The 2002–2003 El Niño recorded in Australian cave drip waters: Implications for reconstructing rainfall histories using stalagmites

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[1] A 30-month study of drip hydrochemistry from Kooringa Cave, eastern Australia, revealed a clear geochemical response to the 2002–2003 El Niño. Through the drought, drip discharge fell to base flow, drip Ca^{2+} concentrations fell by half and drip Mg/Ca and Sr/Ca increased in a co-varying pattern. Calcite Mg/Ca and Sr/Ca predicted from drip waters displayed a marked increase through, and just beyond, the period of greatest moisture deficit. The results suggest that stalagmites from shallow caves in drought-sensitive eastern Australia potentially preserve a valuable record of El Niño-La Niña history. *INDEX TERMS:* 1620 Global Change: Climate dynamics (3309); 1806 Hydrology: Chemistry of fresh water; 1812 Hydrology: Drought; 1829 Hydrology: Groundwater hydrology; 1833 Hydrology: Hydroclimatology. **Citation:** McDonald, J., R. Drysdale, and D. Hill (2004), The 2002–2003 El Niño recorded in Australian cave drip waters: Implications for reconstructing rainfall histories using stalagmites, *Geophys. Res. Lett.*, *31*, L22202, doi:10.1029/2004GL020859.

1. Introduction

[2] Drought is a regular hazard in many parts of Australia where it is intimately related to negative phases of the El Niño-Southern Oscillation (ENSO). The 2002–2003 El Niño drought was one of the worst on record and affected most of the country [*Reid*, 2003]. The greatest rainfall anomalies occurred in winter 2002, when precipitation for 91% of the continent fell below the long-term (post-1900) median, with 46% of the continent scoring in the lowest decile [*Jones*, 2003].

[3] Recent studies have suggested that ENSO is influenced by longer-phase regional ocean-atmosphere circulation phenomena, such as the Inter-Decadal Pacific Oscillation [*Power et al.*, 1999; *Suppiah*, 2004] and the Indian Ocean Dipole [*Godfrey and Rintoul*, 1998]. This may explain why some El Niño-related droughts are more severe (e.g., 1982–1983) than others (e.g., 1997). Yet the reasons why drought severity in Australia is so geographically variable remain poorly understood. Improved forecasts require more data on long-term drought frequency and severity, and on the linkages between drought and regional ocean-atmosphere circulation. However, the brevity of the instrumental weather record, which rarely extends beyond the last ~150 years, hampers this goal. Natural archives provide a potential source of pre-instrumental data, allowing placement of the existing drought record into a longer-term hydroclimatic context.

[4] Speleothems, particularly stalagmites, have been widely used as high-resolution (sub-decadal) paleoclimate proxies [*Roberts et al.*, 1998; *Fairchild et al.*, 2001; *Proctor et al.*, 2002]. Trace-element research suggests that speleothem Mg/Ca and Sr/Ca variations can act as a paleo-recharge proxy [*Roberts et al.*, 1998; *Huang et al.*, 2001; *Treble et al.*, 2003] but the exact relationships between rainfall and speleothem response are complex because drip hydrochemistry during a single event can vary greatly within the same cave [*Baker et al.*, 2000]. *Tooth and Fairchild* [2003] suggested that interpretation of trace-element variations in fossil speleothems can benefit from hydrochemical measurements of active drips. Here we report the results of a 30-month study of drip water hydrochemistry variations through the 2002–2003 El Niño from eastern Australia. The results suggest that the trace-element geochemistry of stalagmites from shallow caves in drought-susceptible eastern Australia have considerable potential for the high-resolution reconstruction of regional drought history.

2. Study Area

[5] Kooringa Cave is part of the Wombeyan karst [*Brunker and Offenberg*, 1970], a ~4 km^2 area of Silurian marble that drains to the eastern seaboard north of Sydney (Figure 1). The region experiences warm to hot summers and cool winters, with mean January maximum and mean July minimum temperatures of 25.7 and 0.6°C respectively. Mean annual precipitation for 1942–2003 is 879 mm (coefficient of variation = 25.8%). Mean summer maximum exceeds the mean winter minimum by ~30%. The cave is a ~50 m-long, shallow, joint-controlled collapse chamber situated ~30 m above local base level. Two drip sites (K1 and K2) located 60 cm apart and overlain by ~14 m of bedrock were studied. The surface above these sites comprises bare rock and soil-filled grikes with patches of low shrubs, forbs and grasses.

3. Methods

[6] Drip discharge was measured using both automated and manual drip counting. Continuous counts were recorded using infra-red (IR) sensors connected to a data logger, whilst manual counts were made at monthly to bimonthly frequency. Condensation and power surges periodically caused sensor malfunctions and interrupted the automated measurements. However, the sensors functioned for most of the study period and generated reliable data whose accuracy

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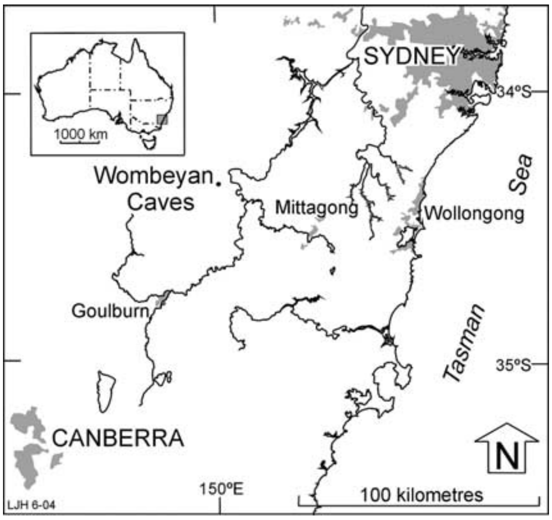

Figure 1. Study site location.

were verified by manual counts. Drip waters were collected in clean glass bottles then acidified with 1% concentrated HNO_3 prior to major cation analysis using an inductively coupled plasma – atomic emission spectrometer at the Australian Nuclear Science and Technology Organisation. Only Ca, Mg and Sr data will be discussed here.

[7] Cave temperature was recorded continuously using a temperature logger. Laboratory-derived coefficients (D) describing $[Mg/Ca]_{drip}$ to $[Mg/Ca]_{calcite}$ and $[Sr/Ca]_{drip}$ to $[Sr/Ca]_{calcite}$ partitioning have been determined in a number of studies [e.g., *Katz*, 1973; *Lorens*, 1981; *Mucci and Morse*, 1983; *Pingitore and Eastman*, 1986; *Huang and Fairchild*, 2001]. Partition coefficients derived from the low-ionic strength solution experiments of *Huang and Fairchild* [2001] were used in this study to calculate theoretical stalagmite $[Mg/Ca]_{calcite}$ and $[Sr/Ca]_{calcite}$, and calcite precipitation vectors [*Fairchild et al.*, 2000]. The predicted $[Mg/Ca]_{calcite}$ ratios were standardized to the mean cave temperature of 11°C. The local water balance was determined from daily rainfall readings taken 130 m from the cave and 'Class A' pan evaporation data from the nearby Australian Bureau of Meteorology station at Goulburn

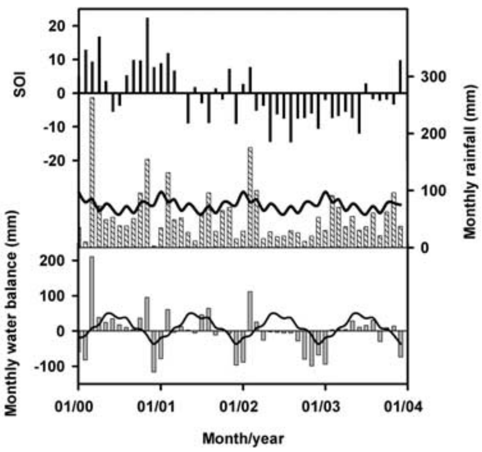

Figure 2. Site hydrology and the Southern Oscillation Index (SOI) (2000–2004). The heavy lines in the second and third panels represent long-term monthly means.

(Figure 1); surface runoff was assumed to be negligible, which is typical of many karst terrains [see *Genty and Deflandre*, 1998].

4. Results

[8] The study site experienced ten consecutive months of below-average monthly rainfall and water deficit (Figure 2) associated with strongly negative Southern Oscillation Indices (SOI). This highlights the site's sensitivity to the 2002–2003 El Niño, which was the most severe drought since 1982–83 and the second worst since 1890. The drips displayed similar discharge behaviour (Figure 3), with a steady decline through the moisture deficit period and increased flows through phases of positive water balance. However, their respective hydrographs differ in detail, with K1 showing a much lower peak-to-base ratio and a much longer recessional limb than K2. These basic differences reflect the unique fracture architecture supplying each drip [*Tooth and Fairchild*, 2003]. The persistence of drip flow through the major water deficit period suggests a significant matrix component to the total marble porosity.

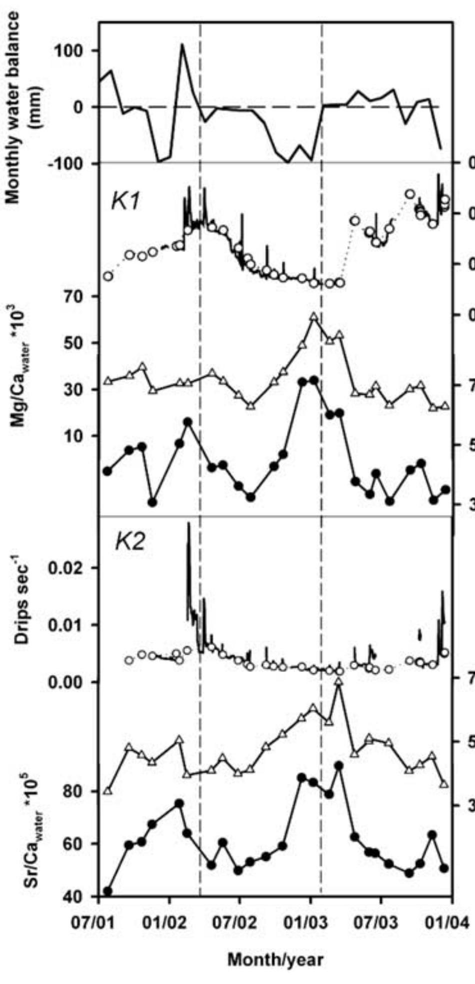

Figure 3. Site water balance (top), drip rate and trace element molar ratios for sites K1 (middle) and K2 (bottom). The period of continuous moisture deficit is bounded by the vertical dashed lines. Open circles are manual drip discharge counts.

Table 1. Summary Hydrochemistry Data for K1 and K2[a]

Parameter	K1	K2
Drips $sec^{-1} \times 10^2$ (man.)	1.3 ± 0.5, 39	0.3 ± 0.1, 35
Drips $sec^{-1} \times 10^2$ (auto.)	1.4 ± 0.5, 39	0.5 ± 0.4, 73
Ca (mmol l^{-1})	2.3 ± 0.6, 27	1.8 ± 0.3, 17
Mg ($\times 10^2$ mmol l^{-1})	7.1 ± 1.0, 13	7.7 ± 0.7, 9
Sr ($\times 10^3$ mmol l^{-1})	0.9 ± 0.2, 19	1.1 ± 0.1, 11
Mg/Ca $\times 10^3$	34.4 ± 10.1, 29	47.2 ± 7.9, 17
Sr/Ca $\times 10^5$	44.9 ± 11.7, 26	61.6 ± 12.5, 20
Mg/Ca vs Sr/Ca (n = 24)	$r = 0.90$, $p < 0.01$	$r = 0.83$, $p < 0.01$

[a]For drip rates, ion concentrations and molar ratios, the numbers represent the mean ± standard deviation and per cent coefficient of variation. Statistics for the automated drip rates are derived from periods when both sensors were functioning (n = 374 days).

[9] The major characteristics of the drip chemistry data are shown in Table 1, whilst $[Mg/Ca]_{drip}$ and $[Sr/Ca]_{drip}$ time-series are shown in Figure 3. Both drips display statistically significant elemental ratio co-variations (Table 1), a trend observed in previous studies [*Baker et al.*, 2000; *Tooth and Fairchild*, 2003]. These ratios show a systematic increase through the drought, with peak values occurring immediately before or just after the water balance shifts into the post-drought positive phase. A less pronounced increase in ratios occurs during a brief pre-drought period of water deficit (Figure 3). The predicted calcite values (Figure 4) show a clear pattern of highest ratios through the latter part of the extreme moisture deficit period of the 2002–2003 El Niño.

5. Discussion

[10] Previous studies have attributed sub-annual shifts in Mg/Ca and Sr/Ca of individual drip points to variations in water-soil and/or water-rock residence time, incongruent and/or differential dissolution of calcite and dolomite, or changes in trace element sources [*Fairchild et al.*, 2000; *Tooth and Fairchild*, 2003]. Incongruent and differential dissolution can be ignored because there is no dolomite in the catchment. An increase in the contribution of Mg^{2+} and Sr^{2+} from exotic sources at the height of the drought cannot explain the observed significant increases in trace element ratios because of the decoupling of recharge and discharge at the time. This leaves changes in residence time as the most likely explanation.

[11] Residence time for a given water-soil-rock system is directly related to recharge and moisture balance: the greater the recharge and more positive the water balance, the shorter the residence time. This has a major impact on drip-water chemistry. Longer residence times (∼dry periods) allow the CO_2-rich percolation waters to move closer to chemical equilibrium with soil carbonate and karst rock, leading to higher dissolved loads. As a period without recharge increases, overlying fractures become dewatered, which causes degassing of CO_2 into air pockets and increases calcite supersaturation. This triggers calcite precipitation along fracture surfaces, preferentially removing Ca^{2+} and leaving the solution enriched in trace elements [*Fairchild et al.*, 2000]. Enhancement of this process may occur because the slower percolation rate increases the time the drip hangs from its exit point, leading to greater CO_2 outgassing. The stalagmite calcite fed by this drip will precipitate from a solution enriched in Mg/Ca and Sr/Ca, leading to higher stalagmite Mg/Ca and Sr/Ca. This so-called 'prior calcite precipitation' effect has been linked directly to variations in site recharge in other studies [*Fairchild et al.*, 2000; *Tooth and Fairchild*, 2003]. We suggest that during the water deficit of the 2002–2003 El Niño, dewatering of fractures and decreased hydraulic heads in the soil and fracture network increased the mean travel time of the

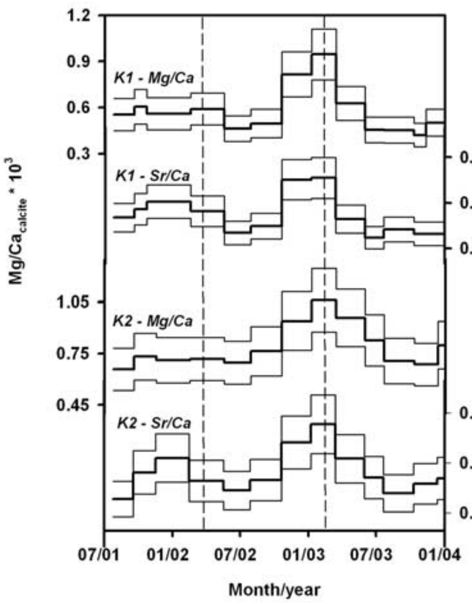

Figure 4. Predicted calcite trace element molar ratios for sites K1 and K2. See text for explanation. The heavy lines are predicted values based on median partitioning coefficients and bounding lines are predicted values based on maximum and minimum coefficients.

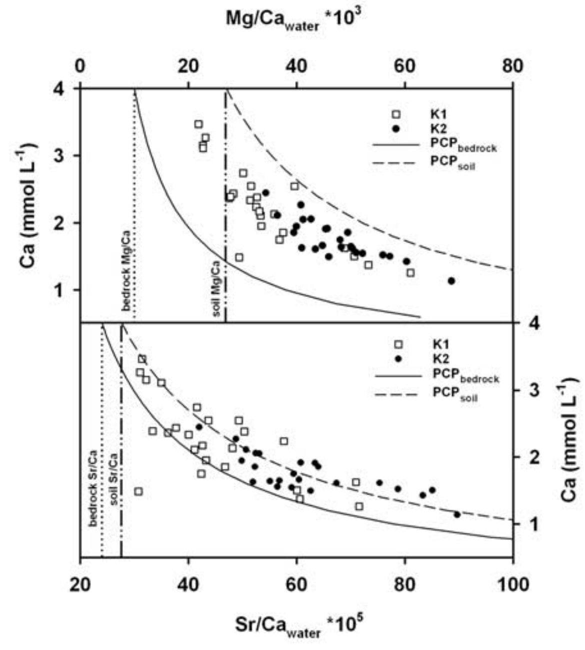

Figure 5. Drip water Ca^{2+} vs. Mg/Ca_{drip} (top) and Sr/Ca_{drip} (bottom), and Mg/Ca and Sr/Ca prior calcite precipitation vectors [*Fairchild et al.*, 2000] based on bedrock and soil end-member values (vertical lines) and median partitioning coefficients [*Huang and Fairchild*, 2001]. All ratios are molar. See text for further explanation.

percolation waters and led to prior calcite precipitation. Support for this interpretation is shown in Figure 5, where Ca^{2+}_{drip} clearly decreases as $[Mg/Ca]_{drip}$ and $[Sr/Ca]_{drip}$ increase. Also shown are vectors defining the evolution of hypothetical drip waters subjected to prior calcite precipitation [*Fairchild et al.*, 2000]. Each vector assumes an initial soil PCO_2 of 0.075 atm necessary to produce percolation waters with an equilibrium Ca^{2+} concentration of ~4 mmol L^{-1} [*Ford and Williams*, 1989], close to the maximum observed drip values. The vector starting points are based on measured bedrock and soil trace element ratios. The drip data clearly run parallel to the soil and bedrock vectors, confirming prior calcite precipitation as the principal mechanism driving the changes in trace element ratios [*Fairchild et al.*, 2000] and suggesting a relatively consistent input from both soil and bedrock sources.

[12] Sensitivity to recharge variations and the predicted $[Mg/Ca]_{calcite}$ and $[Sr/Ca]_{calcite}$ ratios highlight the potential for deriving moisture histories from stalagmites at this and similar shallow-chamber cave environments in drought-sensitive karsts of Australia. The amplitude of the ratio variations is sufficiently large and the length of typical El Niño events (6–12 months) sufficiently long to permit resolution of drought history using laser-based mass spectrometry. The detection of La Niña events should also be possible from the same stalagmites. High rates of recharge during La Niña periods will reduce residence times and refill fractures, reducing or eliminating prior calcite precipitation. Increased drip rates combined with lower dissolved loads would also reduce the amount of prior calcite precipitation on the feeder straws and stalactites. The net effect will be a displacement of $[Mg/Ca]_{drip}$ and $[Sr/Ca]_{drip}$ ratios towards bedrock end-member values. Stalagmite elemental ratios would fall below those recorded here, increasing the amplitude of $[Mg/Ca]_{calcite}$ and $[Sr/Ca]_{calcite}$ between dry and wet spells, thereby improving the capacity to resolve paleo-recharge history.

6. Conclusions

[13] Pre-instrumental data on drought in Australia are needed to improve predictive models and place the historic drought record into a longer-term context. In this study, we have shown how the hydrochemistry of two drip sites within a shallow cave in eastern Australia responded to the 2002–2003 El Niño. At both sites, the drip rate decreased systematically and markedly through the period of greatest moisture deficit and the $[Mg/Ca]_{drip}$ and $[Sr/Ca]_{drip}$ ratios increased significantly as this period persisted. A return to a weakly positive moisture balance resulted in increased drip discharge and lower elemental ratios. Predicted $[Mg/Ca]_{calcite}$ and $[Sr/Ca]_{calcite}$ ratios followed the same pattern. The results suggest that high-resolution trace-element studies of shallow-cave stalagmites in this and similar east Australian karsts, supported by precise radiometric dating [*Hellstrom*, 2003], offer a unique opportunity for exploring the history of drought frequency and magnitude, particularly if robust transfer functions can be derived using instrumental data. Australia appears to be a potentially useful region for such studies because it experiences profound water-balance extremes [*Treble et al.*, 2003], which can amplify trace element signatures in drip waters and, by inference, speleothems.

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