from the groundwater, agree well with calculated ages from the organic carbon fraction of the sediment. We suggest the lake is much older than previously proposed using other dating techniques.

Variations in the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  composition of the authigenic carbonate reflect different residence times of dissolved inorganic carbon and water in the lake caused by changes in the lake level. During periods of hydrologic steady-state, it is suggested that relative changes in the temperature of the lake can be seen in  $\delta^{18}\text{O}$  changes in authigenic carbonate.

Blue Lake has been undergoing sedimentation for at least 28,000 years, including two lengthy periods of hydrologic steady state. The lake, for a large proportion of its existence, was much shallower while for the last 7000 years has maintained a level close to the present one. The influence of pumping from the lake for urban water supply during this century is reflected in the isotopic composition of carbonate in the sediment.

## 1. Introduction

Blue Lake is the largest of three lakes formed in a volcanic complex in south-east South Australia (Fig. 1). Due to its importance as the major source of water for the city of Mount Gambier, there is considerable interest in establishing its water balance. (Turner et al., 1984; Ramamurthy et al., 1985). In addition, there has been considerable effort establishing the geological history of the volcanic complex and that of the surrounding area (Sheard, 1978; Barton and McElhinny, 1980; Barbetti and Sheard, 1981; Blackburn et al., 1982).

This study uses a combination of stable isotope ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for carbonate and organic carbon fractions), and <sup>14</sup>C dating of lake sediment

to establish a hydrological history of the lake from its formation to the present-day.

## 2. The age of the Crater Lakes

Researchers have approached the dating of the crater lakes in this area by either dating material associated with the volcanic activity when the lake was thought to have formed (i.e dating the volcanics) or dating sediment from within the lake.

### 2.1. Dating the volcanics

The volcanic complex, in which the Blue Lake is situated, lies on the western border of the Newer

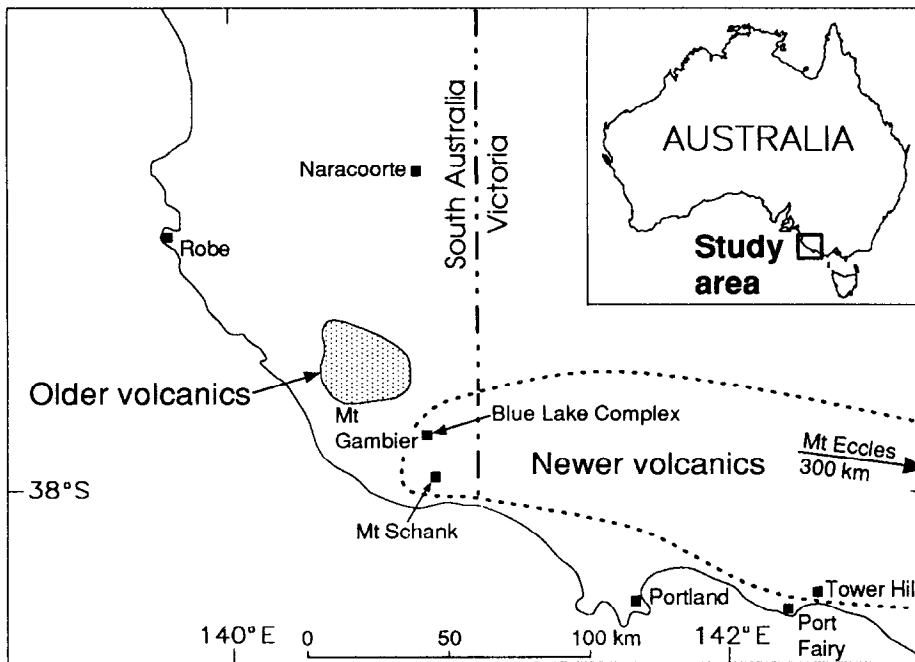


Fig. 1. Location map.

Volcanic region covering a large proportion of central and western Victoria and the south east of South Australia. Included in this group of Newer Volcanics until recently were the volcanic complexes at Tower Hill and Mt. Eccles located approximately 150–200 km east of the Mt. Gambier complex. These areas were thought to be formed 7000–8000 years ago (Gill, 1972). A group of 16 eruptive centres is located approximately 30 km to the northwest of the Blue Lake complex. Although definite ages are unknown for these “Older Volcanics”, they may range from  $10^6$  to 20,000 yr B.P. (Solomon, 1951; Sprigg, 1952; Firman, 1969).

The Blue Lake complex and that of Mt. Schank, located 10 km to the south of the Blue Lake, lie within sands stratigraphically above those of the northern group and are therefore thought to be younger than the Older Volcanics (Barbetti and Sheard, 1981). A radiocarbon age of  $18,100 \pm 350$  yr B.P. (Polach et al., 1978) has been given for a sample of soft charcoal below the associated tuff from Mt Schank. However, dating by thermoluminescence of volcanic debris in the area suggests

an age of about 5000 years (Smith and Prescott, 1987).

Sheard (1978) suggested that the age of formation of the Mt Gambier complex was less than 5000 yr B.P. from 2 dates for charcoal associated with volcanic tuff around the volcanic complex while Blackburn et al. (1982) found a considerable range in  $^{14}\text{C}$  age (400–8000 yr B.P.) for a further 11 samples of charcoal.

Hence, from dating volcanics associated with the its formation, Blue Lake was believed to be included in the “Newer” volcanics and was thought to be, at most, 7000–8000 years old. Moreover, there is a considerable range in the suggested age of the lake from dating this type of material in this environment.

## 2.2. Dating of sediment

There have been few studies dating lake sediments from the “Newer” volcanics region because of difficulties finding large enough samples containing organic carbon to date (pre-AMS) and/or

finding a method to correct for  $^{14}\text{C}$  dilution via dead carbon (see appendix).

Barton and McElhinny (1980) found ages for organic sediment in a shallower lake in the same volcanic complex as Blue Lake increased consistently up to about 6000 yr B.P. with  $^{14}\text{C}$  ages of about 14,000 and 38,000 yr B.P. in layers of aragonite and calcareous tuff respectively recorded at greater depths. At the time of publishing, the older ages were discounted because of the possibility of  $^{14}\text{C}$  “dilution” with dead carbon. More recently, evidence from dating lake sediment (Head et al., 1991) suggests an age of formation of between 20,000 and 30,000 yr B.P., considerably older than the age suggested from dating volcanics.

Clearly, there is a trend in these studies for the sediment to apparently pre-date the formation of the lake as determined from dating volcanics.

### 2.3. This study

The Blue Lake has several attributes which make it particularly interesting to study and applicable to carbon dating. The lake is currently oligotrophic (Turner, 1979). The  $\delta^{13}\text{C}$  signature of the organic matter in the sediment is considerably depleted ( $< -26\%$ , see Fig. 11) indicating that organic material persisting in the sediment had a terrestrial rather than aquatic origin (Gupta and Polach, 1985). Electron microscopy showed that this material was most likely slivers of wood and charcoal 100–500  $\mu\text{m}$  in length and up to 100  $\mu\text{m}$  in diameter. Hence, no dilution effect has been assumed when calculating ages from the  $^{14}\text{C}$  activity of organic material. Hence,  $^{14}\text{C}$  dating of the organic fraction is possible without consideration of the “dilution effect” (sometimes called the hardwater effect). The carbonate in the lake sediment is largely authigenic and hence, dating of this fraction is possible if an estimate for the dilution in the  $^{14}\text{C}$  of the lake water (by incoming groundwater) can be made.

The major aim of this study was to infer historic changes in the water balance of the Blue Lake from the isotopic composition of sediment sampled. Changes in the water balance of the lake were inferred from excursions in the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  composition of the sediment while carbon dating

of organic and inorganic carbon fractions provided a time frame for these changes. Results of  $\delta^{13}\text{C}$  analyses on the carbonate sediment have been used to correct for the reduction in  $^{14}\text{C}$  activity of carbonate precipitating in a groundwater fed lake (the “dilution” effect).

In this paper, we suggest two methods to estimate this dilution effect with each method being applicable to different sections of the sediment core. Using this approach, two semi-independent estimates of age, based on dating the organic and inorganic carbon fractions, may be made for the sediment at any particular depth.

### 3. The environment of Blue Lake

The Blue Lake is located within the Gambier Embayment of the Otway Basin. It has the potential to be fed by two major aquifers: (1) the confined Dilwyn Formation which consists of interbedded sands and lignitic clays and (2) the unconfined Gambier Limestone which is predominantly bryozoal calcarenite (Fig. 2). These are separated by a confining layer of glauconitic silt several metres thick. The hydrogeological description of the region is given by Love (1992) and a detailed stratigraphy by Sheard (1978).

The lake bed is relatively flat with a mean depth of about 70 m, volume of  $37 \times 10^6 \text{ m}^3$  and a surface area of about  $6 \times 10^5 \text{ m}^2$ . The lake is steep-sided with a very small catchment and hence, runoff to the lake is low. Evaporation from the lake has been estimated at  $1200 \text{ mm yr}^{-1}$  (Turner, 1979) and exceeds the average rainfall by about 500  $\text{mm yr}^{-1}$ . The rate of pumping of water from the lake has increased markedly over the last 40 years (Fig. 3) and currently varies between  $3\text{--}4 \times 10^6 \text{ m}^3\text{yr}^{-1}$ . Groundwater input into the lake was estimated at  $5 \pm 1 \times 10^6 \text{ m}^3\text{yr}^{-1}$  in 1977/1978 (Turner, 1979). Despite the increases in pumping, the lake volume has only decreased marginally ( $< 5\%$ ; Turner, 1979) during this century.

While the water level of the Blue Lake is approximately the same as that of the surrounding unconfined aquifer, just north of the lake the potentiometric surface of the confined aquifer is about 9 m higher than the unconfined (Turner,

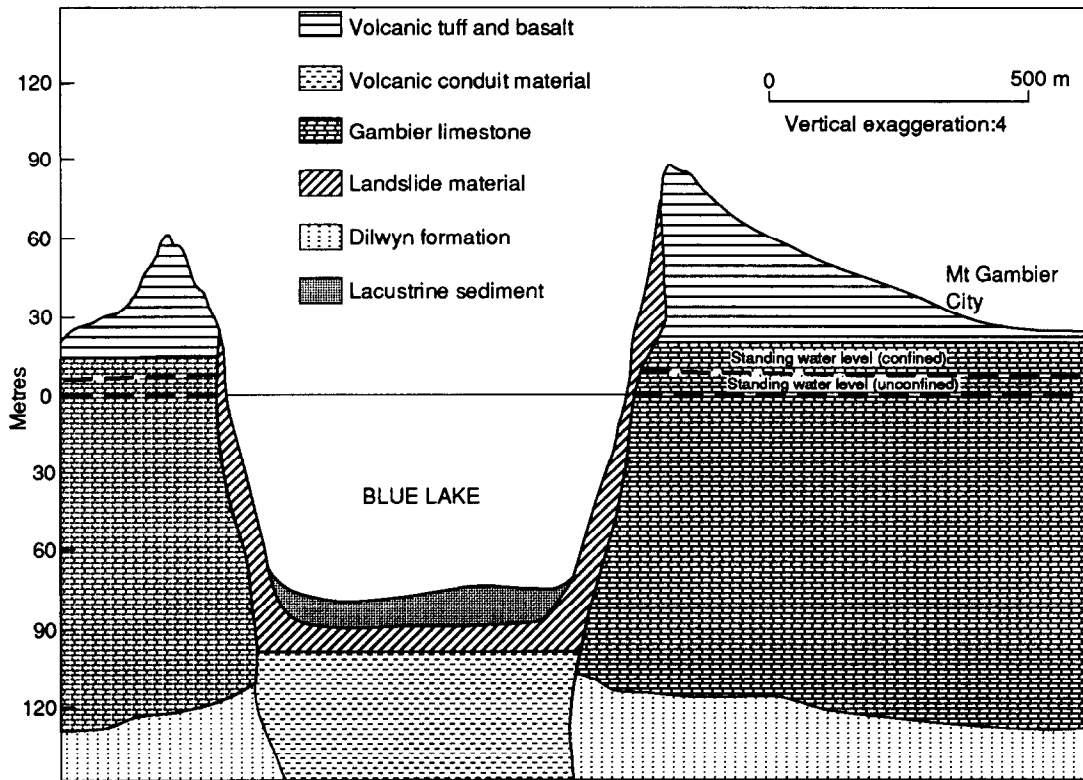


Fig. 2. Hydro-geological cross-section of the Blue Lake (from Sheard, 1978).

1979). Hence, there is hydraulic potential for upward leakage from the confined aquifer water into the lake. The currently accepted estimate for the unconfined:confined groundwater input to the lake is around 4:1 (Ramamurthy et al., 1985).

#### 4. Methods

Three sediment cores, each 5 m in length were taken at equi-spaced locations from the bottom of the lake using a Mackereth corer. The depth of water was 72 m at site 1 (shallowest part of the lake floor) and 78 m at the other two sites. In addition to these cores, a sample of the top 0.30 m of sediment was taken using a cold finger corer.

The Mackereth cores, stored in 50 mm polyvinyl chloride tubes, were frozen then cut lengthwise to give two half cylinders which were stored at a temperature of 3°C to prevent evaporation prior

to sampling and analysis. The cold finger core was sampled at 10 mm intervals, dried at 70°C and stored in glass vials upon arrival at the laboratory.

##### 4.1. Dry bulk density, particle size analysis and electron microscopy

Measurements of dry bulk density were made on all cores, except for the cold finger core, to permit correction for different degrees of compaction that may have occurred during collection or during sediment accumulation. For cores 1 and 2, 10 mm slices of sediment were removed at approximately 100-mm intervals over the length of the core, dried at 70°C for 12 hours and weighed. For core 3, the complete core was divided into 50 mm sections for density measurements.

For particle size analysis, a total of 130 samples were taken from the three cores and allowed to air dry. The relative amounts of sediment in the

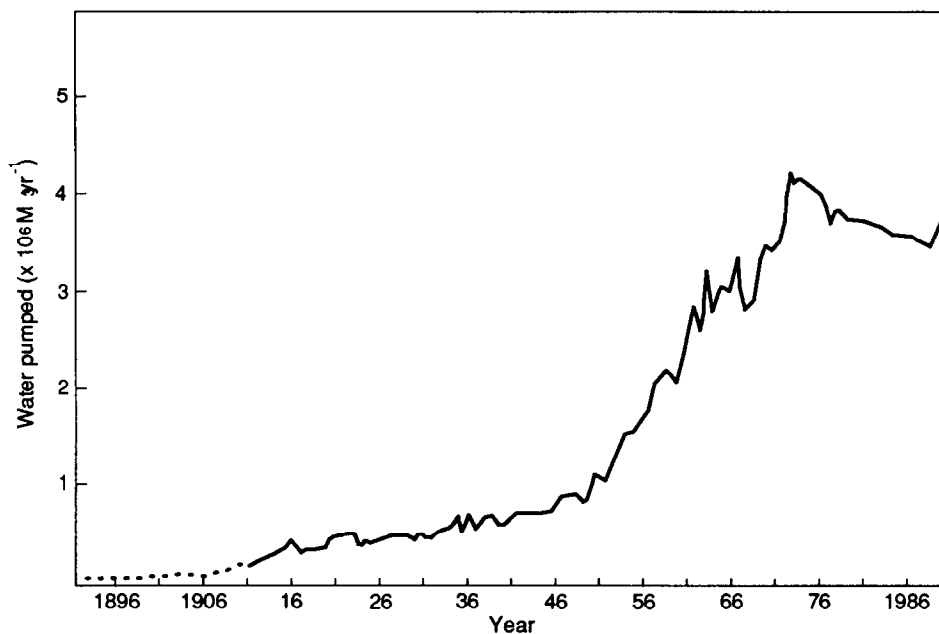


Fig. 3. Extraction of water from the Blue Lake for domestic supply.

ranges  $<20 \mu\text{m}$ ,  $20\text{--}200 \mu\text{m}$  and  $>200 \mu\text{m}$  were measured using a particle size settling method described by Lewis (1983) for 100 of the samples with a further 30 samples analysed in more detail ( $50 \mu\text{m}$  intervals from  $0\text{--}400 \mu\text{m}$ ). The particle fractions for 10 of the samples were determined by electron microscopy.

#### 4.2. $^{14}\text{C}$ analysis on carbonates and organic fractions

Sufficient sediment was sampled to obtain 5 g of inorganic carbon for analysis of  $^{14}\text{C}$ . Nine samples were taken from core 1, 11 samples from core 2 and 7 samples from core 3, pretreated with  $1\text{M}$  NaOCl to remove organic carbon and analysed for  $^{14}\text{C}$  using the method described by Gupta and Polach (1985).

A further 9 sediment intervals from core 2 and two intervals from core 3, each 20 mm, in length were sampled for  $^{14}\text{C}$  analysis of the organic carbon fraction. The sediment was pretreated to obtain the acid/alkali insoluble carbon fraction (Gupta and Polach, 1985) and combusted at  $900^\circ\text{C}$

in an evacuated quartz tube in the presence of CuO wire to form  $\text{CO}_2$  (Boutton et al., 1983). Graphite targets for accelerator mass spectrometric determination of  $^{14}\text{C}$  were prepared by catalytic reduction of  $\text{CO}_2$  according to the method described in Vogel et al. (1987) and subsequently, AMS measurements were made at the Lawrence Livermore National Laboratory Centre for Accelerator Mass Spectrometry (Davis et al., 1990).

#### 4.3. Stable isotope analysis

Samples for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  analysis were taken at 50 mm intervals for cores 1 and 2,  $\sim 300$  mm intervals for core 3, and at 10 mm intervals for the cold finger core. After pretreatment with  $1\text{M}$  NaOCl,  $\sim 100$  mg of each sample reacted with phosphoric acid in a water bath maintained at  $30^\circ\text{C}$  (McCrea, 1950) and the  $\text{CO}_2$  evolved, analysed for  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios using a VG Micromass 602 D mass spectrometer.

The acid/alkali insoluble carbon samples used for  $^{14}\text{C}$  analyses were subsampled then analysed

for  $\delta^{13}\text{C}$  composition using a Europa “Tracer-mass” mass spectrometer after conversion to  $\text{CO}_2$  via a “robo-prep” automatic preparation line. All data is expressed in  $\delta$ -notation as ‰ relative to Pee Dee Belemnite (PDB).

## 5. Results

Results for all of the analyses and measurements are given here with a more detailed explanation of the combined use of these results to provide a hydrologic history of the lake in subsequent sections.

### 5.1. Core description

Cores 1–3, taken at depths of 72, 78 and 78 m, respectively, display similar features with laminae present from the surface of the sediment to a well defined boundary at  $\sim 2.00$  m for core 1,  $\sim 2.88$  m for core 2 and  $\sim 2.63$  m for core 3. The laminae are narrower and more obvious for the bottom third of this interval and appear compressed over a shorter depth interval for core 1. Below the zone where laminae commence, the material is uniformly dark coloured in all cores.

### 5.2. Dry bulk density measurements

There is a relatively uniform increase in dry bulk density from  $\sim 400 \text{ kg m}^{-3}$  at the top of the cores to  $\sim 1400 \text{ kg m}^{-3}$  at varying depths for the 3 cores, and a uniform density of  $\sim 800 \text{ kg m}^{-3}$  for the homogenous dark material at the base of the cores (Fig. 4). For each core, a linear relationship between density and depth was approximated using a least squares fit for the sediment down to the uniform material and constant thereafter (as indicated for core 3 in Fig. 4). While it was not possible to measure density for the cold finger core, it is likely to be less than or equal to the minimum values seen for the Mackereth cores. A value of  $400 \text{ kg m}^{-3}$  was chosen for this section and all subsequent data was plotted against cumulative mass  $M$  ( $\text{kg m}^{-2}$ ) rather than depth.

### 5.3. Particle size analysis and electron microscopy

Each of the three cores display similar particle size distributions. The particle size distribution for core 3 is shown in Fig. 5. From the surface to  $M \approx 1800 \text{ kg m}^{-2}$  the particle size distribution is approximately constant and dominated by  $< 200 \mu\text{m}$  particles. Between  $M \approx 1800$ – $2400 \text{ kg m}^{-2}$ , the particle sizes vary considerably. The dark material below the laminae is homogeneous, dominated by particles  $< 20 \mu\text{m}$  in diameter. Abrupt changes in some parts of the core suggests disruption during sedimentation, the implications of which will be discussed later.

For the 30 samples analysed in greater detail, there was a bimodal distribution of particles with the majority of particles either  $< 150 \mu\text{m}$  or  $> 250 \mu\text{m}$  with most material  $< 150 \mu\text{m}$ . There were few particles in the  $100$ – $200 \mu\text{m}$  size range. When viewed under the electron microscope, rhomboid calcite crystals were clearly present in particle fractions  $< 150 \mu\text{m}$  but were rarely seen in fractions  $> 250 \mu\text{m}$ . Particles larger than  $250 \mu\text{m}$  were typically well-rounded having no well-defined shape. Although individual calcite crystals measured  $10$ – $30 \mu\text{m}$  in diameter, it was common to see several joined together in the  $100$ – $150 \mu\text{m}$  range.

We considered particle fractions  $< 200 \mu\text{m}$  to represent carbonate of authigenic origin and particles  $> 200 \mu\text{m}$  to be detrital. A correction was made to the stable isotope composition and to the  $^{14}\text{C}$  activity of the carbonate analysed (see appendix). We acknowledge, in hindsight, that it would have been easier to sieve the samples prior to analysis and then use only the  $< 200 \mu\text{m}$  fraction. However, the amount of material  $> 200 \mu\text{m}$  is  $< 5\%$  and so the corrections are small, except for the intervals  $\approx 2400$ – $1650 \text{ kg m}^{-2}$  and for the top of the core where corrections are up to 25%.

After acidification of the larger particle size fractions, elongated slivers, most likely being charcoal and wood, were seen when viewed through the electron microscope. This represented the majority of organic material analysed for  $^{13}\text{C}$  and  $^{14}\text{C}$  composition.

### 5.4. Carbon-14 carbonate material

The results for  $^{14}\text{C}$  activities from carbonate precipitate after allowance for the inclusion of

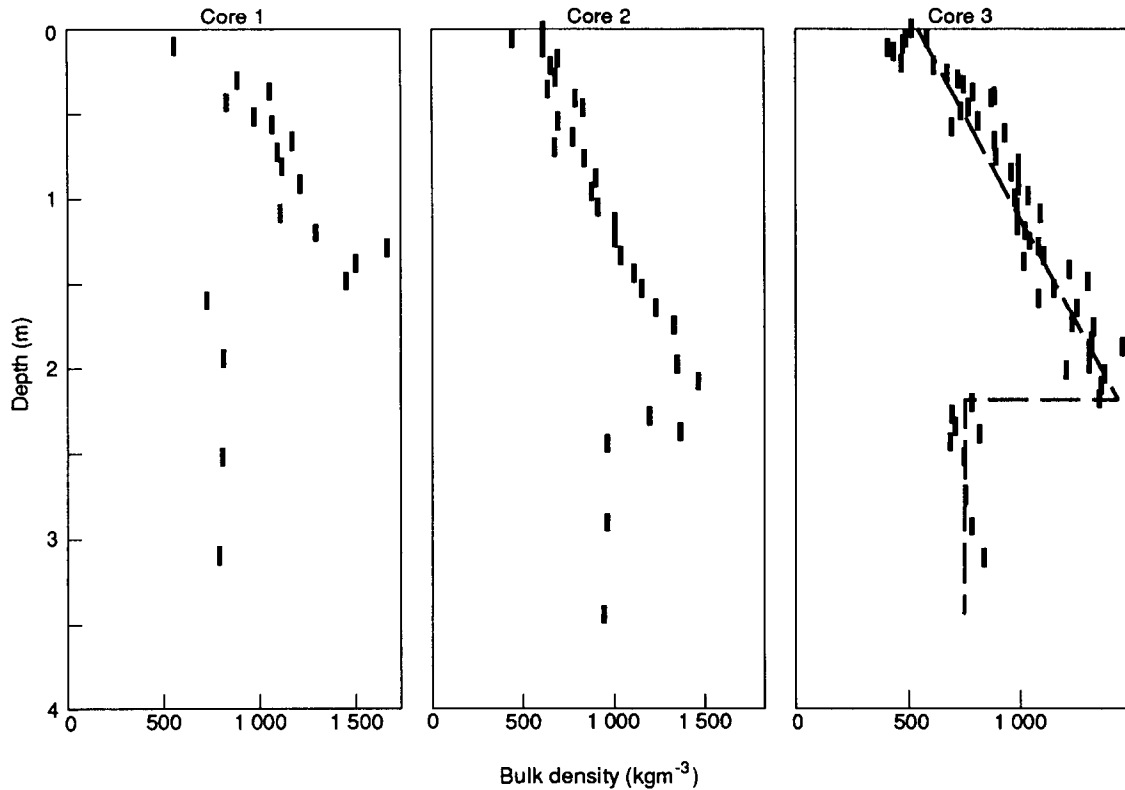


Fig. 4. Depth vs. density profiles for sediment cores.

detrital material, ( $A_{\text{auth}}$ ), are given in Fig. 11. These values cannot be used directly in age determinations because the  $^{14}\text{C}$  activity of the sample may be reduced by dilution with Total Dissolved Inorganic Carbon (TDIC) from the groundwater (see appendix).

Two methods were used to estimate the  $^{14}\text{C}$  activity of the TDIC ( $A(\text{lake})$ ) in lakewater at the time precipitation occurred (see appendix for details). The first method assumes that the lake was in a hydrologically steady-state for a sufficient time to establish a linear relationship between age and cumulative mass, at least over some part of the core (the upper part, in this case). The second method follows an approach by Fontes et al. (1983) using the  $\delta^{13}\text{C}$  composition of the carbonate precipitate to estimate the  $^{14}\text{C}$  activity of the TDIC in the lakewater at the time of precipitation.

#### Using method 1

Using data from all cores, plots of  $M$  against the log of the  $^{14}\text{C}$  activity of the authigenic carbonate ( $\ln A_{\text{auth}}(M)$ ) are linear from the surface to  $M \sim 1650 \text{ kg m}^{-2}$  suggesting a constant sedimentation rate and hydrological steady-state during this time interval. Hence, for this part of the core, method 1 is appropriate for determining the  $^{14}\text{C}$  activity of the TDIC. Using a least-squares fit for the  $^{14}\text{C}$  data for the interval  $M=0\text{--}1650 \text{ kg m}^{-2}$ , we estimate values for the sedimentation rate,  $k$ , and  $A(\text{lake})$  as  $0.229 \text{ kg m}^{-2} \text{ y}^{-1}$  and 71% Modern Carbon (pMC) respectively. ( $r^2=0.98$ , Fig. 6). The error calculated from counting statistics alone is less than 100 yr ( $1\sigma$ ) which is small compared to the overall error using this method of analysis. The overall error associated is estimated at between 500 and 1000 years as seen in the comparison between ages using actual sample activities (solid



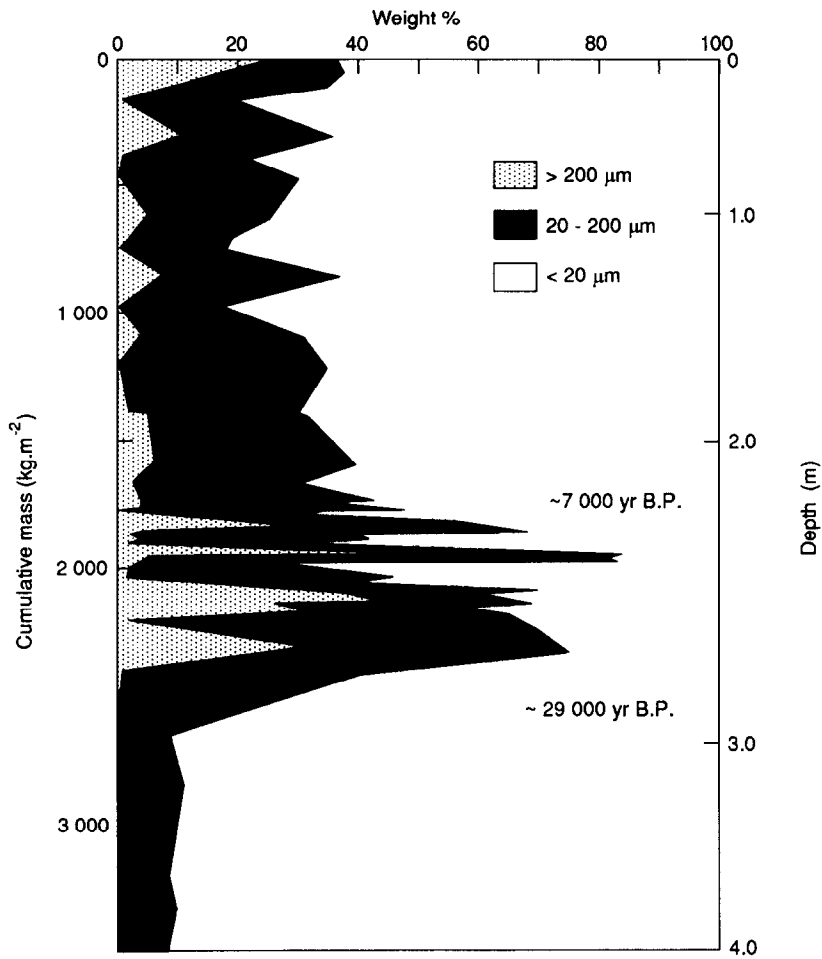


Fig. 5. Cumulative percent particle size distribution for sediment cores.

symbols) and ages averaged over the section (solid line) (Fig. 7 and Fig.11).

#### Using method 2

Fontes et al. (1983) proposed a method for calculating  $A(\text{lake})$  at the time of precipitation from the  $\delta^{13}\text{C}$  composition of precipitate for lakes where there was incomplete re-equilibration between gas and aqueous phase  $\text{CO}_2$ . The lakes were described as being only weakly mixed, had a relatively short carbon residence time, a pH in the vicinity of 7–8 and immobilization of the organic material in the sediments of the basin without recycling of carbon. A description of the method is described in the Appendix.

The Blue Lake is consistent with most of the criteria proposed for this method and has a pH range from  $\sim 8.0$  to 8.4. An estimate for  $A(\text{lake})$  using this method of 77–79% modern carbon (pMC) at the time of sampling agrees well with values measured by Turner (1979) of  $81 \pm 9$  pMC (see Appendix). This suggests that this method provides a reasonable determination of  $A(\text{lake})$  and hence age of the carbonate at any depth in the Blue Lake sediment.

The major error using this method arises from estimating the relative contributions of confined and unconfined groundwater to the lake, as these aquifers have significantly different  $^{14}\text{C}$  activities. In principle, this range may have varied from

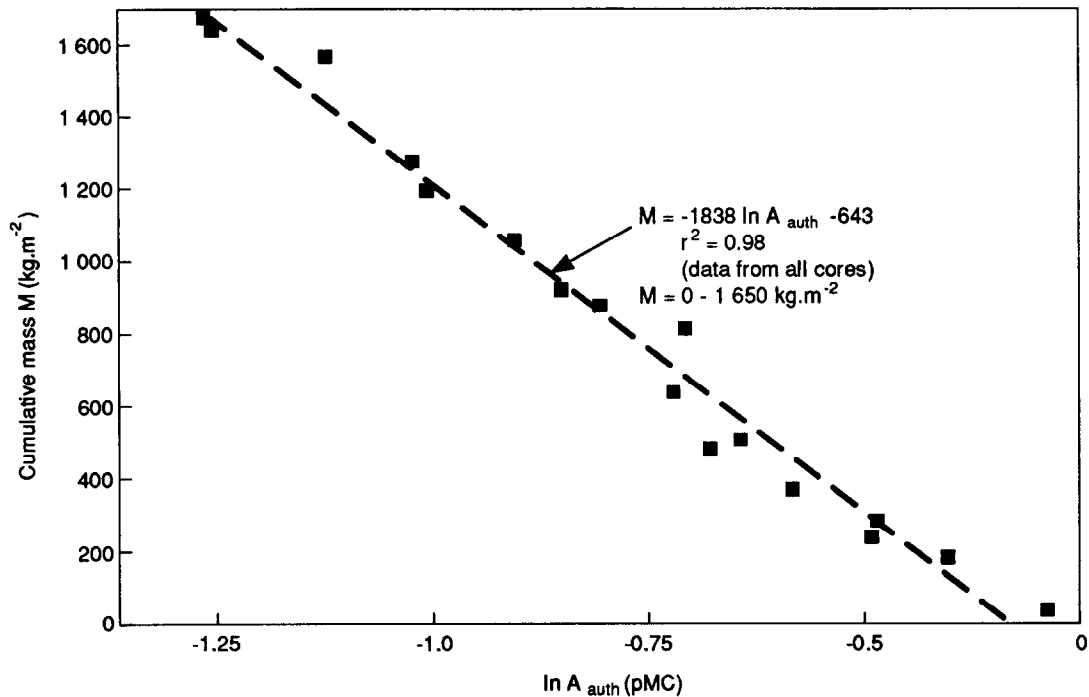


Fig. 6. Cumulative mass  $M$  vs.  $\ln A_{\text{auth}}(M)$  for section 3 of the sediment cores.

totally confined to totally unconfined groundwater input and hence we have calculated an age range based on these extremes (Fig. 11, Ages 2 and 3). Such an error estimate is much more realistic than that calculated from counting statistics alone for dating carbonate sediment. Estimates of the ages for sediment, assuming no hardwater effect, have been included for comparison with corrected ages (Fig. 11, Age 4).

##### 5.5. Carbon-14 organic material

Results from dating bulk organic fractions of the sediment are also presented in Fig. 11. This material has a predominantly terrestrial rather than aquatic origin as seen from electron microscopy and the  $^{13}\text{C}$  composition. Standard counting errors range from 50 to 200 years for these samples.

Ages determined from  $^{14}\text{C}$  analyses for organic and carbonate samples are presented as a function of cumulative mass in Fig. 7 and Fig. 11. Ages indicated by the solid line assumes a constant sedimentation rate and value for  $A(\text{lake})$  (method

1). The joined bars indicate ages calculated using the method of Fontes et al. (1983) with the younger age estimated assuming groundwater input totally from the confined aquifer and the older age assuming input totally from the unconfined aquifer (method 2). The estimates using methods 1 and 2 agree well for the top  $1650 \text{ kg m}^{-2}$  suggesting the mechanism for calcium carbonate precipitation and the estimate for  $A(\text{lake})$  proposed by Fontes et al. (1983) is appropriate for the Blue Lake. Furthermore, there is good agreement between ages determined from  $^{14}\text{C}$  analyses of organic material and the carbonate sediment, except at around 6000–7000 yr B.P. where the  $^{14}\text{C}$  ages determined on organic material are scattered and appear younger than the carbonate material.

##### 5.6. Stable isotope data

Results for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  analyses on samples from cores 1, 2, 3 and the cold finger core are given (Figs. 8 and 9) after correcting for the inclusion of detrital material using the following

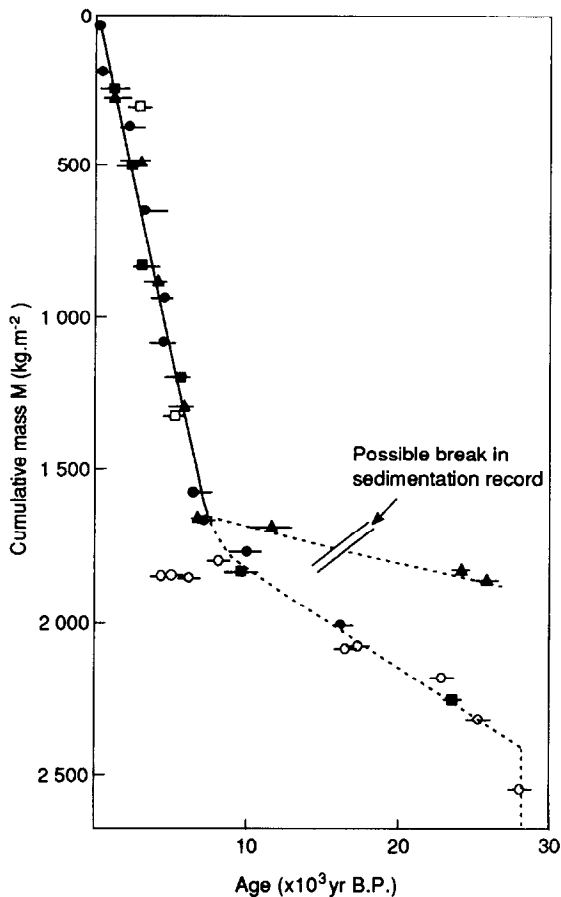


Fig. 7. Estimated age vs. cumulative mass of sediment. Carbonate fraction ( $\blacktriangle$  core 1,  $\bullet$  core 2,  $\blacksquare$  core 3). Organic fraction ( $\triangle$  core 1,  $\circ$  core 2,  $\square$  core 3). For  $M < 1650 \text{ kg m}^{-2}$  age has been estimated using Method 1 (solid symbols) and Method 2 (horizontal bar). For  $M > 1650 \text{ kg m}^{-2}$  age has been estimated using Method 2 only. No "dilution" effect assumed for organic samples.

equation:

$$\delta_{\text{auth}} = (\delta_{\text{meas}} - f_{\text{det}} * \delta_{\text{det}}) / (1 - f_{\text{det}}) \quad (1)$$

where  $\delta_{\text{auth}}$  is the  $\delta^{13}\text{C}$  or  $\delta^{18}\text{O}$  composition of the carbonate sample corrected for inclusion of a weight fraction  $> 200 \mu\text{m}$  ( $f_{\text{det}}$ ) of detrital material.  $\delta_{\text{meas}}$  and  $\delta_{\text{det}}$  are the measured  $\delta^{13}\text{C}$  or  $\delta^{18}\text{O}$  composition of the carbonate sample and the detrital material, respectively. Average values of  $-0.7 \pm 0.2\text{‰}$  for  $\delta^{13}\text{C}$  and  $+0.7 \pm 0.2\text{‰}$  for  $\delta^{18}\text{O}$

were obtained for detrital limestone samples (10 samples).

The results for core 3 analyses (14 samples shown as asterisks in Fig. 8) are similar to those for core 2 (70 samples) at the same cumulative mass and, in the following, the results from core 2 are discussed. Comparing the results for the cold finger core with the other cores indicates that approximately the top  $20 \text{ kg m}^{-2}$  ( $50 \text{ mm}$ ) of the sediment was lost during sampling using the Mackereth corer. Both cores 1 and 2 show similar  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  profiles although samples for core 1 were only analysed to a cumulative mass of about  $2400 \text{ kg m}^{-2}$  and show compressed excursions in parts of the core.

For convenience, results of analyses are presented for four distinct sections of the cores believed to represent different evolutionary stages of the lake (Figs. 8 and 9). The first section concentrates on the uniform dark sediment at the bottom of the core; the second section, the laminae to  $M \sim 1750 \text{ kg m}^{-2}$  ( $\sim 28,000$ – $\sim 7000 \text{ yr B.P.}$ ); the third section, the laminae from  $M \sim 1750 \text{ kg m}^{-2}$  to  $M \sim 80 \text{ kg m}^{-2}$  ( $\sim 7000 \text{ yr B.P.}$ – $\sim 1900 \text{ AD}$ ). The final section examines the surface sediment collected via the cold finger ( $M \sim 0$ – $80 \text{ kg m}^{-2}$ ) and shows the impacts of management-induced changes to the water balance of the lake since pumping began early this century.

The  $\delta^{13}\text{C}$  compositions are  $\sim 0.7\text{‰}$  at depths greater than  $M = 2050 \text{ kg m}^{-2}$  for core 1 and  $M = 2500 \text{ kg m}^{-2}$  for cores 2 and 3 (i.e. section 1;  $> 29,000 \text{ yr B.P.}$ ). The  $\delta^{18}\text{O}$  composition of sediment samples for the same interval ranges from  $\sim 0.0$  to  $0.7\text{‰}$  for all cores. This is approximately that measured for detrital limestone. For section 2 ( $\sim 29,000$ – $\sim 7000$ ) there is little change in  $\delta^{13}\text{C}$  composition until the top where all cores show  $\sim 3\text{‰}$  decrease. Two negative excursions are seen in the  $^{18}\text{O}$  composition of the sediment for this section.

For the interval  $M \approx 80$ – $1750 \text{ kg m}^{-2}$  (section 3,  $50$ – $7000 \text{ yr B.P.}$ ), the  $\delta^{13}\text{C}$  composition is approximately constant except for an  $\sim 1.5\text{‰}$  positive excursion at  $M = 1250 \text{ kg m}^{-2}$  ( $5400 \text{ yr B.P.}$ ). The  $\delta^{18}\text{O}$  composition for samples in this section generally increase toward the surface reaching a plateau value of around  $0.5\text{‰}$  at about  $3000 \text{ yr B.P.}$

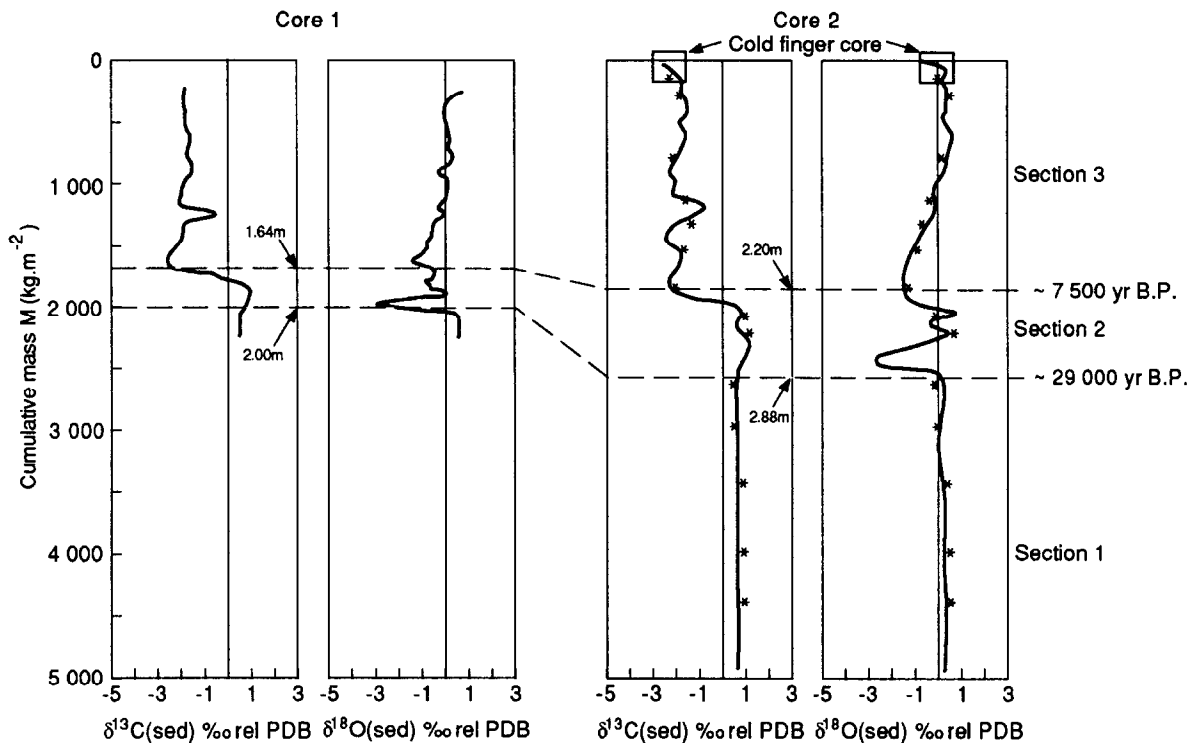


Fig. 8.  $^{13}\text{C}$  and  $^{18}\text{O}$  composition of authigenic carbonate sediment as a function of cumulative mass for core 1 (40 samples @ 50 mm spacing), core 2 (70 samples @ 50 mm spacing) and core 3 (14 samples \*) (sections 2–4). Compositions for carbonate for samples from section 1 are on detrital material.

The cold finger core (section 4) shows a negative shift of  $\sim 3\text{‰}$  in both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  towards the top of the profile.

$\delta_{\text{auth}}$  is determined by the  $\delta^{13}\text{C}$  composition of the lake at the time of precipitation ( $\delta_{\text{bt}}$  from Fontes et al., 1983) and the fractionation between the carbonate and bicarbonate phases  $\epsilon_{\text{s}}$ . If  $\delta_{\text{auth}}$  is close to the  $\delta^{13}\text{C}$  composition of the groundwater,  $\delta_{\text{bs}}$ , the carbon budget of the lake is dominated by groundwater inflow. However, if it is close to the isotopic composition of the bicarbonate in equilibrium with the atmosphere,  $\delta_{\text{ba}}$ , then the carbon budget is dominated by exchange with the atmosphere.

The ratio of carbon input from the groundwater to the lake relative to carbon exchange with the atmosphere is dependent on many factors but in this study we have considered the lake surface area to volume ratio to be most important. As the Blue Lake has very steep sides and is almost cylindrical

(Fig. 2), this ratio approximates to the depth and we suggest that more negative values for  $\delta_{\text{auth}}$  may represent periods when the lake was deeper and/or displayed a shorter mean water residence time. Alternatively, periods when the lake was shallow should result in an enriched signature for  $\delta_{\text{auth}}$ .

## 6. Discussion

### 6.1. Section 1 (uniform dark sediment)

The stable isotope composition of this section is uniform with depth which suggests that this material was homogeneous during deposition. However, as no cores sampled to the bottom of the sediment, we cannot conclude whether or not the sediment is homogeneous over the entire sediment record. The most likely scenario resulting in the formation of such uniform sediment is the

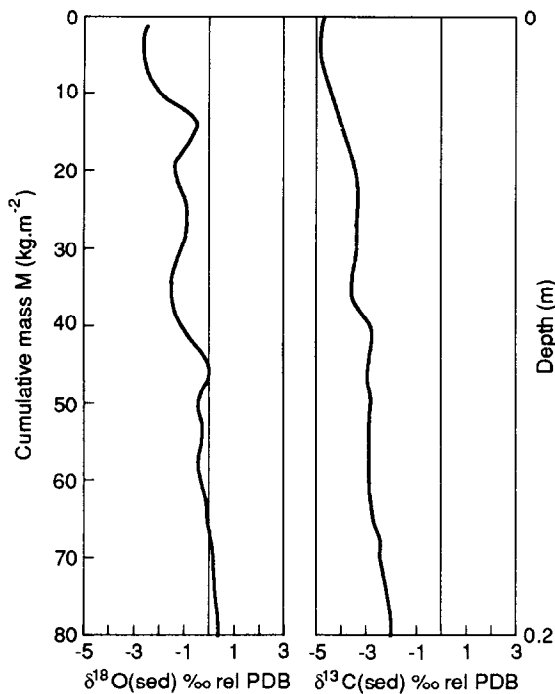


Fig. 9.  $^{13}\text{C}$  and  $^{18}\text{O}$  composition of carbonate sediment as a function of cumulative mass for the cold finger core.

mixing of volcanic debris and material from the aquifer matrix in a mudpool after cessation of geothermal activity.

Electron microscopy does not show any evidence for the precipitation of calcite in this section. Almost 90% of the sediment is  $<20\ \mu\text{m}$  and well rounded which is consistent with the hypothesis above. Under such conditions, the sediment in this section would be the last to settle and would consist of uniform small particles. Hence, although this material consists of small particles, we believe the carbonate in it is detrital limestone, mechanically eroded during the formation of the lake. The isotopic composition of the sediment in this interval being close to that of detrital limestone gives support to this hypothesis.

Because most of the inorganic carbon in this section is likely to be detrital in origin, it is impossible to estimate the age from the carbonate fraction. Similarly, the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  compositions for sediment in this part of the core are unlikely

to provide useful information on the evolution of the lake. The  $^{14}\text{C}$  age of organic carbon for the sample at the top of this section probably provides the most reliable estimate for the time at which the mud pool ceased its activity. As such, it also provides a minimum age of formation of the lake (ie  $>28,000$  yr B.P.).

#### 6.2. Section 2 laminae above the uniform dark sediment to $M = 1750\ \text{kg m}^{-2}$ ( $>28,000$ – $7000$ yr B.P.)

Laminae are clearly present for this section of the core, although they are neither frequent nor regular enough to correspond to seasonal sedimentation or precipitation. More likely, they represent periods ranging from years to possibly centuries during which time precipitation took place at a greater than average rate for this section. These periods were separated by similar intervals during which precipitation was much slower. The large changes seen in the particle size distribution in this part of the core suggests significant changes in the amount of detrital material washed into the lake during this time. This is consistent with a shallower lake and the potential for more erosion during this time from the large steep-sided catchment than seen in subsequent periods.

The analyses for cores 2 and 3 are similar while core 1 shows evidence of a compressed or possibly truncated depositional record. The lower rate of sedimentation (Fig. 7) may be explained by the fact that the surface level of core 1 is approximately 6 metres higher than that of the other cores. In times of very low lake level, the core 1 site may have been exposed and been subject to erosion or at least a much slower rate of deposition. If this was the case, then the amount of sediment in this section of core 1 is likely to be less than the other 2 sites. It is difficult to determine whether the sediment record for core 1 is complete although, from visual observations of the core, there are no obvious discontinuities. The agreement seen in the sedimentation rate for the other two cores and their lower elevation suggests that the records for these are complete. In the following discussion, results from the stable isotopic analysis of core 2

are discussed as sediment from this core appears to represent a more complete history of the lake (Fig. 8).

The  $\delta^{13}\text{C}$  of the authigenic carbonate in the precipitate has a mean value of  $\sim 0.7\text{‰}$  for most of this section. This is more positive than that for most of the precipitate suggesting a much shallower lake during this period. Near the top of this section of the cores ( $M=2000\text{--}1750\text{ kg m}^{-2}$ ; 15,000–7000 yr B.P.) the  $\delta^{13}\text{C}$  of the authigenic carbonate material decreases markedly to about  $-2\text{‰}$  suggesting the lake became deeper during this time.

The  $\delta^{18}\text{O}$  of authigenic carbonate is dependent of the temperature and the water balance of the lake. The historical water balance of the lake is not known well enough to make quantitative estimates of the palaeo lake temperatures. However, it is possible to use the  $\delta^{18}\text{O}$  data of the carbonate sediment to suggest qualitative palaeo-climatic changes during periods where the water balance of the lake is constant. Under steady-state conditions positive excursions for the  $\delta^{18}\text{O}$  composition of the carbonate sediment are indicative of lower lake water temperature while negative excursions indicates a period during the evolution of the lake when the lake temperature was higher.

For the section of the core  $M=2500\text{--}2000\text{ kg m}^{-2}$  (28,000–15,000 yr B.P.), the  $\delta^{13}\text{C}$  composition of the sediment suggests that the lake was consistently shallow or well-mixed and hence, any changes in the  $\delta^{18}\text{O}$  composition of the carbonate sediment should be related to temperature changes. The depleted values seen in the  $\delta^{18}\text{O}$  composition of the carbonate sediment at about  $M=2400\text{ kg m}^{-2}$  (28,000 yr B.P.) suggest a relatively warm lake at this time. The  $\delta^{18}\text{O}$  composition increases from  $-2.8\text{‰}$  at  $M\approx 2400\text{ kg m}^{-2}$  to  $0.2(\pm 0.5)\text{‰}$  at  $M\approx 2250\text{ kg m}^{-2}$  ( $\sim 22,000$  yr B.P.), and approximately constant until  $M\approx 2000\text{ kg m}^{-2}$  ( $\sim 15,000$  yr B.P.). If indeed the hydrological balance was constant during this time, this would suggest a decrease in the lakewater temperature from the time precipitation commenced  $>28,000$  yr B.P. reaching a minimum temperature between 22,000 and 15,000 yr B.P.. This period includes the last glacial maximum ( $\sim 18,000$  yr B.P.).

### 6.3. Section 3; $M=1750\text{--}80\text{ kg m}^{-2}$ (7000 yr B.P.–1900 AD)

The reasonably constant  $\delta^{13}\text{C}$  composition (Fig. 8) for this section suggests the lake water balance was in a relatively steady-state for most of this period. The ratio of the exchange between the lake and atmosphere to the input inorganic carbon from the aquifer system, as indicated from the  $\delta_{\text{auth}}$  composition, suggests a much deeper lake during this period than that prior to 7000 yr B.P.

There is evidence of a disruption to the water balance of the lake at about 5000 yr B.P. ( $M=1250\text{ kg m}^{-2}$ ) as indicated by an increase in  $\delta^{13}\text{C}$  in the sediment of about  $2\text{‰}$ . The apparent reduced water inflows temporarily changed the water balance of the lake and probably lasted for several centuries. There are no obvious changes in the  $\delta^{18}\text{O}$  of the sediment around 5000 yr B.P. However,  $\delta^{18}\text{O}$  values go through a minimum between 7000 and 5000 yr B.P., suggesting that the lake reached its maximum level at a time when temperature was higher than present. Wasson and Donnelly (1991) suggest that 5000–7000 yr B.P. was the warmest period in S.E. Australia during the late Holocene.

Another explanation for the depleted  $\delta^{18}\text{O}$  and to a lesser extent  $\delta^{13}\text{C}$  composition of the sediment at this time would be an increase in the precipitation/evapotranspiration ratio in the area. This is consistent with data for other lakes in S.E. Australia that recorded maximum depths during this period (Wasson and Donnelly, 1991). It is probable that the combined effects of high temperatures and increased precipitation resulted in the depleted isotopic signature of the sediment during this time.

### 6.4. Section 4; $M=80\text{ kg m}^{-2}$ to the surface (1900–1985 AD)

The amount of carbonate in this section of the core was insufficient to allow  $^{14}\text{C}$  dating (AMS was unavailable at time of analysis). Despite this, several changes in the stable isotope composition of the sediment can be explained by the history of pumping from the lake over the last century.

The rate of pumping from the lake during this century (Fig. 3) changed in three stages: (1) a

gradual increase in the rate from 1900 until about 1950 (from  $0.1$  to  $0.8 \times 10^6 \text{ m}^3 \cdot \text{y}^{-1}$ ), (2) a more rapid increase from 1950 until about 1970 (from  $0.8$  to  $4 \times 10^6 \text{ m}^3 \cdot \text{y}^{-1}$ ) and (3) an approximately constant rate of withdrawal since then. Similarly, three regimes may be seen in the  $\delta^{13}\text{C}$  composition for this section of lake sediment (Fig. 9); (1) a slow but gradual decrease in the  $\delta^{13}\text{C}$  composition of the sediment from  $M \sim 80 \text{ kg m}^{-2}$  to  $M \sim 20 \text{ kg m}^{-2}$  followed by (2) a much more rapid decrease from  $M \sim 20 \text{ kg m}^{-2}$  to  $M \sim 6 \text{ kg m}^{-2}$  and (3) a constant composition from there to the surface.

The decrease in  $\delta^{13}\text{C}$  of lake sediment nearer the surface reflects a reduction in the mean residence time of water in the lake resulting in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  approaching that of groundwater. However, we suggest that in this instance, the increase in groundwater flow during this period is induced by pumping from the lake rather than a change in the lake level.

If the three stages of pumping do indeed correspond to the three  $\delta^{13}\text{C}$  regimes, then approximately  $80 \text{ kg m}^{-2}$  of sediment has precipitated in 80 years with a mean sedimentation rate of  $1 \text{ kg m}^{-2} \cdot \text{y}^{-1}$  for this period. This is four times the sedimentation rate suggested prior to pumping and is not unexpected given increased groundwater inflow and hence, TDIC input induced by pumping.

### 6.5. Hydrological history of the Blue Lake

From dates defined in this study, Blue Lake formed  $>28,000$  yr ago. For the period 28,000–15,000 yr B.P., the lake was, on average, shallower than today and at times was probably less than 10 m at the deepest point. At the start of this period, we suggest that the lake water temperature was relatively high and gradually decreased reaching a minimum between 22,000 and 15,000 yr B.P. Sedimentation rate during this time was at most  $0.03 \text{ kg m}^{-2} \cdot \text{y}^{-1}$ . From 15,000 years ago, the level of the Blue Lake increased to a level slightly above that seen at present by about 7000 yr B.P.

From  $\sim 7000$  yr B.P. until pumping from the lake commenced at the start of this century, the lake was in hydrological steady-state with a sedimentation rate of  $\sim 0.224 \text{ kg m}^{-2} \cdot \text{y}^{-1}$ . During

this time, it is likely that the lake water temperature was highest between 7000 and 5000 yr B.P. and decreased until around 4000 yr B.P. It has remained approximately constant since that time. There is evidence that the water balance was disrupted possibly for a period of 500–1000 years at about 5000 yr B.P. This time corresponds to several estimates of  $^{14}\text{C}$  age of charcoal associated with volcanic tuff in the immediate area (Blackburn et al., 1982; Fergusson and Rafter, 1957) and with estimates for volcanic activity from thermoluminescence dating by Smith and Prescott (1987). Hence, it is possible that this disruption may have been a result of renewed volcanic activity in the area.

Since pumping began in about 1900 AD, the hydrological balance of the lake has been perturbed and groundwater inflow has increased. Current sedimentation rates are approximately  $1 \text{ kg m}^{-2} \cdot \text{yr}^{-1}$  considerably higher than that prior to pumping. It is likely that, as pumping rates have levelled off, the lake has reached a new hydrologic steady-state.

The hydrological history of the Blue Lake presented here may be compared with the inferred aquifer response to the lowering of sea level lowering during the last glacial ( $\sim 18,000$  yr B.P., Love, 1992). Love suggested that piezometric heads of the 2 aquifers at the Blue Lake site (Fig. 10) would have been considerably lower than at present for the period prior to 7000 yr B.P. with a minimum at about 18,000 yr B.P. The correlation between calculated groundwater levels and lake level, as indicated from the  $^{13}\text{C}$  signature of the carbonate sediment, suggests that the lake level has been, and continues to be, dominantly groundwater controlled. Moreover, the correlation between sedimentation rate and depth of water suggests that the precipitation of calcite (which contributes the majority of sediment) is and was controlled primarily by the water depth and thus is due chiefly to mixing of inflowing groundwater with lake water. Prior to approximately 15,000 yr B.P., we suggest that the lake probably did not exceed 10 m in depth and at this stage, precipitation at the site of core 1 would have been significantly less than at the other 2 sites as observed.

Changes in lake water temperature, suggested only for the time interval when the carbonate

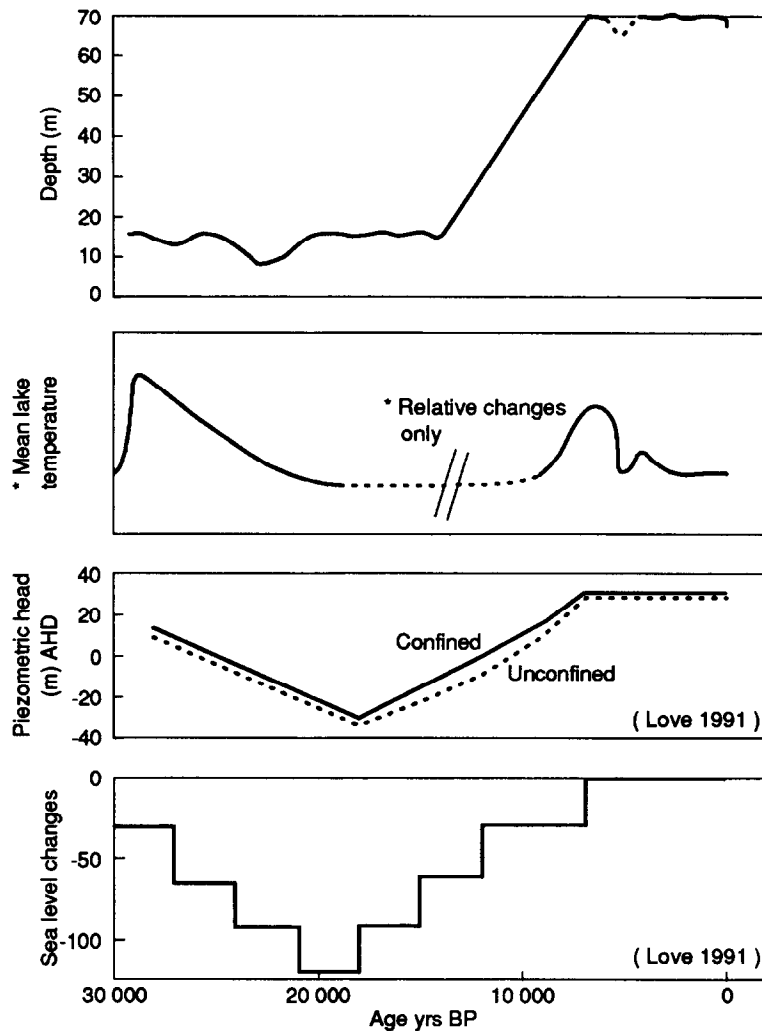


Fig. 10. Hypothesized changes for the Blue Lake during the last 30,000 years. (i) Changes in depth. (ii) Relative temperature changes of water in the Blue Lake. (iii) Changes in groundwater elevation at the Blue Lake site as a response to sea level changes (Love, 1991). (iv) Stepwise sea level changes used by Love (1991).

precipitate displayed constant  $\delta^{13}\text{C}$  composition—indicating a constant water balance but changing  $\delta^{18}\text{O}$  concentration—are relative only. However, the periods of inferred high lake temperature agree well with data summarised by Wasson and Donnelly (1991)(Fig. 10).

## 7. Conclusions

The combined use of  $^{14}\text{C}$ ,  $^{13}\text{C}$  and  $^{18}\text{O}$  analyses, primarily on the carbonate fraction of sediment

from the Blue Lake, has enabled a reconstruction of its hydrological history. The major conclusions from this study are:

—The age of formation of the Blue Lake has been estimated, using a combination of  $^{14}\text{C}$  and stable isotope data, to be at least 28,000 yr B.P. This is much older than that suggested by other workers (Sheard, 1978; Blackburn et al., 1982).

— $^{14}\text{C}$  analyses on carbonate material may be used to date sediment providing the ages are



Core Depth	Cum. Mass	Authigenic Carbon	A <sub>auth</sub>	δ <sub>auth</sub>	Age (1)	Age (2)	Age (3)	Age (4)
(m)	kgm <sub>2</sub>	1-f <sub>det</sub>	pMC	‰PDB	yr B.P.	yr B.P.	yr B.P.	yr B.P.
Carbon Isotope Data and Age Estimation For Carbonate Fraction : Sections 3 and 4								
2 0.0-0.15	35	0.88	73.4	-2.3	Modern	Modern	190	2310
2 0.30-0.40	179	0.97	66.6	-2.0	510	Modern	1240	3270
3 0.41-0.52	240	0.94	61.1	-2.0	1210	560	1990	3950
1 0.38-0.47	283	0.91	61.3	-1.9	1180	640	2040	3930
2 0.65-0.72	372	0.97	55.7	-1.5	1950	1650	2900	4700
1 0.63-0.71	487	0.98	50.6	-2.2	2720	1830	3340	5470
3 0.81-0.91	505	0.98	52.1	-2.2	2490	1670	3180	5240
2 0.99-1.10	645	0.95	48.4	-1.5	3080	3410	4660	5830
3 1.21-1.28	819	0.97	49.0	-1.8	2980	2480	3840	5730
1 1.03-1.11	885	0.94	44.2	-2.0	3810	3180	4620	6560
2 1.35-1.43	929	0.98	42.4	-2.0	4140	3560	4990	6890
2 1.50-1.60	1073	0.97	40.1	-2.3	4590	3690	5240	7340
3 1.61-1.68	1203	0.99	36.2	-2.0	5410	4790	6230	8160
1 1.37-1.41	1287	0.99	35.5	-2.0	5570	4790	6230	8320
2 2.00-2.10	1573	0.94	32.2	-1.5	6350	6150	7400	9100
2 2.10-2.18	1671	0.96	28.2	-2.5	7420	6380	8010	10200
1 1.64-1.72	1646	0.94	28.4	-2.5	7380	6380	8010	10100
Carbon isotope Data and Age Estimation For Carbonate Fraction : Section 2								
1 1.68-1.75	1690	0.96	18.0	-2.1		10280	13030	13800
1 1.79-1.88	1830	0.85	4.8	+1.4		23400	24200	24400
1 1.87-1.95	1850	0.85	3.8	+1.2		25200	26100	26300
1 2.42-2.58	2360	1.00	0.7	+0.9	Estimation of Age Inappropriate			
2 2.18-2.31	1790	0.97	22.4	-1.9		8700	11300	12000
2 2.35-2.50	2000	0.75	11.8	+0.7		15750	16900	17200
2 2.91-3.03	2560	1.00	0.7	+0.6	Estimation of Age Inappropriate			
3 2.26-2.36	1840	0.90	24.3	-1.5		8350	10750	11400
3 2.50-2.56	2260	0.90	4.8	+0.8		23050	24150	24400
3 2.63-2.84	2440	1.00	1.0	+1.0	Estimation of Age Inappropriate			
Carbon Isotope Data and Age Estimation For Organic Fraction : Sections 2 and 3								
3 0.53	300			-31.3				3000
3 1.84	1420			-27.6				5250
2 2.25	1800			-32.5				8000
2 2.33	1860			-27.9				4450
2 2.31	1850			-30.2				6050
2 2.31	1850			-27.9				4800
2 2.50	2090			-27.1				17250
2 2.51	2100			-26.4				16450
2 2.59	2180			-27.1				22850
2 2.71	2330			-26.9				25150
2 2.91	2560			-27.9				28200

- (1) Age estimated using Method 1.
- (2) Age estimated using method 2 with groundwater input assumed to be wholly from the confined aquifer.
- (3) Age estimated using method 2 with groundwater input assumed to be wholly from the unconfined aquifer.
- (4) Age estimated assuming no dilution (hardwater) effect.

Fig. 11. Age estimates for carbonate and organic material from lake sediment.

corrected for detrital carbon and the  $^{14}\text{C}$  dilution from groundwater input.

—The two methods used for estimating the “dilution” effect are valid subject to the limitations presented in this paper. The appropriate conditions for using each method are based primarily on the  $^{13}\text{C}$  composition of the sediment.

—Lake levels for the Blue Lake were much lower than at present prior to 7000 yr B.P. and lake levels for the Blue Lake have been, and continue to be, groundwater controlled.

—The residence time of water in the lake has shortened since pumping began due to induced groundwater flow.

Sedimentation rate for this lake is dependent on the depth of water in the lake with greater depths resulting in greater authigenic carbonate production. Several studies, have used proxy records to establish past variations in lake levels and infer palaeoclimatic changes such as increased precipitation or evaporation rates. This study shows that it is necessary to ensure that the lakes used in such studies are not groundwater controlled and that such lakes are not merely responding to changes in groundwater level that are, in turn, responding to other factors which may not be closely related to regional climatic changes.

### Acknowledgements

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### Appendix—estimating the amount of detrital carbon when dating carbonate sediment

When using carbonate material to date sediment, some of inorganic carbon in the sediment may not

be authigenic carbonate precipitate but limestone which has washed from the walls of the lake. The Gambier Limestone was formed during the late Tertiary and hence has zero  $^{14}\text{C}$  activity. Incorporation of this material into sediment and subsequent analysis for  $^{14}\text{C}$  for the inorganic fraction would result in an apparent age older than that of the authigenic carbonate.

While it is difficult to remove this material quantitatively, a more accurate  $^{14}\text{C}$  activity for the authigenic carbonate may be determined by removing the larger fractions of the sediment prior to analysis. If this is not done prior to analysis, the measured carbon-14 activity of the sample may be corrected after analysis by assuming the coarse fraction ( $>200\ \mu\text{m}$ ) to be inorganic carbon from the Gambier Limestone incorporated in the sediment. In this study detrital material was considered to be  $>200\ \mu\text{m}$ .

The value for the  $^{14}\text{C}$  activity of the authigenic carbonate at cumulative mass  $M$ ,  $A_{\text{auth}}(M)$ , is related to the measured  $^{14}\text{C}$  activity of the sample  $A_{\text{meas}}(M)$  by the following relationship.

$$A_{\text{auth}}(M) = A_{\text{meas}}(M)/(1 - f_{\text{det}}) \quad (2)$$

where  $f_{\text{det}}$  is the sediment fraction greater than  $200\ \mu\text{m}$ .

For this study, the correction to  $^{14}\text{C}$  activity for most of the samples is less than 5%. However, for one sample in section 2, the correction is 33%.

### Estimation of the $^{14}\text{C}$ activity of the dissolved bicarbonate in the lake, $A(\text{lake})$ , at the time of precipitation

The  $^{14}\text{C}$  activities of authigenic carbonate in sediment samples ( $A_{\text{auth}}$ ) cannot be used directly calculate the age of sediment because the activity of the dissolved bicarbonate from which the calcium carbonate has precipitated (the dilution effect) is unknown for all but the present time. This is sometimes referred to as the hardwater effect. If the mean residence time of water in a lake is long,  $^{14}\text{C}$  exchange between the  $\text{HCO}_3^-$  in the lake and atmospheric  $\text{CO}_2$  will result in the  $^{14}\text{C}$  activity of the  $\text{HCO}_3^-$  approaching that of dissolved bicarbonate in equilibrium with atmo-

spheric CO<sub>2</sub> (minimum dilution effect). If the mean residence time of water is short and input of groundwater HCO<sub>3</sub><sup>-</sup> dominates, the <sup>14</sup>C activity of the HCO<sub>3</sub><sup>-</sup> in the lake will be much less and approach that of the groundwater HCO<sub>3</sub><sup>-</sup> (maximum dilution effect). Two possible approaches to estimate this effect can be used.

### Method 1

#### *Estimating the dilution effect during periods when the lake approximates hydrological steady-state*

While uncertainties in the dilution effect limits the use of inorganic <sup>14</sup>C data in dating carbonate precipitate, a relatively accurate estimate for this value may be made if the hydrological balance of the lake has remained steady for a considerable length of time.

If the hydrological balance of any lake is in a steady state for a length of time then it is likely that during that time, precipitation rate, sedimentation rate and the activity of the TDIC in the lake will be constant. This being true then the cumulative mass,  $M$  kg m<sup>-2</sup> will be proportional to the age  $t$  (y) of the sediment and hence:

$$M = kt \quad (3)$$

where  $k$  = rate of sedimentation (kg m<sup>-2</sup> y<sup>-1</sup>).

Also the age may be determined radiometrically as

$$t = -8033 \ln [A_{\text{auth}}(M)/A(\text{lake})] \quad (4)$$

> where  $A(\text{lake})$  = steady-state activity of TDIC in the lake (pMC)

Eq. 4 holds true for any particular depth in the core profile. However, this equation is a good approximation for any discrete sampling interval providing the sampling interval and range of sediment age in the sampling interval is small compared to the overall age of the core section. The cumulative mass at which the sample is taken may then be approximated by the mean of the cumulative mass for the core segment. In this study, the core segments sampled spanned at most 100 kg m<sup>-2</sup> (450 yr) compared to the 1650 kg m<sup>-2</sup> (7000 yr) for section 3 of the cores.

Combining Eqns. 3 and 4:

$$M = -8033 \ln A_{\text{auth}}(M) + 8033k \ln A(\text{lake}) \quad (5)$$

Hence, if a steady state situation prevails, cumulative mass,  $M$ , should be proportional to the log of the activity of the sediment, ie  $\ln(A_{\text{auth}}(M))$ . Hence,  $M$  should be linear with  $\ln(A_{\text{auth}}(M))$ , and the constant sedimentation rate constant can be calculated. The mean <sup>14</sup>C activity can be calculated from the intercept on the cumulative mass axis (=  $\exp(\text{intercept}/8033k)$ ). For this study,  $\delta^{13}\text{C}$  for the authigenic carbonate is approximately constant for all core sections from  $M=0$  to  $-1650$  kg m<sup>-2</sup> suggesting a period of hydrological steady-state during this time.

### Method 2

#### *Using the $\delta^{13}\text{C}$ composition of authigenic carbonate precipitate*

Estimation of the “dilution effect” may also be made by consideration of the <sup>13</sup>C balance of the lake. The  $\delta^{13}\text{C}$  signature of the sediment reflects the <sup>13</sup>C of the lakewater which, in lakes with low biological activity, in turn reflects the ratio of exchange of CO<sub>2</sub> between the lake and the atmosphere compared to input of TDIC from the groundwater.

The following equation was derived by Fontes et al. (1983) to determine  $A(\text{lake})$ .

$$A(\text{lake}) = \left\{ \frac{\delta_{\text{auth}} + \varepsilon_s - \delta_{\text{bs}}}{\delta\text{CO}_{2(a)} - \varepsilon_g - \delta_{\text{bs}}} \left[ \text{ACO}_{2(a)} \left( 1 - \frac{2\varepsilon_g}{10^3} \right) - A_{\text{bs}} \right] + A_{\text{bs}} \right\} \left( 1 - \frac{2\varepsilon_s}{10^3} \right) \quad (6)$$

$\delta\text{CO}_{2(a)}$  is the  $\delta^{13}\text{C}$  composition of atmospheric CO<sub>2</sub> at the time of precipitation and is considered to be  $-6.4\text{‰}$  for the Mackereth cores (pre-1900) and  $-8\text{‰}$  for the top of the cold finger core (Leuenberger et al., 1992).

$\text{ACO}_{2(a)}$  is the activity of atmospheric CO<sub>2</sub> at the time of precipitation and is considered to be 100 pMC for the Mackereth cores and 130 pMC for the top of the cold finger core (Leuenberger et al., 1992)

$\delta_{bs}$  is the  $\delta^{13}\text{C}$  composition of the dissolved bicarbonate in the groundwater.

$A_{bs}$  is the  $^{14}\text{C}$  activity of the dissolved bicarbonate in the groundwater expressed as percent Modern Carbon (pMC).

$$\varepsilon_s = 4232/T(^{\circ}\text{K}) - 15.10 \quad (\text{Mook, 1980}) \quad (7)$$

$$\varepsilon_g = -9483/T(^{\circ}\text{K}) + 23.89 \quad (\text{Mook, 1980}) \quad (8)$$

Possible temporal variations in  $A_{bs}$  and  $\delta_{bs}$  increase the error associated with estimating  $A(\text{lake})$  using this method. Blue Lake is fed by both confined and unconfined aquifers, the relative contributions of which are likely to have changed during the history of the lake.

The unconfined and confined aquifers have  $\delta_{bs} \sim -13.0$  and  $\sim -11.3\%$ , respectively with values for the confined aquifer more uniform than those measured in unconfined (Love, 1992).

Values for the  $^{14}\text{C}$  concentration are again very uniform for the confined aquifer ( $A_{bs} \sim 3$  pMC) in the vicinity of the lake. However, for the unconfined aquifer  $A_{bs}$  varies markedly (20–40 pMC) with a mean value  $\sim 30$  pMC. The error associated with estimation of  $A(\text{lake})$ , if  $A_{bs}$  is unknown, becomes less important as the relative fraction of atmospheric  $\text{CO}_2$  exchange to groundwater derived carbon increases (i.e. as  $\delta_{\text{auth}}$  becomes more positive). To indicate the extent of this induced error we have calculated all ages (Fig.7 and Fig.11) on the basis of both total input from the unconfined aquifer (older age) and total input from the confined aquifer (younger age).

Following the estimation of  $A(\text{lake})$  using either method 1 or 2, the age of the carbonate precipitate expressed as years before present (yr B.P.) is then calculated by the following equation

$$\text{Age}(\text{yr B.P.}) = -8033 \ln [A_{\text{auth}}/A(\text{lake})] \quad (9)$$

No allowance has been made for the possible addition of  $^{14}\text{C}$ -free  $\text{CO}_2$  to the atmosphere due to volcanic activity although for some time intervals this may well have been a possibility.

#### *Testing the $^{14}\text{C}$ dilution correction estimated using method 2*

Seven samples of water from the Blue Lake collected during 1976/1977 had a measured  $^{14}\text{C}$

activity for DIC of  $81 \pm 9$  pMC (Turner, 1979). This may be compared to the estimate for  $A(\text{lake})$  using  $^{13}\text{C}$  data from the carbonate precipitate at the top of the cold finger core Eq. 6.

$\delta_{\text{auth}}$  of surface precipitate (Fig. 9), has been estimated at  $-5\%$ . The ratio of the unconfined:confined groundwater input at this time is estimated at between 0.7:0.3 and 0.8:0.2 resulting in a mean  $^{14}\text{C}$  activity for groundwater entering the lake of between 22–25 pMC (Ramamurthy, 1983; Turner et al., 1983). The value used for  $\delta_{\text{CO}_2(a)}$  and for  $A_{\text{CO}_2(a)}$  are  $-8\%$  and 130 pMC, respectively (Gupta and Polach, 1985). If these values are substituted into Eq. 6,  $A(\text{lake})$  of Blue Lake at this time is estimated to be between 83–93 pMC, in good agreement with that measured by Turner (1979).

## References

- Barbetti, M. and Sheard, M.J., 1981. Palaeomagnetic results from Mounts Gambier and Schank, South Australia. *J. Geol. Soc. Aust.*, 28: 385–394.
- Barton, C.E. and McElhinny, M.W., 1980. Ages and ashes in lake floor sediment cores from Valley Lake, Mt Gambier, South Australia. *Trans. R. Soc. S. Aust.*, 104(6): 161–165.
- Blackburn, G., 1966. Radiocarbon dates relating to soil development, coastline changes, and volcanic ash deposition in south-east South Australia. *Aust. J. Sci.*, 29: 50–52.
- Blackburn, G., Allison, G.B. and Leaney, F.W.J., 1982. Further evidence on the age of tuff at Mt Gambier. *Trans. R. Soc. S. Aust.*, 106(4): 163–167.
- Bottinga, Y., 1968. Calculation of fractionation factors for carbon and oxygen exchange in the system calcite–carbon dioxide–water. *J. Phys. Chem.*, 72: 800–808.
- Bowler, J.M. and Wason, J., 1984. Glacial age environments of inland Australia. In: J.C. Vogel (Editor), *Late Cainozoic Paleoclimates of the Outer Hemisphere*. Balkema, Rotterdam, pp. 183–208.
- Boutton, T.W., Wong, W.W., Hachey, D.L., Lee, L.S., Cabrera, M.P. and Klein, P.D., 1983. Comparison of quartz and pyrex tubes for combustion of organic samples for stable carbon isotope analysis. *Analyt. Chem.*, 55: 1832–1833.
- Chappel, J., 1987. Late Quaternary sea-level changes in the Australian region. In: M.J. Tooley and I. Shennan (Editors), *Sea Level Changes*. Blackwell, New York, NY, pp. 296–331.
- Craig, H., 1965. The measurement of oxygen isotope palaeotemperatures. In: E. Tongiorgi (Editor), *Stable Isotopes in Oceanographic Studies and Paleotemperatures*. Cons. Naz. Ric. Lab. Geol. Nucl., Pisa, pp. 161–182.
- Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus*, 16: 436–469.

- Davis, J.C., Proctor, I.D., Southon, J.R., Caffee, M.W., Heikkinen, D.W., Roberts, M.L., Moore, T.L., Turteltaub, K.W., Nelson, D.E., Loyd, D.H. and Vogel, J.S., 1990. LLNL/UC AMS facility and research program. In: 5th Int. Conf. Accelerator Mass Spectrometry, Paris. Nucl. Instr. Methods, 52: 269–272.
- Fergusson, G.J. and Rafter, T.A., 1957. New Zealand  $^{14}\text{C}$  age measurements. 3. N.Z. J. Sci. Tech., B38: 732–749.
- Firman, J.B., 1969. Quaternary Period In: L. Parkin (Editor), Handbook of South Australian Ecology. Geol. Surv. Aust., pp. 204–233.
- Fontes, J.C., Coque, R., Dever, L., Filly, A. and Mamou, M., 1983. Paléohydrologie isotopique de l'oued el Akariit, Sud Tunisie au Pleistocène supérieur et l'Holocène. Palaeogeogr. Palaeoclimatol. Palaeoecol., 43: 41–62.
- Gill, E.D., 1972. Eruption date of Tower Hill volcano, western Victoria. Vict. Nat., 89: 188–192.
- Gupta, S.K. and Polach, H.A., 1985. Radiocarbon dating practices at ANU. Radiocarbon Lab. Res. School Pac. Stud., ANU, Canberra.
- Head, L., D'Costa, D. and Edney, P., 1991. Pleistocene dates for volcanic activity in Western Victoria and implications for Aboriginal occupation. In: M.A.J. Williams et al. (Editors), The Cainozoic in Australia: a Reappraisal of the evidence. Geol. Soc. Aust. Spec. Publ., 18: 302–308.
- Hutton, J.T., 1974. Chemical characterization and weathering changes in Holocene volcanic ash in soils near Mount Gambier, South Australia. Trans. R. Soc. South Aust., 98 (4): 179–184.
- Leuenberger, M., Siegenthaler, U. and Langway, C.C., 1992. Carbon isotope composition of atmospheric  $\text{CO}_2$  during the last ice age from an Atlantic core. Nature, 357: 488–490.
- Lewis, D.W., 1983. Practical Sedimentology. Hutchinson and Ross, Stroudsburg, Pa.
- Love, A., 1992. Groundwater flow systems: past and present, Gambier embayment, Otway Basin, South-East Australia. Thesis. Flinders Univ. South Australia (unpublished).
- Macumber, P.J., 1977. The geology and palaeohydrology of the Kow Swamp fossil hominid site, Victoria, Australia. J. Geol. Soc. Aust., 25: 307–320.
- McCrea, J.M., 1950. On the isotopic chemistry of carbonates and a palaeotemperature scale. J. Chem. Phys., 18: 849–857.
- Mook, W.G., Bommerson, J.C. and Staverman, W.H., 1974. Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. Earth Planet. Sci. Lett., 22 (2): 169–176.
- Mook, W.G., 1980. Carbon-14 in hydrogeological studies. In: P. Fritz and J.C. Fontes (Editors), Handbook of Environmental Isotope Geochemistry, 1. The Terrestrial Environment, A. Elsevier, Amsterdam, pp. 50–74.
- Polach, H.A., Head, M.J. and Gower, J.D., 1978. ANU radiocarbon date list VI. Radiocarbon, 20: 360–385.
- Polach, H.A., 1979. Correlation of  $^{14}\text{C}$  activity of NBS oxalic acid with Arizona 1850 wood and ANU sucrose standards. In: R. Berger and H.E. Suess (Editors), Radiocarbon Dating. Univ. Calif., Press, Berkeley, pp. 115–124.
- Ramamurthy, L.M., 1983. Environmental isotope and hydrochemical studies of selected catchments in South Australia. Thesis. Flinders Univ. South Australia (unpublished).
- Ramamurthy, L.M., Veeh, H.H. and Holmes, J.W., 1985. Geochemical mass balance of a volcanic lake in Australia. J. Hydrol., 79: 127–139.
- Shackleton, N.J. and Opdyke, N.D., 1973. Oxygen isotope and palaeomagnetic stratigraphy of equatorial Pacific core V28-2.38 oxygen isotope temperatures and ice volumes on a  $10^5$  year and  $10^6$  year scale. Quat. Res., 3: 39–55.
- Sheard, M.J., 1978. Geological history of the Mount Gambier Complex, southeast South Australia. Trans. R. Soc. S. Aust., 102(5): 125–139.
- Solomon, M., 1951. The volcanic deposits of the south-east of South Australia as sources of quarry stone. Min. Rev., 93: 133–137.
- Smith, B.W. and Prescott, J.R., 1987. Thermoluminescence dating of the eruption at Mt. Schank, South Australia. Aust. J. Earth Sci., 34: 335–342.
- Sprigg, R.C., 1952. The geology of the south-east province with special reference to Quaternary coast line migrations and modern beach developments. Bull. Geol. Surv. S. Aust., 29: 30–62.
- Turner, J.V., 1979. The hydrologic regime of Blue Lake, South Eastern Australia. Thesis. Flinders Univ. South Aust. (unpublished).
- Turner, J.V., Allison, G.B. and Holmes, J.W., 1983. Environmental isotope methods for the determination of lake-groundwater relations: applications to determine the effects of man's activities. In: Int. Conf. Groundwater and Man (Conf. Ser., 8). Aust. Water Resour. Council., 1, pp. 341–352.
- Turner, J.V., Allison, G.B. and Holmes, J.W., 1984. The water balance of a small lake using stable isotopes and tritium. J. Hydrol., 70: 199–220.
- Vogel, J.S., Nelson, D.E. and Southon, J.R., 1987.  $^{14}\text{C}$  background levels in an Accelerator Mass Spectrometry System. Radiocarbon, 29: 323–333.
- Wasson, R.J. and Donnelly, T.H., 1991. Palaeoclimatic reconstructions for the last 30,000 years in Australia—A contribution to prediction of future climate. CSIRO Div. Water Resour. Tech. Mem., 91/3.