Adsorbed silica in stalagmite carbonate and its relationship to past rainfall

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Abstract—Despite considerable work on other trace elements, the incorporation of dissolved silicon from cave waters into speleothems has not been previously investigated. In this study, the controls on dissolved Si in cave waters and on adsorbed Si in resulting speleothems are therefore investigated. Bedrock (dolomite), soil water, dripping water, and cave carbonates were retrieved from Heshang Cave situated in the central Yangtze valley of China and were subjected to analysis of dissolved Si content (plus accompanying Ca and Fe analyses). Soil waters have Si/Ca of 45.5 mmol/mol, compared to only 3.2 mmol/mol in the dolomite bedrock, demonstrating that >80% of the dissolved Si must come from dissolution of silicate minerals in the soil. Drip waters have a dissolved Si concentration of $\approx 4.2 \mu\text{g/mL}$, similar to that in the overlying soil water. Actively growing cave carbonates have a Si/Ca of 0.075 mmol/mol suggesting a partition coefficient for incorporation of dissolved silicon of 0.0014, in good agreement with previous laboratory studies. Extrapolating the results of these laboratory studies to the cave environment suggests that changes in Si/Ca in cave carbonates are likely to be primarily controlled by changes in drip-water Si/Ca. The drip-water Si/Ca will, in turn, be controlled by the rate of wind-blown silicate supply; by soil weathering rates; by rainfall dilution; and by precipitation of calcite. The general expectation is that these effects combine to produce high Si/Ca in speleothems during times of low rainfall. A $\delta^{18}\text{O}$ record from a Heshang Cave stalagmite which grew between 20 and 11 thousand years ago allows these controls to be tested. Correlation of high Si/Ca with high $\delta^{18}\text{O}$ demonstrates that regional rainfall exerts significant (but not complete) control on speleothem Si/Ca. With further understanding, speleothem Si/Ca may provide a proxy for past rainfall to complement existing proxies such as $\delta^{18}\text{O}$ and Mg/Ca. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

The concentration of trace elements in cave carbonates is controlled by environmental conditions within the cave such as temperature, humidity, and drip-water chemistry. Trace elements in old carbonates may therefore be proxies for past conditions—a realization that has initiated considerable research into the precise controls on their incorporation. Mg and Sr have received the most attention (Roberts et al., 1998; Huang and Fairchild, 2001; Fairchild et al., 2000) but other elements such as Ba (Finch et al., 2001); P and Na (Fairchild et al., 2001); and U (Ayalon et al., 1999; Treble et al., 2003) have also been studied. Silicon has generally escaped attention. In some studies, total Si has been measured in an attempt to assess the detrital content of the carbonates (Fairchild et al., 2001; Y. Huang et al., 2001; Kuczumow et al., 2003), but no previous study has attempted to measure the concentration of Si incorporated into cave carbonates directly from dissolved Si in drip waters, nor the controls on this incorporation. The content of such adsorbed Si may, however, provide useful information about changes in the past weathering environment and past hydrology of the cave environment. This study presents the first measurements of dissolved Si in cave waters and resulting adsorbed Si in carbonates.

Dissolved silica in the form of monosilicic acid (H_4SiO_4) is found in most natural waters in the Earth's surface environ-

ment, and has traditionally been defined as the silica that reacts with ammonium molybdate within 2 min (Krauskopf, 1956). Previous work has demonstrated that such dissolved silica is incorporated by surface adsorption into calcium carbonate during growth (Bien et al., 1958; Kastner et al., 1977; Kitano et al., 1979). In a comprehensive study of the controls on that incorporation, Klein and Walter (1995) demonstrated that the dissolved Si content of carbonates was influenced by the Si content of the growth solution; the ionic strength of the solution; the surface area of the growing carbonate; and the Mg content of the carbonate. Other variables, such as temperature and the Mg content of the growth solution were found to be unimportant.

In the cave environment, the Si content of the drip water and the amount of prior precipitation of cave calcite are likely to be the primary controls on the adsorbed Si content of growing carbonates. Speleothem Si_d/Ca (where the subscript “d” is used to denote “dissolved” in waters, or “derived from dissolved” in carbonates) is therefore expected to provide a record of past Si concentrations in the cave drip waters. In turn, drip-water Si contents may be controlled by the relative rates of soil weathering versus solute dilution, by the delivery of labile Si to the overlying soil, or by precipitation of calcite.

To understand the incorporation of Si into speleothem carbonate, and to test the expectation that Si_d/Ca responds to changing weathering and rainfall rates, we have measured Si_d/Ca in waters and carbonates from a cave in central China. U/Th chronology of a speleothem from this location demonstrates that its growth encompassed the Younger Dryas (YD),

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Fig. 1. Upper panel: location of Heshang Cave and a schematic representation of the climate system in the region (modified from Johnson and Ingram, 2004). Lower panel shows the typical temperature and rainfall pattern for the area.

and periods equivalent to Heinrich Event 1 (H1) and the Last Glacial Maximum (LGM). Oxygen isotopes indicate changes in rainfall accompanying these climate events. Measurements across these climate changes allow the influence of rainfall on Si_d/Ca to be tested, and provide the first assessment of the

possible use of dissolved Si in speleothems as a proxy for past environmental change.

2. SAMPLE SITE AND PRELIMINARY DATA

This study was conducted on Heshang Cave in the Qingjiang valley of the middle reaches of Yangtze River in southern China at $30^{\circ}26'48.9''\text{N}$, $110^{\circ}25'11.8''\text{E}$, and ≈ 300 m above sea level (Fig. 1). The dominant climatic signal in this area is that of the East Asian Monsoon. This annual pattern is caused by warming of Asia during the Northern Hemisphere summer which causes low atmospheric pressure and moist air-flow from the South China Sea and Bengal Bay, generating high rainfall. The nature and history of this climate system has been extensively discussed and is well summarized in, for instance, An (2000) and Wang et al. (2003). The monsoon generates a strong seasonal rainfall and temperature cycle in the Qingjiang region (Fig. 1) with average annual temperature of 16°C and rainfall of 1460 mm/yr.

Heshang Cave is ≈ 250 m deep with a reasonably large opening and is overlain by ≈ 300 m of Cambrian dolomite. This is capped by a mature 40-cm-thick layer of soil derived from the dolomite but with addition of wind-blown silicate material and organic matter from the abundant vegetation in the area. Several speleothems were collected in 2000. In September 2003, bedrock and soil were sampled, as well as a single drip-water sample collected into a clean polypropylene bottle and directly returned to the laboratory. Between September 2003 and August 2004 a large collection vessel was left under the drip site. Once a week an aliquot was taken from this vessel before emptying it and replacing it under the drip. This collection technique provides a continuous record of drip-water chemistry but allows for the possibility of changes to this chemistry resulting from precipitation of calcite in the collection vessel. Indeed, visible flecks of precipitated calcite were generally observed in the vessel during aliquoting.

Stalagmite HS-2 was selected as the major focus for this study because it grew during a period of changing climate. HS-2 is 61.7 cm long with a basal diameter of 24 cm. It is a calcite speleothem with some porosity and some visible growth banding (Fig. 2). No clear evidence for growth hiatuses is seen, but some changes in coloration are seen, and darker bands may represent periods of slow growth or even cessation of growth. HS-2 was cut along its growth axes, and 10 U/Th samples were

Fig. 2. Stalagmite HS-2, with sampling transect for the $\delta^{18}\text{O}$ and Si_d/Ca data indicated by the dashed line. Numbers are U/Th ages shown in orange. The location of the two points with unusually high Si_d/Ca are also shown for information.

Fig. 3. Growth curve of the HS-2 stalagmite. Points represent U/Th ages with 2σ errors. GR = Growth rate; I1 = Interval 1, 20.1–19.1 ka BP; I2 = Interval 2, 19.1–14.4 ka BP; I3 = Interval 3, 14.4–14.2 ka BP; I4 = Interval 4, 14.2–10.8 ka BP. Gray shading denotes climate periods (after Bard et al., 2000): YD = Younger Dryas; A/B = Allerod/Bolling; H1 = Heinrich 1; LGM = last glacial maximum.

taken from the cut surface. U/Th ages were measured at the University of Minnesota (USA) and have been reported previously in a study of stalagmite lipid concentration (Xie et al., 2003). These U/Th data indicate that the stalagmite grew from 20.1 to 10.8 ka BP (Fig. 3). This period represents the transition from the last glacial to the Holocene and includes major climate events initially recognized in the North Atlantic region such as the YD and H1 (Bard et al., 2000). Despite the limitations of the dating resolution, stalagmite growth can be divided into four intervals with fast growth rate of ≈ 30 cm/ka from 20 to 19 ka and at around 14.3 ka, and slower growth rates of 2 to 4 cm/ka from 19.1–14.4 ka and 14.2–10.8 ka.

Stable isotope analyses were performed on 191 powder samples taken along the growth axis and interspersed between the U/Th age points (Fig. 2). Subsample thicknesses were ≈ 1 mm which corresponds to between 3 and 30 yr depending on the growth rate. Subsamples were measured on a Finnegan MAT 251 mass spectrometer using the 100% H_3PO_4 method (McCrea, 1950) and have been reported previously in Chinese (J. Huang et al., 2001). Both oxygen and carbon isotopes demonstrate significant variability within HS-2 (Fig. 4), as expected for the significant climate reorganizations occurring during this interval.

$\delta^{18}\text{O}$ values in HS-2 range from -4‰ to -9‰ with broad peaks from 17 to 15 ka and 14 to 12 ka, and a sharper peak at ≈ 18.5 ka. In this region, some distance south of the maximum extent of the summer monsoon, oxygen isotopes in rainfall are controlled, on at least a seasonal timescale, by the “amount effect” (Rozanski et al., 1993; Johnson and Ingram, 2004). On longer timescales, secondary control may be exerted by changes in the source water or annual temperature but these effects are likely to be small compared to

Fig. 4. Comparison of Si_d/Ca with Fe/Ca , $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$ in the HS-2 stalagmite. Gray shading denotes major climate events for reference (with chronology from Bard et al., 2000). Two extremely high Si_d/Ca values are omitted from the graph and their positions are marked by their values. The apparent spikiness of the early record may reflect higher resolution in that period due to more rapid sample growth. Note the general tendency for high Si/Ca ratios to be found at times of high $\delta^{18}\text{O}$ values.

the $\approx 5\text{‰}$ amplitude of change observed (Fig. 4). The lack of a clear source effect, for instance, is seen by the similarity of $\delta^{18}\text{O}$ at ≈ 20 ka with that at ≈ 10 ka. These ages represent glacial and Holocene conditions respectively, which should represent the maximum possible change in $\delta^{18}\text{O}$ composition of the source waters in the South China Sea. Temperature changes of 20°C , much larger than expected for this region, would be required to generate the observed 5‰ changes.

Observed carbon isotope variations are large (up to 8‰) and are likely to be related to changes in vegetation above the cave. Interpretation of speleothem $\delta^{13}\text{C}$ records is complex, and further use of this data will not be made in this

Table 1. Si_d , Ca, and Mg content in the carbonate, soil solution, and dripping-water. Samples are described in Section 2 of the text.

Samples	Si_d ($\mu\text{g/mL}$)	Ca ($\mu\text{g/mL}$)	Si/Ca (mmol/mol)
Stalagmite HS-2 ($n = 205$)	56.8		0.20
	429.1		1.53
	17.0		0.06
Actively-forming stalagmite carbonate	21.1		0.075
Bedrock (dolomite)	481.6		3.16
Soil solution	3.6	112.9	45.5
Directly sampled drip water	4.1	103.7	55.9
Aliquots of weekly drip-water samples ($n = 17$)	4.1 (average)	46.1 (average)	127.1 (average)
	4.4 (max)	55.7 (max)	143.2 (max)
	3.6 (min)	40.3 (min)	102.1 (min)

study, although it is shown in Figure 4 for the sake of completeness.

3. ANALYTICAL METHODS

Minimal preparation of samples was required before measurement of dissolved silicon concentration. Calcite speleothem subsamples and dolomite host rocks were measured directly as powders, and drip waters were kept unfiltered. Soil water was extracted from the soil sample in the laboratory immediately after field sampling by squeezing and subsequent centrifuging to removal any particulate material.

Dissolved silica was determined by the molybdenum blue method (Truesdale and Smith, 1976) with an improved technique to eliminate the interference of phosphate as follows. Measurements were performed at room temperature (25°C) with shaking of the solution after addition of each reagent. A mass of sample (≈ 10.0 mg carbonate powder aliquoted from samples previously measured for stable isotopes, or 0.5 mL of water) was carefully weighed into a 10-mL volumetric flask, and 3.0 mL 0.25N HCl was slowly added. After (carbonate) samples were completely dissolved, 0.4 mL 5% ammonium molybdate solution was added. Ten minutes later, 0.2 mL 40% citric acid solution was added to decompose molybdophosphoric acid and remove the phosphate interference. Immediately, 1.0 mL of a reducing solution (0.3% ascorbic acid in 5 mol/L H_2SO_4) was added. After waiting for 40 min, the colored solution was transferred into a 1-cm quartz cell, and absorbance was measured at a wavelength of 720 nm against a blank solution by means of a Hitachi 220A double light beam spectrophotometer. Dissolved silica data were obtained using external standard calibration. The detection limit of the method is 2.3 $\mu\text{g SiO}_2/\text{g}$ carbonate, and relative standard deviation is 4% ($n = 11$) on an 87 $\mu\text{g SiO}_2/\text{g}$ sample. This method was applied to 205 subsamples of speleothem HS-2 ranging in age from 20.1 to 10.8 ka BP as well as to 17 drip-water samples, one soil water, one host bedrock sample, and one actively growing speleothem sample.

An experiment was also performed to investigate the possibility that this measurement technique leaches Si from detritus within the samples. A sample of HS-2 from the very base of the stalagmite was taken which contains clearly visible detritus, presumably incorporated from the cave floor at initiation of growth. 0.5 g of this sample was heated with clean Na_2CO_3 powder at 950°C to break down the detrital silicate, and the resulting mixture was dissolved in water with addition of 2N HCl. This solution was analyzed for Si_d using the Mo-blue method above. Additional aliquots of the sample were then taken and leached with 0.25N HCl, as was the case for all speleothem subsamples, but for times ranging from 5 to 40 min. These samples were then analyzed using the full Mo-blue method to assess the possibility that progressive leaching of silicate material occurs during initial dissolution of the samples.

Additional measurements were made by inductively coupled plasma mass spectrometry and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Ca was measured on drip waters to allow normalization of Si data; Fe in HS-2 to investigate the presence of detritus in the speleothem subsamples; and Si in drip waters for comparison with the Mo-blue technique.

4. RESULTS

Samples measured by the Mo-blue technique are referred to as Si_d (where the subscript refers to “dissolved” silicon on the assumption that this technique does not analyze detrital Si). Samples measured by ICP-AES are referred to as Si_t on the assumption that all Si will be ionized in the plasma (a reasonable assumption given the fine grain size of any detritus that might be present).

Si_d/Ca in the actively growing portion of a stalagmite is 0.075 mmol/mol, whereas in the 205 subsamples from HS-2 it ranges from 0.06 to 1.53 mmol/mol with a mean of 0.20 mmol/mol (Table 1, Fig. 4). Although some single-point minima/maxima are observed in the record (e.g., that at 17.1 ka), data generally define a pattern with, for instance, a consistently low value of Si_d/Ca from 19.6 to 18.6 ka, and a broad peak from 16.4 to 14.8 ka. The latter peak is the most pronounced, but a second broad peak is observed at 18.7–18.1 ka. Somewhat less well-developed peaks also occur at 14.0–13.6 ka and 12.5–12.0 ka. The largest peak of Si_d/Ca falls in the latter half of the peak in $\delta^{18}\text{O}$ related to H1, whereas the second broad peak corresponds to the $\delta^{18}\text{O}$ peak of the LGM.

For comparison, Si/Ca measured in the subsample from the base of HS-2 which underwent Na_2CO_3 heat treatment was 14 mmol/mol, more than 10 times higher than the highest measured Si_d/Ca value in HS-2. Si_d/Ca measurements in this basal subsample conducted with the normal Mo-blue technique but with variable leaching times ranged from 0.62 to 0.74 mmol/mol and demonstrated a slight increase with leaching period (0.62–5 min; 0.64–10 min; 0.69–20 min; 0.68–30 min; 0.74–40 min). These values are therefore significantly lower than the total Si/Ca in this sample, and are similar to other Si_d/Ca measurements from HS-2.

Fe/Ca measurements for HS-2 range from 0.005 to 7.652 mmol/mol with an average of 0.742 mmol/mol. In general, they are low (<2) after 16 kyr with the higher values restricted to the preceding glacial period. No correlation is observed between Fe/Ca and Si/Ca in HS-2.

Si_d in the soil water, the directly collected drip water, and the aliquots of weekly drip-water samples is reasonably similar and ranges from 3.6 to 4.4 $\mu\text{g/mL}$. Ca concentrations, on the other hand, show a marked decrease from 112.9 $\mu\text{g/mL}$ in the soil water, to 103.1 $\mu\text{g/mL}$ in the dripping water, to a range of 40.3–55.7 $\mu\text{g/mL}$ in the weekly drip-

Fig. 5. Si_d and Si_t in aliquots of weekly drip waters. In each case, water was collected in a large vessel for about a week before an aliquot was removed for analysis and the vessel emptied. This collection technique allows precipitation of calcite within the vessel so that Ca concentrations change during the week. Hence the Si data here are not shown normalized to Ca. Si_d was analyzed by the Mo-blue method; Si_t was analyzed by ICP-AES.

water aliquots. The range of Si_t measured in these weekly drip-water aliquots is very similar (Fig. 5) suggesting that little detrital material is present in the waters.

5. DISCUSSION

5.1. Sources of Si in Heshang Cave Drip Water and Speleothems

Before interpretation of speleothem Si_d/Ca data, it is necessary to understand the source of the Si measured by the Mo-blue technique. In particular, an assessment of the potential for leaching of any detrital material present during the laboratory technique is required. The leaching experiment on the dirty basal calcite was performed specifically to test this possibility. In that experiment, Si_d/Ca is only 5% of Si_t/Ca , clearly indicating that most of the detrital material is not leached during the Mo-blue analysis. The Si_d/Ca value is also not unusually high compared to values from the rest of HS-2, despite the fact that this basal portion was visually much dirtier than the rest of the stalagmite. This suggests that Si_d/Ca values are not strongly influenced by the presence of detritus. The lack of any pronounced increase in Si_d/Ca with duration of leaching also suggests that detrital leaching is not responsible for increasing Si_d/Ca values.

The similarity in average drip-water Si/Ca measured by Mo-blue and by ICP-AES indicates that very little detrital material is present in the drip waters found at Heshang Cave. This might be expected for a cave system with a reasonably lengthy recharge, particularly if flow is not occurring in channels. The lack of any seasonal cycle in measured Si/Ca values does suggest that flow is by slow seepage rather than within channels. Slow seepage flow is expected to act as a “filter” to prevent transit of detritus downward into the cave. In this setting, transport of Si into the cave is likely to be dominated by dissolved Si.

Fe/Ca ratios in HS-2 also indicate that very little detrital

material is present. The concentrations of Fe and Ca in average continental crust are similar to one another (i.e., $\text{FeO} = 4.5\%$, $\text{CaO} = 4.2\%$, Taylor and McLennan, 1985), so, even on the assumption that none of the Fe is in dissolved form, measured Fe/Ca , which averages 0.74 mmol/mol, suggests that only $\approx 0.1\%$ of the mass of HS-2 is detrital silicate. In reality, a portion of the Fe is likely to be derived from dissolution of the dolomite bedrock so this represents an upper bound on the detrital contents. Further evidence that Si_d/Ca measurements are not controlled by dissolution of detrital material is provided by the lack of correlation between Fe/Ca and Si_d/Ca ($r = 0.10$). Glacial portions of the record, for instance, have the highest Fe/Ca , but low Si_d/Ca .

In summary, several lines of evidence suggest that the Mo-blue technique used to assess Si_d in this study does not significantly attack detrital Si and is therefore assessing the Si in water samples that is truly dissolved, or in the carbonate samples that was transported and incorporated in dissolved form. Drip-water Si/Ca and speleothem Fe/Ca also indicate that the total flux of detritus into Heshang Cave is low.

If the situation in Heshang Cave is mirrored in other cave settings then caution should be exercised when interpreting speleothem Si concentrations simply in terms of detrital content. It is clear that significant amounts of dissolved Si can be transported to and incorporated in cave carbonates as they form.

5.2. Uptake of Dissolved Silica into Stalagmite Calcium Carbonate

Si_d/Ca in the actively growing stalagmite is significantly lower than that in the drip water from which it is forming. This difference indicates a partition coefficient for dissolved Si incorporation, D_{Si} , of ≈ 0.0014 (where $D_{\text{Si}} = [\text{Si}_d/\text{Ca}]_{\text{calcite}} / [\text{Si}_d/\text{Ca}]_{\text{solution}}$). This value of D_{Si} falls within the range of those assessed in the laboratory during near-equilibrium silica uptake experiments in diverse conditions (Klein and Walter, 1995, their Table 2) and is close to the average laboratory value in that study of 0.0017. This suggests that the growth of the speleothem is close to equilibrium, as expected given its slow growth rate. There are rather few measurements of dissolved Si in other natural carbonates, but a Si_d/Ca of 0.4 mmol/mol has been reported from Bahamas carbonate precipitated from seawater (Klein and Walter, 1995). This equates to a D_{Si} of ≈ 0.0003 , ~ 4 times lower than that observed here.

Several laboratory studies have indicated that the amount of irreversible adsorption of Si into calcium carbonate is proportional to aqueous Si concentration (Lovering and Patten, 1962; Kitano et al., 1979; Klein and Walter, 1995). Other environmental variables might contribute to variability in carbonate Si content but are likely to be less significant in the cave setting. Temperature change, for instance, has been shown to exert no significant control (Klein and Walter, 1995). Similarly, a slight dependence of Si/Ca on calcite growth rate that has been observed at very rapid growth rates (i.e., a doubling of calcite mass in less than 1 h, Klein and Walter, 1995) is unlikely to be a factor during the slow equilibrium growth of speleothems. Complete cessation of growth may, however, cause an increase of Si/Ca . This cannot be ruled out with the limited resolution of the chronology and may explain the unusually high Si/Ca

values observed at two points in the record. Ionic strength and composition of the growth solution also play a role in determining carbonate Si_d/Ca , as suggested by the lower value of D_{Si} observed for natural carbonate formed at the high-ionic strength of seawater. In the cave setting, however, changes in solution chemistry are likely to be reasonably small: ionic strength is largely set by the solubility of carbonate, and the concentrations of ions such as Na^+ , Cl^- , and SO_4^{2-} are generally very low compared to seawater. Klein and Walter (1995) also demonstrated the importance of carbonate surface area on Si_d/Ca ratios, but such surface area will remain broadly constant during the growth of a single speleothem so will not cause temporal variability in the resulting Si_d/Ca . These arguments suggest that changes in the Si_d/Ca of the drip waters will be the major control on speleothem Si_d/Ca .

5.3. Controls on Drip-water Si_d/Ca

Si_d in karst waters is derived predominately from the breakdown of wind-blown silicate minerals found in the overlying soil (Iler, 1979), whereas Ca is derived from the carbonate minerals in the soil and bedrock. This expectation is confirmed for the Heshang Cave by measured Si_d/Ca in the drip waters (56 mmol/mol) which are significantly higher than those in the dolomite (3 mmol/mol). These high soil-water Si_d/Ca values can only be explained by a significant (>80%) contribution to dissolved Si from breakdown of silicate minerals.

Variation in drip-water Si_d/Ca can be envisaged due to four processes. First, the supply of silicate material to the soil might change with time as a result of changing aridity or wind systems. Second, the breakdown rate of this silicate might change. Third, the dilution of dissolved Si may change due to differing rainfall. Finally, Si_d/Ca might be increased by precipitation of calcite within the bedrock or the cave (i.e., prior precipitation; Fairchild et al., 2000). We will consider the role of each of these in turn.

Aridity varies in most regions at a variety of timescales and could influence the supply of silicate material to the soil. In regions with a well-established soil profile which have not been perturbed by processes such as glaciation, the soil acts to average short-term fluctuations by storing silicate material. This does not preclude, however, the possibility that a particularly labile fraction of wind-blown silicate dissolves quickly and influences the drip-water Si_d/Ca .

The rate of silicate breakdown, or weathering, is influenced by several factors. Temperature is often considered the primary control (Berner, 1992) because silicate dissolution is energy limited, requiring an average of 15 kcal/mol activation energy (Lasaga, 1984). Increased temperature is therefore generally expected to increase the Si_d/Ca of drip waters. Soil pH can also significantly influence weathering rates, particularly in acidic soils (White, 1995). In karst soils, however, in which many caves are found (including Heshang), pH is buffered by calcite in a reasonably narrow range of pH (≈ 8) so that changes in pH are unlikely. Changes in vegetation can also influence weathering, both due to physical erosion of rock, and by release of organic acids. In general, vegetation responds to the primary forcing of climate and therefore acts as an amplifier of weathering changes caused by changes in temperature and rainfall.

Higher rainfall may also serve to increase weathering rate

but will cause a larger effect on Si_d/Ca by diluting the Si_d . When soil waters are recharged by rainfall, the Ca content of these waters rapidly approaches saturation, whereas the Si content responds more slowly so that higher rainfall is expected to lead to lower Si_d/Ca .

Upon percolating downwards from the soil environment, water Si_d/Ca may be modified by interaction with the bedrock, and particularly by the process of prior precipitation. Si_d may exchange with surfaces within the bedrock to decrease Si_d/Ca in the water. In a mature karst system, however, surfaces will have achieved equilibrium with the water, so that this process is unlikely to have a large impact. Dissolution of additional carbonate, perhaps driven by organic-matter respiration, might also serve to decrease water Si_d/Ca ratios but is not likely to be a major factor. The most significant process to alter drip-water Si_d/Ca is therefore precipitation of carbonate within the karst system or on the roof of the cave. This prior precipitation will lead to an increase in water Si_d/Ca because of the relative exclusion of Si from the carbonate mineral (i.e., $D_{\text{Si}} \ll 1$). The impact of this prior precipitation is seen in the slight increase in water Si_d/Ca as it flows from the soil to the cave, and by the marked increase seen in the weekly drip-water samples. These samples were left for sufficient time before subsampling that significant CO_2 degassing occurred, causing calcite precipitation and a decrease in Ca concentration of the waters without any marked change to the Si concentration. This process of prior precipitation may become more significant in dry periods when flow rates are slower and there is more time for CO_2 degassing within the recharge zone or on the cave roof.

In summary, dry climatic conditions are expected to cause an increase in drip-water Si_d/Ca as a result of three direct effects: higher supply of wind-blown silicates; less dilution of dissolved Si; and more prior precipitation. A counter-effect may be caused if the drying causes a marked change in vegetation to reduce the weathering rate of silicates, but this effect is unlikely to overwhelm the three direct effects. Climate cooling is also expected to cause a decrease in Si_d/Ca because of its influence on weathering rates. Because cool conditions often accompany dry conditions, this may also serve to dampen the Si_d/Ca signal. In general, however, Si_d/Ca is expected to respond primarily to changes in rainfall at the cave site. Speleothem HS-2 from Heshang Cave provides a test of this expectation.

5.4. Interpreting Variations in Stalagmite Si_d/Ca Ratios

Observed changes in $\delta^{18}\text{O}$ of HS-2 provide information about past rainfall in the Heshang Cave region and allow testing of the relationship between Si_d/Ca and rainfall. From the isotope record, it appears that periods corresponding to the LGM (≈ 18 ka), H1 (17–15 ka), and the early YD (≈ 14 –12) were all relatively dry. This is in agreement with modeling work (Jiang et al., 2003) which suggests rainfall lower by $\approx 30\%$ at the LGM in this region of China. These three periods represent cold phases of the global climate system so the $\delta^{18}\text{O}$ data confirm the general expectation that dryer conditions occur when it is cold.

The relationship between Si_d/Ca and $\delta^{18}\text{O}$ in HS-2 is not completely straightforward but, in general, high values of Si_d/Ca tend to occur during periods of high $\delta^{18}\text{O}$ (Fig. 4). This relationship is confirmed by a plot of Si_d/Ca against $\delta^{18}\text{O}$

Fig. 6. Si_d/Ca versus $\delta^{18}\text{O}$ demonstrating the slight positive relationship between these proxies and suggesting the role of rainfall in controlling Si_d/Ca .

which shows a positive slope ($r = 0.36$; Fig. 6) confirming the general expectation that low rainfall will increase Si_d/Ca in cave carbonates.

The imperfect fit between the two variables can be explained by the fact that neither is controlled by local rainfall alone. $\delta^{18}\text{O}$, for instance, is controlled by cumulative rainfall along the monsoon path rather than local rainfall at Heshang. Furthermore, there are a number of possible controls on Si_d/Ca , as discussed above. In the specific case of Heshang, secondary control might be exerted by weathering caused by temperature or vegetation variation, or by a decoupling of silicate dust supply from Northern China with the local aridity in the Heshang area.

For Heshang Cave (and by implication other caves), the dominant control on Si_d/Ca does appear to be the amount of local rainfall so that measurements of Si_d/Ca may provide information about past rainfall. Further analysis will be required to fully understand the controls on Si_d/Ca and its relationship with rainfall but, armed with such understanding, Si_d/Ca might then provide a complementary proxy to other rainfall proxies in speleothems such as $\delta^{18}\text{O}$ and Mg/Ca (Huang and Fairchild, 2001).

6. CONCLUSIONS

1. The first measurements of dissolved Si in cave drip waters and of adsorbed Si in speleothem carbonate demonstrate a D_{Si} of 0.0014, similar to that observed in previous studies of laboratory-grown calcite.
2. These results indicate that significant transport and incorporation of Si into cave carbonates can occur in the dissolved form and that caution should therefore be exercised in interpreting total Si concentrations in terms of detrital content.
3. Si_d/Ca in speleothems is expected to be controlled dominantly by changes in the Si_d/Ca of the drip waters from which the carbonate is formed.

4. In general, Si_d/Ca in drip waters are controlled by supply of wind-blown silicates; weathering rate; rainfall dilution; and precipitation of calcite. The combined effect is expected to be that dry climatic conditions lead to high Si_d/Ca .
5. A comparison of Si_d/Ca and $\delta^{18}\text{O}$ from a speleothem spanning deglacial climate events confirms the expectation that rainfall exerts significant (but clearly not complete) control on speleothem Si_d/Ca and suggests that Si_d/Ca might therefore provide information about past rainfall.

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