

*D. M. McHardy*

**MINERALOGY AND STABLE ISOTOPE  
COMPOSITION OF RECENT CARBONATE  
SEDIMENTS AND WATERS FROM FIVE SMALL  
LAKES, SOUTH-EASTERN SOUTH AUSTRALIA.**

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## Abstract

The Robe-Woakwine corridor in southeast South Australia, contains a scattering of lakes of varying size. The coastal lakes selected for study are amongst the smallest. Recent carbonate sediment (sub-aqueous surface and sub-surface sediment) and water samples were collected monthly over 6 months, and analysed for their stable carbon and oxygen isotopic composition and mineralogy.

Lake Woolley is an ephemeral lake. Its water is hyper-saline (TDS {total dissolved solids} 40g/L). The  $\delta^{18}\text{O}_{\text{DIC}}$  (DIC = dissolved inorganic C) and  $\delta^{13}\text{C}_{\text{DIC}}$  of the lake water ranges from -4.2‰ to approximately +1.3‰ and the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of the carbonate sediment ranges from +2.2‰ to +4.2‰. The mineralogy of the sediment is aragonite and low Mg-calcite (LMC) with high Mg-calcite (HMC).

Fresh Dip's water is the least saline of the lakes studied (TDS 4g/L). The  $\delta^{18}\text{O}_{\text{DIC}}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  of the waters have remained relatively constant at approximately +1‰ and -1‰ respectively, as have the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of the carbonate sediment, with values of approximately +2‰ and +4‰ respectively. Mineralogy is predominantly aragonite.

Old Man Lake's water is hyper-saline (TDS 30g/L) with  $\delta^{18}\text{O}_{\text{DIC}}$  values of +5‰ to -5‰, whereas  $\delta^{13}\text{C}_{\text{DIC}}$  remains constant at -2‰.  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of the sediment range between +3‰ and +4.7‰ and 0.5‰ to +2.3‰ respectively. Mineralogy is intermediate Mg-calcite (IMC), LMC and aragonite.

Lake Amy and Ghost Lake are both hyper saline (TDS ≈ 70 & 25 g/L respectively). Ghost Lakes is an ephemeral lake, being completely dry in April.  $\delta^{18}\text{O}_{\text{DIC}}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  values range between -2.2‰ to 0‰ and -4.4‰ to 0‰ respectively.  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of the carbonate sediment range from +1.8‰ to +3.5‰ and -5‰ to 5.3‰ respectively. Mineralogy is predominantly HMC with LMC and aragonite. Lake Amy's water's  $\delta^{18}\text{O}_{\text{DIC}}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  range between -4.1‰ and +2.3‰ whereas the sediment  $\delta^{18}\text{O}$  remains constant at +2‰ and the  $\delta^{13}\text{C}$  range between +1.0‰ and +4.1‰. Mineralogy is predominantly HMC with LMC and aragonite. Traces of the unstable carbonate monohydrocalcite (MHC) also occur.

Each lake is influenced by differing combinations of water inflow. These control the salinity, lake level, precipitate mineralogy, biological activity and isotopic signature of the various components.

The DIC isotopic composition of the waters generally represent regional groundwaters which have undergone atmospheric equilibrium fractionation ( $\epsilon \text{CO}_{2(g)} - \text{HCO}_3^-$ ). The stable isotopic signature of the carbonate sediments correspond to values representing inorganic precipitation at an intermediate rate. Calculated sediment equilibrium isotopic values generally compared unfavourably with those observed, reflecting the unique nature of each lake.

The variations in the mineral percentages over the winter indicate conditions favouring the precipitation of LMC and aragonite, and MHC at Lake Amy, prevailing over the winter. The high proportions of HMC present in each lake (except Fresh Dip) indicates that most of the carbonate precipitation occurs during the summer months, when increased salinity favours the precipitation of HMC. The high level of microbialite activity, coupled with the high stable isotope fractionation values of the sediments of Lake Amy is strong evidence for biologically-aided precipitation of MHC. An increase in the proportions of Mg-rich carbonates to the north of the Robe-Woakwine corridor is possible evidence for a decreasing angle of interface between the denser seawater and groundwater, resulting in a groundwater/seawater mixing zone closer to the surface in the north.

## 1. Introduction

The aim of this study on five lakes in the southeast of South Australia was to:

1. determine the variation in the stable isotopic composition of the modern carbonate precipitate;
2. determine the variation in the stable isotopic composition of the dissolved inorganic carbonate (DIC) of the lake waters;
3. monitor the variation in the composition of the precipitating carbonate for each lake;
4. compare and contrast each lake studied.

The Robe-Naracoorte coastal plain of southeast South Australia is characterised by a series of low ridges. They generally increase in age landward (Sprigg 1952). These ridges are predominantly composed of bioclastic carbonates of varying degrees of lithification. The elevation averages 15m (Cann *et al. in submiss.* 1997). The Robe and Woakwine Ranges run roughly parallel to each other and the current shoreline between Robe and Beachport (Fig. 1), forming the Robe-Woakwine corridor. This flat lying corridor is characterised by a scattering of lakes of various sizes. The series of lakes of concern to this study, Lakes Woolley, Old Man, Fresh Dip, Amy and Ghost, are amongst the smallest within the corridor and are situated either within hollows in the eastern (landward) side of the Robe Range (Amy & Ghost) or within the corridor, at the foot of the Robe Range (Woolley, Old Man, Fresh Dip). The lakes are therefore regarded as simply groundwater windows or alternatively as an outcrop of the local watertable. But to consider these lakes as simply an outcrop of the local watertable neglects to take into consideration many important factors which influence the lake's mineralogy, stable isotopic composition, biological activity, salinity, lake level etc.

The study of oxygen isotopic composition of biogenically and inorganically precipitated calcium-magnesium carbonate minerals is an important field of study in sedimentary geochemistry for both economic and scientific reasons. The fractionation of  $^{18}\text{O}$  between the aqueous and solid phases is temperature dependent. Thus it can be used to determine global environmental change from calculations of palaeotemperature.

The use of oxygen stable isotopic values in lake carbonates is relatively widespread and shows interesting and systematic variations (Talbot 1990), but studies that have calculated the stable isotopic variability of the precipitated carbonate over an experimental period using the measured stable isotopic composition of the lake water from concurrently measured saline conditions are rare (Rosen *et al.* 1994). Many studies have monitored the monthly  $\delta^{18}\text{O}$  of lake

waters, but few have calculated the equilibrium stable isotopic composition of the precipitating carbonates from saline basins that are saturated with respect to carbonate. It is these lakes which will be sensitive to climate-induced hydrological variation which may be reflected in the isotopic composition of the precipitated carbonate (Rosen *et al.* 1994).

## 2. Lake Settings

### 2.1 Location, Morphology and Climate

The lakes are located within the Robe-Woakwine corridor, a 50 km long and 5 km wide flat low-lying region defined by the Robe and Woakwine ranges between Robe and Beachport, southeast South Australia. All lakes are situated either at the foot of the landward side of the Robe Range or within hollows on the landward side of the Robe Range. Hence all experience a similar climate. Average annual rainfall ranges between 50 to 60 cm (Appendix 3.c), and temperatures average 10°C in July to 15-20°C in January (Bayly and Williams 1966). The wind direction is dominated by south westerlies blowing off the Southern Ocean (Mazzoleni 1993).

Lake Woolley is an ephemeral lake located within the Beachport Conservation Park, approximately 2.5 km north-west of Beachport (Fig. 1). The lake is oval shaped and covers an area of ~3 ha, with a maximum depth of ~1.0 m (Fig. 2). The lake's water level ranged from scattered surface ponding in April to approaching overflow level in September. There are no permanent streams entering the lake, and, with no connection to Lake George or the Southern Ocean, the lake can be considered hydrologically closed. Possible sources of water inflow are surface and vadose zone run-off from surrounding dunes, direct rainfall input and direct ground water percolation. Lake biota appears minimal with minor algal blooms appearing and breaking down through the winter. Accumulations of the gastropod *Coxiella striata* (Bullock 1994) built up during the winter and in places dominate the first 0.5 m of the lake beach.

Old Man Lake is located several hundred metres south of Fresh Dip Lake within the Little Dip Conservation Park, approximately 14 km south-west of Robe (Fig. 1). Old Man Lake (Fig. 3) and Fresh Dip (Fig. 4) cover areas of ~3 ha and ~5 ha respectively, with maximum water depths of ~2 m and ~3 m respectively. Old Man Lake biota is the same as that of Lake Woolley. The biota of Fresh Dip lake shows the highest density and diversity of the lakes studied, probably due to the favourable water conditions. Fresh water reeds dominate the lake margin, with small fish and tadpoles also observed, indicating an abundance of aquatic fauna and hence nutrients within the lake environment. The lake floor is dominated by a mixture of fragmented shell material from unidentified fauna(s), covered by a mat of algal material which became more abundant through the winter.

Lake Amy and Ghost Lake are located within a kilometre of each other on 'The Hermitage' (Fig. 1), a private property owned by Mr John Enright. 'The Hermitage' is situated a few kilometres south of Robe. Lake Amy covers an area

of ~7 ha, with a maximum water depth of ~4 m in the northern basin (A.J. Brenchley *pers. comm.* 1997)(Fig 5). Ghost Lake is an ephemeral clay pan which covers an area of ~3 ha (Fig 6). The water level has increased from nil in April to ~0.3 m in September, at which time the lake could be considered to be at overflow level. The biota of Ghost Lake appears limited to a mat of salt-tolerant water grass. The northern lake margin was dominated by a thick mat of dead 'grass', accumulated over the summer by the prevailing wind. During the winter, as the water level rose, a fresh mat of the grass appeared and flourished until it covered the entire lake floor in September. Lake Amy biota is dominated by a thick microbialite mat (5-10 cm) which covers the entire lake floor. Similar microbialites are reported by Moore *et al.* (1984) to be currently forming in Lake Clifton, Western Australia, but under considerably less saline conditions. Exposed 'Pustular doughnut' microbial lithoherms occur on the eastern shore of Lake Clifton and associated with a zone of groundwater discharge (Moore *et al.* 1983) have a thrombolitic fabric, similar to those forming on the northern shore of Lake Amy. Lake Amy is thus the host to a unique hyper-saline tolerant thrombolite-forming microbialite, which appears to dominate the entire lake biota.

Each lake within the group underwent an average increase in water level of ~0.3 m over the duration of the study, i.e. April to September. There are no permanent streams entering any of the lakes, and with no connections to larger adjacent lakes or to the Southern Ocean they can all be considered hydrologically closed. The likely source of water inflow consists of varying combinations of run-off from the surface and through the vadose zone, direct rainfall input and ground-water seepage from adjacent aquifers.

## 2.2 Recent Regional History

During the sea level maximum of the Holocene, the low lying region between the Robe and Woakwine ranges was flooded, forming the Robe-Woakwine corridor. The corridor was open to the sea at Guichen Bay in the north and Rivoli Bay in the south (Fig. 1). Thus seawater was free to circulate uninhibited between the Southern Ocean and the corridor, forming inter-tidal and sub-tidal environments in a back-barrier setting. Longshore drift along the coast between Robe and Beachport had no preferred orientation and sands transported by the currents at the coast were deposited either inland as a series of inland migrating aeolian dunes or were transported both north and south along the coast and deposited to form Guichen and Rivoli Bays.

Sedimentation continued within the bays, and at c.6-7000yr BP a phase of sedimentation partially filled the Guichen Bay opening and by c.2000 yr BP sedimentation was completed by a second phase, and thus the Robe-

Woakwine corridor was completely closed at the northern opening. Although sedimentation was completed at c.2000 yr BP, it is believed that by c.4000 yr BP direct marine access at Guichen Bay was effectively halted by the sedimentation process (Cann *et al. in submiss.* 1997). The southern opening of the corridor at Rivoli Bay remained open after the closure of the northern opening for 2000 years. During this time, incoming seawater transported and deposited bioclastic calcareous sediments which progressively filled the corridor until c.2000 yr BP. The southern opening of the Robe-Woakwine corridor was then completely closed, thus ceasing any direct access for seawater to the corridor (Cann *et al. in submiss.* 1997).

The period of closure of the Robe-Woakwine corridor between c.4000 yr BP and c.2000 yr BP would have marked a period of rapidly changing conditions within the corridor. The increasing lower volumes of unrestricted seawater freely circulating the corridor would have caused water temperature and salinity variations. The increasing infill would have reduced the depth of the remaining water. These varying conditions would have prompted variation in the flora and fauna present in the waters.

Recent sedimentation within the corridor is characteristic of lacustrine and wetland style environments, with today's lakes precipitating carbonate mud of varying mineralogy. This precipitation is enhanced by bacterial and algal influences, along with the influences of the various carbonate-precipitating organisms, eg *Coxiella striata*. The lakes remaining today are a result of the ponding of freshwater surface water and groundwater inputs generally located behind the pre-existing series of ranges (Cann *et al. in submiss.* 1997).

## **2.3 Geological setting**

### **2.3.1 Regional Geology**

The flat-lying coastal plain between Robe and Beachport, and defined on the seaward side by the Robe Range and landward side by the Woakwine Range is referred to as the Robe-Woakwine corridor (Fig. 1). The Robe and Woakwine ranges are the two youngest of the 20 emergent stranded calcareous sand barriers found parallel to the coast of south eastern South Australia (Hossfeld 1950, Sprigg 1952, von der Borch *et al.* 1975, von der Borch *et al.* 1980). The ridges are topographically low, on average 15 m in elevation and increase in age landward (Cann *et al. in submiss.* 1997). The ridges are predominantly composed of bioclastic carbonates of varying degrees of lithification (Cann *et al. in submiss.* 1997) and stretch from western Victoria to the Murray mouth, reaching their widest between Robe and Naracoorte at

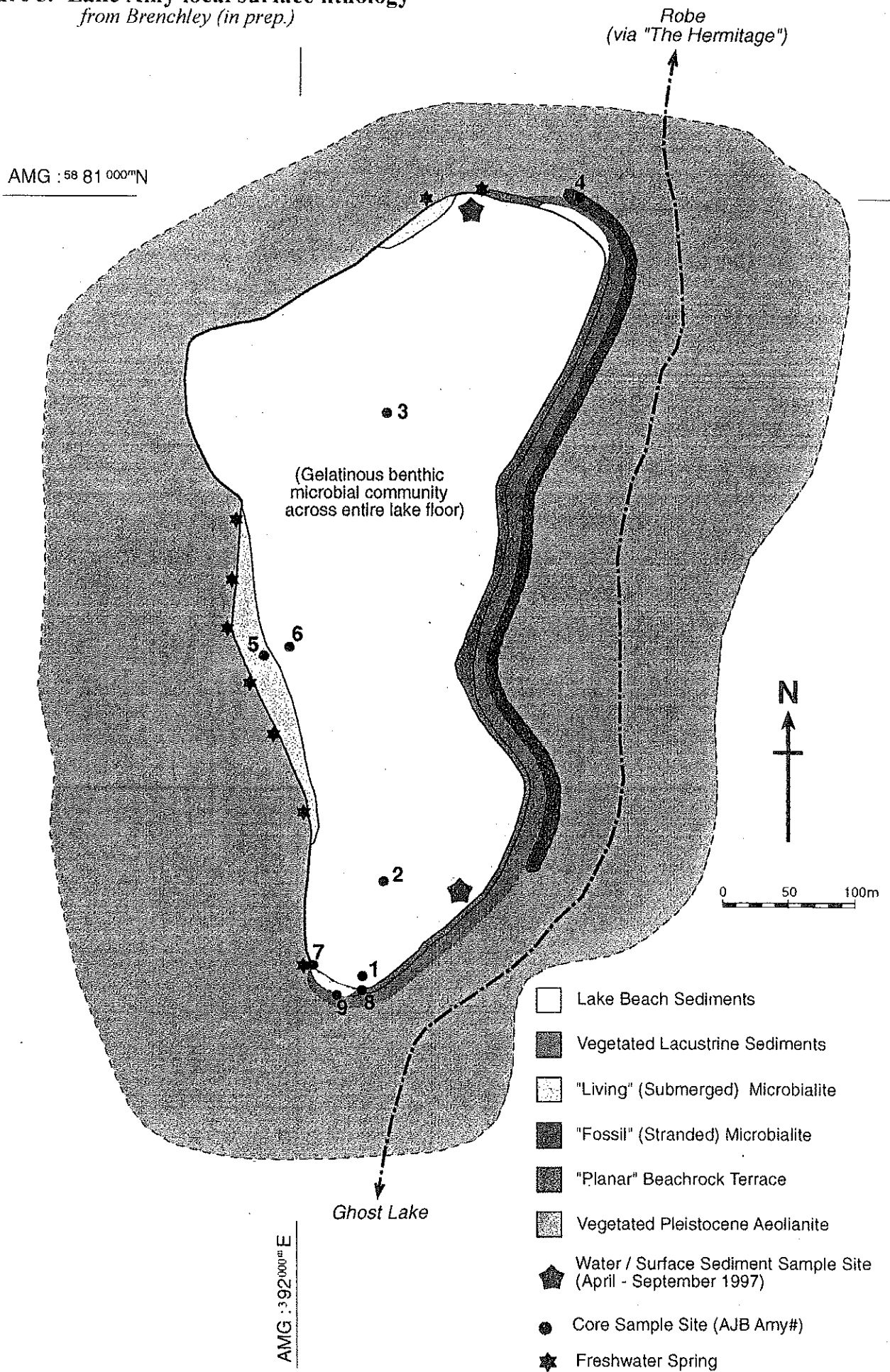


approximately 100 km (Schwebel 1983). The ridges are believed to have originated as shoreline deposits on a low coastal plain undergoing slow tectonic uplift. Each ridge represents a period of high sea-level stand, directly related to glacio-eustatic oscillations that occurred throughout the Quaternary (Hossfeld 1950, Sprigg 1952, von der Borch *et al.* 1980). The gentle regional upwarping of the coastal plain occurred throughout the Quaternary, probably as a result of magma accumulation at regions of basaltic volcanism such as the Millicent region, Mt Gambier and Mt Shank volcanoes. This gentle upwarping, coupled with calcrete development and case hardening, have been major factors in the preservation of the ridges.

### 2.3.2 Local Geology

The relief in the Robe-Woakwine corridor is low, with the ridges producing the topographic highs (Mazzoleni 1993), with the neighbouring Woakwine Range reaching a height of 45 m above sea-level (Burne and Ferguson 1983). Lake Woolley is located at the foot of the Robe Range and is enclosed from the north-west to the south by densely vegetated unconsolidated sand. The remainder of the lake margin is composed of lacustrine beach, with scattered fossil thrombolitic material overlain by calcretised dune sand (Fig. 2). Old Man Lake is situated within a hollow of the Robe Range and is enclosed from the south-east to the north-west by densely vegetated unconsolidated sand (Fig. 3). The remaining margin consists of lacustrine beach and surface hardgrounds, overlain by fossil thrombolitic terrace material. Calcretised dune sands form the final encompassing boundary (Mazzoleni 1993). Fresh Dip Lake lies within a hollow of the Robe Range. The entire lake margin consists of 3-5 m of thick reed beds. Densely vegetated unconsolidated sand encloses the lake from the north-west to the south. The remaining margin consists of fossil thrombolitic terrace material overlain by calcretised dune sand (Fig. 4). Lake Amy is enclosed to the west by vegetated unconsolidated sands, the lake margin consists of lacustrine beach and surface hardgrounds, covered in places with modern thrombolitic material in varying stages of development. This is followed by fossil thrombolitic terrace material which is overlain by calcretised dune sands (Fig. 5). Ghost Lake occupies a hollow within the Robe Range and is bound to the south by vegetated unconsolidated sands. The lake margins consist of lacustrine beach, overlain by fossil thrombolitic material and finally calcretised dune sand (Fig. 6).

**Figure 5. Lake Amy local surface lithology**  
*from Brenchley (in prep.)*



## 2.4 Hydrology

### 2.4.1 Regional Hydrology

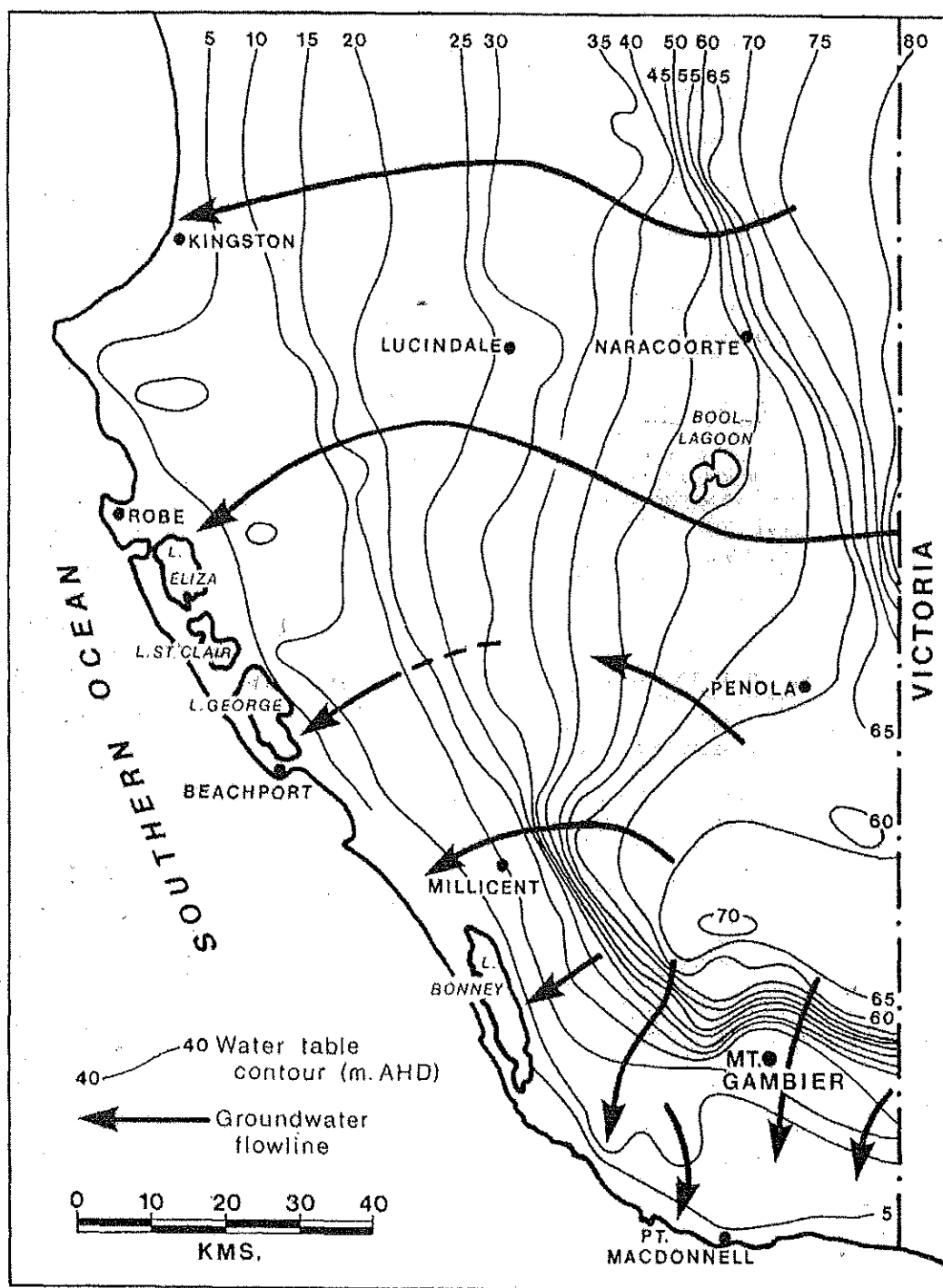
The regional hydrology of the Robe-Woakwine corridor is dominated by a carbonate-rich aquifer referred to as the Upper Gambier Limestone, predominantly a coarse-grained, fossiliferous zone which is porous and permeable, making it one of the best aquifers in Australia (Holmes and Waterhouse 1983). Water within the aquifer flows westward toward the coast (von der Borch *et al.* 1975, Burne and Ferguson 1983, Holmes and Waterhouse 1983), passing across and under the dune ranges (Holmes and Waterhouse 1983)(Fig. 7). The groundwater salinity is extremely variable and dependent upon the local geology, surface conditions above the aquifer, rainfall, recharge rate and origin. In regions of high rainfall and hence high recharge rates, such as the lower South East, TDS in the upper aquifer are low, less than 500 mg/L. These groundwaters exhibit a dominance of  $\text{Ca}^+$  cations, sometimes with  $\text{Mg}^+$ , and  $\text{HCO}_3^-$  as the dominant anion. In the drier northernmost part of the region where recharge is low and groundwater flow slower, the TDS of the groundwaters can reach 5000 mg/L. These groundwaters are dominated by  $\text{Na}^+$  cations and  $\text{Cl}^-$  anions. Within the inter-dune corridors of these regions, the watertable can sometimes be close to the surface, causing a concentration of salts due to evaporation of near-surface groundwater. The salinity of the aquifer increases substantially with depth due to a Ghyben-Herzberg lens of freshwater laying above a denser wedge of seawater (Holmes and Waterhouse 1983). Such an interface exists within the Robe-Woakwine corridor and is currently dipping east at an angle of 14-40° (Nelson 1972).

### 2.4.2 Local Hydrology

Little is known about the local hydrology of each lake. The varying local geology and lake surroundings alter the manner in which waters enter each lake and thus the water's properties. Coupled with the spatial separation of the lakes, varying proximity to the coast and elevation could all cause variability in the composition of the local groundwater entering each lake. A process such as that described by Warren (1982) where the highly permeable unconsolidated dune sand may act as an unconfined aquifer, supplying water to the lake, could be used to describe some of the inflow. The high permeability of the dunes would result in rapid infiltration of waters, not allowing time for evaporation, and would result in fresh water entering the lakes (Nelson 1972). Each lake displays evidence of groundwater seepage in places at the lake margins, which could be attributed to the above process or could be direct percolation of the underlying aquifer water. These locations are sites of reed growth, e.g. the entire margin of Fresh Dip Lake, and indicate the abundance of fresh water in

these locations. The hardgrounds observed at Lake Amy appear similar to those observed by Dutkiewicz and von der Borch (1995) at Lake Greenly on the lower Eyre Peninsula. There, hardgrounds are composed of carbonate and exhibit tepee-like structures, which indicate focal points of groundwater resurgence (Dutkiewicz and von der Borch 1995).

Figure 7. Regional groundwater flow (Holmes and Waterhouse 1983).



### 3. Water Chemistry

#### 3.1 Physical Characteristics

Lake Woolley, an ephemeral lake contained only surface ponding of water in April, which increased through the year. The temperature of the water remaining in April was  $\sim 17^{\circ}\text{C}$ , over May and June the water temperature dropped, to a minimum of  $\sim 12.5^{\circ}\text{C}$  in May. The pH of the water ranged from a minimum of 7.58 during April to a maximum of 8.75 in May, but generally the pH averaged  $\sim 8.1$  (Appendix 3). The TDS ranged from 8.12 g/L in April to a maximum of 79.92 g/L in May, although the general trend is that of a maximum TDS in May which decreased dramatically through to September to TDS  $\sim 21$  g/L (Fig. 8.a). The pH and TDS values recorded in April may not be truly representative as, due to the boggy nature of the exposed lake pan, it was impossible to directly access the ponding surface water. Sampling was carried out on sub-surface water, which possibly was not representative of surface water properties.

Old Man Lake water temperature was at a maximum of  $\sim 19^{\circ}\text{C}$  during April and decreased to a minimum temperature of  $\sim 11.5^{\circ}\text{C}$  in June. The pH of the water remained fairly constant throughout the study, ranging from a maximum of 8.56 in June to a minimum of 7.81 in September, with the average pH of  $\sim 8.1$ . The TDS of the waters ranged from a maximum of 38.85 g/L in April and steadily decreased to a minimum of 20.4 g/L in September (Fig. 8.b).

Fresh Dip's water temperature maximum was  $\sim 17^{\circ}\text{C}$  during April and decreased to  $\sim 11.5^{\circ}\text{C}$  in June. Water pH remained relatively constant, ranging between a maximum of 8.53 in September to a minimum of 7.84 in May. Average pH for the waters was slightly alkaline at  $\sim 8.3$  (Fig. 8.c).

Lake Amy was sampled at two locations, one at the southern shore and one at the north-eastern shore (Fig. 5). The water temperature in the south ranged between  $9^{\circ}\text{C}$  in July to  $\sim 18.5^{\circ}\text{C}$  in April. The north-eastern waters were at a maximum temperature of  $\sim 17.5^{\circ}\text{C}$  during April and decreased to a minimum of  $\sim 10.5^{\circ}\text{C}$  in May. The pH of the southern waters remained almost constant ranging from a maximum of 8.19 in August to a minimum of 7.86 in May, average pH  $\sim 8.0$ . The pH of the north-east waters varied slightly more with a maximum of 8.28 in August to a minimum of 7.63 during April, average pH  $\sim 8.0$ . TDS of the southern water was at a maximum of 76.77 g/L in April and decreased through the year to a minimum of 46.35 g/L. TDS of the north-eastern water ranged from a maximum of 86.85 g/L in April and decreased to a minimum of 45.45 g/L in September (Fig. 8.d & e).

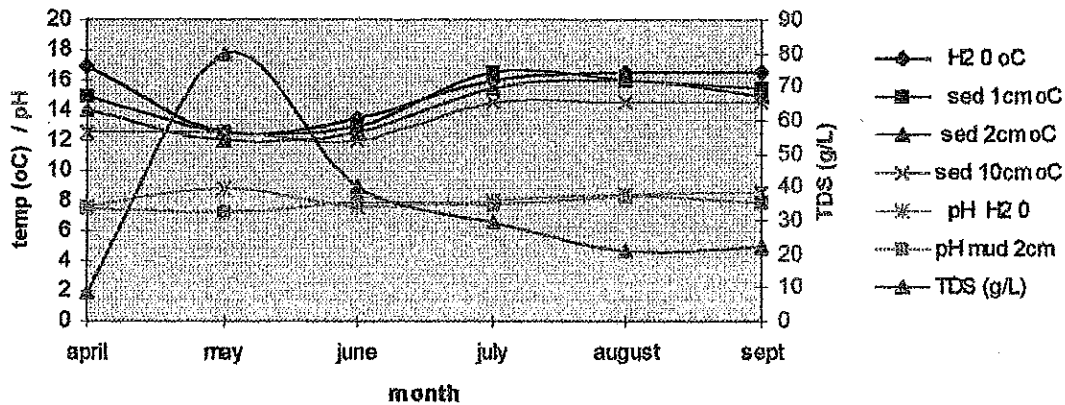
Ghost Lake is an ephemeral lake and was completely dry during April. Water temperature ranged from 17.5°C in May and decreased to a minimum temperature of 10°C in July. The water temperature increased to a maximum of 23°C in September. pH ranged considerably, ranging from slightly acidic (6.97), in June to slightly alkaline (9.68), in September. The TDS ranged from a maximum of 42.7 g/L in May and decreased to a minimum of 15.51 g/L in September (Fig.8. f).

Old Man Lake has an ionic species ratio of  $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$  and  $\text{Cl} > \text{SO}_4 > \text{HCO}_3$  (Mazzoleni 1993), which reflects the species ratios of waters from the northern (Kingston area), more saline regions of the Upper Gambier Limestone aquifer. This correlation could suggest that a major source of ions and possibly water inflow to Old Man Lake is the Upper Gambier Limestone. But with Old Man Lake being located more centrally than in the north of the region this is probably only one source, with possible additional input coming from a regional groundwater/seawater mixing below the lake. Although there is no similar data available for the remaining lakes, due to their close proximity to each other and their similar characteristics, this could also apply for the remaining lakes.

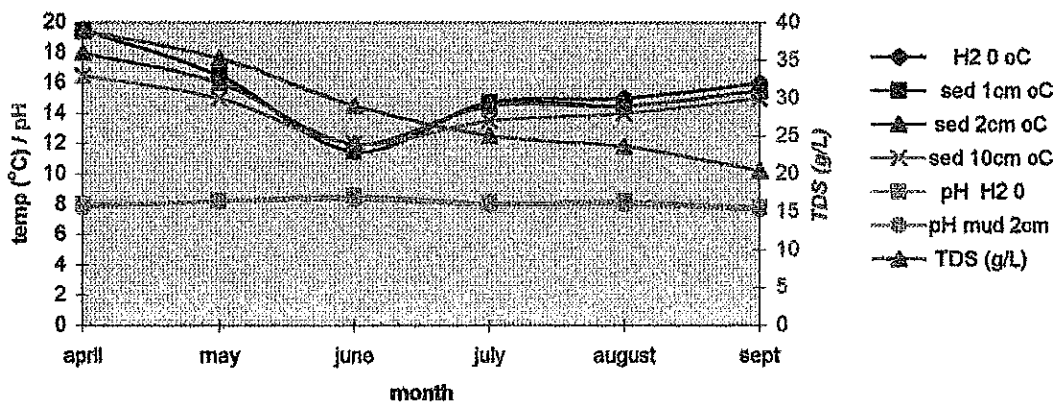
On observation of the TDS trend for each lake, it is apparent that each follows a regular trend. The TDS of the lake waters increase to a maximum over the summer months due to a decrease in precipitation (P) and a dramatic increase in the evaporation (E), i.e., a decrease in the P/E ratio. As precipitation and subsequent run-off increases (a decrease in the P/E ratio) in the months of May and June the TDS decreases dramatically. This decrease continues through the remainder of the winter months, but at a slower rate, reflecting the decrease in the precipitation during this period. The temperature of the waters also exhibit a general trend, reflecting climatic change, decreasing to minimums in the months of May/June/July. This reflects the ambient air temperature. By September, temperatures similar to that of April have again been attained.

Figure 8. Water & sediment temperature, pH & TDS trends

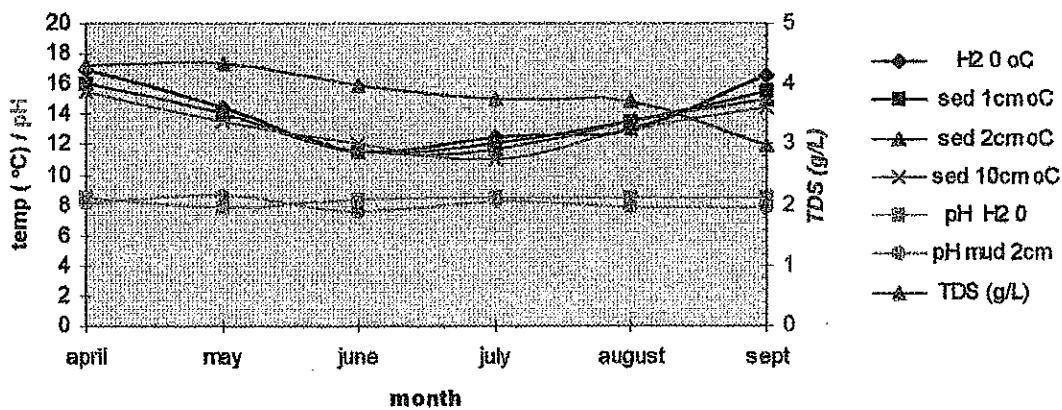
a. Lake Woolley: temp / pH / TDS



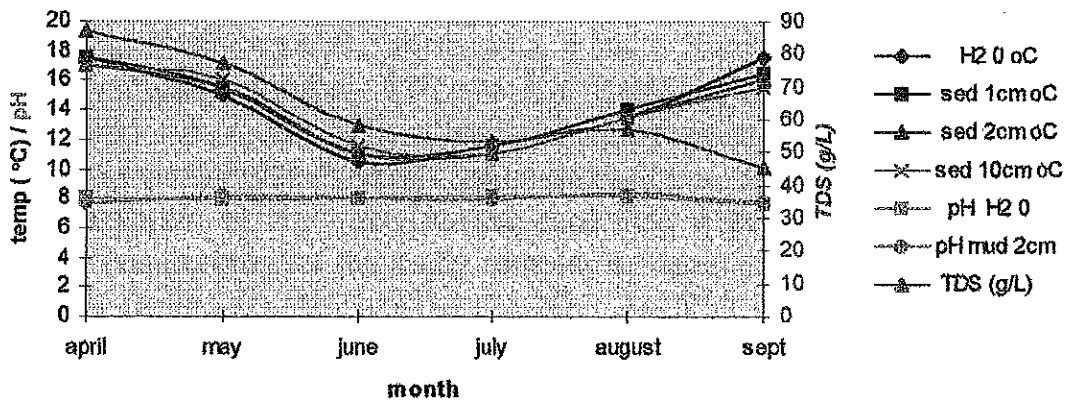
b. Old Man Lake: temp / pH / TDS



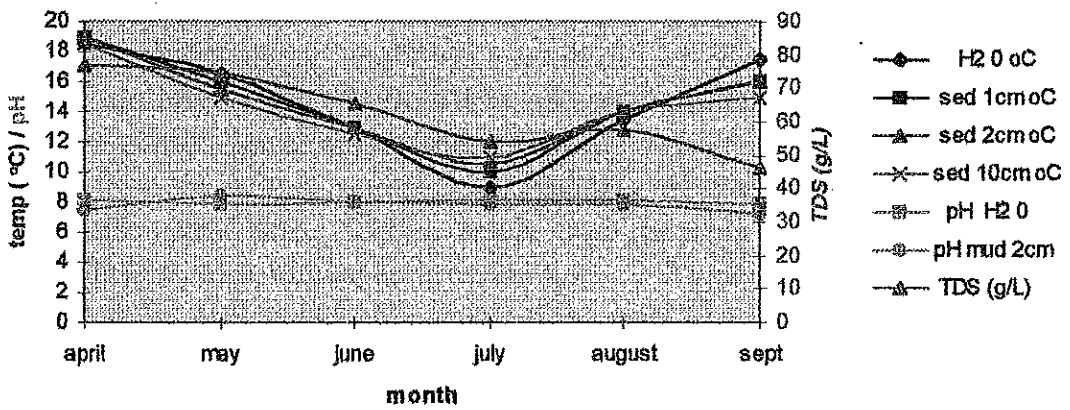
c. Fresh Dip Lake: temp / pH / TDS



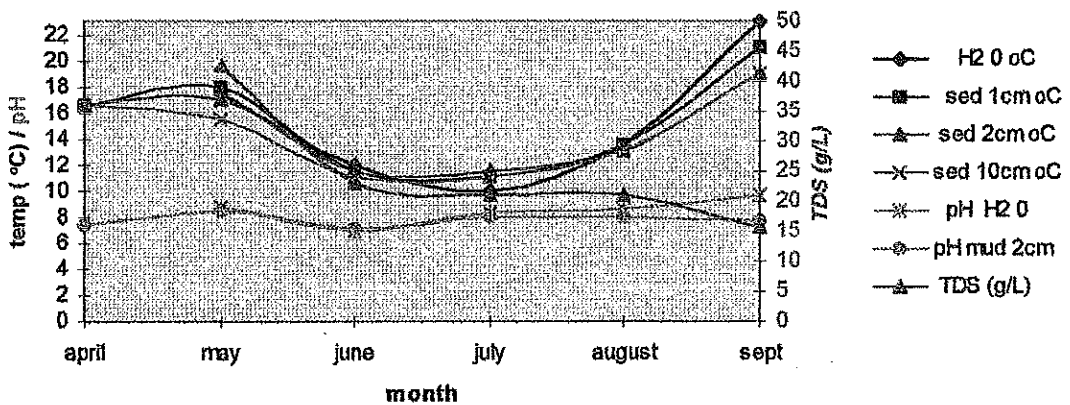
**d. Lake Amy Nth: temp / pH / TDS**



**e. Amy Sth: temp / pH / TDS**



**f. Ghost Lake: temp / pH / TDS**





## 3.2 DIC stable isotopes

### 3.2.1 Introduction

The water samples taken on a monthly basis from each lake were analysed to determine their  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  stable isotopic composition and to monitor any subsequent seasonal variation. Any variation in the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of the lake waters will ultimately cause variability in the composition of these stable isotopes in any precipitation occurring within the lake. The stable isotopic composition of the water samples is determined from the dissolved inorganic carbon (DIC) in the lake water. All  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  stable isotope values are expressed in permil (‰) relative to PDB standards. All quoted stable isotopic enrichment or depletion refer to  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ .

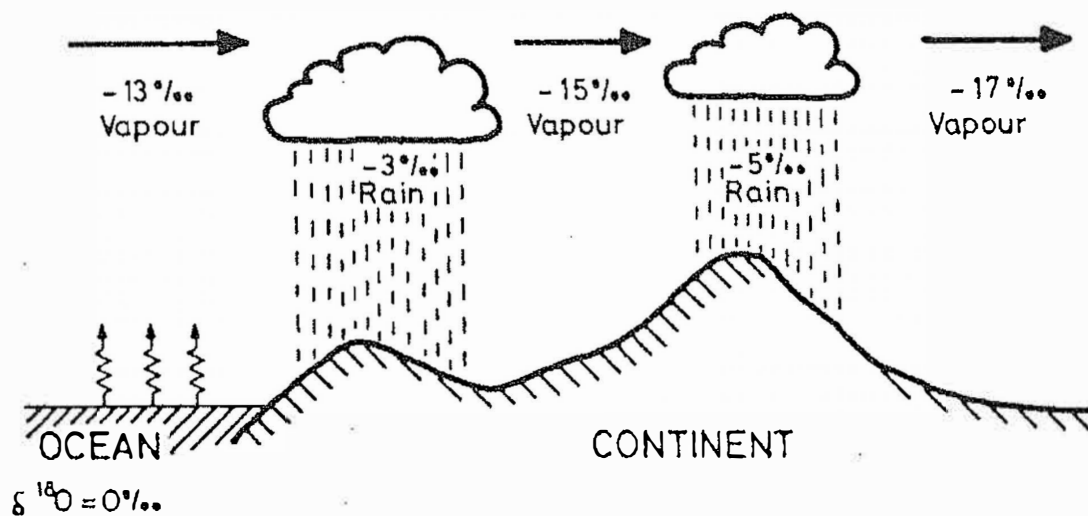
### 3.2.2 DIC stable isotopic equilibrium

Waters entering the lakes are derived from two sources;

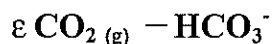
- rainfall, direct input or as a result of surface or vadose zone run-off.
- inflow of groundwaters from adjacent aquifers, from either direct percolation or from surface run-off.

Waters from these two sources are typically in disequilibrium with surface atmospheric conditions. As a result their isotopic signature reflects this disequilibrium with atmospheric conditions. Typically, groundwaters and rainfall exhibit depleted stable isotopic signatures (Fig. 9).

Figure 9. Rain  $\text{H}_2\text{O}$  fractionation (Arthur *et al.* 1983).



Rosen *et al* (1994) quote  $\delta^{13}\text{C}_{\text{DIC}}$  (surface waters) which range from -3.3 to -12.2, and  $\delta^{18}\text{O}_{\text{DIC}}$  from Yadav (1996) are quoted to range from -6.5 ‰ to -3‰. Waters equilibrating with atmospheric conditions, i.e. the DIC of the water equilibrating with atmospheric  $\text{CO}_2$ , undergo a process of stable isotopic fractionation, with the previously depleted DIC undergoing enrichment. Enrichment values vary, depending on the reference, with some typical values listed below.



$^{13}\text{C}$  fractionation (‰)

$-8.13 \pm 0.3$	(T=22°C)	Vogel(1961,1959)
$-8.38 \pm 0.3$	(T=28°C)	Wendt (1968)
-7.92	(T=25°C)	Mook <i>et al</i> (1974)
-7.89	(T=25°C)	Szenan & Zuk (1980)
$-8.27 \pm 0.3$	(T=25°C)	Turner(1982)
$-8.38 \pm 0.12$	(T=20°C)	Emrich <i>et al</i> (1970) & Romanek <i>et al</i> (1992)

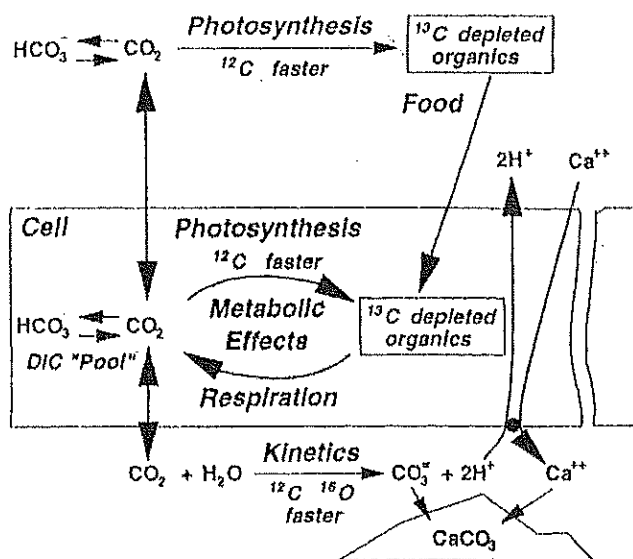
average  $\approx -8.15$  ‰

$^{18}\text{O}$  fractionation (‰)

-7.1	(T=19°C)	Usdowski and Hoefs (1993)
------	----------	---------------------------

The carbon isotopic composition of the aqueous  $\text{HCO}_3^-$  pool can be affected by several important processes (Fig. 10).

**Figure 10. Metabolic and kinetic fractionation effects**  
(McConnaughey *et al.* 1996)



Productivity level alters the  $\text{HCO}_3^-$  pool by the process of photosynthetic removal of  $^{12}\text{C}$ , i.e. the larger the biomass the larger the removal of  $\text{CO}_2$ , leaving the  $\text{HCO}_3^-$  pool enriched in  $^{13}\text{C}$  (Craig *et al.* 1963). Respiration acts in the exact opposite manner to photosynthesis, depleting the  $\text{HCO}_3^-$  pool in  $^{13}\text{C}$  (Andrews *et al.* 1993), although daytime photosynthesis often acts several times faster than respiration (McConnaughey *et al.* 1996) and may possibly mask any effect respiration is having on the  $\text{HCO}_3^-$  pool. Significant amounts of isotopically-light decaying organic matter ( $\delta^{13}\text{C} \sim -25\%$ , Arthur *et al.* 1983), in the water column and in the bottom sediment will result in the  $\text{HCO}_3^-$  pool being depleted in  $^{13}\text{C}$ , i.e.  $\delta^{13}\text{C}_{\text{DIC}}$  depletion (Andrews *et al.* 1993). The dissolution of carbonates ( $\delta^{13}\text{C} \sim 1\%$  to  $2\%$ , Arthur *et al.* 1983) within the basin through kinetic fractionation results in the  $\text{HCO}_3^-$  pool becoming enriched in  $^{13}\text{C}$  (Holmes *et al.* 1997; McConnaughey *et al.* 1996).

Another source of variation to the  $\text{HCO}_3^-$  pool is lake stratification. Stratification could possibly effect the deeper lakes, Lake Amy, Fresh Dip and Old Man Lake. Stratification of the lake waters occurs in the absence of a mechanism to mix the deeper waters with the surface waters, resulting in two chemically and physically distinct waters bodies. The surface waters experience the variations due to evaporation and photosynthesis, while the deeper waters are influenced by the decomposition of organic material. Rosen *et al.* (1994) suggested mixing of lakes similar to those being studied could possibly occur during March to June due to the late stages of evaporation and the inflow of the first winter rains. Mixing of the lake waters results in the flow of depleted bottom waters to the surface, suddenly altering the stable isotopic signature of the lake surface water.

The oxygen stable isotopic composition of the aqueous  $\text{HCO}_3^-$  pool is primarily effected by fractionation arising from evaporation of the water body. The process of evaporation preferentially removes  $^{16}\text{O}$  (Fig. 9), resulting in the aqueous  $\text{HCO}_3^-$  pool becoming enriched in  $^{18}\text{O}$ , i.e.  $\delta^{18}\text{O}_{\text{DIC}}$  enrichment.  $\delta^{18}\text{O}_{\text{DIC}}$  can be seen to vary linearly with salinity (Yadav 1994), presumably as a result of evaporation, until the late stages of evaporation where reduction of the fractionated portion is due to the back-condensation of atmospheric moisture ( $\delta^{18}\text{O} \approx -20\%$ , Craig & Gordon 1965), in addition to the changing chemical activity of the water. This is influenced by the precipitation of hydrated mineral salts (Yadav 1994).

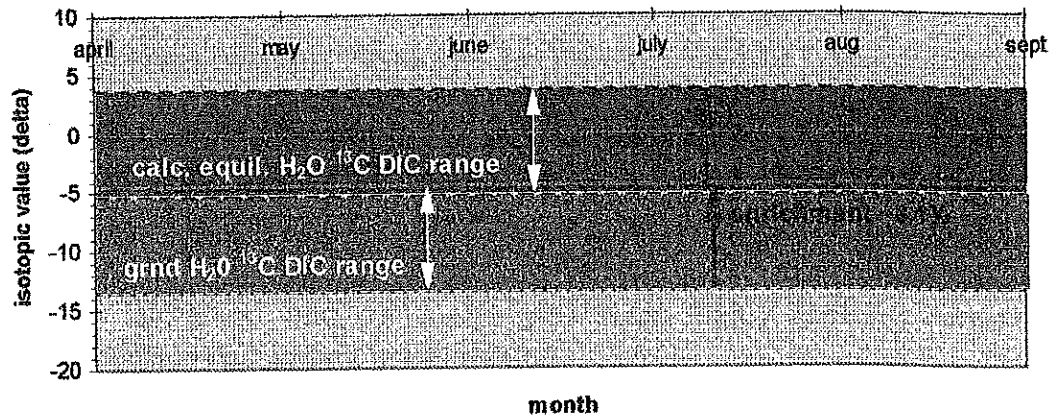
The interplay between these processes, along with other factors such as water inflow and outflow rates, makes trying to decide between mechanisms that control the lake  $\text{HCO}_3^-$  stable isotopic composition problematic. This is well illustrated by the varying stable isotopic values recorded for each lake of the study area.

### 3.2.3 Groundwater DIC stable isotopic composition

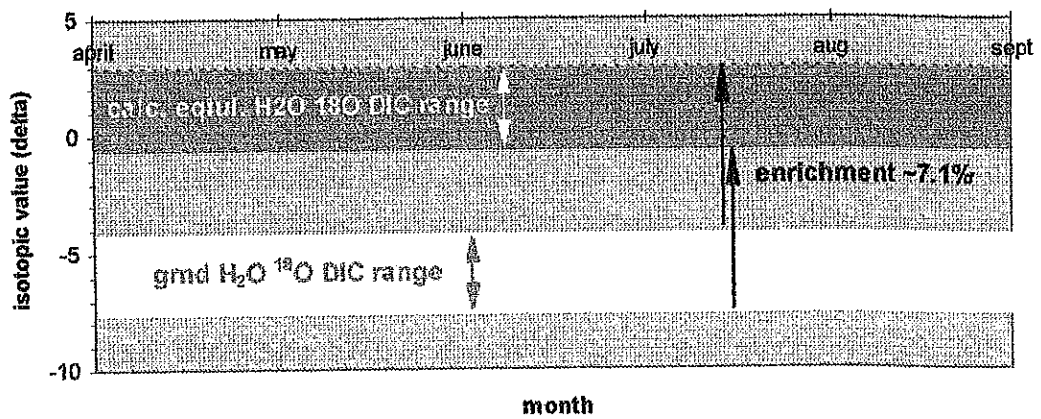
Several sources of groundwaters were sampled throughout the study period. All were freshly sampled from bores to assure a current stable isotopic signature. Groundwaters were sampled from a bore at Little Dip Beach (Fig. 1) and from a bore at the 'The Hermitage', just north of Lake Amy (Fig. 1). Rainwater was also sampled from 'The Hermitage', during periods of rainfall, again to assure a current stable isotopic signature. The  $\delta^{18}\text{O}_{\text{DIC}}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  from these water sources were depleted significantly with respect to lake waters. Groundwater  $\delta^{18}\text{O}_{\text{DIC}}$  values were typically -7.9 ‰ to -4.1 ‰ and  $\delta^{13}\text{C}_{\text{DIC}}$  ranged between -13.4 ‰ to -4.3 ‰. Rainfall values exhibited even larger depletion with  $\delta^{18}\text{O}_{\text{DIC}} \sim -10.0$  ‰ and  $\delta^{13}\text{C}_{\text{DIC}} \sim -21.0$  ‰ (Appendix 2), values which represent waters in disequilibrium with atmospheric conditions. Groundwaters from these sources undergoing  $\delta^{18}\text{O}_{\text{DIC}} (\text{CO}_2 (\text{g}) - \text{HCO}_3^-)$  and  $\delta^{13}\text{C}_{\text{DIC}} (\text{CO}_2 (\text{g}) - \text{HCO}_3^-)$  fractionation of -7.1‰ and -8.15‰ respectively should yield  $\delta^{18}\text{O}_{\text{DIC}}$  values in the range -0.8‰ to 3.0‰ and  $\delta^{13}\text{C}_{\text{DIC}}$  values in the range -5.2‰ to 3.8‰ (Fig. 11 over page).

Figure 11. Groundwater / Surface water stable isotopic equilibrium.

a. *Ground H<sub>2</sub>O / Equilibrium surface H<sub>2</sub>O <sup>13</sup>C DIC*



b. *Ground H<sub>2</sub>O / Equilibrium surface H<sub>2</sub>O <sup>18</sup>O DIC*



### 3.2.4 Lake water DIC stable isotopic composition

Lake Woolley  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{DIC}}$  values vary between -4.2‰ to 1.1‰ and -3.7‰ to 1.3‰ respectively (Fig.13.a & Appendix 2). The DIC stable isotopic signature appears to follow a negative trend from May to September, with a strongly negative excursion in August. April data can be explained as the water sampled was sub-surface and therefore not representative of surface-water. The trend represents a depletion in both  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{DIC}}$ , possibly due to increasing respiration, although this is not likely as there is a lack of lake fauna. An increased inflow of depleted waters not yet fully equilibrated, coupled with lowering evaporation through the winter, could explain the negative DIC trend, and could also explain the highly depleted August data which was sampled during heavy rainfall.

Old Man Lake  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{DIC}}$  values vary between -2.7‰ to -1.6‰ and 2.0‰ to 4.9‰ respectively (Fig.13.b). The  $\delta^{13}\text{C}_{\text{DIC}}$  signature follows a tight trace showing very little deviation, possibly representing well-mixed waters combining quickly and undergoing no major fluctuations in biomass or biotic activity. The  $\delta^{18}\text{O}_{\text{DIC}}$  follows an erratic trace, with April showing an enriched signature possibly representing evaporation and elevated salinity over summer followed by a large (~ 9.5‰) depletion, possibly representing the sudden inflow of depleted waters from ground and meteoric sources, or the result of increased respiration. The following enrichment possibly represents the slowing of mixing allowing waters to equilibrate.

Don Dip Lake  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{DIC}}$  values varied little, with  $\delta^{13}\text{C}_{\text{DIC}}$  ranging between -1.4‰ to -0.3‰ and  $\delta^{18}\text{O}_{\text{DIC}}$  ranging between 0.3‰ to 1.0‰. These constant traces represent a well mixed lake with water in equilibrium. This water is probably experiencing constant influences with no significant changes in salinity, biota or biomass, or source of water inflow.

Don Dip Lake was sampled at two locations. In the north, the  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{DIC}}$  values ranged between -0.5‰ to 2.3‰ and -3.9‰ to 0.7‰ respectively. In the south,  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{DIC}}$  varied between -1.0‰ to 1.2‰ and -4.1‰ to 0.7‰ respectively (Fig.13.d&e). Both locations display similar behaviour with  $\delta^{13}\text{C}_{\text{DIC}}$  being enriched in April/May before achieving a relatively constant trace. The depleted  $\delta^{18}\text{O}_{\text{DIC}}$  in April/May is unexpected, as  $\delta^{18}\text{O}_{\text{DIC}}$  is expected to be enriched with increasing salinity, resulting in  $\delta^{18}\text{O}_{\text{DIC}}$  enrichment, which is not reflected in the  $\delta^{13}\text{C}_{\text{DIC}}$  as would be expected with increased influence. The depleted signature could be due to the inflow of depleted waters resulting in depleted bottom waters combining with surface waters. This trend is not reflected in the  $\delta^{13}\text{C}_{\text{DIC}}$  as would be

expected. The slightly enriched  $\delta^{13}\text{C}_{\text{DIC}}$  in April/May may represent favourable conditions for microbialite growth prevailing during this period increasing photosynthetic activity, or could reflect evaporation effects, both would result in enrichment in the  $\text{HCO}_3^-$  pool.

Ghost Lake's  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{DIC}}$  values range between -4.4‰ to 0‰ and -2.2‰ and 0.1‰ respectively (Fig.13.f). The  $\delta^{13}\text{C}_{\text{DIC}}$  follows a distinct enrichment trend throughout the winter, probably due to increased photosynthesis accompanying the growth of the salt tolerant grass during this period. The  $\delta^{18}\text{O}_{\text{DIC}}$  trace shows enrichment during June and July before achieving a constant trace, this initial enrichment could be the result of evaporation of the first winter waters entering the lake.

The average stable isotopic signatures of the lake water DIC are:

	ave. $\delta^{13}\text{C}_{\text{DIC}}$	ave. $\delta^{18}\text{O}_{\text{DIC}}$
<i>Lake Woolley</i>	-0.8	-0.8
<i>Old Man Lake</i>	-2.0	-0.2
<i>Fresh Dip Lake</i>	-1.0	0.8
<i>Lake Amy Nth</i>	0.95	-0.6
<i>Lake Amy Sth</i>	0.2	0.6
<i>Ghost Lake</i>	-2.3	-1.1

Lake Amy's DIC stable isotopic composition is slightly more enriched relative to the other lakes. This is possibly the result of photosynthetic enrichment, attributable to the large microbialite community inhabiting the entire lake floor (A.J. Brenchley *pers. comm.* 1997), overprinting the atmospheric equilibrium enrichment process. This relative enrichment indicates that the lake has not undergone mixing during the study period, as this would result in a sudden stable isotopic depletion. Without direct measurement of the lake water with depth however, it is hard to determine whether the lake is stratified by simply considering the stable isotopic fluctuations. As the two main processes, photosynthesis and decomposition of biological material result in the opposite effect on the DIC pool, making differentiation between the effects and subsequent interpretation almost impossible. A temperature stratification has been reported by A. Brenchley (1997) at approximately 1 m depth in the north basin. The surface water was  $\sim 22^\circ\text{C}$ , whereas water at 1 m was  $19^\circ\text{C}$ . This temperature inversion was observed in late September/early October 1996 (A.J. Brenchley *pers. comm.* 1997). Due to the size, depth and sheltered environment of the lake it is likely that the lake would be seasonally stratified, presumably during the summer months when water inflow is low.

Ghost Lake's DIC isotopic composition is slightly depleted relative to the other lakes, even after enrichment in August. The depleted nature of the water could indicate that the source of the lake's water is more depleted than those feeding the other lakes. This could either be attributed to a different source of groundwater inflow, possibly a more locally confined aquifer or could simply mean that a greater percentage of the water is meteoric in origin, which is highly depleted relative to ground-waters. Due to the ephemeral nature of the lake, the latter appears more feasible.

Generally the DIC isotopic composition of the lake waters represent surface-waters, originating predominantly from depleted ( $\delta^{13}\text{C}_{\text{DIC}}$  &  $\delta^{18}\text{O}_{\text{DIC}} \approx -12\text{‰}$  to  $-4\text{‰}$ ) groundwater, and particularly in the case of Ghost Lake, rainwaters ( $\delta^{13}\text{C}_{\text{DIC}}$  &  $\delta^{18}\text{O}_{\text{DIC}} \approx -22\text{‰}$  to  $-8.6\text{‰}$ ). The  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{DIC}}$  of the lake waters range between  $-4.5\text{‰}$  to  $+1.0\text{‰}$ , with most values ranging between  $-2.0\text{‰}$  and  $0\text{‰}$ . These values would correspond well to observed groundwater values which have then undergone enrichment due to equilibrium stable isotopic fractionation and fall within the expected calculated range for such depleted ground/rain waters undergoing stable isotopic fractionation, as shown in Fig.11.  $\delta^{18}\text{O}_{\text{DIC}}$  plotted against salinity, as shown in Fig. 12, does not display the linearity suggested by Yadav (1994). Lake Woolley and Old Man Lake are the closest to a linear relationship, while Fresh Dip and Ghost Lake vary independently of salinity change. Lake Amy's results display the opposite relationship with  $\delta^{18}\text{O}_{\text{DIC}}$  increasing with decreasing salinity. These results suggests varying influences upon the  $\delta^{18}\text{O}_{\text{DIC}}$  of each lake which are masking the linearity attributable to evaporation effects.



Figure 12.  $\delta^{18}\text{O}_{\text{DIC}}$  v's Salinity (TDS).

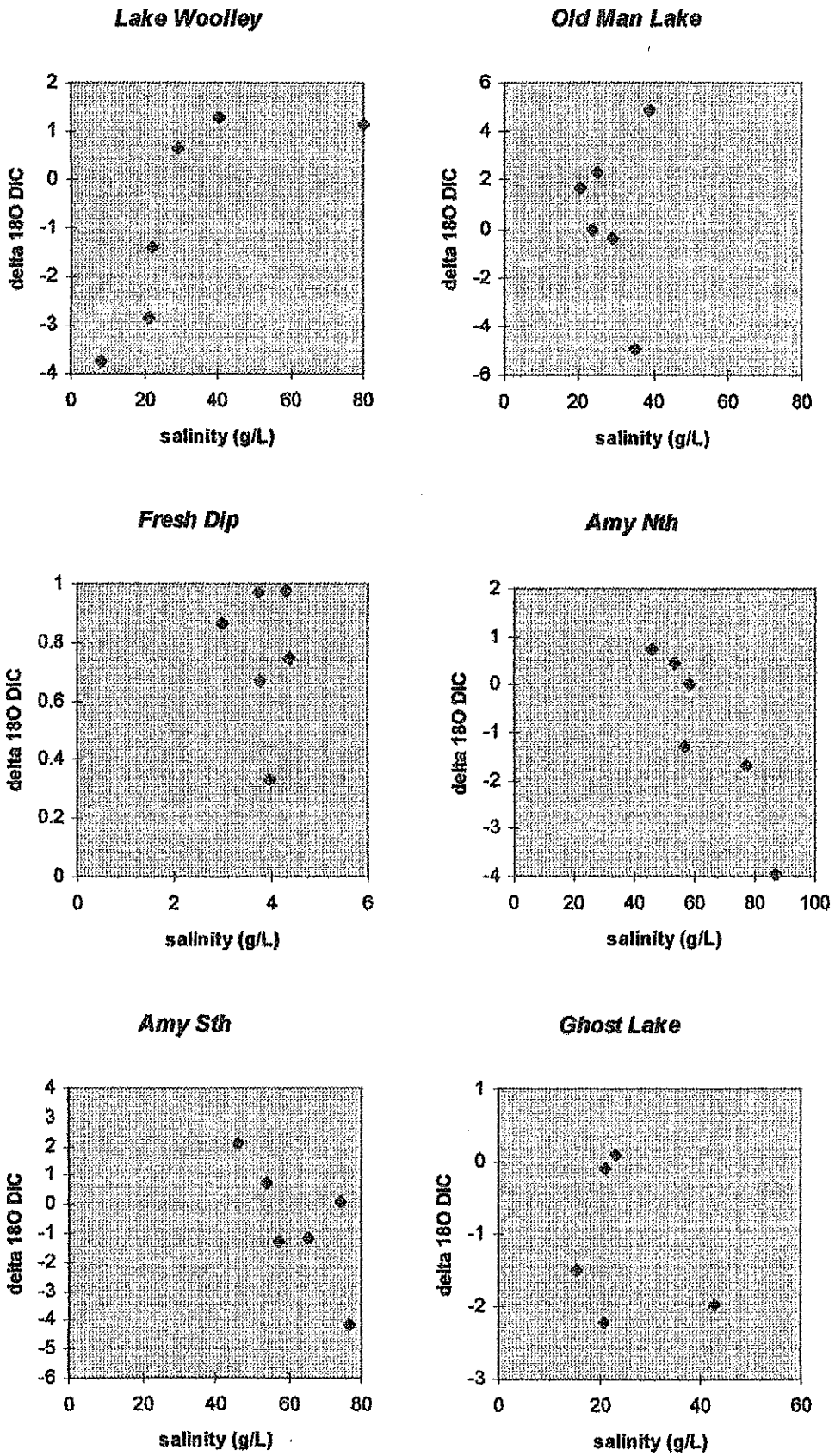
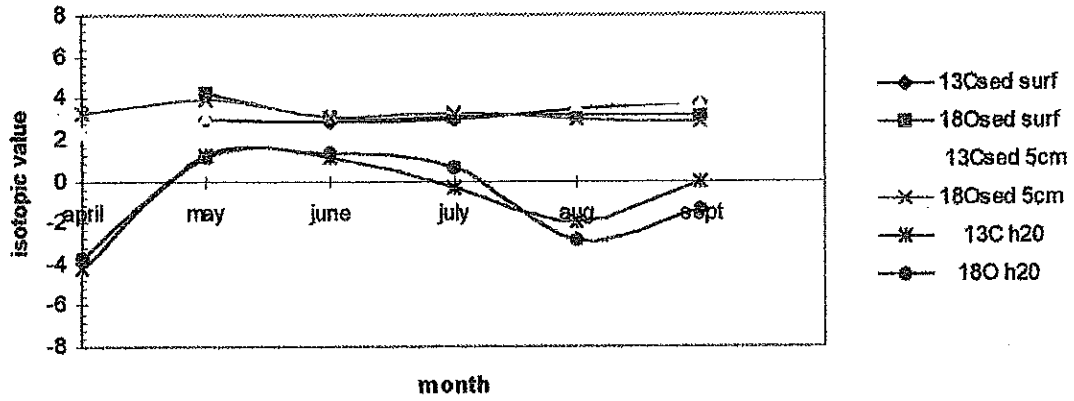
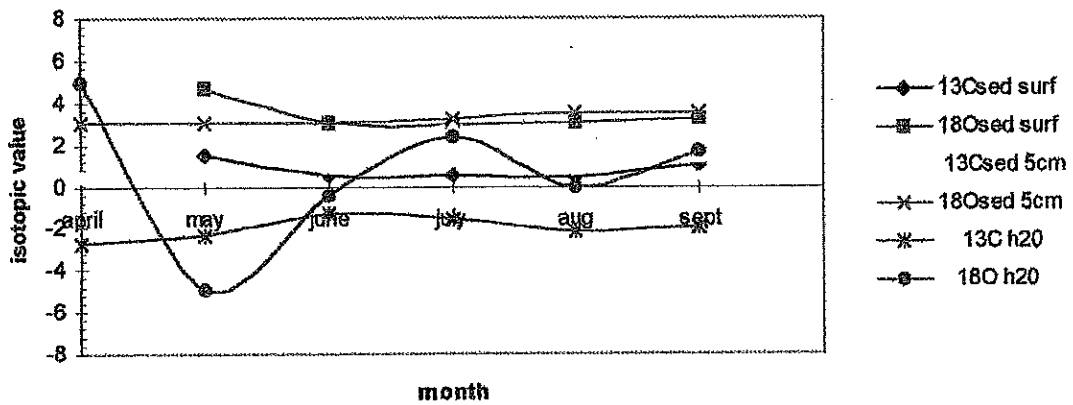


Figure 13. Stable isotope data trends.

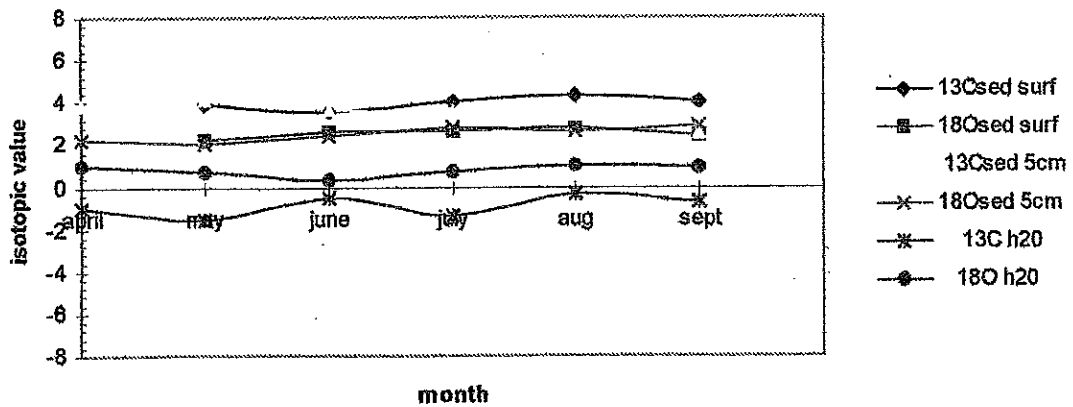
a. Lake Woolley stable isotope data plot



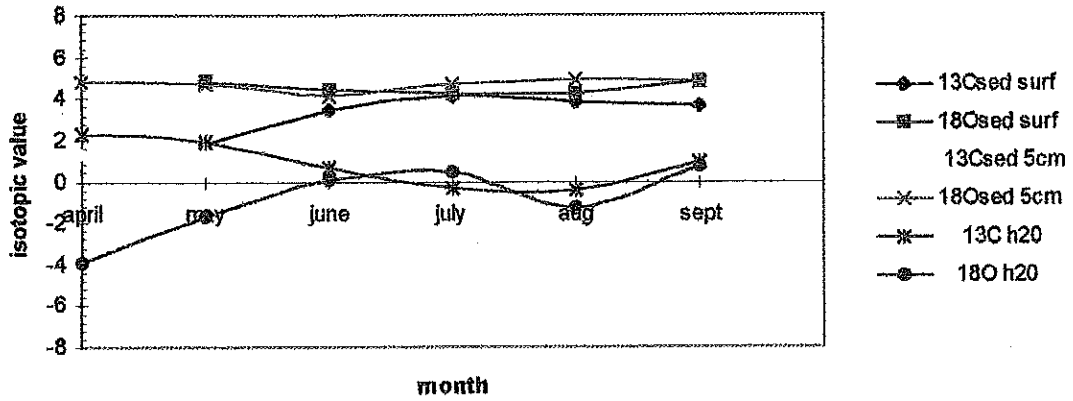
b. Old Man Lake stable isotope plot



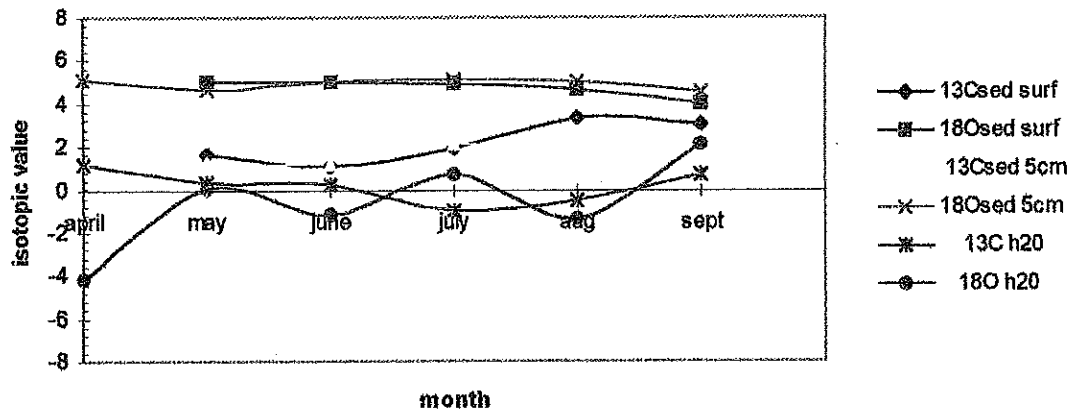
c. Fresh Dip stable isotope plot



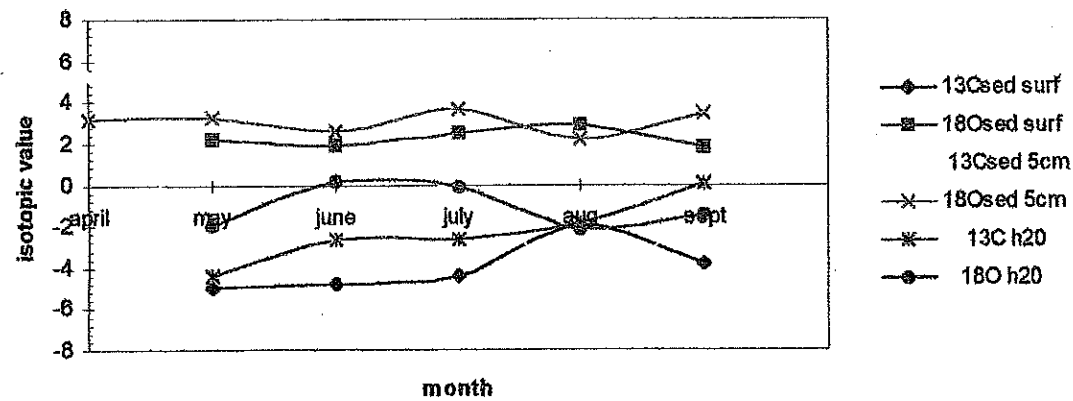
d. *Lake Amy Nth stable isotope data plot*



e. *Lake Amy Sth stable isotope plot*



f. *Ghost Lake stable isotope plot*



## 4.0 Recent carbonate sediments

### 4.1 Physical characteristics

The physical characteristics, namely temperature and pH, of the carbonate sediments were recorded, as with the water samples, at a fixed location and on a monthly basis (Appendix 3). The pH of the sediment was recorded at a depth of 2cm and the temperature was recorded at depths of 1, 2 & 10 cm. As a general trend, the sediment temperatures appear to follow the same trend as the water temperatures, indicating that as the water temperature responds to a decrease in ambient air temperature in the winter months the sediment responds to the changing water temperature. This indicates that water and sediment temperature variations are in response to seasonal ambient temperature changes. The pH of the sediment was almost the same as the water pH, with a marginally more acidic trend (-0.5) in most cases, possibly in response to decaying organic material in the sediment. The pH of the sediment varied little throughout the winter, with most sediments exhibiting minor ( $\pm 0.5$ ) fluctuations.

Lake Woolley sediment temperatures range between 12°C and 16.5°C, with minimum temperatures recorded in May and June. Sediment pH ranged between 7.21 and 8.28, with an average of  $\sim 7.7$ . The maximum separation observed between water and sediment pH was recorded in May ( $\sim 1.5$ ), corresponding to the month of lowest water and sediment temperatures (Fig. 8.a). Old Man Lake's sediment temperature varied between 19.5°C and 11.5°C with minimum temperatures recorded in June. Sediment pH ranged between 7.6 and 8.3, with an average of  $\sim 8.0$ . The sediment pH corresponded almost exactly with water pH values, again with the greatest separation (0.26) occurring during the month of lowest temperatures (Fig. 8.b). Fresh Dip Lake's sediments ranged between 11°C and 16°C, with minimum temperatures observed during June and July. Sediment pH showed greatest variation when compared to water pH of any of the lakes, which is unexpected due to the constant nature of the lake. Values for pH ranged from 7.61 to 8.65, with an average of  $\sim 8.1$  (Fig. 8.c). Lake Amy was sampled at two locations; sediment temperatures in the north-east ranged between 11°C and 17.5°C and in the south ranged between 10°C and 19°C, with minimum temperatures recorded in June and July. Sediment pH in the north ranged from 7.63 to 8.17, average  $\sim 7.9$  and in the south between 7.18 and 8.39, average  $\sim 7.8$ . Sediment pH varied little from water pH (Fig 8.d&e). Ghost Lake sediment temperatures ranged from 11°C to 21°C, with minimum temperatures during June and July. pH ranged from 7.38 to 8.45, with an average of  $\sim 7.8$ . Maximum separation ( $\sim 2.1$ ) occurred during September, as temperatures increased dramatically (Fig 8.f).

## 4.2 Carbonate sediment mineralogy

The carbonate mineralogy of the lake sediment is an assemblage of low magnesium calcite (LMC), intermediate magnesium calcite (IMC), high magnesium calcite (HMC), monohydrocalcite (MHC) and aragonite (Appendix 1). The composition of LMC ranges between 0 and 4 mole % Mg, IMC ranges between 4 and 12 mole % Mg, and HMC  $\approx$  >12 mole % Mg (Bone and James 1993). Halite was also observed in most lakes throughout the study but its occurrence was variable, and percentages would be considered as very minor 'trace' amounts. Surface sediment were sampled as a thin veneer of sediment from the lake bottom. Recent sediments are generally collected using a pan suspended above the lake floor, which collects only recent precipitate. Therefore, the surface samples collected will contain an amount of residual material and are not totally representative of recent precipitation. Recent precipitation has been inferred from variations in the mineral percentages of the sediments.

Lake Woolley's mineral assemblage comprises a combination of aragonite, LMC and HMC. The average mole % Mg of the LMC is ~2.8, and the HMC averages ~24.7 mole % Mg. The average composition of the surface sediment comprises ~38 % aragonite, ~38 % LMC and ~24 % HMC, sub-surface sediment average composition was ~42 % aragonite, ~36 % LMC and ~22 % HMC (Fig. 14.a). The percentage of aragonite decreased during the winter months, while the percentages of LMC increased, indicating conditions more favourable for the precipitation of LMC. The percentage of HMC remained relatively constant indicating conditions not favourable for its precipitation. The decreasing salinity of the waters could account for the decrease in HMC precipitation. The high percentage of aragonite over the summer months is possibly the result of salinity reaching levels which promote aragonite precipitation, but not promote the precipitation of HMC.

Old Man Lake's mineralogy is an assemblage of aragonite, LMC and IMC. Average composition of the LMC is ~2.8 mole % Mg, and the IMC averaged ~9.7 mole % Mg. Composition of the surface sediments averaged ~32 % aragonite, ~28 % LMC and ~40 % IMC, and sub-surface sediment averaged ~29 % aragonite, ~33 % LMC and ~38 % IMC (Fig 14.b). The IMC of both the surface and sub-surface sediment exhibited an overall decreasing trend, compensated by an increasing trend in both aragonite and LMC percentages in both surface and sub-surface sediments. This indicates favourable conditions for LMC precipitation, with minor Aragonite precipitation. The decreasing salinity could account for the decreasing precipitation of IMC during the winter.

The mineralogy of Fresh Dip Lake is dominated by aragonite with LMC and IMC. LMC averaged ~2.4 mole % Mg, while IMC averaged ~9.5 mole % Mg. Surface sediment composition averaged ~83 % aragonite, ~7 % LMC and ~10 % IMC and sub-surface sediment averaged ~88 % aragonite, ~6 % LMC and ~6 % IMC (Fig 14.c). The sediments at both surface and sub-surface levels exhibited almost no variation throughout the year, this could be as a result of the fresh nature of the waters (TDS ~4.0 g/L) currently present in the lake not favouring carbonate precipitation. The aragonite which comprises the vast majority of the lake sediment is possibly derived from fragmented shell material from fauna inhabiting the lake and not from recent inorganic carbonate precipitation.

The mineralogy of Lake Amy is unique in that it not only comprises the expected aragonite, LMC & HMC but also MHC, with IMC observed in trace amounts in some months. Mole % Mg of the LMC and HMC were ~2.9 and ~23.9 respectively in the south of the lake and ~2.3 and ~21.7 respectively in the north. Surface sediment averages ~12 % aragonite, ~16 % LMC, ~58 % HMC and ~14 % MHC in the south and ~9 % aragonite, ~12 % LMC, ~39 % HMC and ~40 % MHC. The sub-surface sediment composition averages ~6 % aragonite, ~15 % LMC, ~77 % HMC and ~2 % MHC in the south and ~11 % aragonite, ~25 % LMC, ~61 % HMC and ~3 % MHC in the north (Fig 14.d&e). In the south general trends of the sediments vary with depth as do the mineral percentages. The surface sediment exhibits a decrease in HMC and aragonite, coupled with an increase in LMC and MHC percentages. Thus indicating conditions favouring the precipitation of LMC and MHC, possibly the result of decreasing salinity and increasing biological activity. Whereas, in the sub-surface sediment HMC decreases slightly and MHC and aragonite increase slightly. LMC remains relatively constant with the one isolated increase corresponding with a major isolated decrease in HMC, possibly a result of exsolution of Mg from HMC. In the north, general percentage trends remain constant at depth for all minerals except LMC, and MHC. The percentage of aragonite decreases, while HMC initially decreases dramatically during April to June followed by an increase during the remaining months. The decreasing salinity could account for the decrease in precipitation of HMC and aragonite and increase in precipitation of LMC. The MHC percentages at the surface increased dramatically, reflecting favourable conditions for its precipitation during winter, again, possibly the result of biological activity. At depth the percentages of MHC remain constantly below the surface percentages, possibly indicating its decomposition to a more stable carbonate phase on burial. LMC percentages at the surface remain constant. At depth the initially high percentages of LMC correspond to a decrease in HMC, possibly the result of exsolution of Mg from the HMC and recrystallization as pure calcite during the summer and early winter.

Ghost Lake mineralogy is an assemblage of aragonite, LMC & HMC. Average mole % Mg of the LMC is ~2.6 whereas the HMC averaged ~12.3. Surface sediment composition averaged ~19 % aragonite, ~21 % LMC and ~60 % HMC, and the sub-surface sediment averaged ~20 % aragonite, ~17 % LMC and ~63 % HMC (Fig 14.f). The trend of mineral percentages indicates a slight increase in precipitation of LMC and aragonite, while HMC remains relatively constant, indicating little HMC precipitation. In general little variation occurs in the mineral percentages possibly indicating little precipitation, this is expected due to the small volume of water contained within the lake. The majority of the precipitation (especially HMC) probably occurs during the summer months where evaporation greatly increases the salinity of the waters.

During the study period the temperature of the lake water decreased, lowering evaporation, and rainfall increased resulting in lower salinities. These conditions appear to favour the precipitation of LMC and Aragonite, and in the case of Lake Amy precipitation of MHC. While the precipitation of the Mg-rich carbonates occur during the summer months when salinities are higher. Considering that the mineralogy of each lake, except for Fresh Dip and Woolley are dominated by Mg-rich carbonates suggests that the majority of carbonate precipitation in these lakes occurs during the summer months when salinities are highest.

The abundance of Mg-rich carbonates precipitating in the lakes is a result of a high concentration of the elements of the carbonate minerals in the groundwaters feeding the lakes, coupled with climatic conditions of low rainfall and high evaporation rates (Ahmad 1993). High evaporation increases the salinity of the waters and increases the concentration of the carbonate ionic species to a point where saturation concentrations are achieved and precipitation occurs. The controlling mechanism of carbonate mineral formation, proposed by von der Borch (1965), is repeated flux of concentrated and chemically evolved brines from the lake to the groundwater, resulting in haloes of unusually saline groundwater around the lakes. These then control the types of carbonate minerals forming. Salinity data obtained from groundwaters adjacent to Lake Amy show low TDS and hence it shows no saline halo surrounding the lake. Since Lake Amy is the most saline lake studied, it would be unlikely the process would occur elsewhere. The occurrence of monohydrocalcite ( $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ ) in Lake Amy suggests there are two possible modes for carbonate formation in this lake, since MHC has two proposed modes of formation:

- a) chemical precipitation from either airborne water droplets (lake shore) or at the solution / atmosphere interface.
- b) biological activity (Taylor 1975).

MHC is also present in Lake Fellmongery, near Robe. This lake also contained living thrombolitic material, until its recent connection to Guichen Bay (A.J. Brenchley *pers. comm.* 1997). With MHC found in two lakes exhibiting thrombolite formation, it suggests that biologically-aided formation of MHC, in association with microbialite formation, is the dominant mode of formation of MHC in Lake Amy.

The source of the calcium and carbonate minerals carried within the groundwaters is likely to be from the dissolution of  $\text{CaCO}_3$  within the calcareous sediments of the regional aquifer (von der Borch & Lock 1979; von der Borch *et al* 1975). Several possible sources of magnesium ions exist:

- a) the ocean, either directly, or possibly due to seawater / groundwater mixing within the underlying aquifer or possibly seaspray;
- b) exsolution of Mg from the unstable HMC allochems within the aquifer.

A third proposed source of  $\text{Mg}^{2+}$  ions is the Quaternary basalts and tuff which occur immediately southeast and up-gradient (groundwater flow) of the region (von der Borch & Lock, 1979; von der Borch *et al.* 1975), but this theory has been disproved by recent Sm/Nb isotope work (Y. Bone, *pers. comm.* 1997).

The percentage of Mg-rich carbonates in the lake sediment appears to decrease toward the south, with the exception of Fresh Dip Lake. Lake Amy and Ghost Lake both exhibit a mineralogy dominated by Mg-rich carbonates (>60% HMC), Old Man Lake's mineralogy is equal parts aragonite, LMC and Mg-rich carbonates, but Lake Woolley's sediment consists of only ~20% Mg-rich carbonates. This trend cannot be explained by the regional hydrology, as the groundwater concentration of  $\text{Mg}^{2+}$  ions increases to the south (Holmes and Waterhouse 1983). The ephemeral nature of Lake Woolley could explain the lack of Mg-rich carbonates as a result of a diagenetic process of exsolution of Mg from Mg-carbonates associated with dissociation and recrystallization as pure calcite (Ahmad 1993), although the same process does not appear to be effecting Ghost Lake.

When considering the mole % Mg of the Mg-rich carbonates of the sediments, a differing trend appears. Lake Amy still exhibits the greatest proportions of Mg-rich carbonates (~50 % HMC @ ~22 mole % Mg), and the proportions of Ghost Lake and Lake Woolley (~60 % HMC @ ~12 mole % Mg, and ~23 % HMC @ ~25 mole % Mg respectively) still correspond well with the previous models of a lower Mg concentration of groundwaters to the south. But Old Man Lake (~39 % IMC @ ~10 mole % Mg) shows a lower Mg concentration than Lake Woolley, thus suggesting that the fresher influences on Fresh Dip Lake may also be influencing the sediments of Old Man Lake, and therefore suggest these conditions may be more a local effect rather than



simply being an isolated influence on a single lake, as these two lakes are close together (Fig. 1).

A possible explanation for the varying mineralogy could be an increased influence of the zone of groundwater/seawater mixing upon the waters entering the lakes in the north. This could be the result of a thinner wedge of freshwater above the denser seawater occurring in the north, resulting in a shallower mixing zone. Considering that the lakes are relatively equal distance from the coast, this would mean that a shallowing seawater/groundwater interface angle trends toward the north within the Robe-Woakwine corridor.

The composition of Fresh Dip sediments are possibly the result of freshwater recharging the lake at a greater rate than that being experienced by the other lakes. This coupled with water outflow, decrease the residence time of the lake water, and thus does not allow time for Mg accumulation through evaporation. This suggests that Fresh Dip Lake, rather than being a hydrologically closed system is an open system with water inflow matched by water outflow. This could be explained if Fresh Dip was to be topographically lower than the other lakes. Resulting in it being below the regional watertable at all times during the year and not only during periods of high recharge when the watertable rises, as is possibly the case with the other lakes.

## 4.3 Sediment stable isotopes

### 4.3.1 Carbonate sediment stable isotopic equilibrium

The process of carbonate precipitation results in stable isotopic fractionation, with the precipitated carbonate undergoing enrichment with respect to the DIC of the parent waters, major influences are listed below. Biogenically precipitated carbonate displays a differing  $\delta^{18}\text{O}$  fractionation value to inorganically precipitating carbonate at a rate which is determined primarily by temperature (Arthur *et al* 1983). The difference is only exhibited below  $\sim 10^\circ\text{C}$ , and since water temperature generally remained above this, fractionation due to temperature can be ignored. As with enrichment values for DIC atmospheric equilibrium stated previously, there is a wide range of values quoted for enrichment associated with carbonate precipitation.  $\delta^{13}\text{C}$  enrichment during precipitation displays a wide range of values as fractionation is affected by the rate of precipitation, with slow precipitation exhibiting greater enrichment than carbonates precipitating quickly (Turner 1982). Some typical values are listed below.

#### $\epsilon \text{HCO}_3^- - \text{calcite}$

##### $^{13}\text{C}$ fractionation (‰)

-2.4	Turner(1982)
-0.55 fast ppt rate	Turner(1982)
-4.0 slow ppt rate	Turner(1982)
-1.27	Emrich(1970)
-0.4 fast ppt rate	Grossman <i>et al.</i> (1986)
-3.4 slow ppt rate	Grossman <i>et al.</i> (1986)
-2.26	Rahimpour-Bonab(1997)

#### $\epsilon \text{ calcite} - \text{aragonite}$

##### $^{13}\text{C}$ fractionation (‰)

-1.6	Turner(1982)
-1.8	Rubinson & Clayton (1969)
-1.7	MacConnaughey <i>et al.</i> (1996)
-1.2	Gonzales & Lohmann (1985)

##### $^{18}\text{O}$ fractionation (‰)

-1.3	Turner(1982)
-0.6	Tarutani <i>et al.</i> (1969)

## $\epsilon$ LMC – HMC

$^{18}\text{O}$  fractionation (‰)

+0.06 / mole % Mg

Tarutani *et al.* (1969)

The above enrichment values are added to the known  $\delta^{13}\text{C}$  of the DIC of the lake water to obtain equilibrium  $\delta^{13}\text{C}$  for precipitating carbonates. Equilibrium  $\delta^{18}\text{O}$  of precipitated carbonates are calculated by using paleotemperature equations. These equations vary for precipitating mineralogy, with different equations for calcite and aragonite. The equations also vary depending upon the reference. Some typical equations follow.

### aragonite

$$T(^{\circ}\text{C}) = 20.6 - 4.34 (\delta^{18}\text{O}_{\text{arag}} - \delta_w) \quad \text{Rahimpour-Bonab (1997)}$$

$$T(^{\circ}\text{C}) = 19.0 - 5.32 (\delta^{18}\text{O}_{\text{arag}} - \delta_w) + 0.03 (\delta^{18}\text{O}_{\text{arag}} - \delta_w)^2 \quad \text{Arthur *et al.* (1983)}$$

### calcite

$$T(^{\circ}\text{C}) = 16.9 - 4.2 (\delta^{18}\text{O}_{\text{calcite}} - \delta_w) + 0.10 (\delta^{18}\text{O}_{\text{calcite}} - \delta_w)^2 \quad \text{Rahimpour-Bonab (1997)}$$

$$T(^{\circ}\text{C}) = 16.9 - 4.2 (\delta^{18}\text{O}_{\text{calcite}} - \delta_w) + 0.13 (\delta^{18}\text{O}_{\text{calcite}} - \delta_w)^2 \quad \text{Arthur *et al.* (1983)}$$

$$T(^{\circ}\text{C}) = 15.7 - 4.36 (\delta^{18}\text{O}_{\text{calcite}} - \delta_w) + 0.12 (\delta^{18}\text{O}_{\text{calcite}} - \delta_w)^2 \quad \text{O'Neil *et al.* (1969)}$$

Equilibrium values were calculated using the following method;

-  $^{13}\text{C}$  fractionation (‰)

$\epsilon \text{HCO}_3^- - \text{calcite} \sim -2.26$  ‰ (intermediate ppt rate)

$\epsilon \text{calcite} - \text{aragonite} \sim -1.2$  ‰

-  $^{18}\text{O}$  value obtained using paleotemperature equations for calcite and aragonite as per Rahimpour-Bonab (1997), with

$\epsilon \text{LMC} - \text{HMC} \sim +0.06$  ‰ / mole % Mg

- final values were then calculated by combining aragonite and calcite values in the proportions observed in the sediments.

(Table 1, Fig. 15.a to f)

### 4.3.2 Carbonate sediment stable isotopic composition

Lake Woolley surface sediment  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  range between 2.8 ‰ to 3.7 ‰, and 3.0 ‰ and 4.2 ‰ respectively, whereas sub-surface sediment ranges between 2.2 ‰ to 3.7 ‰ and 2.8 ‰ and 3.9 ‰ respectively (Fig. 13.a). Surface sediment and sub-surface have constant  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , whereas the

surface sediment  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  are enriched by  $\sim 1.6\text{‰}$  and  $\sim 3.0\text{‰}$  respectively, when compared to the calculated equilibrium values (Fig. 15.a).

Surface sediment  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of Old Man Lake range between  $0.5\text{‰}$  to  $1.5\text{‰}$  and  $3.0\text{‰}$  to  $4.7\text{‰}$  respectively, and sub-surface values range between  $0.4\text{‰}$  to  $2.3\text{‰}$  and  $3.0\text{‰}$  to  $3.5\text{‰}$  respectively (Fig. 13.b). On average, the surface sediment is slightly enriched compared to the sub-surface sediment and generally matches the calculated equilibrium values, whereas the  $\delta^{18}\text{O}$  of the surface sediment is enriched  $\sim 1.8\text{‰}$  compared to equilibrium values (Fig. 15.b).

Fresh Dip Lake surface sediment  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  range between  $3.5\text{‰}$  to  $4.3\text{‰}$  and  $2.2\text{‰}$  to  $2.6\text{‰}$  respectively, and sub-surface  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  vary between  $2.5\text{‰}$  to  $4.1\text{‰}$  and  $2.2\text{‰}$  and  $2.9\text{‰}$  respectively (Fig. 13.c). No major enrichment occurs between the surface and sub-surface sediments or between the  $\delta^{18}\text{O}$  of the surface sediment and its calculated equilibrium value, whereas the  $\delta^{13}\text{C}$  of the surface sediment is enriched  $\sim 1.8\text{‰}$  compared to the calculated equilibrium values (Fig. 15.c).

Lake Amy surface sediment  $\delta^{13}\text{C}$  values ranged from  $1.8\text{‰}$  to  $4.1\text{‰}$  in the south and  $1.0\text{‰}$  to  $3.3\text{‰}$  in the north, whereas the  $\delta^{18}\text{O}$  range between  $4.2\text{‰}$  and  $4.8\text{‰}$  in the south and  $4.6\text{‰}$  and  $4.9\text{‰}$  in the north (Fig. 13.d & e). Surface sediment is  $\delta^{13}\text{C}$  enriched on average by  $2.0\text{‰}$  in the south and by  $0.6\text{‰}$  in the north and  $\delta^{18}\text{O}$  remains constant with depth. In the south  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of the surface sediment is enriched by  $\sim 1.3\text{‰}$  and  $\sim 3.8\text{‰}$  respectively when compared to the equilibrium values, in the north enrichment is  $\sim 2.4\text{‰}$  and  $\sim 3.8\text{‰}$  compared to equilibrium values (Fig. 15.d & e).

Ghost Lake surface sediment  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  range between  $-5.0\text{‰}$  to  $-2.0\text{‰}$ , and  $1.8\text{‰}$  to  $2.8\text{‰}$  respectively, sub-surface sediment  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  range between  $-5.0\text{‰}$  to  $5.3\text{‰}$  and  $2.2\text{‰}$  and  $3.5\text{‰}$  respectively (Fig. 13.f). Surface sediment is  $\delta^{13}\text{C}$  enriched  $\sim 3.0\text{‰}$  compared to sub-surface and  $\delta^{18}\text{O}$  enriched  $\sim 0.9\text{‰}$ . The surface sediments are  $\delta^{13}\text{C}$  depleted  $\sim 4.3\text{‰}$  and  $\delta^{18}\text{O}$  enriched  $\sim 1.6\text{‰}$  when compared to the calculated equilibrium values (Fig. 15.f).

The carbonate sediments generally display little deviation in either surface or sub-surface  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  trends. The  $\delta^{18}\text{O}$  values are generally more enriched than the  $\delta^{13}\text{C}$  values. In each lake, except Ghost Lake, the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  are enriched compared to the  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{DIC}}$ , as is expected. Average enrichment values are listed over the page.

$\epsilon \text{HCO}_3^-$ -carbonate(observed)

$^{13}\text{C}$ fractionation (‰)	$^{18}\text{O}$ fractionation (‰)	
-3.9	-4.1	Lake Woolley
-2.8	-3.0	Old Man Lake
-5.0	-3.2	Fresh Dip Lake
-2.1	-3.0	Lake Amy Nth
-1.9	-4.2	Lake Amy Sth
+1.7	-3.2	Ghost Lake
<hr/>		
<i>average</i> ~ -2.4	~ -3.8	

The average  $\delta^{13}\text{C}$  fractionation values corresponds well with those quoted previously, and as a general trend indicates a intermediate rate of precipitation.

The average  $\delta^{13}\text{C}$  fractionation of -5.0 ‰ at Fresh Dip compares poorly to the calculated equilibrium values (Table 1 & Fig.15.c) and corresponds to an exceptionally slow rate of precipitation (Turner 1982). This result is expected, as Fresh Dips current conditions seem unfavourable for high carbonate precipitation. The high proportion of aragonite could also explain a higher degree of fractionation. Hence, this would require the aragonite source to be recent inorganic precipitation and not from an organic source as previously expected, as organic aragonite generally exhibit equilibrium with the DIC. Ghost Lakes  $\delta^{13}\text{C}$  fractionation of +1.7 ‰ again disagrees dramatically with the calculated equilibrium value (Table 1 & Fig.15.f) and indicate the incorporation of isotopically light carbon into the carbonate phase. This could be attributed to the large amount of decomposing water grass present in the lake, which could have a large effect on the lakes stable isotopic signature due to the small volume of the lake. Lake Amy's  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  trends were generally well above those of the other lakes and the calculated equilibrium  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  trends, except in the south where the  $\delta^{13}\text{C}$  matched reasonably well (Table 1 & Fig.15.d&e). Although, the fractionation values still corresponded well to those quoted previously. The variation in  $\delta^{13}\text{C}$  from the equilibrium values could be attributed to fast precipitation rates, but coupled with such large variations in  $\delta^{18}\text{O}$  suggests a differing influence, possibly as a result of microbialite-aided MHC precipitation within the lake. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of Old Man Lake correspond well to those calculated and to the previously quoted values (Table 1, Fig.15.b). This could be due to the lack of any extensive flora or fauna in the lake altering the sediments stable isotopic signature, and also indicates that the precipitation is inorganic, at a intermediate rate. The  $\delta^{13}\text{C}$  and

$\delta^{18}\text{O}$  trends of Lake Woolley were below the calculated equilibrium values, and slightly higher than those of the other lakes (Table 1 & Fig.15.a). This is possibly due to a faster than expected precipitation rate, or as a result of the precipitation of aragonite increasing the fractionation experienced by the sediment relative to the DIC. Due to the lack of lake flora an increased fractionation due to biological-aided precipitation is unlikely.

**Table 1.  $\delta^{13}\text{C}$  &  $\delta^{18}\text{O}$  stable isotope calculated equilibrium values**

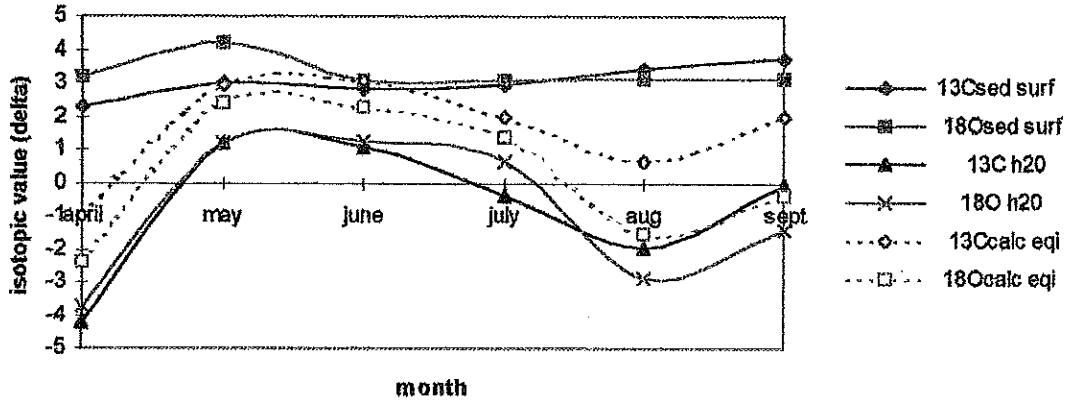
DATE	<i>Ghost Lake</i>		<i>Old Man Lake</i>		<i>Fresh Dip Lake</i>	
	$\delta^{13}\text{C}$ calc.equi	$\delta^{18}\text{O}$ calc.equi	$\delta^{13}\text{C}$ calc.equi	$\delta^{18}\text{O}$ calc.equi	$\delta^{13}\text{C}$ calc.equi	$\delta^{18}\text{O}$ calc.equi
April	-0.97	-2.39	0.09	2.35	2.23	1.70
May	2.97	2.37	0.34	-2.08	1.70	2.00
June	3.08	2.26	0.69	0.91	2.53	2.17
July	1.96	1.34	0.75	2.13	1.77	2.28
Aug	0.64	-1.53	0.49	0.75	2.79	2.48
Sept	1.96	-0.39	0.68	1.91	2.30	1.57

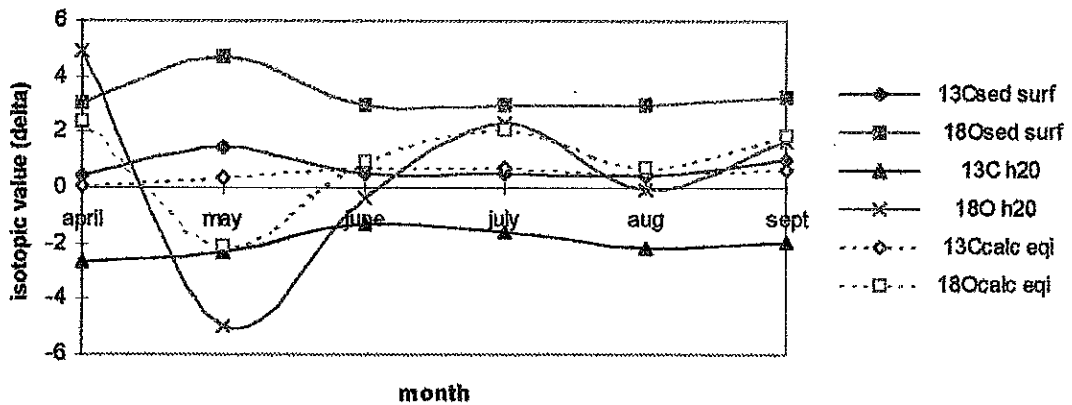
DATE	<i>Lake Amy Nth</i>		<i>Lake Amy Sth</i>		<i>Ghost Lake</i>	
	$\delta^{13}\text{C}$ calc.equi	$\delta^{18}\text{O}$ calc.equi	$\delta^{13}\text{C}$ calc.equi	$\delta^{18}\text{O}$ calc.equi	$\delta^{13}\text{C}$ calc.equi	$\delta^{18}\text{O}$ calc.equi
April	1.83	-0.38	0.46	0.64	1.17	2.34
May	1.18	0.61	0.88	1.16	-0.72	-0.31
June	0.86	0.98	0.57	1.13	0.15	0.94
July	0.60	0.71	0.72	1.86	0.07	1.10
Aug	0.33	0.45	0.64	0.45	0.56	-0.14
Sept	0.54	0.71	1.01	1.35	0.77	-0.36

Figure 15. Stable isotope calculated equilibrium.

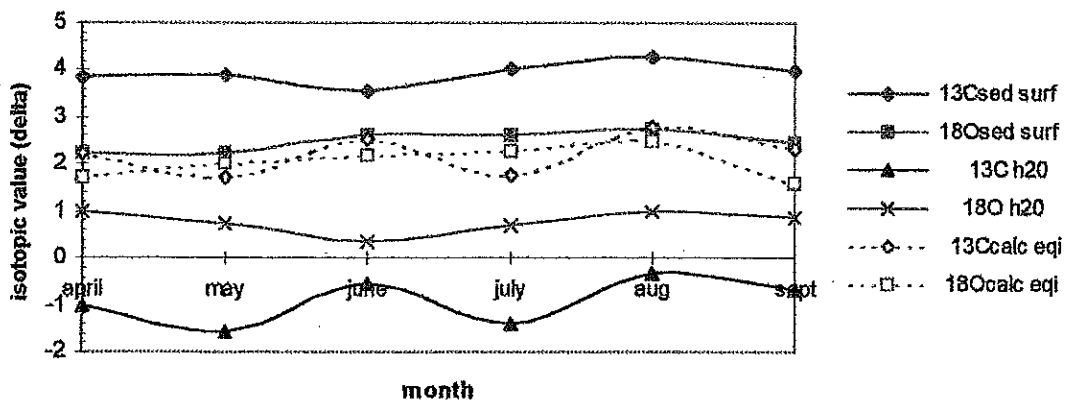
a. *Lake Woolley sediment equilibrium*



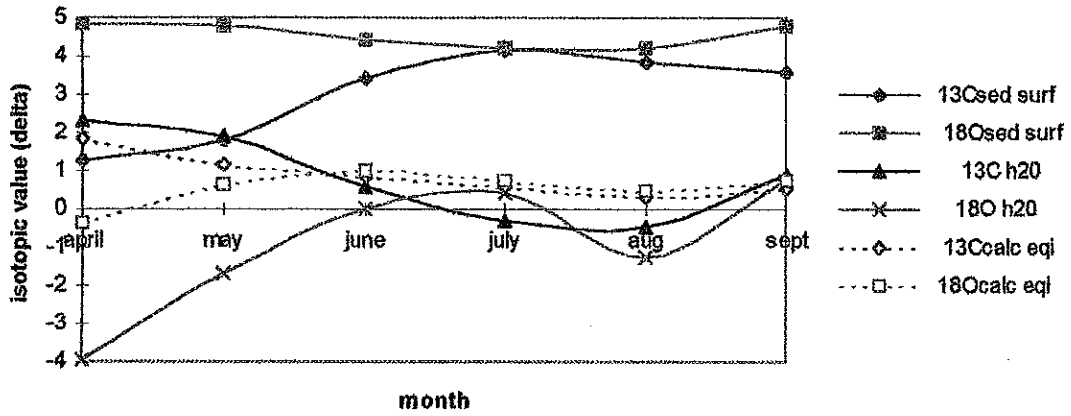
b. *Old Man Lake sediment equilibrium*



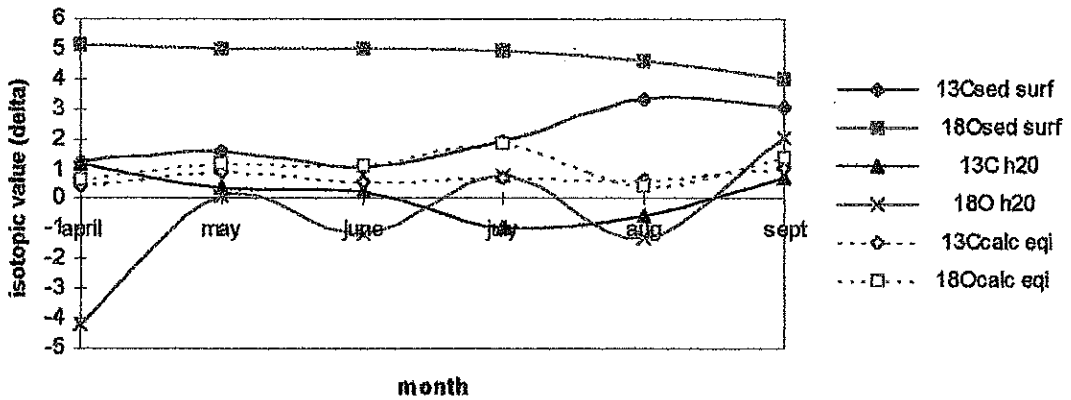
c. *Fresh Dip sediment equilibrium*



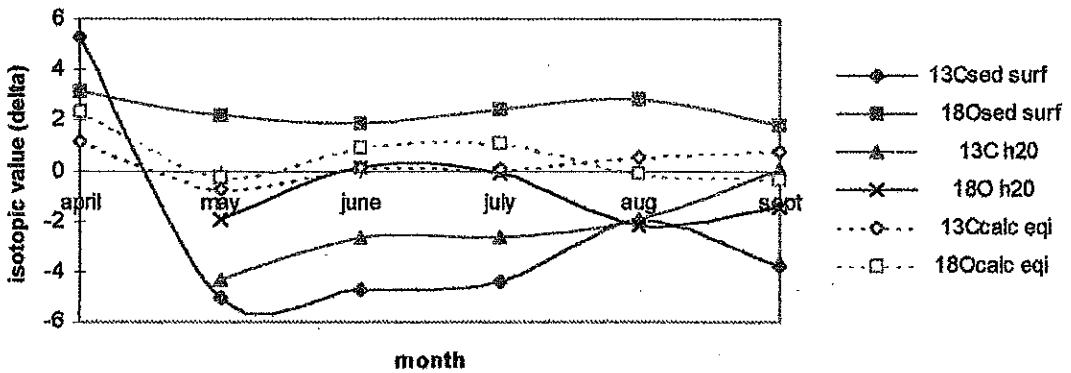
**d. Lake Amy-North sediment equilibrium**



**e. Lake Amy-South sediment equilibrium**



**f. Ghost Lake sediment equilibrium**





## 5.0 Discussion

### a) Stable isotopes

The DIC stable isotopic composition of the lake waters represent surface waters that have originated predominantly from depleted groundwater, or, in the case of Ghost Lake, from highly depleted rainwaters. The  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{DIC}}$  of the lake waters correspond well to observed groundwaters which have undergone enrichment due to atmospheric equilibrium stable isotopic fractionation. They fall within the expected calculated range for such depleted ground/rain waters undergoing stable isotopic fractionation. The similar DIC stable isotopic composition of each lake, except Ghost Lake, suggests that each lake is fed by waters originating from the same source. Monthly variations in the DIC stable isotopic signature of the lake water represent the stable isotopic effects of differing rates, and sources of water inflow, evaporation, biological activity, decomposition of biological material and respiration. The stable isotopic composition of the lake sediments correspond to precipitation from an inorganic source that is precipitating in disequilibrium to the lake waters. The surface sediments do not display the consistent stable isotopic behaviour of the waters. Although the traces display relatively consistent behaviour, each lake's sediment underwent unique fractionation of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  relative to the  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{DIC}}$  of the lake waters. Only in very few cases did the calculated equilibrium  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  match the observed values. This result is expected, as each lake is highly individual and has its own unique combination of influences governing precipitation. Thus disequilibrium precipitation confirms the varying nature of carbonate precipitation in each lake. The average observed  $\text{HCO}_3^-$  - carbonate  $\delta^{13}\text{C}$  fractionation value of  $\sim -2.4\text{‰}$  corresponds well with values from other similar locations, whereas the  $\delta^{18}\text{O}$  fractionation value of  $\sim -3.8\text{‰}$  again confirms non-equilibrium carbonate precipitation.

### b) Mineralogy

Each lake displays a unique mineralogical assemblage, which again confirms the unique influences on each lake which govern its characteristics. Variation in the mineral percentages from each lake indicates a general increase in the percentages of LMC and aragonite, and in the case of Lake Amy MHC. This indicates favourable conditions for the precipitation of these minerals prevailing over the winter months. The high percentages of Mg-rich carbonates present in each lake (except Fresh Dip) indicates that the majority of the carbonate precipitation occurs in the summer months when the higher salinity of the lake water favour such precipitation. The decrease in the abundance of Mg-rich carbonates associated with the lakes southward is of particular interest. The concentration of  $\text{Mg}^{2+}$  within the groundwaters feeding

the lakes would be expected to display the opposite behaviour to this, with decreasing  $Mg^{2+}$  concentration to the north. Although Mg-rich carbonate diagenesis associated with evaporation is a possible explanation, the ephemeral Ghost Lake located in the north still displayed high amounts of Mg-rich carbonates. A possible explanation is the increasing role of seawater/groundwater mixing within the supplying aquifer to the north of the Robe-Woakwine corridor. A decrease in the interface angle between the denser intruding seawater and groundwater would result in a zone of mixing closer to the surface in the north. Hence, the influence of the surface waters is greater in this region. Another explanation could be the increasing depth to the watertable in the south, which would decrease groundwater ion concentration due to evaporation thus decreasing the concentration of the waters entering the lakes. The constant nature of Fresh Dip's mineralogy coupled with a constant DIC isotopic signature is possibly the result of freshwater recharge of the lake at a rate faster than that of the other lakes. This is possibly the result of it being located lower topographically than the other lakes. This would result in it lying below the regional watertable at all times and not only during periods of watertable elevation, as is possibly the case with the other lakes. The occurrence of MHC in Lake Amy, coupled with the high level of microbialite activity, enriched sediment stable isotopic values and high stable isotope fraction between DIC and the precipitated carbonate, is strong evidence for the biologically aided precipitation of MHC. This reflects the findings of Taylor (1975) where the occurrence of HMC in Lakes Butler and Fellmongery, also near Robe, was also associated with, and attributed to microbial activity.

## 6.0 Conclusions

The DIC stable isotopic composition of the lakes surface water varied from lake to lake and each lakes DIC stable isotopic signature varied on a monthly basis. Monthly variations in the DIC stable isotopic signature of the lake water represent the stable isotopic effects of differing rates, and sources of water inflow, evaporation, biological activity, decomposition of biological material and respiration. The DIC stable isotopic signatures of the lake waters reflect waters that have originated primarily from highly depleted groundwater and rainwater. The water has undergone isotopic fractionation and subsequent enrichment on equilibrating with atmospheric CO<sub>2</sub>. Variations in the DIC stable isotopic signature observed between lakes reflect the varying nature of the lake environments.

The stable isotopic composition of the lake sediments also varied between lakes. Sediments displayed precipitation at disequilibrium with the DIC of the lake waters, reflecting inorganic precipitation at an intermediate rate. Calculated equilibrium stable isotopic values of the sediments compared poorly with the observed trends. This reflects the varying nature of each lake environment, indicating a limitation in applying generalised modelling techniques to such variable systems.

The mineralogy of each lake is a unique assemblage of LMC, IMC, HMC, aragonite and MHC. Variations in the mineral percentages indicate conditions favourable for the precipitation of LMC and aragonite, and MHC in the case of the Lake Amy, prevailing over the winter months. The high percentages of HMC present in each lake (except Fresh Dip) indicate that the majority of the carbonate precipitation occurs during the summer months. The occurrence of MHC in Lake Amy, which has a high level of microbialite activity, is strong evidence for the biologically aided precipitation of MHC. This is reflected in the high stable isotopic fractionation values of the precipitating carbonate. The increase in the concentration of Mg-rich carbonates to the north of the region is possible evidence for a decreasing interface angle between dense seawater and groundwater in the north. This results in a seawater/groundwater mixing zone closer to the surface in the north of the Robe-Woakwine corridor.

c. Calcite precipitate mole % Mg values

*Lake Woolley*

DATE	mole % Mg					
	surface sediment			sub-surface sediment		
	LMC	IMC	HMC	LMC	IMC	HMC
April				3.9		29.7
May	1.8		25.5	4.0		27.5
June	2.7		24.1	1.8		23.3
July	2.1		23.3	1.8		22.2
Aug	3.6		25.0	2.7		23.0
Sept	1.3		23.6	3.0		24.4

*Old Man Lake*

DATE	mole % Mg					
	surface sediment			sub-surface sediment		
	LMC	IMC	HMC	LMC	IMC	HMC
April				1.8	10.0	
May	3.9	10.2		1.8	10.0	
June	3.3	10.0		1.2	10.0	
July	3.6	10.0		1.3	8.8	
Aug	3.3	10.5		4.0	9.4	
Sept	2.1	10.0		3.0	7.4	

*Fresh Dip Lake*

DATE	mole % Mg					
	surface sediment			sub-surface sediment		
	LMC	IMC	HMC	LMC	IMC	HMC
April				1.4	9.4	
May	2.1	4.7		2.1	10.0	
June	3.6	9.4		2.4	7.1	
July	3.0	9.1		3.0	10.2	
Aug	1.8	10.0		2.7	12.0	
Sept	2.7	9.7		1.8		12.5

*Lake Amy Nth*

DATE	mole % Mg					
	surface sediment			sub-surface sediment		
	LMC	IMC	HMC	LMC	IMC	HMC
April				3.9		25.5
May	4.2		23.6	2.1		24.1
June	0.0		23.6	3.9		24.7
July	3.9		23.0	2.1		24.4
Aug	0.0		24.1	2.4		23.3
Sept	0.0		23.6	3.3		24.1

## Lake Amy Sth

### *mole % MgCO<sub>3</sub>*

DATE	<i>surface sediment</i>			<i>sub-surface sediment</i>		
	LMC	IMC	HMC	LMC	IMC	HMC
April				3.0		23.9
May	2.7		23.0	3.0		24.4
June		4.8	24.4	3.7		24.4
July	3.6		23.9	3.3		25.2
Aug	3.6		23.0	1.8		22.7
Sept	0.4		23.3	2.4		25.0

## Ghost Lake

### *mole % MgCO<sub>3</sub>*

DATE	<i>surface sediment</i>			<i>sub-surface sediment</i>		
	LMC	IMC	HMC	LMC	IMC	HMC
April				2.4		15.4
May	2.7		15.4		6.8	16.5
June	0.0		12.1	3.0		14.3
July	0.0	8.9		1.6		16.2
Aug	3.3		14.3	3.3		14.3
Sept	3.6		12.2	2.7		16.0

a.  $\delta^{13}\text{C}$  &  $\delta^{18}\text{O}$  stable isotope values

LAKE WOOLLEY

DATE	Isotopic value (‰)					
	$\delta^{13}\text{C}_{\text{sed surf}}$	$\delta^{18}\text{O}_{\text{sed surf}}$	$\delta^{13}\text{C}_{\text{sed 5cm}}$	$\delta^{18}\text{O}_{\text{sed 5cm}}$	$\delta^{13}\text{C}_{\text{h20}}$	$\delta^{18}\text{O}_{\text{h20}}$
April			2.29	3.21	-4.21	-3.74
May	2.99	4.19	3.04	3.91	1.17	1.16
June	2.83	3.04	3.19	3.09	1.07	1.27
July	2.94	3.03	3.50	3.24	-0.38	0.65
Aug	3.40	3.12	3.62	2.94	-1.99	-2.87
Sept	3.75	3.12	3.73	2.84	-0.08	-1.41

OLD MAN LAKE

DATE	Isotopic value (‰)					
	$\delta^{13}\text{C}_{\text{sed surf}}$	$\delta^{18}\text{O}_{\text{sed surf}}$	$\delta^{13}\text{C}_{\text{sed 5cm}}$	$\delta^{18}\text{O}_{\text{sed 5cm}}$	$\delta^{13}\text{C}_{\text{h20}}$	$\delta^{18}\text{O}_{\text{h20}}$
April			0.40	3.06	-2.70	4.89
May	1.47	4.69	2.34	3.01	-2.31	-4.96
June	0.48	2.99	0.91	2.99	-1.29	-0.39
July	0.52	2.94	2.97	3.22	-1.62	2.31
Aug	0.44	2.99	0.79	3.50	-2.15	-0.07
Sept	1.02	3.22	1.40	3.49	-1.98	1.67

FRESH DIP LAKE

DATE	Isotopic value (‰)					
	$\delta^{13}\text{C}_{\text{sed surf}}$	$\delta^{18}\text{O}_{\text{sed surf}}$	$\delta^{13}\text{C}_{\text{sed 5cm}}$	$\delta^{18}\text{O}_{\text{sed 5cm}}$	$\delta^{13}\text{C}_{\text{h20}}$	$\delta^{18}\text{O}_{\text{h20}}$
April			3.84	2.25	-1.03	0.98
May	3.90	2.22	4.14	2.07	-1.57	0.74
June	3.53	2.59	3.68	2.44	-0.53	0.33
July	4.00	2.63	3.54	2.76	-1.40	0.67
Aug	4.28	2.76	3.39	2.62	-0.32	0.97
Sept	3.98	2.44	2.54	2.89	-0.67	0.86

LAKE AMY - NORTH

DATE	Isotopic value (‰)					
	$\delta^{13}\text{C}_{\text{sed surf}}$	$\delta^{18}\text{O}_{\text{sed surf}}$	$\delta^{13}\text{C}_{\text{sed 5cm}}$	$\delta^{18}\text{O}_{\text{sed 5cm}}$	$\delta^{13}\text{C}_{\text{h20}}$	$\delta^{18}\text{O}_{\text{h20}}$
April			1.27	4.84	2.32	-3.95
May	1.78	4.77	1.49	4.68	1.89	-1.68
June	3.44	4.43	1.50	4.09	0.59	0.02
July	4.15	4.20	0.89	4.72	-0.29	0.43
Aug	3.85	4.22	1.41	4.91	-0.46	-1.27
Sept	3.59	4.81	1.33	4.76	0.88	0.75

### LAKE AMY - SOUTH

DATE	Isotopic value (‰)					
	$\delta^{13}\text{C}_{\text{sed surf}}$	$\delta^{18}\text{O}_{\text{sed surf}}$	$\delta^{13}\text{C}_{\text{sed 5cm}}$	$\delta^{18}\text{O}_{\text{sed 5cm}}$	$\delta^{13}\text{C}_{\text{h20}}$	$\delta^{18}\text{O}_{\text{h20}}$
April			1.24	5.15	1.20	-4.18
May	1.59	4.99	1.26	4.62	0.35	0.09
June	1.03	4.98	1.20	5.00	0.25	-1.20
July	1.89	4.90	2.12	5.12	-0.95	0.74
Aug	3.29	4.61	1.62	4.97	-0.55	-1.32
Sept	3.02	3.98	0.96	4.52	0.68	2.07

### GHOST LAKE

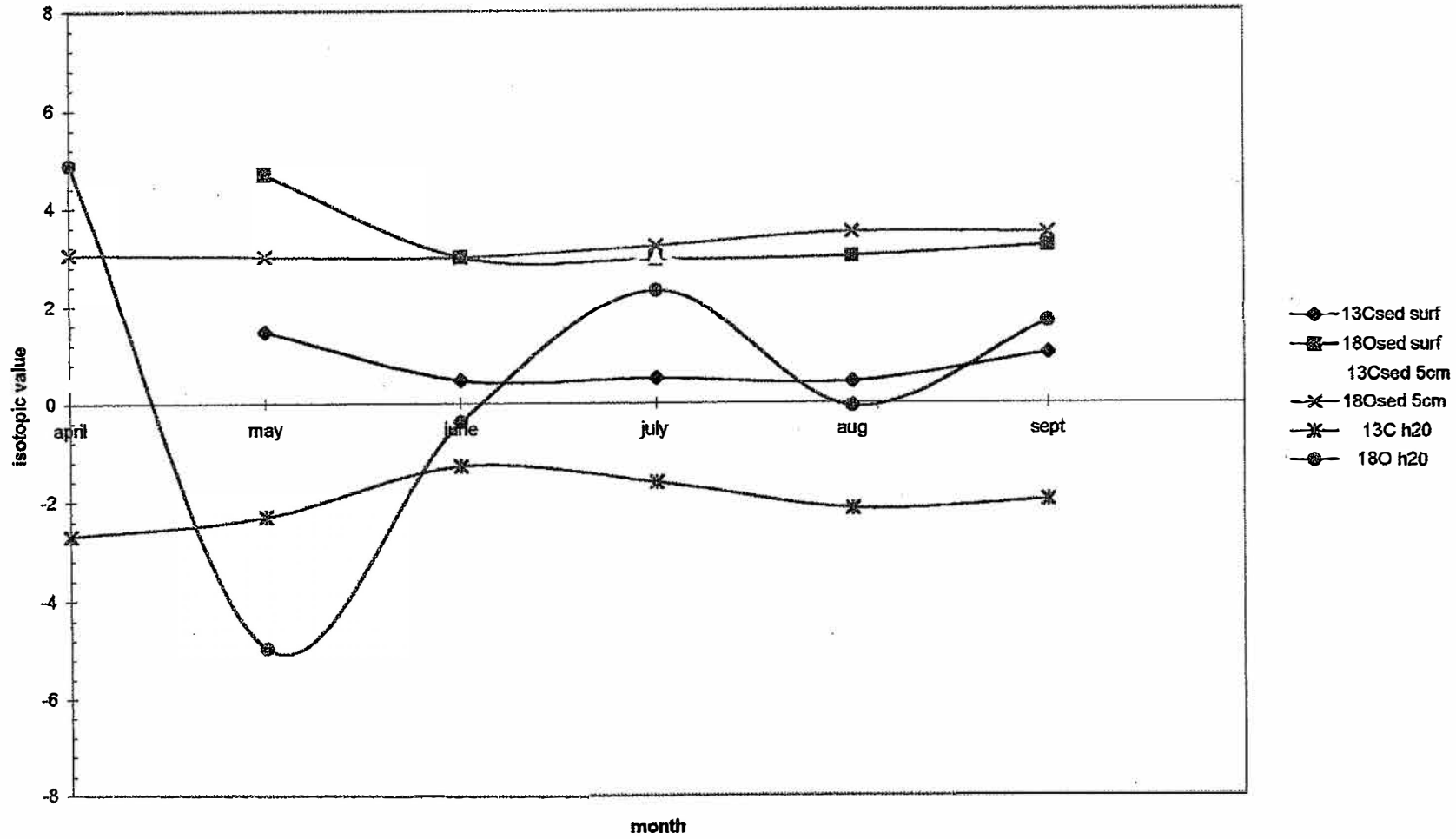
DATE	Isotopic value (‰)					
	$\delta^{13}\text{C}_{\text{sed surf}}$	$\delta^{18}\text{O}_{\text{sed surf}}$	$\delta^{13}\text{C}_{\text{sed 5cm}}$	$\delta^{18}\text{O}_{\text{sed 5cm}}$	$\delta^{13}\text{C}_{\text{h20}}$	$\delta^{18}\text{O}_{\text{h20}}$
April			5.31	3.15		
May	-5.03	2.21	-2.92	3.26	-4.37	-1.98
June	-4.76	1.86	-2.64	2.61	-2.64	0.10
July	-4.42	2.46	-0.01	3.63	-2.64	-0.10
Aug	-2.01	2.83	-4.91	2.19	-1.94	-2.22
Sept	-3.81	1.78	-1.12	3.47	0.00	-1.50

### GROUND / RAIN H<sub>2</sub>O: ISOTOPIC DATA

DATE	Isotopic value (‰)					
	Grnd-Little Dip track		Grnd-The Hermitage		Rain H <sub>2</sub> O - Robe	
	$\delta^{13}\text{C}_{\text{h20}}$	$\delta^{18}\text{O}_{\text{h20}}$	$\delta^{13}\text{C}_{\text{h20}}$	$\delta^{18}\text{O}_{\text{h20}}$	$\delta^{13}\text{C}_{\text{h20}}$	$\delta^{18}\text{O}_{\text{h20}}$
April						
May						
June	-13.39	-7.57				
July	-11.84	-7.43	-4.29	-5.06		
Aug	-12.04	-5.97	-9.35	-4.14	-21.93	-8.64
Sept	-10.89	-7.95	-9.10	-8.00	-21.19	-12.76

**OLD MAN LAKE ISOTOPIC DATA PLOT**

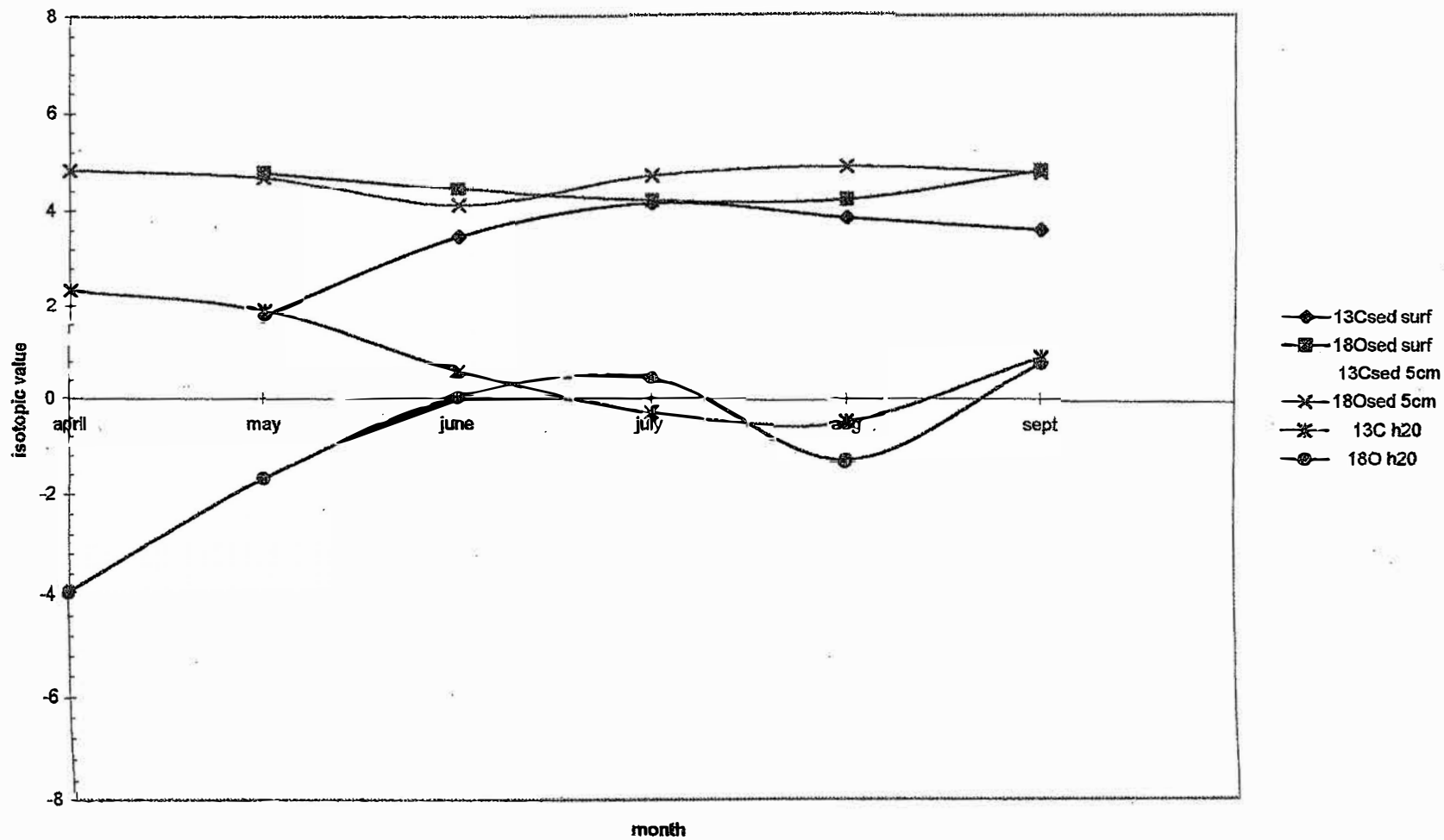
Old Man Lake





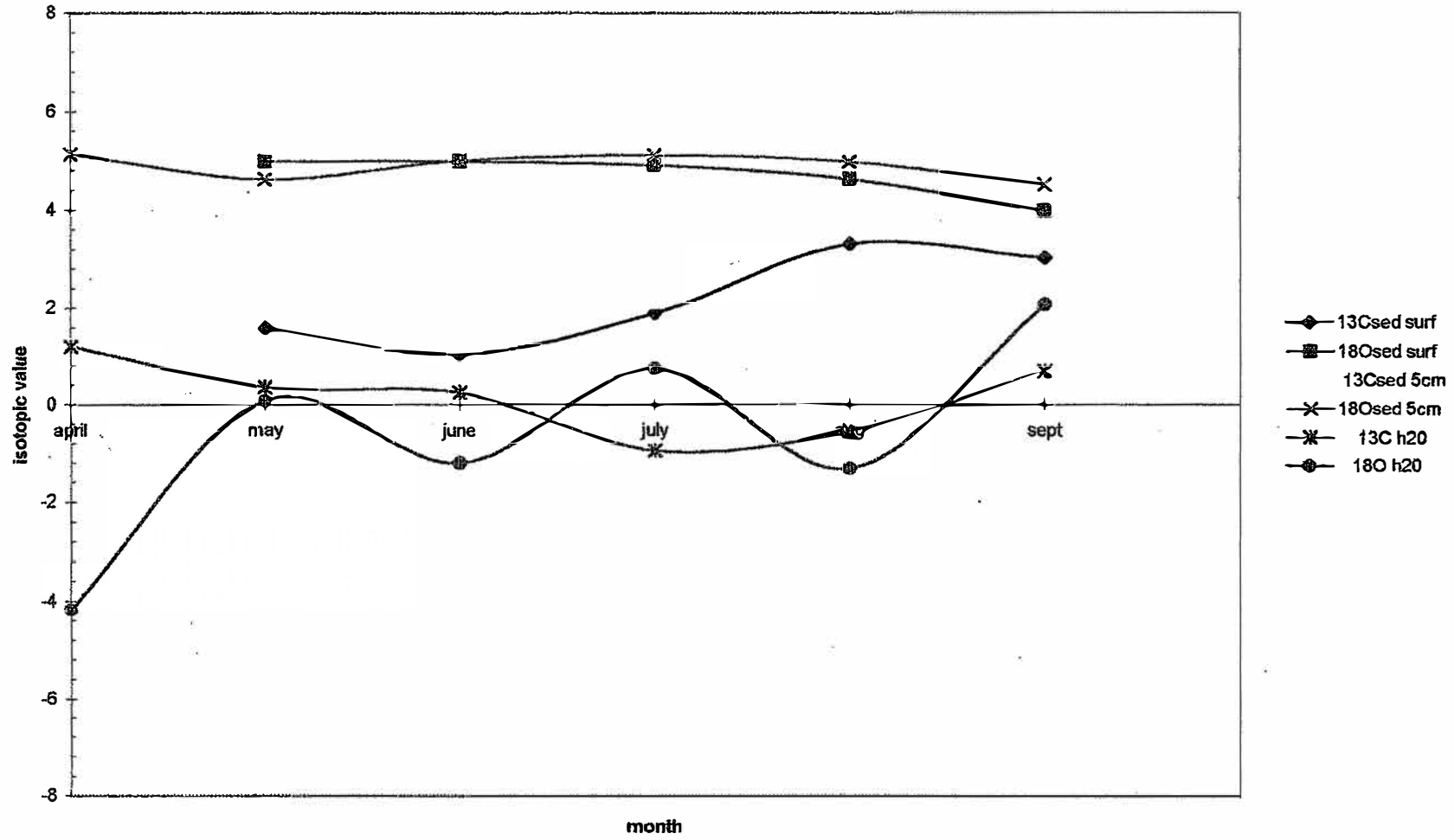
LAKE AMY-NORTH ISOTOPIC DATA PLOT

Lake Amy Nth



LAKE AMY-SOUTH ISOTOPIC DATA PLOT

Lake Amy Sth



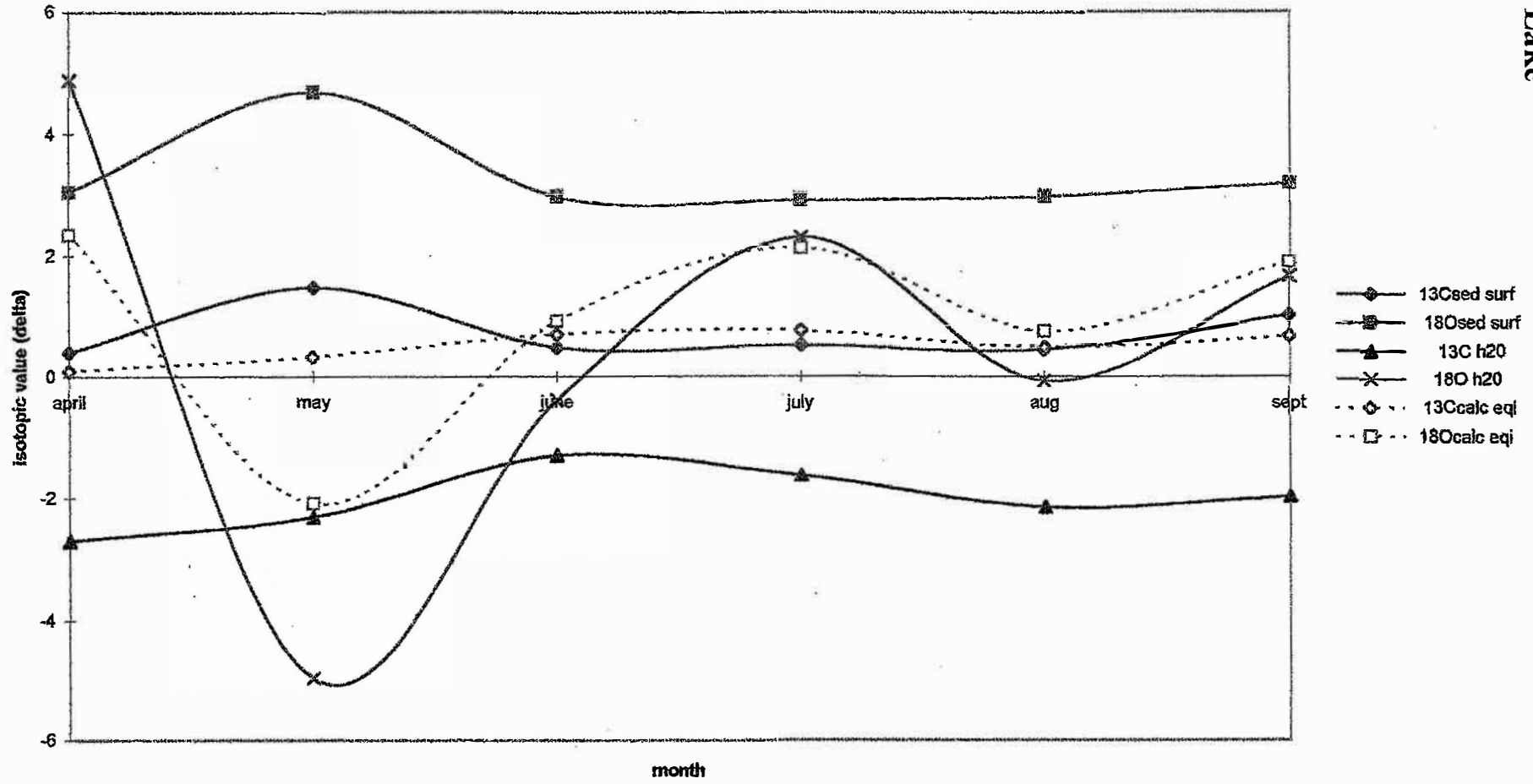
c.  $\delta^{13}\text{C}$  &  $\delta^{18}\text{O}$  stable isotope equilibrium values

DATE	<i>Ghost Lake</i>		<i>Old Man Lake</i>		<i>Fresh Dip Lake</i>	
	$\delta^{13}\text{C}$ calc.equi	$\delta^{18}\text{O}$ calc.equi	$\delta^{13}\text{C}$ calc.equi	$\delta^{18}\text{O}$ calc.equi	$\delta^{13}\text{C}$ calc.equi	$\delta^{18}\text{O}$ calc.equi
April	-0.97	-2.39	0.09	2.35	2.23	1.70
May	2.97	2.37	0.34	-2.08	1.70	2.00
June	3.08	2.26	0.69	0.91	2.53	2.17
July	1.96	1.34	0.75	2.13	1.77	2.28
Aug	0.64	-1.53	0.49	0.75	2.79	2.48
Sept	1.96	-0.39	0.68	1.91	2.30	1.57

DATE	<i>Lake Amy Nth</i>		<i>Lake Amy Sth</i>		<i>Ghost Lake</i>	
	$\delta^{13}\text{C}$ calc.equi	$\delta^{18}\text{O}$ calc.equi	$\delta^{13}\text{C}$ calc.equi	$\delta^{18}\text{O}$ calc.equi	$\delta^{13}\text{C}$ calc.equi	$\delta^{18}\text{O}$ calc.equi
April	1.83	-0.38	0.46	0.64	1.17	2.34
May	1.18	0.61	0.88	1.16	-0.72	-0.31
June	0.86	0.98	0.57	1.13	0.15	0.94
July	0.60	0.71	0.72	1.86	0.07	1.10
Aug	0.33	0.45	0.64	0.45	0.56	-0.14
Sept	0.54	0.71	1.01	1.35	0.77	-0.36

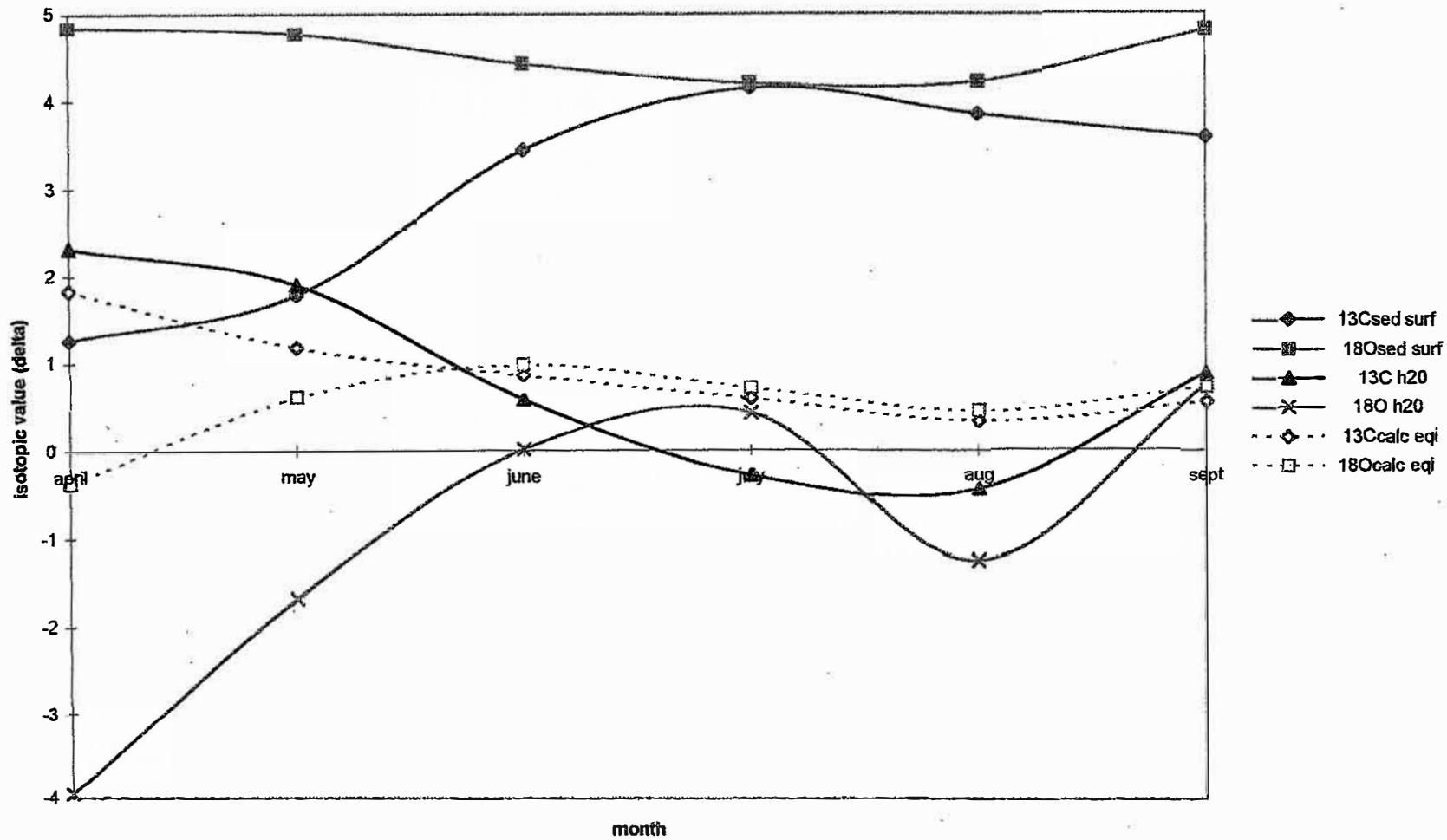
Old Man Lake

Old Man Lake sediment equilibrium



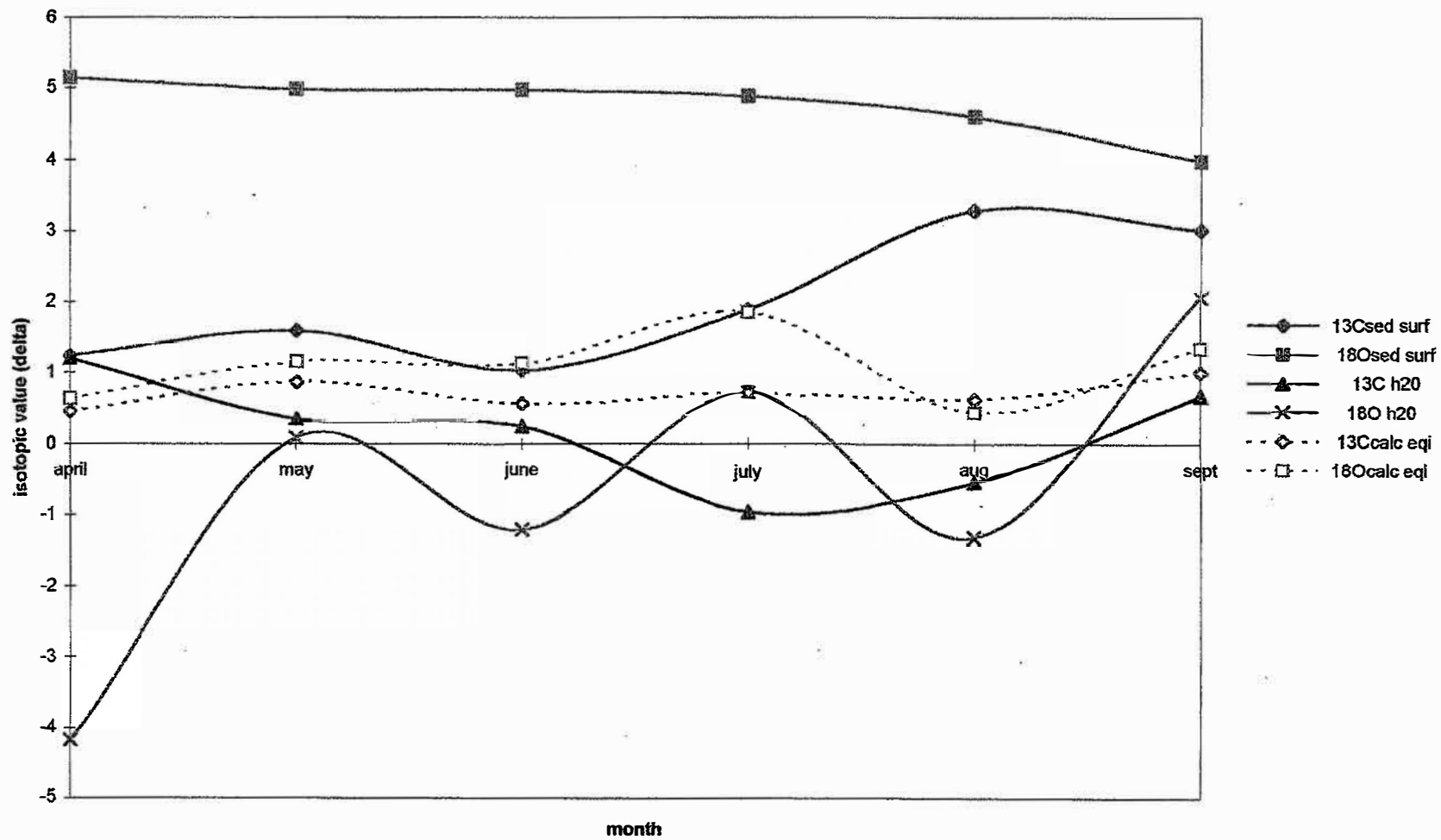
Lake Amy-North sediment equilibrium

Lake Amy Nth



*Lake Amy-South sediment equilibrium*

Lake Amy Sth



## a. Temperature, pH & TDS values

### *Lake Woolley*

DATE	<i>TEMPERATURE deg Celcius</i>				<i>pH</i>		<i>TDS (g/L)</i>
	H <sub>2</sub> O °C	sed 1cm	sed 2cm	sed 10cm	pH H <sub>2</sub> O	pH sed 2cm	
april	17.0	15.0	14.0	12.5	7.58	7.42	8.12
may	12.5	12.5	12.0	12.5	8.75	7.21	79.92
june	13.5	13.0	12.5	12.0	7.62	7.93	40.40
july	16.0	16.5	15.5	14.5	7.99	7.73	29.10
august	16.5	16.0	16.0	14.5	8.38	8.28	21.30
sept	16.5	15.5	15.0	14.5	8.53	7.87	21.99

### *Old Man Lake*

DATE	<i>TEMPERATURE deg Celcius</i>				<i>pH</i>		<i>TDS (g/L)</i>
	H <sub>2</sub> O °C	sed 1cm	sed 2cm	sed 10cm	pH H <sub>2</sub> O	pH sed 2cm	
april	19.5	19.5	18.0	16.5	7.97	7.8	38.85
may	16.5	16.5	16.0	15.0	8.24	8.15	35.25
june	11.5	11.5	12.0	12.0	8.56	8.3	28.95
july	14.7	14.7	14.5	13.5	8.08	7.96	25.05
august	15.0	14.5	14.5	14.0	8.2	7.98	23.61
sept	16.0	15.5	15.5	15.0	7.81	7.6	20.40

### *Fresh Dip Lake*

DATE	<i>TEMPERATURE deg Celcius</i>				<i>pH</i>		<i>TDS (g/L)</i>
	H <sub>2</sub> O °C	sed 1cm	sed 2cm	sed 10cm	pH H <sub>2</sub> O	pH sed 2cm	
april	17.0	16.0	16.0	15.5	8.49	8.1	4.29
may	14.5	14.0	14.0	13.5	7.84	8.65	4.35
june	11.5	11.5	11.5	12.0	8.34	7.61	3.96
july	12.5	12.0	11.7	11.0	8.45	8.25	3.75
august	13.0	13.5	13.5	13.0	8.5	7.85	3.72
sept	16.5	15.5	15.0	14.5	8.53	7.87	2.97

### *Lake Amy Nth*

DATE	<i>TEMPERATURE deg Celcius</i>				<i>pH</i>		<i>TDS (g/L)</i>
	H <sub>2</sub> O °C	sed 1cm	sed 2cm	sed 10cm	pH H <sub>2</sub> O	pH sed 2cm	
april	17.5	17.5	17.0	17.0	8.06	7.63	86.85
may	15.0	15.5	15.5	16.0	7.89	8.13	77.20
june	10.5	11.0	11.0	11.5	8.01	8.05	58.45
july	11.5	11.5	11.0	11.0	8.12	7.84	53.04
august	13.5	14.0	13.5	13.5	8.17	8.28	56.64
sept	17.5	16.5	16.0	15.5	7.65	7.7	45.45

### *Lake Amy Sth*

DATE	<i>TEMPERATURE deg Celcius</i>				<i>pH</i>		<i>TDS (g/L)</i>
	H <sub>2</sub> O °C	sed 1cm	sed 2cm	sed 10cm	pH H <sub>2</sub> O	pH sed 2cm	
april	18.5	19.0	19.0	18.5	8.07	7.43	76.77
may	16.5	16.0	15.5	15.0	7.86	8.39	74.24
june	13.0	13.0	13.0	12.5	8	8.02	65.24
july	9.0	10.0	10.5	11.0	8.12	7.84	53.90
august	13.5	14.0	14.0	14.0	8.19	7.82	57.52
sept	17.5	16.0	16.0	15.0	7.89	7.18	46.35

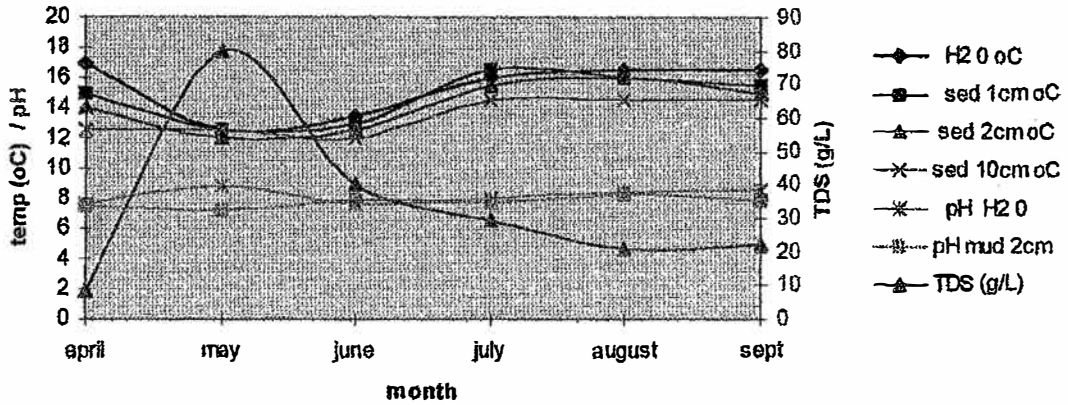
### *Ghost Lake*

DATE	<i>TEMPERATURE deg Celcius</i>				<i>pH</i>		<i>TDS (g/L)</i>
	H <sub>2</sub> O °C	sed 1cm	sed 2cm	sed 10cm	pH H <sub>2</sub> O	pH sed 2cm	
april		16.5	16.5	16.5		7.38	
may	17.5	18.0	17.0	15.5	8.75	8.45	42.70
june	12.0	11.5	11.5	11.0	6.97	7.06	23.04
july	10.0	11.0	11.5	11.0	8.21	8.01	21.15
august	13.5	13.5	13.0	13.0	8.56	8.01	20.95
sept	23.0	21.0	19.0	19.0	9.68	7.6	15.51

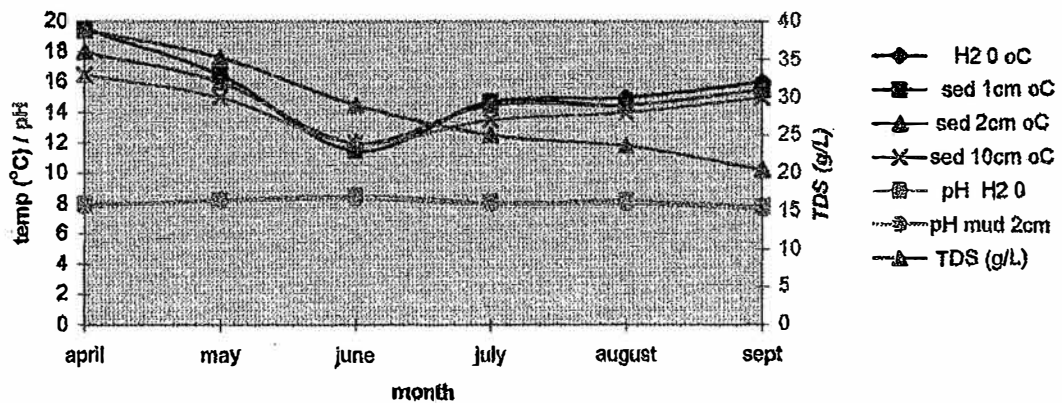


**b. Temperature, pH & TDS trends**

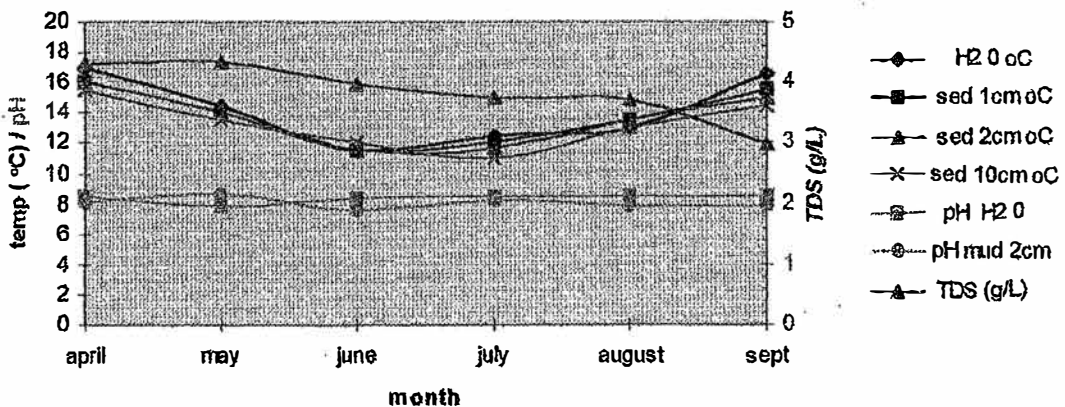
**a. Lake Woolley: temp / pH / TDS**



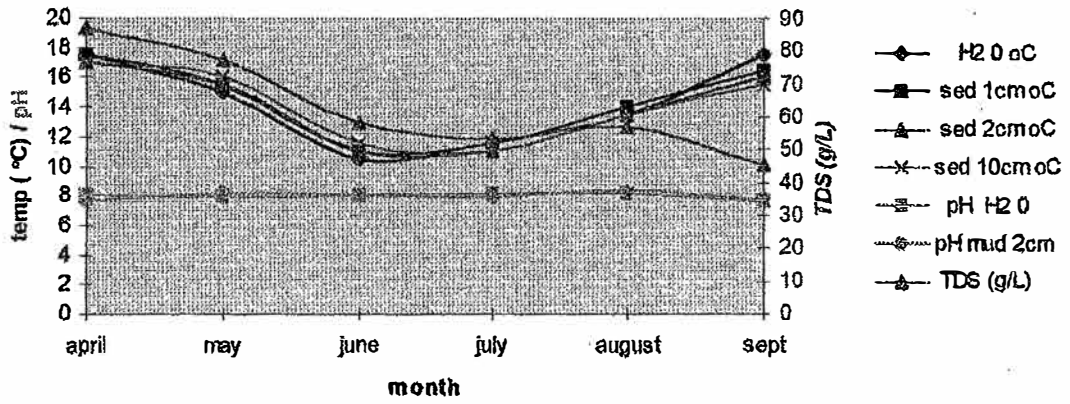
**b. Old Man Lake: temp / pH / TDS**



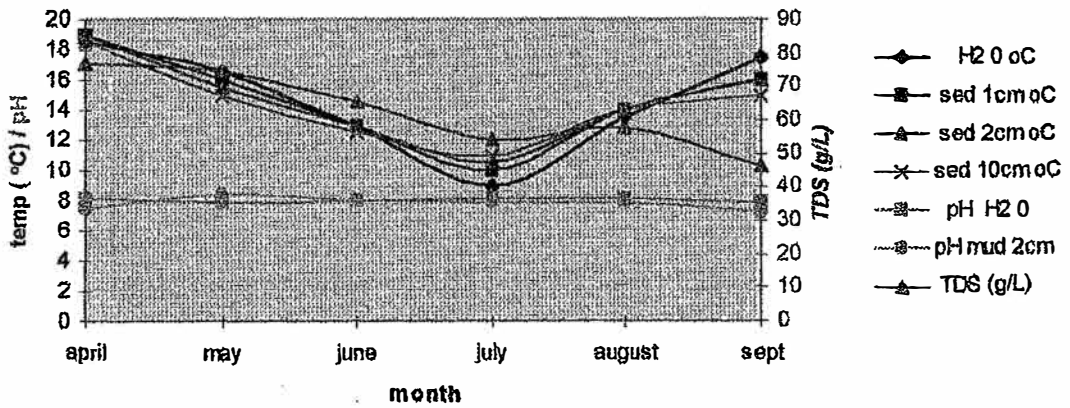
**c. Fresh Dip Lake: temp / pH / TDS**



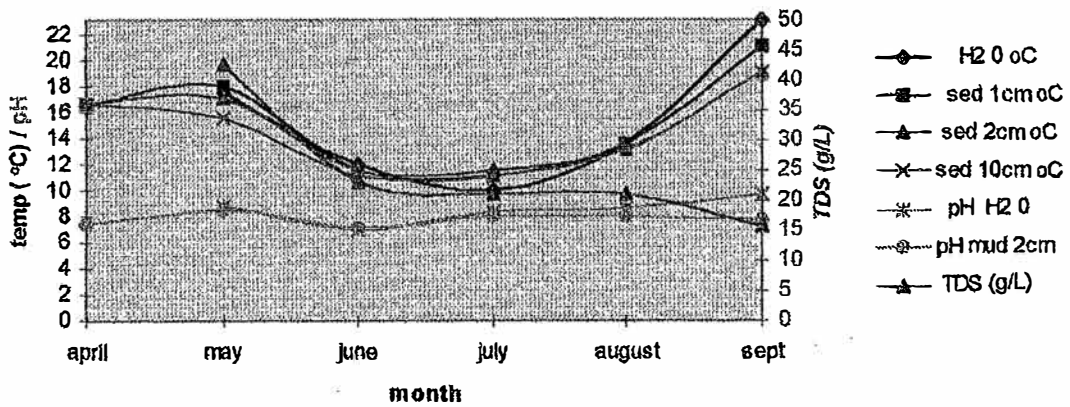
**d. Lake AmyNth: temp / pH / TDS**



**e. AmySth: temp / pH / TDS**

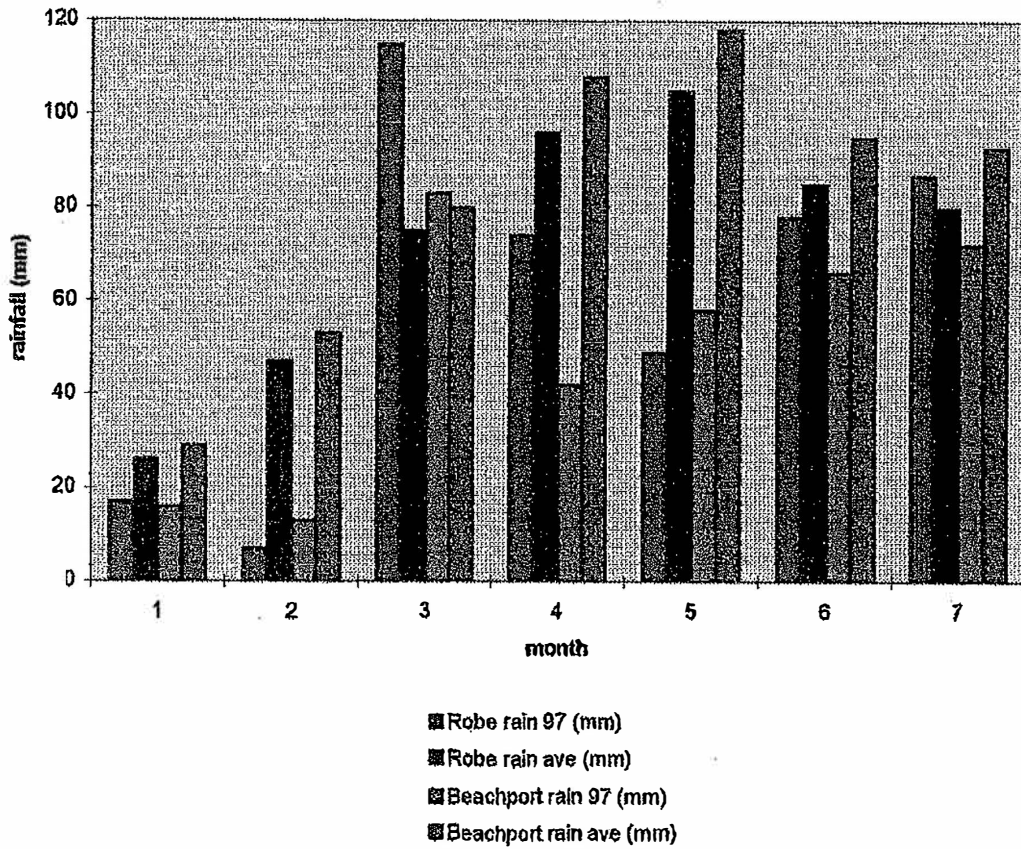


**f. Ghost Lake: temp / pH / TDS**



**c. Robe-Beachport rainfall**

month	<i>Robe</i>		<i>Beachport</i>	
	rain 97 (mm)	rain ave (mm)	rain 97 (mm)	rain ave (mm)
march	17	26	16	29
april	7	47	13	53
may	115	75	83	80
june	74	96	42	108
july	49	105	58	118
aug	78	85	66	95
sept	87	80	72	93



## ANALYTICAL TECHNIQUES

### 1. X-ray Diffraction (XRD) Analysis

Five drops of deionized water were added to two heaped microspatular amounts of sample and then ground by pestle to form the required slurry. The slurry was then smeared over 2/3 of a clean and labelled slide. Once dry the sample was then subjected to XRD analysis under the following conditions:

Defractometer	Phillips PW 105
Monochromator	Graphite
Radiation Source	Cobalt K $\alpha$ radiation. Wavelength 1.7902 Å
2- $\theta$ Scanning Range	25° to 40° @ 0.5/min (slow scan) 3° to 75° @ 2.0/min (normal scan)

JCPDS Manuals were used in the identification of minerals.

A modification of the below equations were used to determine mineral percentages

$$\% \text{ Aragonite} = \frac{5P(A).100}{5P(A) + P(C) + P(Q)}$$

$$\% \text{ Calcite} = \frac{P(C)}{5P(A) + P(C) + P(Q)}$$

$$\% \text{ Quartz} = \frac{P(Q)}{5P(A) + P(C) + P(Q)}$$

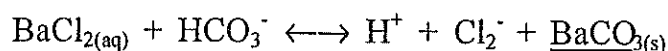
(Adapted from von der Borch 1976)

Where P(A), P(C) and P(Q) are equal to the peak heights of aragonite, calcite and Quartz respectively. Mg mol % were determined by dosing the samples with quartz and utilising the pc program 'Mg Calc'.

## 2. Isotopic Analysis

Isotopes are atoms whose nuclei contain the same number of protons but a differing number of neutrons, hence they have differing mass numbers (ie, sum of protons and neutrons) but occupy the same position in the periodic table. They are denoted for oxygen as  $^{18}\text{O}$  and  $^{16}\text{O}$  and for carbon as  $^{13}\text{C}$  and  $^{12}\text{C}$ , directly noting the differing mass number. The isotopes of carbon and oxygen are "stable" isotopes as opposed to unstable (radioactive) isotopes which spontaneously decay with time. Carbon has two stable isotopes  $^{13}\text{C}$  and  $^{12}\text{C}$ , with the latter accounting for ~98.9% of natural carbon. Oxygen has three stable isotopes  $^{18}\text{O}$ ,  $^{17}\text{O}$  and  $^{16}\text{O}$  with abundances of 0.1995%, 0.0375% and 99.763% respectively, it is due to higher abundance and greater mass difference that the  $^{18}\text{O}/^{16}\text{O}$  ratio is determined (Hoefs 1996).

Stable isotopic analysis of lake waters was undertaken on Barium Carbonate ( $\text{BaCO}_3$ ) precipitated from the waters.  $\text{BaCO}_3$  was precipitated by the addition of 100 ml of 10% Barium Chloride ( $\text{BaCl}_2$ ) solution to 600 ml of filtered lake water.



Approximately 2500  $\mu\text{g}$  of precipitate was weighed into buckets then subjected to 'off-line' stable isotope analysis, utilising the auto-run option of the 'Fisons Mass Spectrometer' (Dept. Geology & Geophysics, Adelaide University). The  $\delta^{18}\text{O}_{\text{DIC}}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  values were obtained from  $\text{CO}_2$  liberated when the resultant  $\text{BaCO}_3$  was reacted with 100% Hypochloric acid within the mass spectrometer reaction vessel.

Stable isotopic analysis of the sediments was undertaken on approximately 500  $\mu\text{g}$  of sample which had been air dried and ground by mortar and pestle, then subjected to 'off-line' stable isotope analysis, utilising the auto-run option of the 'Fisons Mass Spectrometer' (Dept. Geology & Geophysics, Adelaide University).

$\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  were expressed in permil (‰) relative to the PDB standards, after the correction for  $^{17}\text{O}$  following the method of Craig (1957).