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In situ measurement of seasonal $\delta^{18}O$ variations and analysis of isotopic trends in a modern speleothem from southwest Australia

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Abstract

We present a record of seasonal and inter-annual oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) isotope ratios from an 81-year-old stalagmite from Moondyne Cave, southwest Australia. The growth history of stalagmite MND-S1 is known since it grew on a cave boardwalk that was installed in 1911 and removed in 1992. This stalagmite provides an excellent test of speleothem climate proxies because the regional climate is strongly seasonal (wet winter/dry summer) and has experienced a 200 mm (20%) reduction of mean rainfall since the mid-1960s, and a 0.8 °C temperature rise since ~1953. Seasonal variations in calcite $\delta^{18}O$ were measured in situ by high spatial resolution ion microprobe, whilst inter-annual variations of $\delta^{18}O$ and $\delta^{13}C$ were measured by conventional gas-source mass spectrometry.

Comparison of the speleothem stable isotopes and instrumental temperature records reveals that $\delta^{18}O$ variations are too large to be driven by temperature alone, and are in the opposite sense. However, daily rainfall $\delta^{18}O$ measurements show that the mean seasonal range in $\delta^{18}O$ of rainfall in southwest Australia is large (2‰) and inversely correlated with rainfall amount. A rainfall driver for the speleothem $\delta^{18}O$ is confirmed by the detection of seasonal shifts of 0.7–1.5‰ in speleothem $\delta^{18}O$ that track rainfall $\delta^{18}O$, smoothed by storage in the overlying limestone. The seasonal range in speleothem $\delta^{18}O$ is larger than any inter-annual and decadal variation observed in the record. The prominent annual cycles in speleothem $\delta^{18}O$ revealed by ion microprobe analysis indicate that subtle changes in the frequency of intense winter rainfall events, or possibly also moisture sources, could produce significant changes in mean speleothem $\delta^{18}O$. The ion microprobe results also raise the possibility that the masses of speleothem calcite deposited in winter and summer could vary as a function of the seasonal drip rate and carbonate saturation state of these waters. If this is the case, then small changes in the relative masses of calcite deposited in winter and summer could produce significant shifts in mean $\delta^{18}O$ and $\delta^{13}C$ that have a complex relation to climate. This finding should be generally applicable to the interpretation of long-term trends in speleothem geochemical records for shallow cave

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sites where seasonal variations in geochemical tracers are relatively large, including most of the sub-tropical monsoon belts and mid to high latitudes with distinct rainfall seasons.

Keywords: speleothem; oxygen isotopes; carbon isotopes; annual cycle; rainfall; ion microprobe

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1. Introduction

The stable isotopes of carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) in speleothem carbonates are widely regarded as climate proxies and are routinely measured [1–7], yet few modern records exist to test their veracity against the instrumental climate record. This step is critical for understanding climate proxies, particularly those reflecting cumulative signals of complex processes. Speleothem $\delta^{18}O$ records the combined signatures of rainfall $\delta^{18}O$ and cave temperature, provided the calcite is precipitated in oxygen isotopic equilibrium [1]. Methods for separating the two effects, such as the analysis of fluid inclusions that represent the original drip water [8], are complicated and not routinely performed. Thus, many speleothem records are interpreted as combined records of rainfall and temperature [4,5], while some are recognised as being clearly dominated by rainfall [6].

Speleothem $\delta^{13}C$ is also a composite signal, reflecting biogenic fractionation of the soil carbon pool [9], limestone dissolution under open- or closed-system conditions [10,11], prior carbonate precipitation from groundwater [12], and the rate of CO_2 degassing from drip waters over a speleothem surface [10,11]. The term open system or closed system refers to limestone dissolution conditions where groundwaters either remain in contact with soil CO_2 (open) or are isolated from soil CO_2 (closed) after acidification [11]. Biogenic CO_2 produced under C3 vegetation has an average $\delta^{13}C$ value of $-27‰$, but may vary by approximately $\pm 5‰$ depending on the environmental effects on photosynthesis [13,14]. Soil CO_2 is dominated by biogenic CO_2 but can be mixed with atmospheric CO_2 when soil respiration rates are low [15]. The contribution of carbon atoms from limestone dissolution is negligible under open-system conditions and small under closed-system conditions [11,16]. By contrast, degassing of CO_2 before drip water reaches the speleothem, and the subsequent conversion of HCO_3^- to $CO_{2(aq)}$, may substantially raise the $^{13}C/^{12}C$ of the precipitating solution. This may be driven by a reduction in the partial pressure of CO_2 in drip waters when they enter the cave [11,16], or because calcite has been lost from solution in aquifer pore spaces or over other formations (prior calcite precipitation) [12].

A critical factor in interpreting speleothem $\delta^{13}C$ and $\delta^{18}O$ records is determining whether disequilibrium isotopic fractionation caused by rapid CO_2 degassing or, rarely, by evaporation of the precipitating solution [11], overprints climatic signals. Isotopic disequilibrium is indicated by a simultaneous increase of $\delta^{13}C$ and $\delta^{18}O$ down a growth layer from the speleothem apex, and by correlation between $\delta^{13}C$ and $\delta^{18}O$ along a growth axis [11]. This is because $\delta^{13}C$ and $\delta^{18}O$ are affected simultaneously if the removal of $CO_{2(g)}$ outpaces the conversion of $CO_{2(aq)}$ to HCO_3^- [11]. However, these tests tend not to be definitive in practice because it is almost impossible to sample coeval calcite along a growth layer. Moreover, climatic factors conceivably can simultaneously affect axial profiles of both speleothem $\delta^{18}O$ and $\delta^{13}C$.

To improve our understanding of isotopes in speleothems, we examined seasonal variations of $\delta^{18}O$, and inter-annual variations of $\delta^{18}O$ and $\delta^{13}C$ in a modern speleothem of known growth history. Our test sample is a 33 mm tall, 59 mm wide stalagmite (MND-S1) that grew from 1911 to 1992 on a boardwalk in Moondyne Cave, southwest Western Australia (34°16′S, 115°05′E; Fig. 1). The calcite crystal fabric of MND-S1 is columnar palisade [17], with inclusions between crystallites preserved in the mid-section (open columnar palisade fabric; 1930–1970), and dense, compact inclusion-free (closed columnar palisade fabric) calcite above and below this (Fig. 2).

Stalagmite MND-S1 preserves clear trace element cycles (P, Mg, U, Sr, Ba, and Na) previously analysed by excimer laser ablation inductively coupled plasma mass spectrometry (ELA-ICPMS) [18]. These cycles were determined to be annual based on the agreement between the number of cycles in MND-S1 and the