



# Calcium isotopes in caves as a proxy for aridity: Modern calibration and application to the 8.2 kyr event



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## ABSTRACT

We present the first study of Ca isotope cycling in a natural cave system, with measurements of bedrock, dripwater and recently formed carbonate, coupled to a first stalagmite time-series spanning the 8.2 kyr event. Dripwaters at Heshang Cave (Central China; 30°27'N, 110°25'E) are isotopically heavy relative to the dolomite bedrock, the result of prior calcite precipitation (PCP) occurring earlier in the drip flow path. A simple Rayleigh fractionation model quantifies the extent of PCP in the modern environment at 36% Ca removal. The observed in situ calcium isotope fractionation factor between dripwater and carbonate is  $\Delta^{44/42}\text{Ca} = -0.63 \pm 0.03\text{‰}$  and does not vary during the annual cycle.

Measurements of speleothem carbonate spanning the 8.2 kyr event show the response of Ca isotopes to changing climate.  $\delta^{44/42}\text{Ca}$  increases by 0.35‰ at the onset of the event, coeval with changes in  $\delta^{18}\text{O}$  and Mg/Ca, and remains high for 80 yr. This change is explained by decreased rainfall leading to increased PCP; an interpretation supported by established PCP proxies (Mg/Ca, Sr/Ca and Ba/Ca). Ca isotopes indicate that PCP increased to 60% Ca removal during the event, which, from application of a simple box model, suggests mean annual rainfall decreased by approximately a third in Central China during the 8.2 kyr event. The response of Ca isotopes across this event demonstrates their potential for the assessment of past conditions, including past dripwater flow rates and rainfall.

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## 1. Introduction

Speleothem carbonates are continental palaeoclimate archives. Numerous speleothem-based climate proxies have been developed and applied including  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  analyses (e.g. Hendy, 1971; Wang et al., 2001), trace metal contents (e.g. Ayalon et al., 1999; Gascoyne, 1983), fluid inclusion chemistry (e.g. Schwarcz et al., 1976) and clumped isotope measurements (e.g. Affek et al., 2008). Of these, carbon and oxygen isotope analyses are the most widely used.  $\delta^{18}\text{O}$  records have shed light on past changes in precipitation patterns and atmospheric moisture transport (e.g. Bar-Matthews et al., 1999; Dykoski et al., 2005; Wang et al., 2001). These records are highly informative, but the controls on speleothem  $\delta^{18}\text{O}$  are complex and often non-local, complicating their interpretation (Dreybrodt and Scholz, 2011; Pausata et al., 2011).

To address these uncertainties, speleothem  $\delta^{18}\text{O}$  records are increasingly being complemented with minor and trace element data

(Hellstrom and McCulloch, 2000; Liu et al., 2013; Moreno et al., 2010). The concentrations of certain trace elements (for example Mg, Sr and Ba) in dripwaters and calcite precipitates have been shown to vary in a range of settings, on seasonal and inter-annual timescales, in response to rainfall change (Fairchild et al., 2001; Treble et al., 2005; Tremaine and Froelich, 2013). This is due to precipitation of secondary carbonate minerals in the overlying aquifer and/or on the cave roof, a process termed prior calcite precipitation (PCP) (Fairchild et al., 2000). Preferential removal of Ca into calcite during PCP enriches dripwaters in Mg, Ba and Sr relative to Ca. The extent of PCP is related to local effective rainfall; during periods of aridity, decreased pressure head leads to increased water residence times and may increase the proportion of air-filled porosity in the aquifer – both factors that encourage PCP (Cruz et al., 2007; Tooth and Fairchild, 2003). The chemical signature of PCP preserved in speleothems has the potential to reconstruct past aridity and disentangle local from regional controls on  $\delta^{18}\text{O}$  records. However, while highly informative, trace element based PCP reconstructions have so far been limited to qualitative interpretation about rainfall change.

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An additional geochemical proxy with potential to assess past PCP and local rainfall is the isotopic composition of calcium in speleothems. While speleothem carbon and oxygen isotope signals have been studied extensively, no systematic study has yet investigated isotope fractionation of Ca, the third major element of calcite, in the cave environment or speleothem archive. Speleothem Ca is primarily sourced from the host carbonate rock, dissolved by CO<sub>2</sub>-charged waters in the soil and upper epikarst. As waters percolate through the unsaturated zone, PCP may occur. Ca isotopes are fractionated during incorporation into calcite, with light isotopes preferentially incorporated into the solid phase (Gussone et al., 2005; Lemarchand et al., 2004; Marriotti et al., 2004; Reynard et al., 2011; Tang et al., 2008). Thus we expect PCP to isotopically enrich dripwater relative to its initial composition. Ca isotopes in speleothems may record this signal.

The 8.2 kyr event is the largest natural climate perturbation in the Holocene. First identified in Greenland ice cores (Dansgaard, 1987), the event is known globally (Dixit et al., 2014; Ljung et al., 2008; Pross et al., 2009; Spooner et al., 2002). In China the event is recorded as a period of increased aridity, interpreted as a weakening of the monsoon (Cheng et al., 2009; Hu et al., 2008b; Liu et al., 2013; Morrill et al., 2011). This perturbation to the hydrological cycle provides an excellent test case to assess the speleothem Ca isotope response to climate change.

## 2. Methods

### 2.1. Study site and sample selection

Our study site is Heshang Cave, Central China (30°27'N, 110°25'E; 294 m) (Hu et al., 2005, 2008a). It is an active cave system approximately 250 m long overlain by ~300 m of Cambrian dolomite and a well-vegetated soil horizon ~30 cm thick. Local rainfall is dominated by the East Asian Monsoon. Monitoring of the cave indicates that it is well ventilated and exhibits a large seasonal cave air temperature cycle (7.5 °C) about a mean value of 19 °C (Hu et al., 2008a).

Speleothem samples were taken from stalagmite HS4 – an extensively studied Holocene stalagmite previously described in the literature (Hu et al., 2008b, 2005; Johnson et al., 2006; Li et al., 2014; Liu et al., 2013). Liu et al. (2013) established a chronology for the 8.2 kyr event in stalagmite HS4 and characterised the event based on an ultra-high-resolution δ<sup>18</sup>O and Mg/Ca record. They identify the 8.2 kyr event as a period of enhanced PCP at the site, suggesting a decrease in rainfall. Based on this record we selected 44 micromilled speleothem samples spanning the 8.2 kyr event from the residual powders milled during the study of Liu et al. (2013). Each sample averages 4–5 yr of stalagmite growth.

In addition, nineteen dripwater samples (acidified immediately after sampling) and twenty farmed glass-plate calcite samples were taken from the HS4 drip-site at monthly intervals over the course of two years (2005–2007) to understand seasonal controls on dripwater and speleothem Ca isotopes (Hu et al., 2008a). A block of dolomite bedrock was powdered and subsampled to characterise the source of calcium.

### 2.2. Sample preparation

Carbonate samples (200–300 μg CaCO<sub>3</sub> each) were dissolved in 2% HNO<sub>3</sub>. Samples to be processed through column chemistry were dried and re-dissolved in 2N HCl. Dripwater and glass plate samples were processed through the two-step column procedure of Chu et al. (2006) to isolate their Ca content. Briefly, BioRad AG50W-X12 resin is used to separate Ca and Sr from other matrix elements, notably Mg. This is followed by Eichrom SrSpec resin to separate Ca from Sr. Subsequent testing (described in Section 2.3)

showed trace element contents were sufficiently low that only the first step of chemistry was necessary for the dolomite bedrock, and no processing was necessary for speleothem samples.

### 2.3. Calcium isotope analysis

Calcium isotope ratios were analysed using a Nu Instruments MC-ICPMS with Aridus desolvating nebuliser at the University of Oxford, largely following the method of Reynard et al. (2011). Samples were analysed for <sup>42</sup>Ca, <sup>43</sup>Ca and <sup>44</sup>Ca allowing calculation of δ<sup>44/42</sup>Ca and δ<sup>43/42</sup>Ca.

$$\delta^{44/42}\text{Ca} (\text{‰}) = \left( \frac{(^{44}\text{Ca}/^{42}\text{Ca})_{\text{sample}}}{(^{44}\text{Ca}/^{42}\text{Ca})_{\text{standard}}} - 1 \right) * 1000 \quad (1)$$

$$\delta^{43/42}\text{Ca} (\text{‰}) = \left( \frac{(^{43}\text{Ca}/^{42}\text{Ca})_{\text{sample}}}{(^{43}\text{Ca}/^{42}\text{Ca})_{\text{standard}}} - 1 \right) * 1000 \quad (2)$$

Samples were analysed relative to NIST SRM 915a using a sample-standard bracketing routine, concentration matched to 10 ± 1 ppm Ca. Each sample was analysed a minimum of 5 times. During ICP-MS analysis of carbonates the sample matrix is dominated by <sup>40</sup>Ca<sup>+</sup>. Concentration-matching samples and standards is therefore sufficient to limit variability in space-charge effects – the dominant source of instrumental mass bias during ICP-MS analysis (Boulyga, 2010). In addition we consider potential interferences on <sup>42</sup>Ca<sup>+</sup>, <sup>43</sup>Ca<sup>+</sup> and <sup>44</sup>Ca<sup>+</sup>. For clean speleothem samples potential isobaric interferences are limited to ArH<sub>2</sub><sup>+</sup>, MgO<sup>+</sup>, Sr<sup>2+</sup> and various organic polyatomic species. The effects of some potential interferences on Ca isotopes are shown in Fig. 1.

Strontium interferences were corrected for using the <sup>87</sup>Sr<sup>2+</sup> beam at mass 43.5 following Reynard et al. (2011). The correction was calibrated using a Sr ICP standard. Sr doping experiments showed this correction to be accurate up to Sr/Ca = 0.34 mmol/mol, the maximum ratio tested. Mg doping experiments showed no influence of Mg contamination on δ<sup>44/42</sup>Ca or δ<sup>43/42</sup>Ca up to Mg/Ca = 118 mmol/mol. Ca isotope triple plots (e.g. Fig. 1) were used to monitor for uncorrected isobaric interferences.

For speleothem and bedrock samples secondary standard NIST SRM 915b and an internal secondary standard (HPS Ca – a High Purity Standards Ca standard) were used to determine accuracy and external precision after Sr correction. Measured values for SRM 915b were δ<sup>44/42</sup>Ca = 0.35 ± 0.11‰ and δ<sup>43/42</sup>Ca = 0.19 ± 0.13‰ (2s, n = 40), and for HPS Ca were δ<sup>44/42</sup>Ca = 0.27 ± 0.07‰ and δ<sup>43/42</sup>Ca = 0.14 ± 0.11‰ (2s, n = 39). Dripwaters and glass plate calcite samples were analysed at a different time and HPS Ca was used to determine external precision giving δ<sup>44/42</sup>Ca = 0.34 ± 0.14‰ and δ<sup>43/42</sup>Ca = 0.23 ± 0.18‰ (2s, n = 184).

HPS Ca is a relatively clean calcium standard while NIST SRM 915b contains significant strontium (Sr/Ca = 0.24 mmol/mol). Our Sr-corrected SRM 915b value (δ<sup>44/42</sup>Ca = 0.35 ± 0.11‰) matches values obtained by TIMS, δ<sup>44/42</sup>Ca = 0.36 ± 0.02‰ (2se; Heuser and Eisenhauer, 2008), and by MC-ICPMS using a column-purified Ca solution, δ<sup>44/42</sup>Ca = 0.42 ± 0.02‰ (2se; Schiller et al., 2012). Neither of these alternative methods suffer from Sr<sup>2+</sup> interferences; the agreement between values demonstrates the accuracy of the Sr correction. Use of the Sr correction allows for Ca isotope analysis of sufficiently clean samples by MC-ICP-MS without column chemistry, greatly increasing sample throughput relative to alternative methods.

Fig. 1 shows data processed with and without the Sr correction on a triple-isotope plot. Without the Sr correction samples are off-set parallel to the Sr<sup>2+</sup> interference vector; corrected data fall close to the mass-dependent fractionation line. Without the correction, reproducibility on Sr-bearing samples is poor due to variation in the Sr<sup>2+</sup>/Sr ionisation ratio. Sr correction reduces the uncertainty

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