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Climatic and Anthropogenic Impacts on $\delta^{13}C$ Variations in a Stalagmite from Central China

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ABSTRACT

In this paper, we present a $\delta^{13}C$ record that covers the past 750 years at a resolution of 2 - 3 years which was preserved in a precisely dated stalagmite (DY-1) obtained from the Dayu Cave on the south flank of the Qinling Mountains in central China. Between 1249 AD and 1800 AD, climate-induced vegetation changes appear to have been the primary control on $\delta^{13}C$ values at a centennial scale. Variations in precipitation amounts control the residence time of seepage water and may have affected the dissolution of bedrock, prior carbonate precipitation in the unsaturated zone above the cave, and the degassing of CO_2 within the cave. These hydrogeochemical processes are likely to have been the most important controls on $\delta^{13}C$ levels over annual to decadal scales, and may also have influenced centennial-scale variations. The reduced $\delta^{13}C$ value of atmospheric CO_2 since the Industrial Revolution may have caused the decreasing trend in $\delta^{13}C$ values seen in stalagmite DY-1 after 1800 AD. Increased visitor numbers in the unventilated Dayu Cave over time produced a large amount of CO_2, and maintained a raised level of pCO_2 in the cave air. This artificially enhanced pCO_2 may have decreased the fraction of CO_2 degassing, and hence carbonate precipitation, which could partly cause the decreasing trend in the stalagmite $\delta^{13}C$ seen over the past 200 years.

Key words: Stalagmite, Carbon isotopes, Climate, Anthropogenic impact

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1. INTRODUCTION

Speleothems represent reliable natural archives of changing continental paleoclimatic and paleoenvironmental conditions because of their precisely associated ^{230}Th dates and high-resolution proxy records (e.g., Dorale et al. 1998; Lauritzen and Lundberg 1999; McDermott et al. 2001; Wang et al. 2001; Baldini et al. 2002; Fleitmann et al. 2003; Cruz et al. 2005; Cai et al. 2006; Cheng et al. 2009). Carbonate rocks are common in China, and the monsoon climate favors the development of caves and speleothems. Over the past decade, speleothem research in China has greatly improved our understanding of the history and variability of the Asian monsoon (e.g., Wang et al. 2001, 2005, 2008; Tan et al. 2003, 2009, 2011; Yuan et al. 2004; Dykoski et al. 2005; Cai et al. 2006, 2010a, b, 2012; Zhou et al. 2008; Cheng et al. 2009, 2012). For example, stalagmite oxygen isotopic records from China have revealed the patterns of variations in the Asian monsoon over the last 500 ka years (Yuan et al. 2004; Wang et al. 2008; Cheng et al. 2009, 2012). The results showed a dominant 23 ka cycle suggesting that the East Asian monsoon responded predominantly and directly to changes in the Northern Hemisphere summer insolation on orbital timescales. (Wang et al. 2008; Cheng et al. 2009, 2012). On a millennial scale, the oxygen isotope records of Chinese stalagmites correspond well with the Greenland ice core records (e.g., Wang et al. 2001, 2008; Cai et al. 2012). In addition to the clear link to the climate of the high northern latitudes, stalagmite $\delta^{18}O$ records from southwest China suggest that some millennial-scale Indian monsoon events during the last glacial period were linked to the climate of the high southern latitudes (Cai et al. 2006). Holocene stalagmite records indicate that solar activity played an

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important role in Asian monsoon variability over decadal to centennial timescales (Wang et al. 2005; Tan et al. 2009; Cai et al. 2010a, 2012).

In contrast to the wide use of stalagmite oxygen isotopes, fewer studies have considered stalagmite carbon isotopes from China (Li et al. 1997; Kong et al. 2005; Cosford et al. 2009). This is primarily due to the multiple sources of carbon involved, such as soil CO_2, atmospheric CO_2, and dissolved carbonate bedrock, as well as complicating factors such as vegetation type and density, soil biological activity, and hydro-geochemical processes including the seepage water in the vadose zone, cave ventilation, and the degassing of CO_2 from seepage water, prior carbonate precipitation in the vadose zone (Bar-Matthews et al. 1996; Baker et al. 1997; Dorale et al. 1998; McDermott 2004; Cosford et al. 2009; Luo and Wang 2009; Frisia et al. 2011; Li et al. 2011; Tremaine et al. 2011). Here, we present the carbon isotope record from a precisely dated stalagmite (DY-1) collected from the Dayu Cave on the south flank of the Qinling Mountains in central China, and discuss the climatic and anthropogenic impacts on speleothem $\delta^{13}C$ values.

2. CAVE SITE AND LOCAL CLIMATE

Dayu Cave (33°08’N, 106°18’E; 870 m above sea level at the entrance) is located on the south flank of the Qinling Mountains, 40 km north of Ningqiang County, Shaanxi Province, central China (Fig. 1). The cave is 2 km long, with many branched passages and small chambers, and is formed in Upper Proterozoic dolomite. The cave has a high humidity (ca. 100%), and contains a variety of modern and fossil speleothems. The CO_2 concentration in the center of the cave was around 1600 ppm during our last visit on 22 September 2009, while the temperature in the center of the cave was 13.0°C, consistent with the local annual mean temperature (12.9°C).

At present, the climate in the region of the Dayu Cave is strongly affected by the East Asian monsoon (Liu et al. 2003); mean annual precipitation in this area is 1100 mm. Water balance modeling (Thornthwaite 1948; McCabe and Markstrom 2007) indicates that most of the water surplus in this area occurs between July and October (Tan et al. 2013). Consequently, recharge of the aquifer above Dayu Cave occurs mainly as a result of the summer monsoon precipitation. Vegetation above the cave is primarily comprised of Chinese pine, oak, and shrubs.

3. SAMPLE AND METHODS

Stalagmite DY-1 (Fig. 2) was 10.9 cm long, between 4.5 and 6.0 cm in diameter, and was collected from the central area of Dayu Cave in 2005, before being halved and polished. To evaluate the primary mineralogy and check for post-depositional alteration, six contiguous subsamples were taken along the entire length of the stalagmite and analyzed using X-ray diffraction (XRD).

A further nine subsamples, including two replicates, were drilled along the growth axis of the stalagmite for ^{230}Th

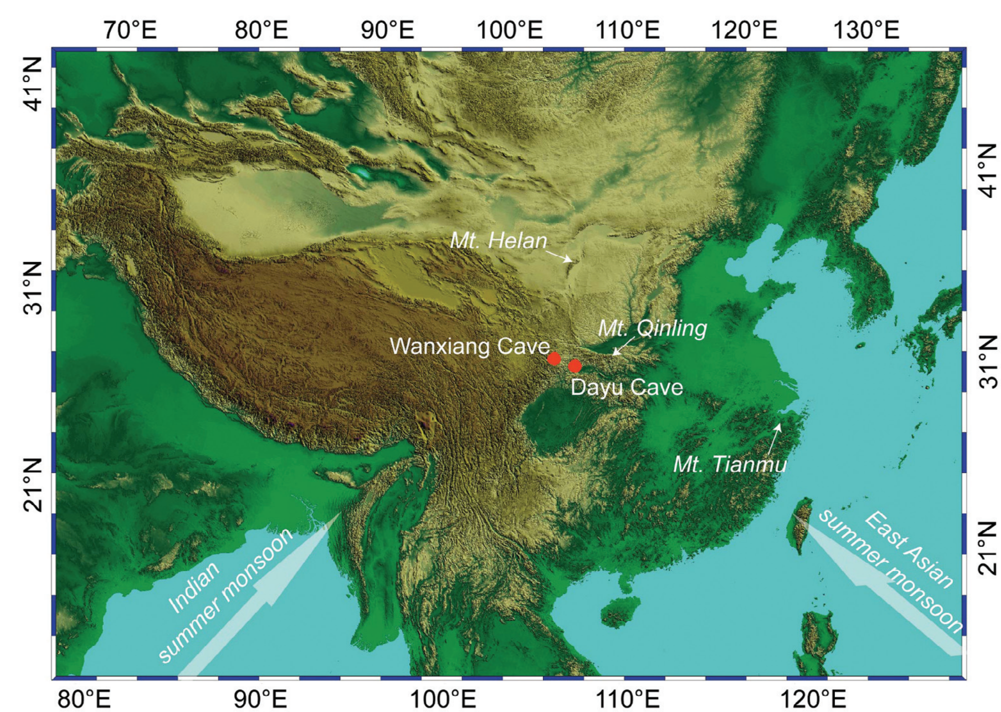

Fig. 1. Location map showing Dayu Cave and other sites referred to in the text.

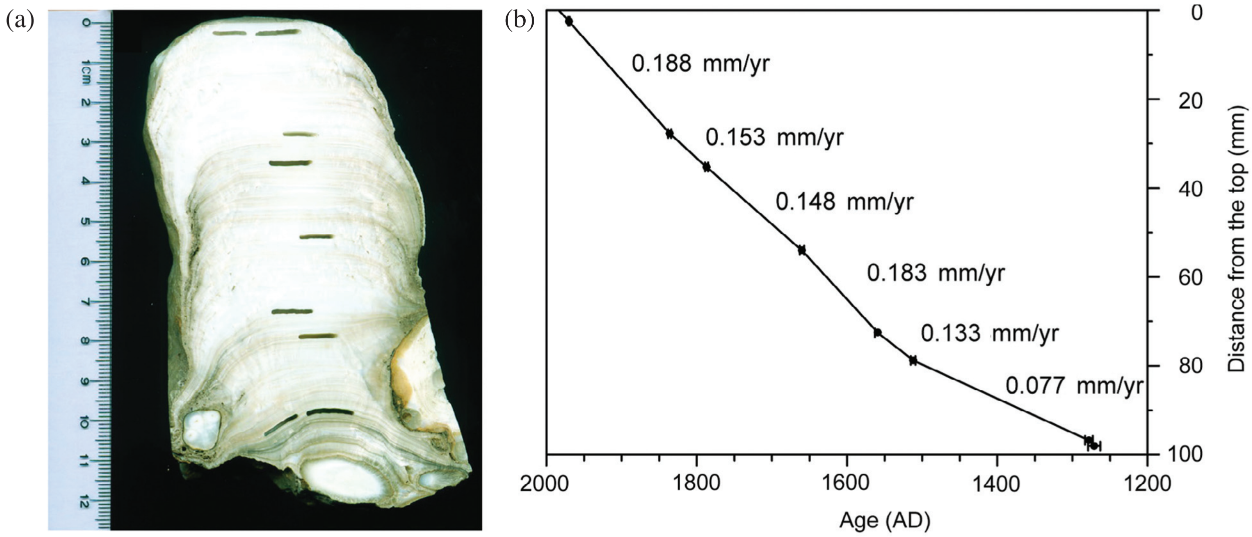

Fig. 2. (a) Section and (b) growth rate of stalagmite DY-1 from Dayu Cave. The locations of the nine dated subsamples, including two replicates, are shown in (a).

dating, and about 300 subsamples were processed for stable isotope analysis to give a temporal resolution of 2 - 3 years (see Tan et al. 2009 for details). Subsamples from two horizons at a depth of 1.9 cm and 4.1 cm were selected for the Hendy test (Hendy 1971), which evaluates the state of isotopic equilibrium during carbonate precipitation. Repeated measurements of one internal laboratory standard (TTB1) showed that the long-term reproducibility of the $\delta^{13}C$ analysis was better than ±0.1‰ (2σ).

4. RESULTS

4.1 Chronology

The majority of the ^{230}Th dating errors were of the order of 1 - 3 years (Table 1), although when the drilling thickness (ca. 1 mm) is taken into account, the average age errors increase to around 3 - 8 years. The growth model of DY-1 was developed using a linear interpolation method (Fig. 2). The model shows that DY-1 grew at a rate of 0.077 - 0.188 mm yr^{-1} between 1249 AD and 1983 AD (Tan et al. 2009).

4.2 Mineralogy

The XRD traces from DY-1 (Fig. 3) change little along the length of the stalagmite, indicating that the mineralogical composition remained homogeneous throughout the growth period; DY-1 is composed of aragonite, with negligible calcite.

4.3 The $\delta^{13}C$ Record

Figure 4 shows that the $\delta^{13}C$ values of DY-1 range from -1.1 to -3.6‰, with an average of -2.52‰. There is a gradual decrease in $\delta^{13}C$ from 1249 to 1380 AD followed by an increase to higher levels which are maintained between 1415 and 1490 AD. After 1490 AD, the $\delta^{13}C$ values decrease again and exceed the average value at around 1520 AD. Between 1520 and 1700 AD, the $\delta^{13}C$ record exhibits lower values except for two positive excursions at around 1590 and 1630 AD. The $\delta^{13}C$ record is dynamically variable during the 18^{th} century. Within this period, there are five prominent, high-amplitude excursions that last for about 20 years each. Two prominent negative excursions are evident around 1735 and 1775 AD, and there are three positive excursions around 1715, 1755, and 1795 AD. Since the 19^{th} century, the $\delta^{13}C$ record shows a progressively decreasing trend, with some decadal-scale fluctuations.

5. DISCUSSION

5.1 Controls on Speleothem $\delta^{13}C$

Speleothem $\delta^{13}C$ values have bedrock, atmospheric, and soil gas sources (McDermott 2004), and different vegetation types above caves produce distinctive ranges in the $\delta^{13}C$ of speleothems (Baker et al. 1997; Dorale et al. 1998; Denniston et al. 2000): typically -14 to -6‰ for speleothems associated with C3 plants, and -6 to +2‰ for those associated with C4 plants (McDermott 2004). Dense (sparse) vegetation cover promotes (reduces) the production of soil biogenic CO_2, which is relatively depleted in ^{13}C, resulting in lower (higher) $\delta^{13}C$ values in speleothems (Hellstrom et al. 1998; McDermott 2004; Baldini et al. 2005; Genty et al. 2006; Cosford et al. 2009; Springer et al. 2010; Li et al. 2012). The concentration and $\delta^{13}C$ value of atmospheric CO_2 have changed over geologic time (Francey et al. 1999; Kawamura et al. 2007; Lüthi et al. 2008) especially over the past 200 years. These changes are recorded in the $\delta^{13}C$ of the dissolved inorganic carbon (DIC) in the seepage water due to exchange between soil CO_2 and atmospheric CO_2, as well as the photosynthesis and respiration of plants above the cave; consequently, they may ultimately be recorded in the $\delta^{13}C$ of speleothems (Baskaran and Krishnamurthy 1993; Li et al. 1997). In addition, the extent of dissolution of the host rock will affect the $\delta^{13}C$ of the speleothem because the $\delta^{13}C$ value of host limestone/dolomite is much higher than the soil gas $\delta^{13}C$ value (Genty et al. 2001; McDermott 2004;

Table 1. ^{230}Th dating results of stalagmite DY-1 from the Dayu Cave. The errors are 2σ errors. Decay constant values are: $\lambda_{230} = 9.1577 \times 10^{-6}$ yr^{-1}, $\lambda_{234} = 2.8263 \times 10^{-6}$ yr^{-1} (Cheng et al. 2000) and $\lambda_{238} = 1.55125 \times 10^{-10}$ yr^{-1} (Jaffey et al. 1971). Corrected ^{230}Th ages assume the initial $^{230}Th/^{232}Th$ atomic ratio of $4.4 \pm 2.2 \times 10^{-6}$. Depths along the growth axis are relative to the top (youngest surface) of the stalagmite. Year BP: year before present (1950 AD).

Depth (mm)	^{238}U (ppb)	^{232}Th (ppt)	$^{230}Th/^{232}Th$ (ppm)	$\delta^{234}U$ (measured)	$^{230}Th/^{238}U$ (activity)	^{230}Th Age (yr) (uncorrected)	^{230}Th Age (yr BP) (corrected)	^{230}Th Age (yr AD) (corrected)	$\delta^{234}U_{Initial}$ (corrected)
98	20378 ± 195	1364 ± 11	4228 ± 36	1551 ± 9	0.01714 ± 0.00017	735 ± 8	679 ± 8	1271 ± 8	1554 ± 9
96.75	15556 ± 23	1537 ± 21	2841 ± 42	1555 ± 3	0.01700 ± 0.00012	729 ± 5	672 ± 5	1278 ± 5	1558 ± 3
78.75	21893 ± 46	927 ± 16	4527 ± 81	1570 ± 4	0.01161 ± 0.00008	494 ± 3	438 ± 3	1512 ± 3	1572 ± 4
72.5	12398 ± 86	384 ± 11	5523 ± 158	1536 ± 6	0.01036 ± 0.00009	447 ± 4	391 ± 4	1559 ± 4	1538 ± 6
54	17096 ± 35	612 ± 18	3716 ± 113	1546 ± 4	0.00806 ± 0.00007	346 ± 3	290 ± 3	1660 ± 3	1547 ± 4
35.25	17660 ± 128	585 ± 10	2528 ± 46	1526 ± 7	0.00507 ± 0.00005	219 ± 2	163 ± 2	1787 ± 2	1526 ± 7
27.75	21618 ± 39	400 ± 21	3504 ± 186	1526 ± 3	0.00393 ± 0.00005	170 ± 2	114 ± 2	1836 ± 2	1527 ± 3
2.5	13190 ± 85	309 ± 10	592 ± 24	1538 ± 6	0.00084 ± 0.00002	36 ± 1	-20 ± 1	1970 ± 1	1538 ± 6
2.5	12429 ± 20	3247 ± 24	59 ± 4	1547 ± 3	0.00093 ± 0.00006	40 ± 2	-19 ± 3	1969 ± 3	1548 ± 3

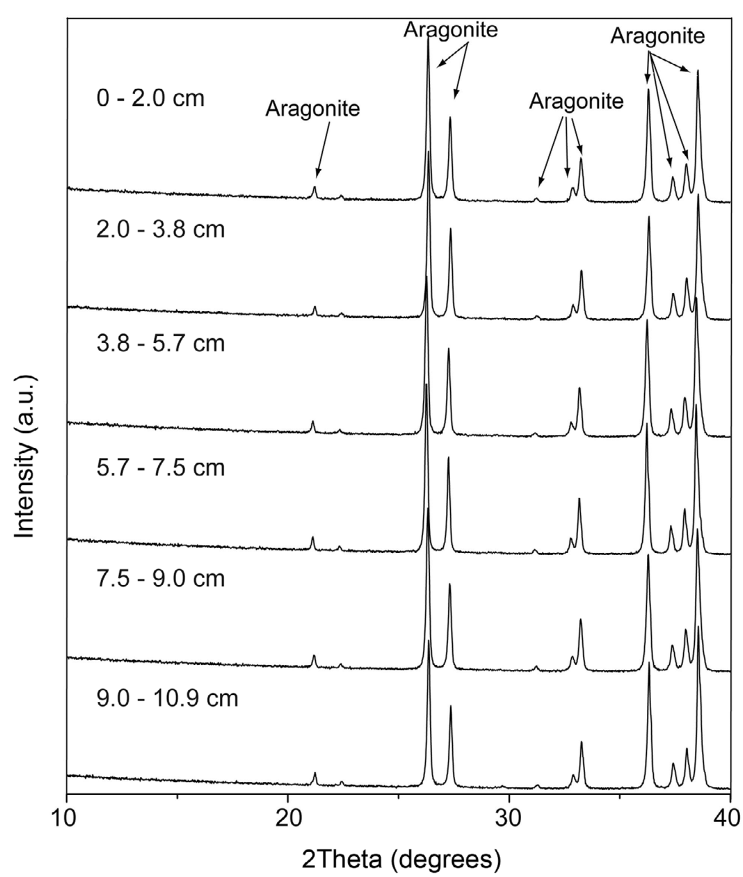

Fig. 3. Results of XRD analysis for DY-1.

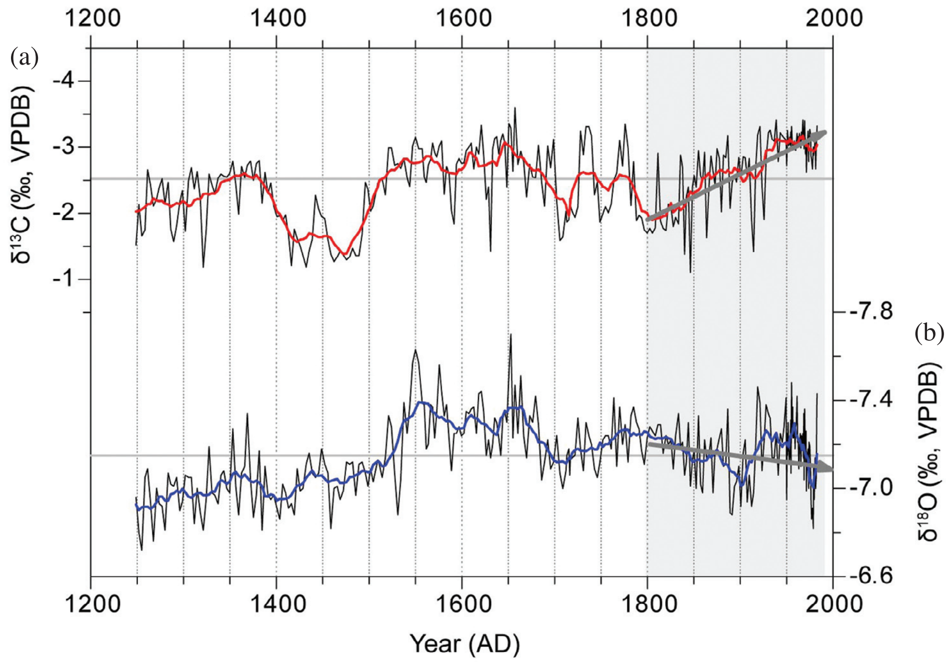

Fig. 4. (a) $\delta^{13}C$ and (b) $\delta^{18}O$ records obtained from stalagmite DY-1. The red and blue lines are the 10-point running means. The light horizontal gray lines indicate the average $\delta^{18}O$ (-7.15‰) and $\delta^{13}C$ (-2.52‰) values for the whole series. The grey arrows indicate the different trends in the $\delta^{13}C$ and $\delta^{18}O$ variations over the past 200 years, respectively. .

Rudzka et al. 2011). On millennium to orbital scales, this effect may be masked by the effect of vegetation changes (Dorale et al. 1998), but it may have an important influence on speleothem $\delta^{13}C$ on annual to decadal scales.

Other processes, such as the evaporation and rapid degassing of cave drip waters within the cave (Hendy 1971; Spötl et al. 2005; Mattey et al. 2008; Mühlinghaus et al. 2009), and prior carbonate precipitation in the unsaturated zone, may also produce heavy carbon isotope signatures (Baker et al. 1997; McDermott 2004). Recent cave monitoring work indicates that cave ventilation may force degassing of CO_2 from the dripwater resulting in ^{13}C enrichment of the speleothem (e.g., Spötl et al. 2005; Frisia et al. 2011; Li et al. 2011; Tremaine et al. 2011).

5.2 Climatic and Anthropogenic Impacts on $\delta^{13}C$ Variations in DY-1

5.2.1 1249 - 1800 AD

Samples that formed under conditions of high humidity and the gradual degassing of CO_2 are commonly found in oxygen and carbon isotopic equilibrium (Hendy 1971). Although there are limitations to the Hendy test (Dorale and Liu 2009), $\delta^{13}C$ and $\delta^{18}O$ remained constant along the growth layers of DY-1 (Fig. 5) indicating that the stalagmite was deposited under equilibrium conditions of isotopic fractionation (Hendy and Wilson 1968). Furthermore, the $\delta^{13}C$ and $\delta^{18}O$ records of DY-1 correlate well with another calcite stalagmite isotopic record from Shizi Cave, 120 km southeast of Dayu Cave (Houyun Zhou, personal communication), which offers further support for this conclusion (Hendy and Wilson 1968; Dorale et al. 1998; Dorale and Liu 2009). Previous studies found that the $\delta^{18}O$ variations in DY-1 were closely correlated to local instrumental rainfall indicating that the $\delta^{18}O$ data can be used as a proxy for rainfall with lower $\delta^{18}O$ values representing greater amounts of precipitation, and vice versa (Tan et al. 2009). Figure 4 shows that the pattern of variation in the speleothem $\delta^{13}C$ record is very similar to the centennial-scale variations in $\delta^{18}O$ before the 19th century. This suggests that climate-induced vegetation changes may have been the primary long-term control on $\delta^{13}C$ in DY-1 during this period. From the latter half of the 13th century to the 15th century, a dry and/or warm climate reduced the vegetation density and decreased the C3/C4 plant ratio (Cerling 1984; Cerling et al. 1989), causing relatively high $\delta^{13}C$ values in DY-1. From the 16th century to the 17th century, the climate turned wet and/or cold. The resultant increase in vegetation density and the C3/C4 plant ratio led to a relative reduction in $\delta^{13}C$ values during this period. The climate fluctuated around an average condition during the 18th century.

On annual to decadal timescales, there is a significant positive correlation ($r = 0.57$, $P < 0.01$, $N = 187$) between the $\delta^{13}C$ and the $\delta^{18}O$ records of DY-1. As kinetic fractionation was negligible during the deposition of the stalagmite, climatic factors dominated the co-variation of the $\delta^{13}C$ and

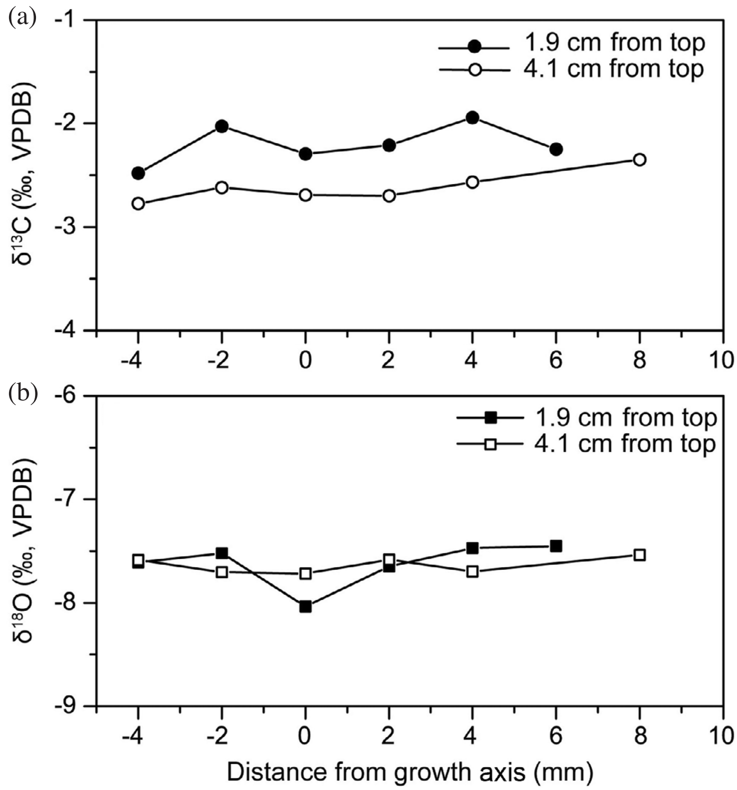

Fig. 5. Results of the Hendy test on the (a) $\delta^{13}C$ and (b) $\delta^{18}O$ records from two horizons of the stalagmite DY-1.

$\delta^{18}O$ records. As discussed above, the $\delta^{18}O$ of DY-1 may reflect local precipitation variations with lower $\delta^{18}O$ values representing higher precipitation, and vice versa (Tan et al. 2009). In arid regions, where the soil is usually thin and the vegetation above the cave is sparse, rapid throughput of meteoric water during deluge events may allow little interaction between seepage water and soil CO_2, resulting in high $\delta^{13}C$ values in stalagmites (Bar-Matthews et al. 2003). However, the situation is quite different in an area such as the Qinling Mountains, where the thick soil and dense vegetation above the cave lead to significant interaction between seepage water and soil CO_2. The decreased residence time of the seepage water during wetter conditions may cause less bedrock to be dissolved resulting in the low $\delta^{13}C$ values of DY-1. In addition, a wet climate favors vegetation growth and biological productivity which may also contribute to the relatively low $\delta^{13}C$ values in DY-1 on a decadal scale. In contrast, the increased residence time of the seepage water during drier condition may allow more bedrock to be dissolved resulting in the heavy $\delta^{13}C$ values in DY-1 (Li et al. 1997; McDermott 2004; Rudzka et al. 2011). Lower levels of precipitation may also reduce vegetation cover, and favor prior carbonate precipitation in the unsaturated zone above the cave, and enhanced degassing of CO_2 within the cave (Bar-Matthews et al. 1996; Baker et al. 1997), also resulting in higher $\delta^{13}C$ values. These hydrogeochemical effects over annual to decadal scales, may also contribute to speleothem $\delta^{13}C$ variations on centennial scale in the same manner.

5.2.2 1800 AD to the Present-Day

Variations in $\delta^{13}C$ correspond well with those of $\delta^{18}O$ in stalagmite DY-1 over both decadal and centennial scales before the 19th century ($r = 0.57$, $P < 0.01$, $N = 187$) because of their common climatic control; however, this close relationship was disturbed over the past 200 years. Since 1800 AD, $\delta^{13}C$ values show a sustained decreasing trend on centennial scale. In contrast, $\delta^{18}O$ values show a slightly increasing trend which indicates decreasing monsoon precipitation (Fig. 4), despite synchronous decadal variations between the $\delta^{18}O$ and the $\delta^{13}C$ values ($r = 0.35$, $P < 0.01$, $N = 119$). These discrepancies suggest factors other than climate may have controlled the long-term trend in $\delta^{13}C$ variations over the past 200 years.

Since the Industrial Revolution, human-induced emissions, particularly from the burning of fossil fuels with relatively low $\delta^{13}C$ values, have been discharged to the atmosphere (Longinelli et al. 2005). These emissions have caused the $\delta^{13}C$ value of atmospheric CO_2 to decrease by about 2.3‰ since 1750 AD (IPCC 2001). The declining trend in the $\delta^{13}C$ record of DY-1 over the past 200 years may reflect the decreasing $\delta^{13}C$ value of atmospheric CO_2

beginning with the Industrial Revolution. The similar declining trend was also recorded in a stalagmite from Wanxiang Cave (33°19'N, 105°00'E; An 2007) and a tree-ring series taken from the Helan Mountains in Northwest China (Liu et al. 2004) and the Tianmu Mountains in southeast China (Zhao et al. 2005) (Fig. 6). The fall in the δ^{13}C levels of atmospheric CO_2 after 1950 is the most prominent aspect of the record over the past 200 years (Francey et al. 1999); however, our stalagmite δ^{13}C record from DY-1 did not show this trend. This may be due to the decreasing amounts of precipitation over the past 50 years. As shown in Fig. 4, δ^{18}O has increased dramatically over the past 50 years, and this indicates decreased monsoon precipitation. On decadal to annual timescales, the decrease in precipitation may reduce vegetation cover, and increase bedrock dissolution, resulting in increased δ^{13}C values. These influences may have counteracted the decrease in atmospheric δ^{13}C, resulting in the slightly increasing trend in the DY-1 δ^{13}C record. Furthermore, the rapid growth of the Chinese population over the past 300 years has led to a large expansion in land use and caused severe degradation of vegetation and soils in most of the very fragile karst environments such as the Yunan-Guizhou plateau (Wei et al. 2006). This damage to vegetation and soils can cause a remarkable increase in speleothem δ^{13}C values (Liu 2008) masking the impact of the decrease in the δ^{13}C value of atmospheric CO_2.

Another possible factor may be human activities within the cave. Dayu Cave was discovered early, and large numbers of people have visited the cave. At least 72 visits are recorded in the inscriptions inside the cave (Fig. 7), most of which occurred during the Ming (1368 - 1644 AD) and Qing (1644 - 1911 AD) Dynasties. Further inscriptions refer to the 19th century, indicating more frequent human activities in the cave. Early visitors used burning torches to light the cave, and produced large amounts of CO_2, which would have raised the pCO_2 of the cave air. Observed temperature and CO_2 data suggest that Dayu Cave is a relatively closed system, and air exchange between the cave and the free atmosphere is slow. Increasing visitor numbers to the cave over the past 200 years may have maintained the raised cave air pCO_2, thus decreasing the fraction of CO_2 degassing and carbonate precipitation (Spötl et al. 2005; Johnson et al. 2006; Mattey et al. 2008; Cosford et al. 2009), and may be partly responsible for the decreasing trend in the stalagmite δ^{13}C values.

6. CONCLUSIONS

Stalagmite DY-1 from the Dayu Cave on the south flank of the Qinling Mountains in central China provides a valuable record of the climatic and anthropogenic impacts on stalagmite δ^{13}C variations over the past 750 years. From

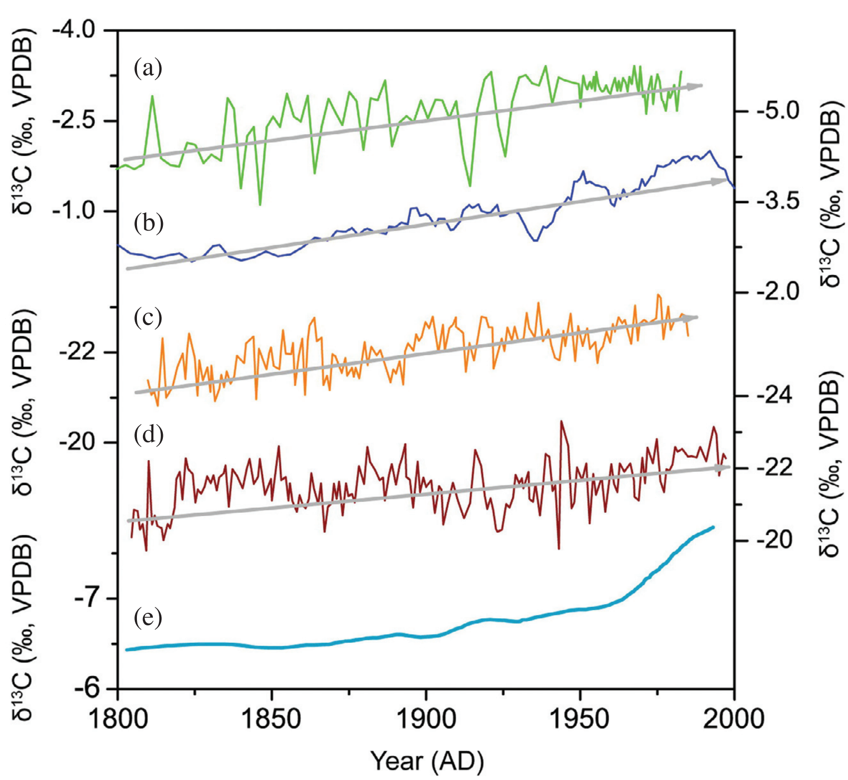

Fig. 6. Comparison of (a) the δ^{13}C record from DY-1 with: (b) stalagmite δ^{13}C record from Wanxiang cave (An 2007), (c) tree ring δ^{13}C record from the Tianmu Mountains (Zhao et al. 2005), (d) tree ring δ^{13}C record from the Helan Mountains (Liu et al. 2004), and (e) δ^{13}C record of atmospheric CO_2 extracted from an Antarctic ice core and fern samples (Francey et al. 1999).

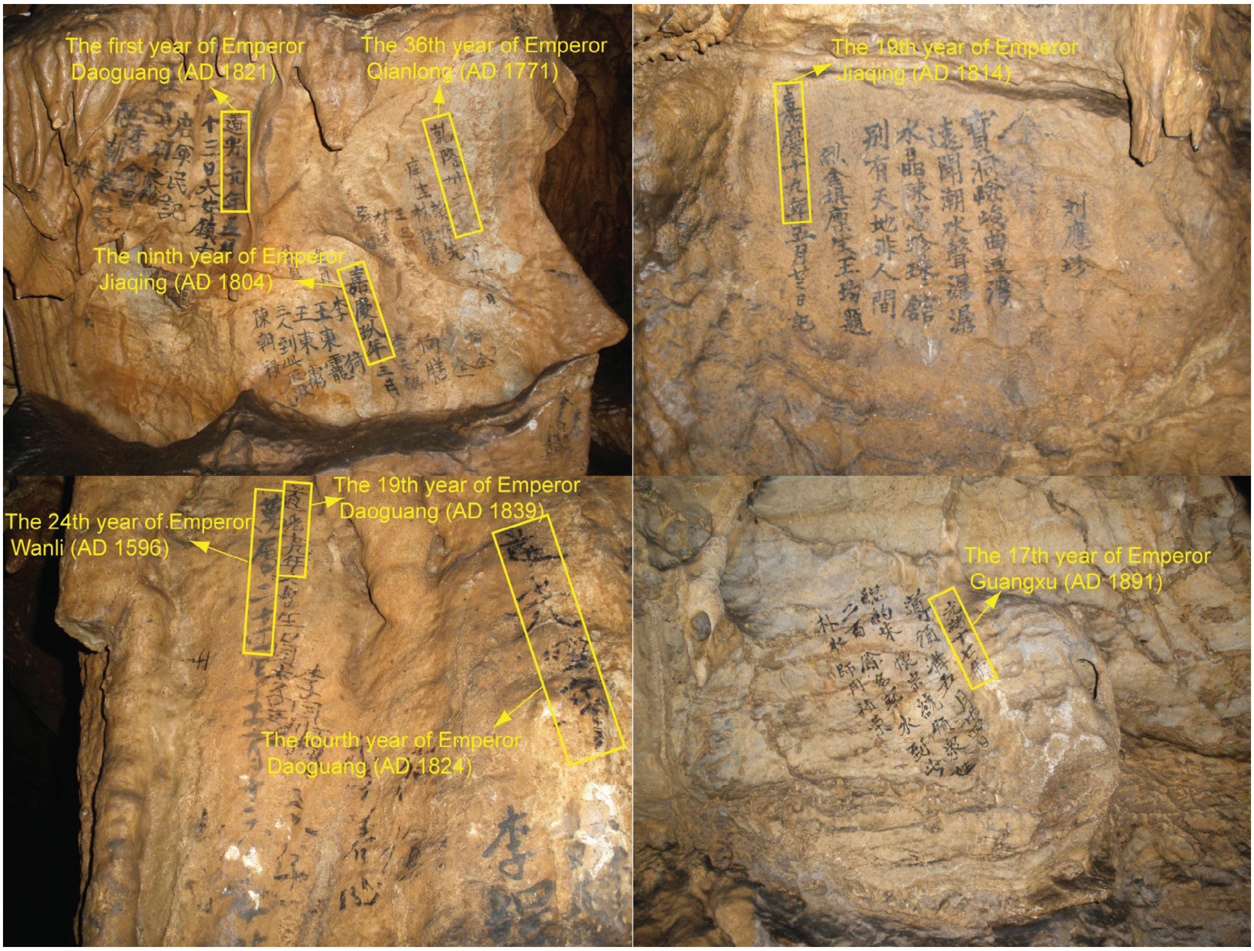

Fig. 7. Examples of inscriptions from Dayu Cave.

the latter half of the 13th century to the 15th century, a dry and/or warm climate reduced the vegetation density and decreased the C3/C4 plant ratio, causing relatively high $\delta^{13}C$ values in DY-1. From the 16th to the 17th century, the climate turned wet and/or cold, and the increased vegetation density and C3/C4 plant ratio caused relatively low $\delta^{13}C$ values during this period. The climate fluctuated around an average condition during the 18th century. Variations in precipitation controlled the residence time of the seepage water, and may have affected the dissolution of bedrock, prior carbonate precipitation in the unsaturated zone above the cave and, the degassing of CO_2 within the cave which ultimately influenced the $\delta^{13}C$ values of DY-1 on annual to decadal scales, and even at the centennial scale.

The reduction in the $\delta^{13}C$ value of atmospheric CO_2 since the Industrial Revolution may have caused the decreasing trend in the $\delta^{13}C$ of stalagmite DY-1 after 1800 AD. Early visitors to the Dayu Cave used burning torches for lighting, which produced large amounts of CO_2 inside the cave. Increased visitor numbers to the cave over time may have sustained the raised pCO_2 cave air, and led to a decrease in the fraction of CO_2 degassing and carbonate precipitation, which may be partly responsible for the decreasing trend in stalagmite $\delta^{13}C$ over the past 200 years.

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