The influence of diurnal temperatures on the hydrochemistry of a tufa-depositing stream

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Abstract:

At-a-station diurnal variations in carbonate hydrochemistry were measured during four observation periods at Davys Creek, a tufa-depositing stream in central NSW, Australia. Major ion concentrations and continuously logged measurements of specific conductivity, pH and temperature showed that changes in the amount of CaCO₃ deposited upstream of the study reach were directly related to changes in diurnal water temperatures, which control the rate of CO₂ efflux to the atmosphere. The greatest upstream losses occurred during the mid-afternoon water temperature peak, whereas the lowest upstream losses occurred at sunrise, when water temperatures were at their lowest. Cloudy days at all times of the year produced small diurnal water temperature ranges (*c.* 2–5 °C) and, consequently, relatively small changes in upstream CaCO₃ loss (23–50 mg L⁻¹) through the day. Clear sunny days, especially during summer months, produced large diurnal water temperature changes (up to *c.* 11 °C), which in turn triggered diurnal changes in upstream CaCO₃ loss of up to 100 mg L⁻¹. By implication, the active reach of tufa deposition must advance downstream and increase in length during the evening and *vice versa* during the day. Given that the temperature of Davys Creek waters are a function of insolation, changes in the reach of tufa deposition under baseflow conditions are a direct function of the prevailing weather. This has implications for the palaeoclimatic interpretation of fossil tufa deposits. Copyright © 2003 John Wiley & Sons, Ltd.

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INTRODUCTION

Tufa is a chemical sedimentary deposit formed from CaCO₃-rich spring waters emerging from aquifers bearing a high proportion of karst rock (Altunel and Hancock, 1994; Liu *et al.*, 1995; Pentecost, 2001). The source groundwaters rise to the surface with CO₂ levels much higher than those of the overlying atmosphere. As a consequence, rapid CO₂ outgassing occurs immediately upon emergence, causing the waters to become supersaturated with respect to CaCO₃ as they move downstream. This triggers carbonate deposition (usually in the form of calcite) as crusts on streambeds, lake floors and valley sides (Chafetz and Folk, 1984; Pentecost and Viles, 1994; Ford and Pedley, 1996). In some instances, deposition may be mediated by biological processes, particularly the photosynthetic behaviour of microbes (Pedley, 2000). However, tufa deposition always takes place in waters that thermodynamically favour calcite precipitation, so determining the extent of the biotic role is difficult (Spiro and Pentecost 1991; Pentecost, 1994, 1995).

Tufas are well represented in the Late Quaternary geological record, where they constitute a potentially valuable source of palaeoclimate information (Pedley *et al.*, 2000; Arenas *et al.*, 2000; Szabo *et al.*, 1996). However, the interpretation of tufa palaeoenvironments is hindered by an incomplete understanding of modern tufa-deposition processes. Although the general physico-chemical mechanisms of deposition are well

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understood (Lorah and Herman, 1988), the way in which deposition responds to shifts in climatic parameters at a range of temporal scales remains largely unresearched.

Studies of seasonal changes in stream-water evolution indicate that rates of downstream increase in calcite supersaturation levels vary throughout the year, which has implications for the length of reach over which active tufa deposition occurs (Lorah and Herman, 1988; Drysdale, 2001). In a recent study, the rate of stream-water evolution and, consequently, the length of reach over which tufa deposition occurs was shown to vary positively with discharge (Drysdale *et al.*, 2002), which has significant palaeoenvironmental implications. Only a few studies to date have examined how tufa deposition varies over smaller temporal scales, such as the diurnal cycle (e.g. Barnes, 1965; Dandurand *et al.*, 1982; Lorah and Herman, 1988; Spiro and Pentecost, 1991; Pentecost, 1994; Drysdale *et al.*, 2002). Most such studies show that at-a-station stream chemistry can vary significantly through the diurnal cycle. This can influence longitudinal sampling campaigns because the hydrochemistry at a sampling point will reflect both time- (i.e. period of the day) and space-dependent (i.e. distance from spring) components of stream-water evolution. If this is ignored, the validity of both qualitative and quantitative analyses of downstream trends may be compromised. In addition, at-a-station diurnal variations may be of profound importance with regards to factors controlling the pattern of diurnal variations over periods greater than a single day. Identification of such factors may prove useful for interpreting tufa palaeoenvironments.

Of the diurnal studies in tufa-depositing streams to date, most have been conducted over single periods of 24 h or less (e.g. Barnes, 1965; Dandurand *et al.*, 1982; Lorah and Herman, 1988; Spiro and Pentecost, 1991; Pentecost, 1994); some have involved only a few measurements through the diurnal cycle (e.g. Cole and Batchelder, 1969; Amundson and Kelly, 1987). We are unaware of any study that documents diurnal changes in tufa-depositing streams over extended periods (i.e. days to weeks), although carbonate groundwater-fed streams that do not deposit tufa have been the subject of recent investigations (e.g. Neal *et al.*, 2000, 2002).

The logistical difficulties of diurnal studies are immediately obvious: in order to evaluate longer term changes in stream chemistry without the need for persistent water sampling, continuous measurements of stream parameters are required. These measurements must be related to ion data from shorter term water sampling campaigns. In this study, we use a combination of water sampling and continuously logged measurements of pH, specific conductivity and temperature to study the diurnal hydrochemistry of Davys Creek, a small tufa-depositing stream in central NSW, Australia. We address the following questions: (i) to what extent does at-a-station stream chemistry vary during the diurnal cycle? (ii) what factors control these diurnal changes? (iii) what controls the magnitude of diurnal changes over extended periods (days to weeks) under baseflow conditions; (iv) what are the implications of each of the above for CaCO_3 deposition? As far as we are aware, this is the first comprehensive study of its type anywhere.

STUDY AREA

Davys Creek ($32^{\circ}40'S$, $148^{\circ}40'E$) is a tributary of the Belubula River, a major subcatchment of the Lachlan River in the central-east portion of the Murray–Darling Basin, south-eastern Australia (Figure 1). The upper and middle reaches of the creek's catchment comprise Middle Ordovician volcanics (Walli Andesite), whereas the lower reaches are underlain principally by Late Ordovician limestones (Cliefden Caves Limestone Group), which rest unconformably on the volcanics (Webby and Packham, 1982; Figure 1).

Tufa deposition occurs along two reaches of the creek. The upper reach is fed perennially by a series of discrete in-channel and streambank seepages. For most of the year, the uppermost segment of this reach consists of a chain of pools, which only become interconnected following sustained rainfall. Perennial flow commences at Twin Gully, about 2.5 km downstream of the most upstream seepages (Figure 1). Tufa deposition commences c. 500 m downstream of Twin Gully and has formed small dams and cascades over a c. 350 m segment of the channel.

Figure 1. Location and geology of the study area. The bottom segment is a long section of Davys Creek showing the position of the data-logging site and the major hydrogeological features

The upper reach is separated from its lower counterpart by a dry-valley section, above which upstream surface waters sink progressively into the creek bed within a few hundred metres of the limestone–andesite contact. A fault brings groundwaters to the surface a further *c.* 300 m downstream (Figure 1). This resurgence represents a combination of the sinking waters derived from the upstream andesite subcatchment and autogenic recharge of the limestone subcatchment. Rapid CO₂ outgassing results in tufa precipitation for *c.* 500 m along the lower reach before the waters reach the Davys Creek–Belubula River junction.

The upper reach, which is the focus of this study, is unusual in the sense that the tufa source waters rise in volcanics, and are not of karstic origin. However, stable carbon isotope values from the tufas ($-9.7 \pm 0.4\text{‰}$; $n = 11$; Drysdale, unpublished data) suggest that the total dissolved carbon is of biogenic origin (Hoefs, 1997), and is close to the mean value for local speleothems ($-8.3 \pm 1.2\text{‰}$, $n = 154$; McDonald, 2000). In addition, the groundwater temperature is *c.* 16 °C all year, which is identical to air temperatures within local caves (McDonald, 2000). Taken together, these data rule out a geothermal source for the waters. The most probable origin of the spring waters is rising water tables brought about by progressive post-European land clearance. Dryland salinity is widespread in the region (Hill, 1999). The upper reaches of Davys Creek contain salinity scalds, and boreholes and groundwater seepages have relatively high specific conductivities (up to 2000 $\mu\text{S cm}^{-1}$) dominated by Na⁺ and Cl⁻. These waters also contain abundant dissolved Ca²⁺ and HCO₃⁻ (up to 328 mg L⁻¹ of CaCO₃ equivalent) and CO₂ levels approaching 100 times that of the open atmosphere. It is the significant downstream outgassing of the latter that triggers tufa deposition along sections of the streambed.

The instrumentation and water-sampling site chosen for this study is situated along a small bedrock channel segment at the downstream limit of tufa deposition along the study reach. Dye-tracing experiments show that the waters take approximately 3–6 h to reach the site from Twin Gully (Figure 1). All sampling was conducted during non-drought conditions, when this reach carries a near-stable baseflow discharge of 3–5 L s⁻¹. Any effects of discharge variability on the downstream evolution of the waters (Drysdale *et al.*, 2002) can be ignored. During El Niño (drought) conditions, flow reduces to 1–2 L s⁻¹; no sampling was conducted under these conditions.

Based on dye-tracing, the flow time along the perennial reach is estimated to be 3–6 h. The deployment site is ideal for studying diurnal changes in water properties because it represents the position where the waters attain their maximum residence time for that specific tufa-depositing reach, and is thus where diurnal changes should be maximized (Barnes, 1965; Pentecost, 1994). By contrast, locations closer to the groundwater source would experience little exposure to ambient conditions, and hydrochemical changes would be minimized (Barnes, 1965). Therefore, under baseflow or near-to-baseflow conditions, seepage-water composition should alter very little, and at-a-station diurnal fluctuations in both specific conductivity (SC) and Ca²⁺–HCO₃⁻ will reflect diurnal changes in the amount of CaCO₃ deposited by the waters upstream, i.e. before they reach the station. However, the seepage-water composition will change during storm events as a result of surface runoff (i.e. diluted SC) and immediately following such events as a result of the flushing of salts from the salinity-affected unsaturated zone (i.e. increased SC). When these salt pulses enter the stream system, diurnal changes may be absent or depressed.

METHODS

Field campaigns were conducted in February, April, July and December 2000 (Table I). During each campaign, a Greenspan Technology CTD300 data logger was programmed to collect continuous readings of SC (as $\mu\text{S cm}^{-1}$ at 25 °C), pH and temperature at 15-min intervals for periods ranging from 5 to 26 days (Table I). The logger was calibrated prior to deployment using pH (6.86 and 9.18) and conductivity (0 and 1412 $\mu\text{S cm}^{-1}$) standards.

Hand-held water quality meter measurements were undertaken to check the reliability of data logger measurements. Laboratory calibration experiments showed that relative changes in the pH and conductivity

Table I. Summary of sampling periods and data collection for each field campaign

Parameters	February 2000	April 2000	July–August 2000	December 2000
Logging period	13:15 12/2/00 to 08:00 27/2/00	05:00 24/4/00 to 20:45 29/4/00	17:45 26/7/00 to 00:00 5/8/00	19:30 6/12/00 to 00:00 1/1/01
Hand-held meter measurements	Yes	No	Yes	Yes
Water sampling period	n.a.	00:00 29/4/00 to 21:00 29/4/00	16:40 26/7/00 to 17:35 28/7/00	16:50 6/12/00 to 14:30 8/12/00
Number of water samples	n.a.	12	15	34
Ca ²⁺ + HCO ₃ [−]	No	Yes	Yes	Yes
Other major anions	No	No	Yes	Yes
Other major cations	No	No	Yes	Yes

of a continuously varying solution recorded by bench-top meters matched those recorded by the data logger, but were 'offset' according to the ionic composition of the waters. In addition, the logger usually took between 1 and 2 h to stabilize following calibration. Although the logger recorded true fluctuations in solution composition once it stabilized, the absolute values were not precisely the same as those of the bench-top meters. In the belief that an offset would persist in the field, a programme of hand-held meter measurements was included to verify the logger data. In February, July and December, the pH, temperature and SC were measured at regular intervals using hand-held meters, which were calibrated using the same standards as those used for the data logger. A YSI 100 SC/temperature and a Metrohm 704 pH meter were used during these campaigns. In April 2000, SC, pH and temperature were measured using a Eutech Cyberscan PC10. However, this pH sensor could not be calibrated satisfactorily in the field, so hand-held pH meter data from this campaign are not reported here.

In all campaigns except February, water samples for ion analyses were collected so that diurnal changes in SC could be quantified in terms of relative changes in upstream CaCO₃ deposition (Table I). Samples were collected at intervals during the diurnal cycle in clean acid-rinsed plastic containers. In April, samples were collected for Ca²⁺ and HCO₃[−] analyses only, whilst for July and December major anions (Cl[−], SO₄^{2−} and NO₃[−]) and cations (Mg²⁺, Na⁺ and K⁺) were also measured. Bicarbonate was measured potentiometrically to the pH c. 4.5 endpoint within 30 min of collection using standardized c. 0.02 M HCl. Remaining anions were measured using a Waters ion chromatograph. All cations were measured on HNO₃-acidified sample aliquots using an ARL 3520 ICP–AES (inductively coupled plasma–auger electron spectroscopy). In cases where SC fluctuations could be attributed solely to Ca²⁺ and HCO₃[−] changes, paired Ca²⁺ and conductivity values were correlated and, where considered valid, regression was used to establish a time-series of diurnal CaCO₃ changes.

The full hydrochemical data sets for July and December were processed through the program PCWATEQ (Rollins, 1984), which calculates the charge-balance error, dissolved CO₂ (as both total CO₂ and PCO₂) and calcite saturation index (SI_{calcite}) for each sample. Although Ca²⁺ and HCO₃[−] analyses were conducted on April samples, we were unable to generate these indices owing to the lack of pH data.

PCO₂ is calculated from

$$\text{PCO}_2 = \frac{\alpha \text{HCO}_3^- \alpha \text{H}^+}{K_1 K_{\text{CO}_2}}$$

where the prefix α is the activity, and K_1 and K_{CO_2} are the equilibrium constants for carbonic acid (H₂CO₃) and CO₂ respectively (White, 1988). The values of these and other reaction constants in the CaCO₃–H₂O–CO₂ system are known for the full range of ambient temperatures (Drever, 1982), whereas the activities are determined from measured HCO₃[−] concentrations and pH.

SI_{calcite} is calculated from

$$SI_{\text{calcite}} = \log \left(\frac{\alpha \text{Ca}^{2+} \times \alpha \text{CO}_3^{2-}}{K_{\text{calcite}}} \right)$$

where K_{calcite} is the equilibrium constant for calcite. Q3

PCO₂• and SI_{calcite} are derived from *in situ* measurements of pH and temperature, and analysis of Ca²⁺ and HCO₃⁻ from water samples (Ford and Williams, 1989). In carbonate waters, the dominant control on PCO₂• is pH. Thus, if pH changes recorded by a data logger can be validated using hand-held meter measurements, a surrogate time-series of PCO₂ can be derived from continuous measurements of pH alone. Establishing a time-series for SI_{calcite} is slightly more complex. However, if SC can be shown to change principally because of variations in Ca²⁺ (and HCO₃⁻), then αCa^{2+} can be estimated from SC data because αCa^{2+} is principally a function of Ca²⁺ concentration (Drever, 1982). The parameter, αCO_3^{2-} , is calculated from HCO₃⁻ and pH. However, αCO_3^{2-} variations are a direct function of pH in the normal pH range of carbonate waters. Given that K_{calcite} is known for ambient temperatures (White, 1988), SC and pH can be used as surrogates for αCa^{2+} and αCO_3^{2-} respectively, and a reliable SI_{calcite} time-series generated. At the very least, these time-series should provide an indication of *relative* diurnal shifts in PCO₂• and SI_{calcite}. Similar time-series have been generated by Neal *et al.* (2002) but using a slightly different approach from that utilized here. Q3

RESULTS

Logger data and hand-held meter measurements

February 2000. The data logger was deployed for a 16-day period in February 2000 (Table I). The SC, pH and temperature data were collected by hand-held meters on six occasions over the first 30 h of logging, covering almost the full range of logged values for the same period. The time-series for each logged parameter is shown in Figure 2 with the hand-held meter measurements superimposed over their respective time-series. The correlation coefficients for each pair of measurements (Table II) show that the fluctuations recorded by the logger, although offset on an absolute scale, match closely those measured by the hand-held meter.

Logged SC, pH and temperature each show consistent diurnal changes (Figure 2), although the magnitude of change varies through the observation period. For a given cycle, peak conductivities typically occur between 0700 to 0800 hours (Table III) and decrease steadily until the late afternoon to early evening (1630 to 1900 hours), after which they increase. The water temperature follows a similar although not identical trend, with minimum and maximum temperatures recorded 1–2 h earlier than the maximum and minimum SC values respectively. The pH also fluctuates throughout the day, with minima occurring between 2230 and 0130 hours (Table III). The pH rises through the morning, steadily at first then rapidly, and peaks between midday and mid-afternoon (1100–1500 hours). Thus, although all three parameters show clear diurnal fluctuations, none is in perfect phase with either of the other two. Days recording the lowest diurnal fluctuations in pH and SC experienced the lowest water temperature ranges. In addition, SC and water temperature are closely inversely

Table II. Correlation coefficients for each pair of hand-held-meter and data-logger measurements

Parameters	February 2000	April 2000	July 2000	December 2000
T_{logger} versus $T_{\text{hand-held}}$	1.00	0.98	0.99	1.00
$\text{pH}_{\text{logger}}$ versus $\text{pH}_{\text{hand-held}}$	0.95	n.a.	0.96	0.90
$\text{SC}_{\text{logger}}$ versus $\text{SC}_{\text{hand-held}}$	0.99	0.92	0.98	0.97
Ca^{2+} versus $\text{SC}_{\text{logger}}$	n.a.	0.96	0.34	0.96
HCO_3^- versus $\text{SC}_{\text{logger}}$	n.a.	0.92	0.65	0.99
Observations	6	12	14	33

Figure 2. Logged and hand-held meter measurements of SC, temperature and pH for February 2000

Table III. The timing of temperature, SC and pH minima and maxima for each logging period

Parameter	February 2000	April 2000	July 2000	December 2000
SC minimum	1630–1900	1700–1900	1530–1700	1500–1800
SC maximum	0700–0800	0830–0930	0800–0900	0700–0800
Temperature minimum	0600–0800	0730–0830	0830–0900	0730–0800
Temperature maximum	1530–1730	1515–1600	1500–1545	1530–1630
pH minimum	2230–0130	n.a.	2000–0100	2200–0000
pH maximum	1100–1500	n.a.	1300–1500	1400–1600

related. Together, these suggest that water temperature plays an important role in controlling the diurnal chemistry.

April 2000. The data logger was deployed for six consecutive days at the end of April 2000. Neither hand-held nor logger pH measurements are available for April 2000 owing to calibration problems. The temperature and SC observations using the hand-held meter are superimposed over their respective logger time-series in

Figure 3. The similarity in patterns and the high correlation coefficients (Table II) demonstrate the excellent agreement between logger and hand-held meter values, although as for February, the values are slightly offset.

The logged parameters show systematic diurnal variations. The SC values again virtually mirror those of temperature. Maximum water temperatures occur between 1500 and 1600 hours each day (Table III), whereas SC minima occur around 2–3 h later; minimum water temperatures occur around 1–2 h before maximum conductivities.

July–August 2000. The data logger measured continuously for 9 days over July–August 2000 (Figure 4). Spot measurements of temperature, pH and SC during the initial part of this period mirrored the logger patterns and returned high correlation coefficients (Table II), despite the large absolute differences in values. Consistent diurnal changes prevail for all parameters for most of the logging period. The timing of maximum and minimum values for pH is comparable to those from February (Table III). Water temperatures reach their lowest further into the morning and their maximum slightly earlier in the afternoon compared with other periods (Table III), reflecting the shorter winter insolation period. Minima in SC also occur slightly earlier, suggesting that water temperature is at least partly controlling conductivity shifts.

During this campaign a longer term decline in SC, in addition to the diurnal signal, is evident for all but the first day and a half of measurement. Although the magnitude of diurnal changes in SC match those of temperature, there is no obvious longer term temperature shift that might explain the longer term decline in SC. Thus, other factors appear to be controlling this decline, a point that will be addressed further in a later section.

December 2000. The data logger continuously measured water quality for 25 days during December 2000, with hand-held meter measurements carried out over the first 2 days (Figure 5). Very strong correlations between paired hand-held meter and logger measurements for all three parameters (Table II) again confirm the reliability of the logger to record genuine diurnal hydrochemical changes. As with previous campaigns, all

Figure 3. Logged and hand-held meter measurements of SC and temperature for April 2000

Figure 4. Logged and hand-held meter measurements of SC, temperature and pH for July 2000

three parameters fluctuate consistently throughout the diurnal cycle. Not surprisingly, the timing of maxima and minima of all three parameters is comparable to February (Table III).

Lower amplitude diurnal shifts in both pH and SC tend to coincide with days when water temperature ranges were also relatively low (Figure 5). In addition, longer term changes in SC are evident, although unlike July these appear to mirror longer term shifts in maximum and minimum temperatures. The relationship between the magnitude of diurnal SC changes and stream temperatures will be considered further in the discussion.

Water sample data

Major ions. The complete ion analyses, including calcite saturation indices, charge balance errors and carbon dioxide concentrations, can be viewed at the following web address: http://www.newcastle.edu.au/discipline/geography/staff_students/staff/r-drysdale/table.htm. Only pH, temperature, SC, Ca^{2+} and HCO_3^- data are reported here (Table IV). During each campaign, both Ca^{2+} and HCO_3^- fluctuate throughout the day, reflecting absolute changes in the degree of upstream loss of CaCO_3 prior to the waters reaching the measurement site. The lowest values occur during the mid- to late afternoon period (1500 to 1800 hours), whereas the highest values were recorded from waters sampled between 0500 and 1000 hours (Table IV). These closely match the timing of maximum and minimum changes in SC recorded by the data logger (Table III).

Figure 5. Logged and hand-held meter measurements of SC, temperature and pH for December 2000

Correlations between logger SC and both Ca^{2+} and HCO_3^- for all three campaigns were statistically significant (Table II), indicating that coupled changes in these ions owing to changes in upstream CaCO_3 loss are largely responsible for the fluctuations in SC. However, the correlations for July are much weaker than those for both April and December, suggesting that changes in other ions also may be forcing SC variations. The Na^+ , Cl^- and, to a lesser extent, Mg^{2+} data for both July and December show longer term trends, which can be attributed to recent recharge. For July, these ions increased steadily over the water-sampling campaign (Figure 6c), which was a period of light but persistent rainfall. Water-depth values recorded by the data logger also show a small but steady increase in relative creek levels between 26 and 29 July (Figure 6a), no doubt in response to the recharge. Thus, the water-sampling period of July occurred at the onset of a salt pulse, which moved slowly through the system in the days following, as shown by the declining logger SC values from 28 July onwards (Figure 4). In December, the sampling period occurred 5 days after a 3-day rainfall event (28.8 mm recorded over 3 days at nearby Cowra: Australian Bureau of Meteorology data). Figure 6d shows that the same ions and water depth *decrease* over the water sampling period, indicating the 'tail-end' or recessional stage of a similar salt-flushing episode. The *c.* 2-day pattern for Mg^{2+} in both July and December is confounded by diurnal changes (Figure 6c and f), which probably result from its incorporation into calcite

Table IV. Summary of hand-held meter measurement and water sample Ca^{2+} and HCO_3^- data for April, July and December 2000. The ion data are in mg L^{-1} . SI_c and PCO_2 are the log calcite saturation indices (dimensionless units) and CO_2 partial pressures (in log atmospheres)—see text for explanation

Date and time	°C	pH	SC	Ca^{2+}	HCO_3^-	Date and time	°C	pH	SC	Ca^{2+}	HCO_3^-
April 2000						December 2000					
29/04/2000 0:00	15.5	n.a.	1181	98	522	06/12/2000 16:50	28.2	8.22	1203	70	478
29/04/2000 2:00	15.1	n.a.	1184	97	525	06/12/2000 18:20	26.7	8.21	1226	76	500
29/04/2000 4:00	14.8	n.a.	1193	99	528	06/12/2000 19:20	25.5	8.15	1244	78	515
29/04/2000 6:00	14.5	n.a.	1201	100	530	06/12/2000 20:20	24.2	8.08	1260	82	535
29/04/2000 8:00	14.0	n.a.	1212	101	536	06/12/2000 22:00	22.1	8.01	1283	90	556
29/04/2000 10:00	14.9	n.a.	1200	101	529	06/12/2000 23:30	21.1	8.03	1286	92	566
29/04/2000 12:00	16.9	n.a.	1179	98	520	07/12/2000 5:20	18.4	8.08	1299	100	582
29/04/2000 14:00	18.8	n.a.	1160	95	506	07/12/2000 7:00	18.0	8.08	1296	100	575
29/04/2000 16:00	19.5	n.a.	1148	92	501	07/12/2000 9:00	19.3	8.22	1282	95	564
29/04/2000 18:00	18.9	n.a.	1155	92	505	07/12/2000 10:00	20.6	8.20	1266	92	557
29/04/2000 20:00	17.1	n.a.	1172	94	508	07/12/2000 11:00	21.9	8.27	1225	88	540
29/04/2000 21:00	16.7	n.a.	1178	95	512	07/12/2000 12:00	23.0	8.32	1223	84	517
July 2000						07/12/2000 13:00	23.4	8.25	1208	81	507
						07/12/2000 14:00	23.3	8.28	1205	78	498
						07/12/2000 15:00	23.3	8.28	1206	78	498
						07/12/2000 16:00	24.1	8.23	1203	77	501
						07/12/2000 17:00	24.4	8.25	1195	74	490
						07/12/2000 18:00	24.2	8.26	1194	72	487
						07/12/2000 19:00	23.4	8.18	1207	77	494
						07/12/2000 20:00	22.2	8.08	1233	83	520
						07/12/2000 21:00	20.8	8.02	1256	88	542
						07/12/2000 22:00	19.7	8.06	1271	91	555
26/07/2000 16:40	10.6	8.39	1230	87	522	07/12/2000 23:00	18.7	8.06	1276	92	563
26/07/2000 19:10	9.3	8.29	1247	92	531	08/12/2000 0:00	17.9	8.05	1287	100	578
26/07/2000 21:05	8.8	8.28	1251	93	540	08/12/2000 5:10	15.5	8.08	1290	100	581
26/07/2000 23:15	8.4	8.33	1274	95	554	08/12/2000 6:15	15.4	8.11	1290	99	584
27/07/2000 7:06	7.1	8.33	1305	94	543	08/12/2000 7:30	15.5	8.14	1286	98	579
27/07/2000 9:10	6.9	8.39	1243	89	521	08/12/2000 8:30	16.3	8.21	1279	97	575
27/07/2000 11:20	8.6	8.46	1258	88	522	08/12/2000 9:30	17.9	8.29	1261	93	558
27/07/2000 13:10	9.6	8.53	1245	84	502	08/12/2000 10:30	19.8	8.26	1237	88	540
27/07/2000 15:30	10.0	8.51	1207	79	481	08/12/2000 11:30	22.2	8.33	1213	81	519
27/07/2000 17:30	9.0	8.47	1244	86	497	08/12/2000 12:30	24.0	8.34	1192	76	494
27/07/2000 19:50	8.3	8.36	1285	87	518	08/12/2000 13:30	25.9	8.38	1171	70	480
27/07/2000 22:45	6.9	8.35	1312	90	531	08/12/2000 14:30	27.0	8.38	1156	66	464
28/07/2000 7:30	6.2	8.34	1386	94	561						
28/07/2000 9:10	6.7	8.41	1387	95	563						
28/07/2000 17:35	10.6	8.33	1340	84	528						

during CaCO_3 deposition (Figure 6b and e). The relative variations in Na^+ , Mg^{2+} and Cl^- for December are less than half those for July; variation in K^+ is similar for both periods, but this ion has little bearing on SC owing to its very low concentration. The net result is that the influence on SC of 'background' variations in Na^+ , Mg^{2+} and Cl^- is less significant for December than for July (Figure 6g–i): the December Ca^{2+} and HCO_3^- data explain 96% and 99% of the total variation in logger SC respectively, whereas the corresponding values for July are 34% and 65% (Table II). For April, when no other ion data are available, the power of Ca^{2+} and HCO_3^- in explaining variations in SC is similar to that of December. Consequently, SC can be used as a surrogate for continuous CaCO_3 variations for both April and December (but not for July), and reliable time-series of diurnal at-a-station CaCO_3 changes have been compiled for both periods (Figure 7b and c).

Figure 6. Diurnal Na^+ , Cl^- and Mg^{2+} ion patterns for July 2000 (a–c) and December 2000 (d–f), and correlations between SC and Cl^- (g), Na^+ (h) and Mg^{2+} (i) for both July and December 2000. Note that all ion data are plotted in milli-equivalents per litre

Figure 7. Derived diurnal CaCO_3 variations for February, April and December 2000

For February 2000, no water samples were collected. However, given the strong relationships between hand-held meter SC and logger SC (February), and between SC and Ca^{2+} for April and December (Table II), it is possible to compile a similar CaCO_3 time-series for February by, first, converting all logger SC data for February 2000 into hand-held SC values using regression, then transforming the latter into CaCO_3 -equivalent using the regression equation of SC versus Ca^{2+} for December 2000. The SC versus Ca^{2+} data for April was not considered because the hand-held SC meter used for the April campaign differed from that used in December and February, and we cannot verify its relationship to the YSI meter. The resulting time-series for February is shown in Figure 7a.

Table V summarizes the changes in CaCO_3 for each of the three campaigns. The highest diurnal CaCO_3 changes occurred during December, when the station experienced an amplitude of 101 mg L^{-1} ; three other days in December experienced fluctuations of 100 mg L^{-1} . The lowest maximum diurnal changes occurred in

April (31 mg L⁻¹), which also recorded the lowest minimum change (23 mg L⁻¹). There is a general tendency for the diurnal CaCO₃ changes to reflect water temperature ranges: in terms of the maximum CaCO₃ ranges for each period, December scored the highest and had the highest temperature range, whereas April scored the lowest and had the lowest temperature range. This pattern breaks down when one examines the minimum diurnal changes: December had the highest minimum CaCO₃ change (50 mg L⁻¹), yet the temperature range was only 3.6 °C, whereas the lowest minimum (April: 27 mg L⁻¹) had the highest diurnal temperature range (5.5 °C). Clearly, temperature range alone may not explain all CaCO₃ changes. This will be explored further in the discussion.

Diurnal changes in PCO₂ and the calcite saturation index. Changes in the CaCO₃ composition of tufa-depositing waters are driven by CO₂ flux from the stream waters to the atmosphere and the consequent effect of this flux on SI_{calcite}. Figure 8a and b shows the diurnal trends in PCO₂ and SI_{calcite} for the 2-day water-sampling periods of July and December. There is no PCO₂ and SI_{calcite} data for February or April because water samples were not collected for the former and there are no pH data for the latter. Although the data in Figure 8a and b are limited in continuity and temporal resolution, the diurnal patterns for both parameters are quite consistent. The greater temporal resolution of the December series permits more precise estimates to be made of the timing of SI_{calcite} and PCO₂ changes. The highest PCO₂ values occur during the late evening, whereas the lowest occur during the early to mid-afternoon. For SI_{calcite}, the minimum values occur in the late evening and the highest are confined to the late morning to early afternoon period.

A better understanding of the nature and timing of PCO₂ and SI_{calcite} changes can be gained by generating time-series of PCO₂ and SI_{calcite}, which would provide greater temporal resolution than the grab-sample data. As noted earlier, PCO₂ is largely a function of pH. Figure 8c and d indicates that PCO₂ derived from the water samples collected in July and December is strongly correlated with the corresponding instantaneous pH values of the data logger. The standard errors of estimate for the independent variable (pH) for July and December are 0.04 and 0.05 respectively, which is insignificant compared with typical diurnal ranges of up to 10 times these values (Figures 2, 3 and 5 and Table IV). Therefore, logged pH can be used legitimately as a surrogate for PCO₂ for these two campaigns. As discussed previously, the major requirements for a reliable time-series of SI_{calcite} are strong correlations between αCa²⁺ and logger SC, and between αCO₃²⁻ and logger pH. Only the December data satisfy these criteria (Figure 8e and f); for the July campaign, the correlation between αCa²⁺ and logger SC is insignificant owing to longer-term variations in non-carbonate ions, and a lack of reliable pH data precludes us from generating a SI_{calcite} time-series from the April data.

It is now possible to deconstruct the precise detail of the diurnal changes. The temperature, SC and derived PCO₂ and SI_c data for one randomly chosen day in December is sufficient to elucidate this detail (Figure 9) because the diurnal changes are consistent for each day of each respective campaign. The SC value reaches

Table V. Maximum and minimum diurnal CaCO₃ changes, and the corresponding temperature maximum, minimum and range, for each logging period

Parameter	February 2000	April 2000	December 2000
Max. diurnal change in CaCO ₃ (mg L ⁻¹)	67	31	101
Temperature minimum and maximum (°C)	17.3–25.7	9.4–15.8	18.5–29.1
Temperature range (°C)	8.4	6.4	10.6
Min. diurnal change in CaCO ₃ (mg L ⁻¹)	26	23	50
Temperature minimum and maximum (°C)	20.4–22.7	12.3–17.6	21.2–24.8
Temperature range (°C)	2.3	5.3	3.6
Mean diurnal change in CaCO ₃ (mg L ⁻¹)	49	27	87
Mean diurnal temperature range (°C)	5.4	5.5	11
Number of days	15	6	25

Figure 8. (a and b) Diurnal variations in PCO_2 and calcite saturation for July and December 2000. (c and d) Correlations between PCO_2 and logger pH for July and December. (e and f) Correlations between SC and both αCa^{2+} and αCO_3^{2-} for December 2000.

a maximum by early morning (a in Figure 9) and decreases to a minimum by mid- to late afternoon (b). The decline in SC commences shortly after water temperatures begin to rise (c). This temperature increase is accompanied by a sharp decrease in PCO_2 (d). Water temperature peaks by mid-afternoon (e), but by this stage PCO_2 has reached its minimum (f). As temperature falls, PCO_2 rises. However, this rise occurs (f) before SC has reached its minimum (b). The SC value begins to rise in the late afternoon and continues steadily until reaching a plateau in the evening. The temperature fall virtually mirrors the rise in SC. However, the sharp rise in PCO_2 , which commenced mid-afternoon, is arrested during the evening and begins to decrease steadily (g). The likely factors controlling these diurnal changes will be discussed in the next section.

Figure 9. Diurnal variations in temperature, SC, PCO_2 and calcite saturation for 17 December 2000. See text for explanation of a to g

DISCUSSION

Controls on an individual diurnal cycle

The general nature of the diurnal trends observed at Davys Creek is similar to that documented at other sites around the world (Barnes, 1965; Dandurand *et al.*, 1982; Spiro and Pentecost, 1991; Pentecost, 1994): at-a-station minima in dissolved ions (measured as SC or dissolved CaCO_3) usually occur in the mid-afternoon when water temperature reaches its maximum and PCO_2 is closest to atmospheric levels, whereas maximum ion concentrations between sunrise and mid-morning coincide with minimum water temperatures and PCO_2 peaks.

At Davys Creek, continuous measurements show that increasing water temperatures in the morning trigger reductions in PCO_2 . This in turn produces a sharp increase in $\text{SI}_{\text{calcite}}$, shortly after which SC begins to fall as a result of CaCO_3 deposition. The recorded fluctuations in CaCO_3 are attributed to variations in the amount of carbonate deposited upstream before the waters reach the monitoring site. Thus, under conditions of near-constant seepage water composition, which holds true for baseflow conditions, the reach of carbonate deposition retreats upstream during the day and advances downstream during the evening, as shown schematically in Figure 10. The entire diurnal cycle is driven by insolation via water temperature changes, which control the rate of CO_2 outgassing and the amount of CaCO_3 held in solution via the inverse relationship between temperature and dissolved CaCO_3 and CO_2 . During the evening, the temperature-induced increase in PCO_2 cannot be the result of extra CO_2 uptake by the stream water. Instead, it is caused by a reduction in the amount of upstream CO_2 loss, which gives rise to the apparent PCO_2 increase in Figure 9. The stream is a net loser of CO_2 and will remain so as long as its PCO_2 is greater than that of the coexisting atmosphere. Similarly, the stream is not gaining dissolved CaCO_3 during the evening, but is losing less to the solid phase along the reach upstream of the monitoring station (Figure 10).

The only unexplained anomaly from Figure 9 is the slow but steady decrease in PCO_2 that commences mid- to late evening (g in Figure 9). This persists until mid-morning, after which the rate of decrease increases markedly. The mid-evening reduction in PCO_2 contradicts the trend in water temperature, which is decreasing at the same time and thus should promote CO_2 retention. The answer is apparent when total CO_2 is plotted against temperature and PCO_2 for December. The PCO_2 starts to decrease when total CO_2 reaches maximum levels (Figure 11a). Total CO_2 mimics water temperatures for most of the cycle (Figure 11b). From approximately midnight, total CO_2 reaches a plateau, even though water temperature continues to decrease. The plateaux of dissolved CO_2 represent the minimum amount of outgassing that occurs along the reach upstream of the monitoring site during the two diurnal cycles. The total CO_2 cannot increase further without an additional source of CO_2 . This source is not available: the stream is always a net loser of CO_2 along its

Figure 10. Conceptual model of downstream changes in dissolved CaCO_3 during the diurnal cycle

entire length because of the large pressure gradient that exists between the stream and the atmosphere. As total CO_2 remains approximately constant, PCO_2 must decrease as temperature decreases because PCO_2 is positively related to total CO_2 concentration but inversely related to temperature (White, 1988). Therefore, although PCO_2 slowly decreases over the period mid-evening to dawn for each of the logging periods (Figure 9), total CO_2 remains approximately constant.

Longer term controls on diurnal changes

It is clear from the above that water temperature is the driving force behind the diurnal changes in the amount of CaCO_3 deposition occurring upstream of the monitoring site. To what extent do changes in day-to-day diurnal temperature ranges affect the amount of day-to-day CaCO_3 losses? The data in Figures 2–5 and Table V suggest that day-to-day changes in water temperature range are synchronous with and sympathetic to the diurnal ranges in CaCO_3 deposition: as the water temperature range decreases (e.g. owing to one or more consecutive cloudy days), the amount of diurnal CaCO_3 change also decreases. In Figure 12a, temperature range and CaCO_3 range are plotted for February, April and December. For each individual monitoring period, the correlation coefficients are statistically significant ($p < 0.05$; $r = 0.84, 0.73, 0.62$ respectively), and the correlation coefficient for the composite data is stronger again ($r = 0.85$). Therefore, water temperature variations not only account for the diurnal change observed during a single day, but day-to-day changes in water temperature range explain about three-quarters of the variation in day-to-day changes in the amount of upstream CaCO_3 deposition. In addition, the amount of upstream diurnal CaCO_3 loss is positively related to maximum water temperature (Figure 12b). This is largely because the highest water temperature ranges tend to occur on days with the highest maxima at a given time (i.e. season) of the year (Figure 12c). The correlation in Figure 12b relates only to data from December and February, both summer months that experienced comparable mean maximum (31.2 versus 32.0°C) and minimum air temperatures (14.5 versus 18.2°C), and mean diurnal air temperature ranges (16.3 versus 13.7°C) for the year of observation (Australian Bureau of Meteorology data for Cowra, located 40 km west-south-west of Cliefden). For these two periods, greater upstream CaCO_3 losses occur as maximum daily water temperature increases. This is partly because diurnal water temperature ranges tend to increase as maximum water temperatures increase at a given time of the year (Figure 12c).

Figure 11. (a) Total CO₂ and PCO₂, and (b) total CO₂ and temperature through the December 2000 water sampling period

Given that stream-water temperature is a direct function of ambient temperatures, the amount of tufa deposited along the upstream reach at Davys Creek is therefore a function of daily weather patterns for a given set of seepage-water conditions. When diurnal ranges are low owing to cloud cover, the amount of tufa deposited between the seepage zone and the monitoring site decreases, whereas the opposite occurs during sunny days when the temperature range is greater. Furthermore, days with higher air temperatures coincide with larger diurnal water temperature ranges, with consequent higher diurnal CaCO₃ ranges. This should translate into lower rates of upstream deposition during winter months compared with summer months, although we cannot confirm this here because the daily SC variations for the July time-series are affected by significant changes in non-carbonate species. This is certainly an area for further study.

Implications for climate change

The above results have implications for interpreting tufa palaeoenvironments and on predicting the likely response of tufa-depositing streams to future climate change. Under warmer climate conditions, tufa deposition along a given stream will be focused along segments more proximal to the springs because the waters will evolve more rapidly. Conversely, during periods of increased cloudiness or decreased temperatures, downstream migration of deposition will prevail. However, such situations will only prevail if base-flow discharges and water composition do not change markedly (Drysdale, 2001; Drysdale *et al.*, 2002). Discharge increases will extend the reach of tufa deposition for waters of a given initial composition because the waters will require a much longer stream distance over which to evolve to a highly supersaturated state, whereas the opposite will occur under lower discharges (Drysdale *et al.*, 2002). Clearly, future work could be directed towards determining the relative importance of discharge and temperature. In terms of seepage-water composition, increased Ca²⁺ and HCO₃⁻ concentrations under a fixed temperature and discharge regime will

Figure 12. Diurnal changes in CaCO_3 versus (a) diurnal water temperature range and (b) maximum water temperature. (c) The relationship between maximum daily water temperatures and diurnal water temperature range for each of the observation periods

result in the upstream migration of the tufa reach because it will stimulate more rapid CaCO_3 deposition (Baker and Smart, 1995); the converse will be the case under conditions of diluted concentrations (Drysdale, 2001). A combination of lower effective rainfall (and therefore lower baseflow discharges) and higher temperatures have been postulated for southern Australia during interglacial intervals of the Quaternary (Ayliffe *et al.*,

1998). Under such conditions, increased ion concentrations are also likely. This combination of hydroclimatic conditions would almost certainly cause the reach of tufa deposition to migrate upstream.

CONCLUSIONS

In this study we have shown that the amount of tufa deposition that occurs along a given stream reach varies over the diurnal cycle according to insolation-driven shifts in water temperature, which controls the rate of downstream CO₂ efflux. The greatest daily changes in deposition for each observation period occurred when diurnal water temperature ranges were at their maximum, whereas the lowest values coincided with minimum temperature ranges. Furthermore, the highest water temperature ranges correlated with days of highest maximum temperatures, with the greatest ranges in summer. Therefore, diurnal variations in CaCO₃ should be greatest in summer, although this needs to be tested more rigorously in a future study. Given that water temperatures are an indirect function of air temperatures via solar radiation receipt, day-to-day variations in tufa deposition at Davys Creek under approximately constant discharge conditions are dependent upon the prevailing weather. The next step is to determine the nature and magnitude of diurnal trends under contrasting discharge/water composition conditions.

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