High-resolution stalagmite $\delta^{13}\text{C}$ record of soil processes from southwestern China during the early MIS 3

LIU DianBing^{1*}, WANG YongJin¹, CHENG Hai^{2,3} & EDWARDS R L³

¹ College of Geography Science, Nanjing Normal University, Nanjing 210046, China;

² Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an 710049, China;

³ Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota 55455, USA

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Knowledge of the evolution of pedogenic processes in the carbonate area is important to understand the dynamics of rock desertification. A precisely-dated stalagmite $\delta^{13}\text{C}$ record between 61.3 and 50.5 ka BP from southwestern China, potentially related to soil biogenic CO_2 production, shifts within a narrow range between -9‰ and -7‰ , and exhibits a prominent cycle of 350–470 a, independent of the Asian monsoon changes. This indicates that a threshold effect might control the amplitude of calcite $\delta^{13}\text{C}$ variability, likely associated with the vertical soil loss in the carbonate area. The periodic $\delta^{13}\text{C}$ changes reflect that the loss/recovery of soil cover can operate on centennial scale. Thus, the rock desertification in southwestern China might at least initiate 60 ka ago and should be of natural origin.

Wulu Cave, stalagmites, stable carbon isotope, centennial changes, soil processes

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Stable carbon isotopes ($\delta^{13}\text{C}$) in the stalagmites have multiple controls [1,2], among which site-specific factors often play a dominant role. At climatically- or environmentally-sensitive locations, however, the speleothem $\delta^{13}\text{C}$ values can exhibit large and periodic shifts on orbital to inter-annual scales through changes in the vegetation and/or soil processes above the cave [3–6], which has a wider regional significance. Hence, the $\delta^{13}\text{C}$ signal in these stalagmites can record spatial changes of biological activities and soil conditions.

In the karst zone, where the underground water often flows vertically through conduits and fractures, the soil particles can be carried straight down into the hydrologic systems rather than laterally transported [7–10]. This mode of soil loss was proposed to be impacted by land use, land cover, rainfall regimes and topography in the observation studies [11,12]. Apparently, the soil erosion in southwestern China is currently related to human activities, yet it still

remains unclear to what extent the natural soil development and forming processes contribute to the rock desertification in the Yun-Gui Plateau. Recently, we collected two stalagmites from Wulu Cave, Guizhou Province, the $\delta^{18}\text{O}$ records of which were reported in Liu et al. [13]. Here we present a precisely-dated stalagmite $\delta^{13}\text{C}$ record between 61.3 and 50.5 ka BP, allowing an assessment on the natural evolution of pedogenic processes when anthropogenic influence was negligible.

1 Location and samples

Wulu Cave (26°03'N, 105°05'E, 1440 m above sea level) is located at the Yun-Gui Plateau, Guizhou Province, which is a southeastward extension of the Tibetan Plateau, and climatically influenced by the East Asian and Indian summer monsoons [14]. The studied site is suffered from severe rock desertification and the local flora is mostly composed of deciduous herbs (C_4 -type vegetation). The cave is about

*Corresponding author (email: ldb9921@njnu.edu.cn)

800 m long, overlain by 40 m of Triassic limestone bedrock (at a slope of 40°–50°) with a thin soil cover (5–10 cm). In the cave chamber, the later part (500–800 m from the entrance) is covered by 2-m-high deposits of clay and debris, while the former part (0–500 m) is mainly covered by rocks. Field work found little active calcite deposited in the cave. Local precipitation distinctly increases in late spring as the Indian monsoon intensifies, while in summer, regional meteorological conditions are dictated by both the Indian and East Asian summer monsoons. Current mean annual temperature at this site is about 14°C, with a maximum in July (20.8°C) and a minimum in January (4.3°C). The annual precipitation ranges between 1100 and 1700 mm, peaking (920 mm) during the summer months (June through September), reaching a minimum (80 mm) in the winter (December through February).

The two stalagmites, Wu23 and Wu26, were collected 5 m apart and 650 m from the entrance. Sample Wu23 is 66.7 cm in length. It has a “candlestick” shape with a diameter of 6.5 cm, indicating a stable deposition history. Sample Wu26 is 83 cm long and has a larger diameter, varying from 9 cm to 10 cm. When halved and polished, couplets of faint transparent/dark layers are apparent between 52 and 81.6 cm in Wu26 [13]. At 25, 41 and 50 cm, changes in color suggest a growth cessation or changes in the growth rate at these depths. In Wu23, black organic-rich bands are evident at 8 cm from the top, indicative of a growth hiatus. At 36 cm, horizontal bands are gradually replaced by curved ones, suggesting a shift in moisture conditions and/or growth rate.

2 Analytical methods

Fifteen calcite powder samples were drilled along the growth axis of stalagmites (6 for Wu23 and 9 for Wu26) with 0.9 mm-diameter carbide dental burs for ^{230}Th dating. The measurements were performed by inductively coupled plasma mass spectrometry (ICP-MS) on a Finnigan-MAT Element at the Department of Geology and Geophysics, University of Minnesota, USA. The procedures are similar to those described in Shen et al. [15], with results listed in Table 1 in [13]. All dates are in stratigraphic order with typical analytical errors (2σ) ranging from 130 to 400 a. For stable isotopic measurements, 1200 subsamples were drilled with 0.3 mm-diameter carbide dental burs along the central growth axis. Analyses were performed on a Finnigan-MAT 253 mass spectrometer fitted with a Kiel Carbonate Device at the College of Geography Science, Nanjing Normal University. Spatial resolution is 0.5–1 mm for Wu23 and 1–2 mm for Wu26. This corresponds to a temporal resolution of 2–40 a for different portions of the two samples. The results are reported relative to Vienna Pee Dee Belemnite (VPDB) with standardization determined relative to NBS 19. Precision of $\delta^{18}\text{O}$ values is 0.06‰ and 0.03‰ for $\delta^{13}\text{C}$, at the 1-sigma level.

3 Results

3.1 U/Th chronology

Fifteen ^{230}Th dates reveal that two stalagmites grew between

Table 1 ^{230}Th dating results for two stalagmites from Wulu Cave, southwestern China^{a)}

Sample No.	Depth (cm)	^{238}U (ng/g)	^{232}Th (pg/g)	$\delta^{234}\text{U}$ (measured)	$^{230}\text{Th}/^{238}\text{U}$ (activity)	^{230}Th age (a BP) (uncorrected)	^{230}Th age (a BP) (corrected)	$\delta^{234}\text{U}_{\text{Initial}}$ (corrected)
Wu23-11	1.1	620±1	211±3	1384±4	0.533±0.002	26980±130	26970±130	1494±5
Wu23-100	10.0	500±1	347±3	1311±4	0.964±0.003	55750±260	55740±260	1534±5
Wu23-261	26.1	405±1	488±15	1371±3	1.014±0.004	57370±310	57360±310	1611±4
Wu23-373	37.3	443±1	165±2	1331±5	1.010±0.004	58430±290	58430±290	1570±6
Wu23-480	48.0	530±1	327±13	1320±4	1.020±0.005	59470±390	59470±390	1561±4
Wu23-645	64.5	596±1	204±3	1293±4	1.011±0.003	59810±250	59800±250	1531±4
Wu26-54	5.4	711±1	3855±7	1273±4	0.890±0.003	51630±220	51560±220	1473±5
Wu26-149	14.9	636±1	421±8	1240±2	0.903±0.001	53460±120	53450±120	1442±3
Wu26-238	23.8	628±1	411±3	1249±4	0.915±0.003	54110±260	54110±260	1455±5
Wu26-259	25.9	479±1	295±3	1276±4	0.936±0.004	54840±290	54830±280	1489±5
Wu26-430	43.0	434±1	322±6	1256±2	0.962±0.001	57270±130	57260±130	1476±3
Wu26-490	49.0	581±1	342±3	1271±4	0.974±0.003	57720±280	57710±280	1497±5
Wu26-526	52.6	556±1	107±3	1258±4	0.990±0.004	59400±300	59400±300	1488±5
Wu26-663	66.3	522±2	182±6	1280±6	1.011±0.005	60120±400	60120±400	1517±7
Wu26-817	81.7	646±1	445±3	1247±4	1.008±0.003	61200±260	61190±260	1482±5

a) Errors are 2σ analytical errors. Decay constant values are $\lambda_{230}=9.1577\times10^{-6}\text{ a}^{-1}$, $\lambda_{234}=2.8263\times10^{-6}\text{ a}^{-1}$, $\lambda_{238}=1.55125\times10^{-10}\text{ a}^{-1}$. Corrected ^{230}Th ages assume an initial $^{230}\text{Th}/^{232}\text{Th}$ atomic ratio of $(4.4\pm2.2)\times10^{-6}$. Corrected ^{230}Th ages are indicated in bold.

61.3±0.26 and 27±0.13 ka BP (Table 1), with most of the deposition occurring from 61.3 to 50.5 ka BP, covering the early Marine Isotope Stage (MIS) 3. These dated calcite powders have high uranium (400–710 ng/g) and relatively low thorium concentrations (110–490 pg/g). Thus, initial ^{230}Th age corrections are trivial (generally less than 15 a), ensuring high-precision dating results. The two stalagmites are closely situated, and influenced by similar climatic and edaphic conditions. A considerable discrepancy of corrected $\delta^{234}\text{U}_{\text{Initial}}$ values (an indicator of the ratio of excess ^{234}U to ^{238}U in the seepage water when calcite deposited) observed between them might have little climatic/edaphic origin. One possibility is due to different types of conduit feeding two stalagmites and associated water-rock interactions [16], which is clearly reflected in their different diameters.

An age model was developed for the stable isotope data by linear interpolation between adjacent ^{230}Th dates. The youngest age at 8 cm in Sample Wu23 (26.97±0.13 ka BP), above an apparent hiatus, was not used in constructing the

age model. Below the hiatus, growth rate of Sample Wu23 ranges from 100 to 660 mm/ka (Figure 1). Between 52 and 81.6 cm depth of Wu26, an average of 4 to 5 couplets of light/dark layers can be identified per millimeter. If these are annual bands, they would indicate a growth rate of 200–250 mm/ka [13], which agrees reasonably well with our estimate of 163 mm/ka from the bounding U/Th dates (59.4±0.3 ka BP; 61.2±0.3 ka BP). The growth periods for two samples overlap between 59.8 and 55.5 ka BP, with a discontinuity in Wu26 from 59.4 to 57.7 ka BP.

Sample Wu23 exhibits little variability in lithological features below the hiatus, partly reflected by a near-linear age model and a slight shift in the growth rate at 48 cm (Figure 1). Occasional changes in lithology in Sample Wu26 (above 50 cm) may account for large variation of growth rate, ranging between 20 mm/ka and 130 mm/ka. Below this depth, the age model is practically linear. Consequently, the age model we established from an interpolation between adjacent dating points is roughly supported by

Figure 1 Comparison of $\delta^{13}\text{C}$ (a) and $\delta^{18}\text{O}$ (b) records, and their growth rates (c). The grey bar in (a) and (b) indicates a continuous growth period and is well constrained by ^{230}Th dates. The horizontal grey line in (a) shows the mean value of $\delta^{13}\text{C}$ data. Error bars are indicated respectively on top of (b).

the observed lithological variations.

3.2 Carbon isotopic sequence

The $\delta^{13}\text{C}$ values for two samples shift from -10‰ to -4‰ , mostly within a range of -9‰ and -7‰ (Figure 1(a)). Over their growth periods, the $\delta^{13}\text{C}$ values show high-frequency (centennial) and high-amplitude (over 2‰) variability around -8‰ in contrast to $\delta^{18}\text{O}$ changes (Figure 1(b), [13]). This pattern of $\delta^{13}\text{C}$ variability persists throughout the early MIS3. The $\delta^{18}\text{O}$ record, however, exhibits distinct millennial-scale changes. This discrepancy between them suggests that they have different dynamics, partly supported by a low correlation between them (Figure 2, $r^2 = 0.07$ for Wu23, 0.003 for Wu26).

“Hendy tests” [17] performed on seven growth lamina (four for Wu23, three for Wu26) show little variability in $\delta^{18}\text{O}$ within a radius of 3 cm from the central axis (indicated by 0 cm in Figure 2) to the edges, with a standard deviation of less than 0.23‰ along each layer. In contrast, $\delta^{13}\text{C}$ values

shift by 0.7‰ – 2.6‰ along these same layers. A potential interpretation for these observed large $\delta^{13}\text{C}$ changes is different CO_2 degassing rate at the stalagmite surface [18] and/or errant sampling beyond the targeted growth layer, which more substantially impacts calcite $\delta^{13}\text{C}$ than $\delta^{18}\text{O}$ [19]. However, the well-duplication of their $\delta^{18}\text{O}$ records (Figure 1) indicates that calcite most likely precipitated under equilibrium conditions, although a kinetic effect probably occurs at their edges. Even so, the isotopically kinetic effect and growth dynamics should have little impact on the $\delta^{13}\text{C}$ variability along the central axis, because both factors can not precisely result in periodic $\delta^{13}\text{C}$ changes. During their initial growth, both stalagmites have larger growth rates (Figure 1(c)). But their $\delta^{13}\text{C}$ variability exhibit similarly cyclic changes as during the younger intervals, seldom influenced by shifts in the Asian monsoon intensity and their growth dynamics.

Over their contemporaneous growth periods, the reproduction of $\delta^{18}\text{O}$ records can be applied as a reference, resulting in a composite $\delta^{13}\text{C}$ record at the coeval depths. The

Figure 2 Correlation analysis between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ for Samples Wu23 (a), Wu26 (b) and the results of “Hendy tests” (c), (d) on seven layers. The grey lines in (c) and (d) represent variations in $\delta^{13}\text{C}$ along the same lamina, and the black lines illustrate changes in $\delta^{18}\text{O}$. r^2 values are listed in (a) and (b), the $\delta^{18}\text{O}$ standard deviations are labeled in parentheses on the right.

growth rate of Wu26 during 55.9 ka BP downwards shows larger changes, hence we focus on a spectral analysis on the composite $\delta^{13}\text{C}$ data between 61.3 and 55.9 ka BP (grey bar in Figure 1). During this time, the $\delta^{13}\text{C}$ variability shows a distinct periodicity of 350 to 470 a. Within each cycle, times of depleted $\delta^{13}\text{C}$ values last about 200 to 300 a and remain stable, while the enriched period appears to be one third of the former. Furthermore, variations in the $\delta^{13}\text{C}$ in each cycle apparently confine to a narrow range with a rapid enrichment/depletion transition (about 20 to 50 a, Figure 3).

4 Discussion

4.1 Environmental significance of stalagmite $\delta^{13}\text{C}$

Carbon in speleothem calcite has three main sources: (1) atmospheric CO_2 ; (2) soil CO_2 which is controlled by atmospheric CO_2 , plant respiration, and organic matter degradation; and (3) bedrock carbonate (CaCO_3) that is dissolved during seepage [20]. On millennial scale, the speleothem $\delta^{13}\text{C}$ variability was thought to reflect climate-driven changes in vegetation (relative abundance of C_3/C_4 -type plant assemblages [4,21]).

At the Wulu site, the modern vegetation is mainly composed of deciduous herbs. Although it is now not acknowl-

edged whether this type of vegetation dominated in the distant time, the pattern of Wulu $\delta^{13}\text{C}$ variability clearly does not support the explanation of C_3/C_4 -type vegetation changes. First, this assumption probably does not hold on the centennial scale observed in our calcite $\delta^{13}\text{C}$ record (Figure 3) or needs to be further testified. Second, the rapid transition of enriched/depleted $\delta^{13}\text{C}$ values (20–50 a) can not be caused by natural degradation/recovery of C_3 vegetation, which should be more gradual. Third, changes in the vegetation are closely associated with the climate, yet this relationship breaks down as different frequencies identified in the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records (Figure 1). Additionally, the narrow range of $\delta^{13}\text{C}$ (-7‰ to -9‰), to some extent, suggests that monotypic vegetation should dominate during the distant time. A modern stalagmite grown under a grass field from Villars Cave, France exhibited constant $\delta^{13}\text{C}$ changes (around -9.2‰) between 1910 and 1990 AD in contrast to a forest-covered stalagmite [22], which implies that the grass field did not change significantly during the past century. Our calcite $\delta^{13}\text{C}$ values during the early MIS3 fall within those of C_4 -type vegetation (-6‰ to -23‰ , [23]), partly suggesting a contribution as those from the modern vegetation. Previous studies showed that the soil biogenic CO_2 production has an important impact on the speleothem $\delta^{13}\text{C}$ variations [2,20], which is 10–100 times the concentration

Figure 3 The composite Wulu $\delta^{13}\text{C}$ record between 61.3 and 55.9 ka BP. The grey bars show periods of depleted $\delta^{13}\text{C}$ values, corresponding to increased soil biogenic CO_2 production, and the dotted and solid lines indicate the narrow range of $\delta^{13}\text{C}$ variability and the mean value, respectively. The subplot indicates the spectral analysis result for the composite $\delta^{13}\text{C}$ record.

of the atmospheric CO_2 [24]. Therefore, the Wulu $\delta^{13}\text{C}$ record most likely reflects the biogenic CO_2 production related to soil processes, although the confirmation of this interpretation via cave monitoring is currently restricted by deficit of active calcite deposition. Changes in the CO_2 degassing rate may also contribute to changes in the calcite $\delta^{13}\text{C}$ [25], however, larger variations were only observed at the edge of stalagmites [13,26], sub-sampling along the central growth axis of stalagmite may effectively avoid this influence [27]. Even that the stochastic changes of CO_2 degassing contribute to the calcite $\delta^{13}\text{C}$, it can not result in the periodic variability observed in our record.

In the previous investigations, the biomass effect was extensively proposed to control the carbonate $\delta^{13}\text{C}$ on shorter timescales [28–31], among which four caves in Guizhou Province with different vegetation covers revealed a negative relationship between them [31]. In Figure 3, periods of depleted calcite $\delta^{13}\text{C}$ values (indicated by the grey bars) likely correspond to strong biogenic CO_2 production, because increased soil biogenic CO_2 production leads to more negative $\delta^{13}\text{C}$ values [2,20]. Consequently, the thickness of soil cover over the cave probably reached an appropriate level at this time, to provide a prerequisite and habitat for vegetation growth and microbial activity. The enriched times (periods between the grey bars) indicate weaker microbial activity and less soil CO_2 production.

4.2 Implication of periodic $\delta^{13}\text{C}$ changes

The most prominent for Wulu $\delta^{13}\text{C}$ record is a striking periodicity of about 400 a (above a confidence level of 95%), stably fluctuating around -8‰ (between -7‰ and -9‰ , Figure 3). This centennial $\delta^{13}\text{C}$ variability, independent of Asian monsoon changes (Figure 1), might be related to karstic dynamics and processes. If the modern C4-type vegetation at this site persisted during the early MIS 3, one possible driving factor for the calcite $\delta^{13}\text{C}$ is from the centennial-scale solar activity [32–34], because the soil moisture and grass development is sensitive to solar output by regulating the surface temperature [35]. This forcing, however, has limited impact on the millennial climate changes [36], although this speculation still remains debatable [33,34,36].

Furthermore, the large (2‰) and rapid (20–50 a) $\delta^{13}\text{C}$ variations might involve a pedogenic and/or ecological threshold. In Guizhou Province, the erosion rate of carbonate rock is about 0.06–0.1 mm/a, while the pedogenesis rate is about 0.01–0.02 mm/a [37], hence a negative soil growth can be pervasively found [8]. A process of “vertical soil loss” through creeping and sliding at the crust/bedrock interface, caused by chemical and gravitational erosion [10], hinders a continuous accumulation of weathering crust. Thus, the soil only deposited in the later part of Wulu cave chamber should source directly from the limestone fissures and fractures, yet not transport from the cave entrance. This

suggests that periodic absence/deficit of soil cover might further reduce the soil biogenic CO_2 production, resulting in positive excursion of calcite $\delta^{13}\text{C}$ values.

Therefore, the cyclicity of 350–470 a in the $\delta^{13}\text{C}$ record possibly reflects a loss/recovery rate of soil cover at this site. This pattern of $\delta^{13}\text{C}$ variability remains unchanged during other time windows from the site-specific stalagmite records (unpublished data). Apparently, our data, if proven to be mechanically associated with soil processes, are of particular importance to understand the evolution and dynamics for rock desertification in southwestern China. Recently, Liu et al. [38] suggested that carbonate weathering might be significant in controlling the short-term climate changes. This means that in the typical carbonate area, the weathering rate is probably fast. Hence, the centennial-scale of soil recovery/erosion might further validate this conclusion, and the rock desertification in southwestern China is probably of natural origin, and at least began 60 ka ago. The anthropogenic influence in the modern times potentially aggravated this process. As explained above, our studied site is sensitively located, and the $\delta^{13}\text{C}$ record might represent the local signal, regional significance needs to be further tested with more spatially separated cave records.

5 Conclusions

A composite $\delta^{13}\text{C}$ record from two ^{230}Th -dated stalagmites in southwestern China reveals a detailed history of soil processes between 61.3 and 50.5 ka BP. The $\delta^{13}\text{C}$ record is characterized by a notable cycle of 350–470 a, and shifts between -9‰ and -7‰ . During each cycle, the period of depleted $\delta^{13}\text{C}$ values spans 200 to 300 a, and the enriched lasts 100 to 200 a, with a rapid transition between them.

The periodic $\delta^{13}\text{C}$ variability, in some degree, suggests that the erosion/recovery of soil cover at the studied site can work at centennial scale, supporting the previous assumption that the carbonate weathering can influence the climate on shorter timescales [38]. The rapid transitions are likely caused by the vertical soil loss proposed as a main transporting mode of soil particles through the hydrologic systems [7–10]. Thus, our record provides a new line of evidence that the rock desertification might be of natural origin, and at least began 60 ka ago.

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