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Carbon isotopic records from stalagmites and the signification of paleo-ecological environment in the area of Guangxi—Guizhou, China

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Abstract High resolution carbon isotopic records in millennial, centennial and decadal timescales from three stalagmites from three different caves under a similar monsoon climate in Guangxi–Guizhou, China, provided detailed information on the paleo-ecological environmental conditions in the past 15,000 years. The results indicate that during the glacial period, or cold-dry period, such as Heinrich event H1 and Younger Dryas event karst development was poor as was pedogenesis, C3 vegetation didn't grow well, resulting in C4 plants dominating and with heavy $\delta^{13}C$ values in stalagmites. In a warm-humid stage, C3 vegetation grew well and predominated with negative $\delta^{13}C$ values. The $\delta^{13}C$ records from stalagmites could be indicative of sensitive vegetation changes and reflective of climate changes in precipitation, temperature, etc. The $\delta^{13}C$ records may also be used to distinguish different effects from nature or human activity. Particularly since the late Holocene, human activities have increased disturbances to environment, even more than natural factors. Forest vegetation was destroyed, C4 plants became dominant, and rock desertification was aggravated because of severe water and soil loss, all resulting in sharply increasing $\delta^{13}C$ values of stalagmites that are heavier than pre-middle Holocene $\delta^{13}C$ values.

Keywords Stalagmites · Carbon isotopic records · Rock desertification · Guangxi—Guizhou

Introduction

Speleothem in karst caves is regarded as valuable archives of climatic conditions, ecological environments, surface karst processes, rock desertification, and so on. Compared with other continental climate-environment records such as tree rings, ice cores, loess, lake sediments and peat sediments, speleothem retains the full climate information with little influence from surface short-term climate changes such as high-frequency changes in temperature and precipitation. Precise U-series dating on speleothem also makes them remarkable for research on climatic and ecological environment changes.

Speleothem $\delta^{13}C$ as a record of vegetation

Previous studies have demonstrated that carbon isotopes are significant environmental indicators of the variation in vegetation. Hendy (1971) discussed the origin, effect, and geologic significance of carbon isotopes from cave carbonates. Carbon isotope variations in stalagmites have much with $\delta^{13}C$ values of dissolving atmospheric CO_2 in rainfall, and soil CO_2 released by plant respiration and soil organic matter decomposition (Hendy 1971). The concentration of atmosphere CO_2 is much lower than soil CO_2—300–350 ppm as compared to 800–10,000 ppm. The results from Yaji Experiment Site in Guilin indicate the hydrochemical variations of karst springs as the output of karst process are controlled by precipitation and the shift of soil CO_2 concentration. In warm-humid stages, microbe levels rise and give high soil CO_2 concentration, causing the pH of karst springs to rise, and vice-versa. This proves that precipitation and biologic soil CO_2 are the important driving forces that power the karst dynamic system (He et al. 1997). Quade et al. (1989) found that soil CO_2 and the dissolved bicarbonate of the soil solution reach almost isotopic equilibrium, which means that the dissolution of limestone has little obvious influence on carbon isotopic equilibrium for secondary deposition of calcium carbonate. So the shift of $\delta^{13}C$ value of speolothems reflects that of soil CO_2 during the same period or with a regular lag. Previous studies demonstrated that environmental factors such as precipitation and the portion of C3 plants and C4 plants with different C-cycle routes have significant impacts on $\delta^{13}C$ value of soil CO_2 (Wang and Han 2001). And differences in respired CO_2 for C3 photosynthetic pathway plants and C4 plants have a vital role in variation of $\delta^{13}C$ value, but the shift of temperature is negligible (Yuan et al. 2003). Therefore, $\delta^{13}C$ value from stalagmites is a proxy of the changes in vegetation, which is indirect consequence of climate changes in temperature, precipitation, etc. The shift of the $\delta^{13}C$ caused directly by global climate change, especially temperature, is so tiny that a variation of about 10°C in temperature could cause an $\sim$1‰ shift of the $\delta^{13}C$ (He et al. 1997), but vegetation is sensitive to climate variation, especially to relative humidity. Variation on climate recorded by $\delta^{13}C$ value of CO_2 is preserved in stalagmite carbonates, which magnifies the direct influence of climate variation, especially in humid climates. The $\delta^{13}C$ values of speleothem calcite are dependent on the carbon isotopic composition that are controlled by the different vegetation ratios above or near the cave (Li et al. 1998).

Because C3 vegetation (arbors, shrubs, forbs, and cool season grasses) have lower $\delta^{13}C$ values in soil CO_2 than C4 vegetation (sedge, gramineous plants and dry season grasses), changes in vegetation type lead to variation in the carbon isotopic composition of soil organic matter, and also $\delta^{13}C$ value of speolothem (Boutton 1991; Brook et al. 1990; Dorale et al. 1998). C3 plants absorb carbon in the C3 photosynthetic pathway following Calvin's carbon cycle, and an increase in moisture makes $\delta^{13}C$ levels descend. The $\delta^{13}C$ value of soil CO_2 is between $\sim$−32 and −23‰ with an average of −25‰, and the more negative the $\delta^{13}C$, the more humid and hot, the climate. C4 plants absorb carbon in a C4 photosynthetic pathway following Hatch-Slack's carbon cycle, and an increase in moisture causes heavy $\delta^{13}C$ values. The $\delta^{13}C$ value of soil CO_2 is about in the range of $\sim$−14 to −8‰, representing an arid climate. Differences in hydrologic conditions among caves make different fractions of carbon isotopes in infiltrating fluids. When CO_2 gas is recorded into speleothem carbonate by chemical reactions, $\delta^{13}C$ values change a lot according to fraction laws. But similar trends in carbon isotopic compositions of different cave speleothems agree strongly with regional vegetation changes to $\delta^{13}C$ values of speleothems. So the shifting tendency of $\delta^{13}C$ values is more valuable than numerical $\delta^{13}C$ values in interpreting the variation of vegetation types (Denniston et al. 2000).

In this study, the $\delta^{13}C$ records of stalagmites in Guangxi–Guizhou area demonstrate that the forest vegetation in karst region used to be flourishing, then degenerated, but is now in a regeneration period.

Location, samples and methods

Three speleothems were sampled from three different caves with more than 80 m overlays and the stable temperatures inside caves corresponded well to the surface annual average temperature. In fact, the three caves, Dongge Cave, Xiangshui Cave, and Fengyu Cave, are located in the similar climate of East-Asian monsoon and Indian monsoon. Their locations are shown in Fig. 1. Stalagmite D4, 304 cm high, is from Dongge Cave (25°17′N, 108°5′E) 18 km SE of Libo, Guizhou Province. Dongge Cave is at an elevation of 680 m, with karst forest vegetation with mean annual precipitation of 1,753 mm (Yuan et al. 2004). Stalagmite X1, 70 cm high, is from Xiangshui Cave (25°15′N, 110°55′E) at an elevation of 400 m in Guanyang, Guilin, where brushwood and tussock predominate, but stone desertification has taken place at a few peaks. Actively forming stalagmite F4, 14 cm high, is from Fengyu Cave (24°30′N, 110°20′E) at an elevation of 380 m in Lipu, Guilin, where brushwood and tussock grow well in karst peak-clusters. The three stalagmites have been studied for different vegetation and effects in similar climates.

Each stalagmite was sawed vertically in half along the growth axes of deposition, and polished for visual inspection. The three stalagmites are composed of white, gray, and dark obvious calcite crystals while stalagmites D4 and X1 are characterized primarily by dense, optically clear calcite with clear deposition-cycles. No sign of recrystallization is apparent in any sample. Each stalagmite was sampled for dating and $\delta^{18}O$, $\delta^{13}C$ analysis along its central axis from its top. Samples were dated by TIMS-U series at the University of Minnesota isotope Laboratory and ^{210}Pb techniques at the University of Southern California (Tables 1, 2). The average precision of dating is 87a, particularly the F4 stalagmite with a high precision of 11a. As for stalagmite D4, two long hiatuses of about 28 and 49 ka occurred and here we study the upper 193 cm continuous deposition in the last 15,600 years. Calcite powder sampled in the same intervals (0.5–5 mm) along the central axis was analyzed at the isotope laboratory of Institute of Karst Geology,

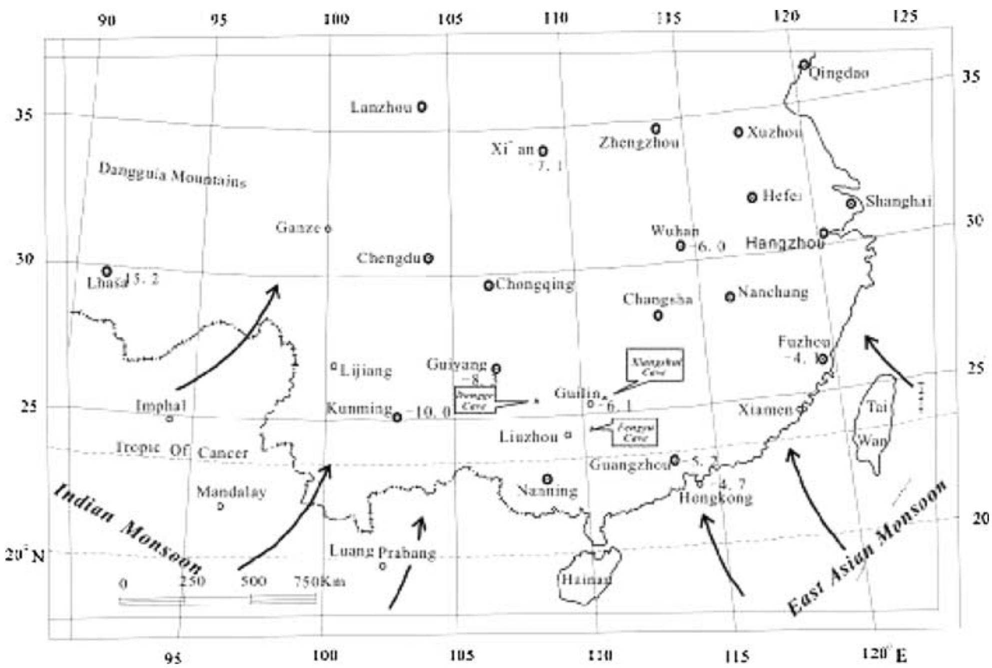

Fig. 1 The position of caves in Guangxi–Guizhou and moving route of the moisture source of the summer monsoon in the south of China. The numbers are the mean annual δ^{18}O values of the precipitation (Zhang et al. 2004a; Yuan et al. 2004). *Arrow* route of the summer monsoon

Table 1 Dating by using TIMS-U series from D4 stalagmite sampled from Dongge cave in Libo, Guizhou

Sample	Distance from the top of stalagmites	^{238}U (μg/g)	^{232}Th (ng/g)	δ^{234}U (measured value)	^{230}Th/^{238}U (activity)	δ^{234}U (initial value)	^{230}Th(age) (a BP)
D4-26	0.5 cm	600.0 ± 0.5	249 ± 13	−2.0 ± 1.1	0.00147 ± 0.0004	−2.0 ± 1.1	130 ± 40
D4-25	11 cm	488.0 ± 0.5	129 ± 9	−6.9 ± 1.4	0.00380 ± 0.0001	−6.9 ± 1.4	380 ± 10
D4-24	13 cm	387.2 ± 0.4	316 ± 10	−5.6 ± 1.7	0.00441 ± 0.00023	−5.6 ± 1.7	420 ± 30
D4-23	25 cm	438.5 ± 0.3	263 ± 10	−8.6 ± 1.1	0.01430 ± 0.00023	−8.7 ± 1.1	1540 ± 30
D4-21	30 cm	341.9 ± 1.8	433 ± 11	2.0 ± 9	0.02165 ± 0.00020	2.2 ± 9.0	2280 ± 40
D4-20	45.5 cm	475.7 ± 0.8	208 ± 9	8.8 ± 25	0.03651 ± 0.00025	8.9 ± 2.6	3990 ± 30
D4-19	47 cm	335.5 ± 0.2	120 ± 8	0.9 ± 0.9	0.03745 ± 0.00027	0.9 ± 0.9	4140 ± 30
D4-28	62 cm	509.6 ± 1.2	56 ± 7	−12.6 ± 1.3	0.04682 ± 0.00031	−12.8 ± 1.3	5300 ± 40
D4-18	86 cm	420.2 ± 5.3	70 ± 8	−62 ± 16	0.05236 ± 0.00079	−63.0 ± 16	6260 ± 150
D4-17	102 cm	443.3 ± 0.3	57 ± 8	−20.6 ± 0.9	0.05839 ± 0.00035	−20.9 ± 1.0	6700 ± 40
D4-16	122 cm	344.7 ± 0.5	13 ± 9	−9.4 ± 2.5	0.06520 ± 0.00033	−9.6 ± 2.5	7430 ± 40
D4-15	144 cm	468.0 ± 0.6	213 ± 8	−23.8 ± 1.8	0.07182 ± 0.00034	−24.3 ± 1.8	8310 ± 50
D4-29	162 cm	488.8 ± 1.0	320 ± 9	−0.5 ± 1.4	0.07971 ± 0.00052	0.5 ± 1.5	9020 ± 60
D4-13	164 cm	482.2 ± 0.4	116 ± 7	−12.5 ± 10	0.08130 ± 0.00032	−12.8 ± 1.0	9360 ± 40
D4-30	174 cm	406.3 ± 0.8	70 ± 7	−11.7 ± 1.2	0.09952 ± 0.00067	−12.1 ± 1.3	11580 ± 80
D4-12	176 cm	458.0 ± 0.6	292 ± 8	−18.9 ± 1.8	0.10176 ± 0.00056	−19.5 ± 1.8	11910 ± 70
D4-31	181 cm	441.2 ± 0.9	247 ± 9	−21.9 ± 1.5	0.10690 ± 0.0011	−22.7 ± 1.5	12600 ± 140
D4-11	186 cm	521.7 ± 0.6	213 ± 7	−3.7 ± 1.5	0.11546 ± 0.00037	−3.8 ± 1.6	13420 ± 50
D4-32	190 cm	535.5 ± 1.0	40 ± 8	−20.9 ± 1.2	0.12087 ± 0.00076	−21.7 ± 1.3	14390 ± 100
D4-33	193 cm	424.9 ± 0.9	1353 ± 13	−3.9 ± 1.7	0.13359 ± 0.00091	−4.1 ± 1.7	15470 ± 130

China. Carbonic isotopic resolution of whole stalagmites ranged from 35 to 110a, even in special section 7a. δ^{13}C values are normalized to the Pee Dee Belemnite standard (PDB).

Modern carbonate deposits from above two caves for four years from 2000 to 2004 were also analyzed. The value of δ^{18}O is from −7.7 to −8.2‰ and δ^{13}C −5.2 to −6.2‰ from modern carbonate in Dongge Cave. The δ^{18}O is from −6.46 to −7.2‰ and δ^{13}C −5.88 to −6.06‰ from modern carbonate in Xiangshui Cave. The δ^{13}C values from modern carbonate in the two caves have little difference with the average δ^{13}C values of stalagmite carbonate. Provided that modern vegetation is a reference, the average δ^{13}C will stand for a base line to vegetation conditions or ratio of C3 and C4 plants. Other questions concerned stalagmite F4 because the average δ^{13}C value is quite different from δ^{13}C values of modern carbonate. So we regard its δ^{13}C values of

Table 2 Dating by using TIMS-U series from X1 stalagmite sampled from Xiangshui cave in Guanyang, Guilin

Sample	Distance from the top of stalagmites	^{238}U (ppb)	^{232}Th (ppt)	$\delta^{234}U$ measuring	$^{230}Th/^{238}U$ (activity)	$\delta^{234}U$ initial value	^{230}Th(age) (k a BP)
X1-1	2.80 cm	69.0 ± 0.2	923 ± 8	503.2 ± 4.6	0.0103 ± 0.0005	503.9 ± 4.6	0.49 ± 0.14
X1-2	38.0 cm	55.7 ± 0.1	687 ± 8	505.2 ± 2.5	0.0370 ± 0.0007	509.1 ± 2.5	2.48 ± 0.13
X1-3	64.0 cm	173.1 ± 0.5	1956 ± 13	433.9 ± 3.1	0.0715 ± 0.0009	440.5 ± 3.2	5.35 ± 0.14
X1-4	69.5 cm	110.0 ± 0.5	1711 ± 8	420.0 ± 5.2	0.0800 ± 0.0011	427.1 ± 5.3	6.00 ± 0.18

$\lambda_{230} = 9.1577 \times 10^{-6}\ Y^{-1}$, $\lambda_{234} = 2.8263 \times 10^{-6}\ Y^{-1}$, $\lambda_{238} = 1.55125 \times 10^{-6}\ Y^{-1}$

Ages of stalagmites using TIMS-U-Series, analyzed by isotope laboratory in the department of geology and physical geography, Minnesota University, USA

modern carbonate as a reference to discuss the variation on vegetation.

Results from the $\delta^{13}C$ value of three stalagmites

$\delta^{13}C$ records from the three stalagmites provided an opportunity to deduce the history of the paleo-vegetation within 15,000a, from initial flourish, decay, comeback, then flourish. Both nature and human activity played important roles in the evolvement of the environment. In general, nature is more important, but sometimes human effect predominates by putting on human disturbance to nature.

$\delta^{13}C$ records from D4 stalagmite in Dongge Cave in Libo, Guizhou

Figure 2 shows the curves of carbon and oxygen isotopic records. A good relationship between the isotopic records, stalagmite deposited cycles and the shape are apparent. The $\delta^{13}C$ average value −5.23‰ during its whole growing period is close to the $\delta^{13}C$ values of modern carbonate (−5.2 to −6.2‰). We use the modern vegetation (karst forest) as the reference condition. The heavier $\delta^{13}C$ than average denotes the reducing precipitation or arid environment with C4 plants dominant, and vice-versa. The varying $\delta^{13}C$ curve reveals that stalagmite D4 went

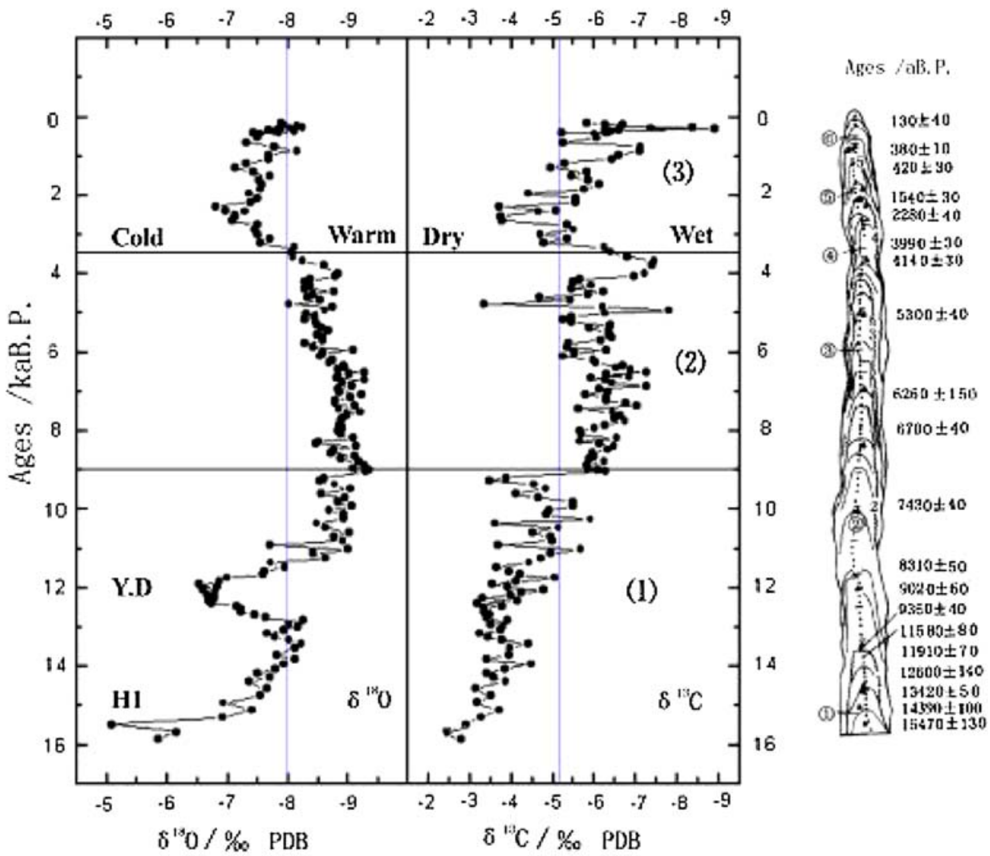

Fig. 2 The records of carbon and oxygen isotope from D4 stalagmite of Dongge cave, Libo (Zhang 2004a), **1** Vegetation was slow recovering (15,000–9,000a BP), **2** vegetation was flourish (9,000–3,500a BP), **3** vegetation was degenerating (3,500–2,000a BP) and coming back to flourish (since 2,000a BP

through three long periods: (1) Sub-humid stage (15,000a–9,000a BP) with the $\delta^{13}C$ average value −3.6‰ including Heinrich event H1 and Younger Dryas event (Yuan et al. 2004; Zhang et al. 2004a). The severe East-Asia winter monsoon made for a cold climate and reduced available precipitation. In this condition, the C4 vegetation was dominant (Yuan et al. 2004) and vegetation was in a slow recovery and improvement process. (2) Warm-humid stage (9,000a–3,500a BP) with an $\delta^{13}C$ average value −6.23‰. The strong East-Asia summer monsoon brought more available precipitation, resulting in C3 plants to over 95%. In this stage there were little climatic shifts and cold events except a short cool-aridity during 4,770a–4,600a BP with the heavy $\delta^{13}C$ value up to −3.5‰. (3) Transition from cold-aridity to warm-humid (since 3,500a BP). There was an aridity-cold period of about 3,500a–2,000a BP similar to the Younger Dryas event regarded as the third Neoglacial age. This cold event allowed C4 vegetation to quickly replace forest and $\delta^{13}C$ rose abruptly from approximately −6.23 to −3 or −4.5‰. Since 2000a BP, East-Asian summer monsoon strengthened slightly with rising temperatures and increasing available precipitation since 2000a BP Vegetation took a turn for the better and recovered with a low $\delta^{13}C$ of −6.18‰. At present there is a preferential vegetative pattern of evergreen broadleaf forest above Dongge cave.

$\delta^{13}C$ records from X1 stalagmite in Xiangshui Cave in Guilin

The records of carbon and oxygen isotopes from stalagmite X1 reveal dentate shifts in Fig. 3, and correspond well to the stalagmite cycle. Records of stalagmite D4 and X1 suggest that $\delta^{18}O$ formed under similar climate conditions, but $\delta^{13}C$ formed under different vegetation conditions. The whole average $\delta^{13}C$ of −8.29‰ in its 6,000a has little variation with an average $\delta^{13}C$ of −8.96‰ from modern carbonate in 1997. Provided that modern vegetation is taken as a relative stable condition for reference, we regard the whole average $\delta^{13}C$ of −8.29‰ as a base line for relative abundance of C3 and C4 plants.

According to the $\delta^{13}C$ changes of Stalagmite X1, its 6,000a was divided into two stages: (1) flourishing vegetation (6,000a–1,000a BP) with a $\delta^{13}C$ average of −9.12‰. In this stage, the $\delta^{18}O$ records suggests a warm-humid climate cooled down slowly and kept cool, and the $\delta^{13}C$ records indicate that there was similar vegetation to modern brushwood-tussock. The 2,000a–1,000a BP shows a good improvement occurred and there would probably be forest-brushwood vegetation. But six peaks with the heavy $\delta^{13}C$ values manifest several little shifts on the ecological environment, especially the period from 3,800 to 1,000a BP. was divided into five sub-stages, showing a similar-cycle of about 400a responding to a dentate-like shift on $\delta^{18}O$. (2) Vegetation degeneration (1,000a–373a BP) with abruptly rising $\delta^{13}C$ value. The $\delta^{13}C$ of stalagmite X1 increased rapidly from −9.02‰ to −5.21‰, to −3.81‰, then $\delta^{13}C$ oscillated about −3 to −5‰. It's believed to be a result of more serious disturbance from human activity because population increased, the forest had fallen excessively, and much land was used for food. Forest vegetation (C3 plants) degenerated to shrubs, then to grass, even rock desertification. Now the poor vegetation overlaying the cave is only

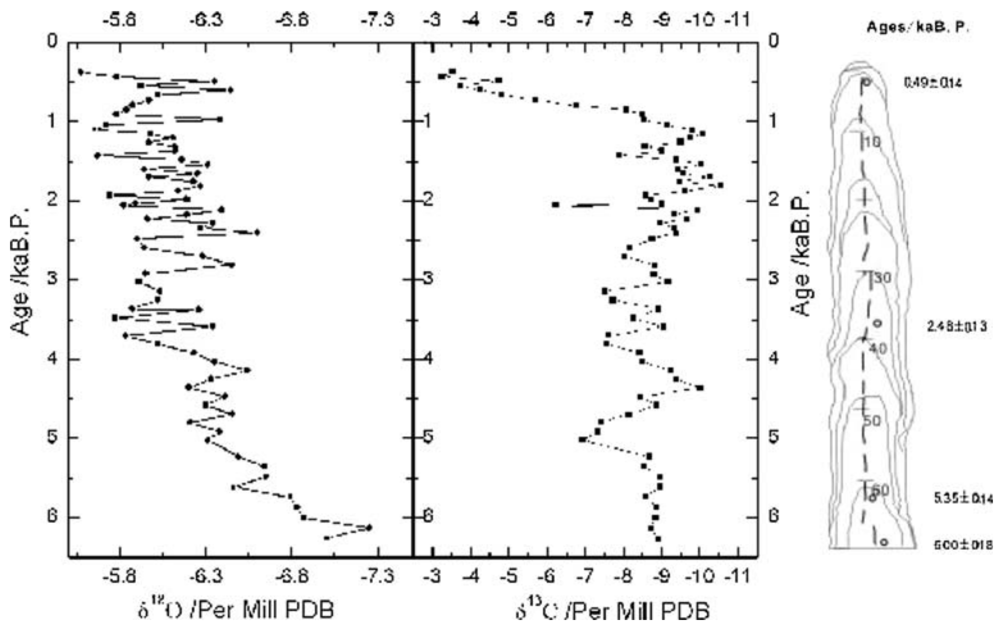

Fig. 3 The records of carbon and oxygen isotope from stalagmite X1 of Xiangshui cave, Guanyang(Zhang 2004b). During 6,000–1,000a BP, vegetation flourish suggested natural cycles about 400a. In the following stage (1,000–373a BP) vegetation degeneration was mainly caused by human activity

grass and a few shrubs with surface dolomitization due to soil erosion and vegetation loss in some sites.

δ^{13}C records from stalagmite F4 in Fengyu Cave, Guilin

The actively growing Stalagmite F4 was collected from Fengyu Cave, Guilin. The samples in stalagmite top were dated by ^{210}Pb techniques to calculate its deposition rate and other samples were dated by TIMS-U series showing that the initial growth occurred about 500a ago. The stalagmite was sampled twice for carbon and oxygen isotope analysis. The first 47 samples and the second 51 samples had almost identical results. The δ^{13}C value of modern carbonate in Fengyu Cave is $-5.21‰$, which is heavier than the average δ^{13}C of $-10.25‰$. The δ^{13}C value of modern carbonate is denotable of modern brushwood-tussock and is regarded as a reference to discuss variation on vegetation.

In Fig. 4, the δ^{13}C records from stalagmite F4 display variation of the ecological environment. In the early 300a, a low δ^{13}C of about $-12‰$ demonstrated that local vegetation was in a quite good condition. A slow ascendance to the δ^{13}C values occurred in the early glacial age (1530–1790 AD). However, in the following 100 years, the δ^{13}C increased rapidly, reaching $-5.8‰$, suggesting serious human disturbance because of the population explosion in the Qing Dynasty and forest over-utilization to compensate for freezing temperatures in the little glacial age. Forest degeneration occurred rapidly resulting in brushwood, tussock, and rock desertification. At the beginning of the modern warm period (the early 20th century), the warm-humid climate allowed C3 plants to grow well and caused the δ^{13}C to drop to $-9.7‰$. Continuous damage to vegetation made it impossible for the δ^{13}C value to go back to the initial low values and δ^{13}C values were more elevated about $2‰$ in the past 30 years because of aridity.

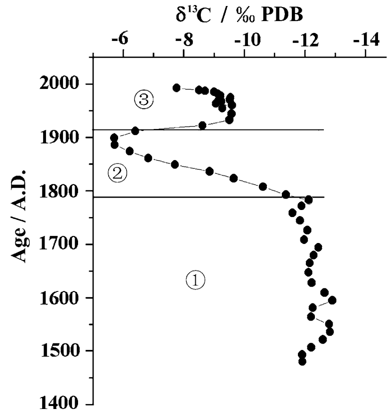

Fig. 4 The records of carbon isotope from stalagmite F4 of Fengyu cave, Lipu, **1** early stage with good C3 vegetation, **2** little glacial age with degeneration of C3 vegetation affected by nature and human activity, **3** modern warm age with good development of C3 plants

Conclusion

The δ^{13}C values from stalagmites in caves preserve information on the history of karst processes, vegetation, and rock desertification and also record indirect climatic effect of vegetation. Studies for the δ^{13}C records of three stalagmites from different caves of Guangxi—Guizhou area demonstrate that in the last 15,000a, local vegetation changed from initial luxuriant, to degeneration, and subsequent regeneration and so on under the united control of nature (climate) and human activity. Since the late Holocene, human activity has played a dominant role over nature. It is continuous damage to forest vegetation and excessive land used for food that has resulted in the degeneration of vegetation, aggravation of rock desertification, serious soil erosion, and depletion of water resources in karst regions. Karst ecological environments are sensitive to human activity, and the carbon isotope records from stalagmites in karst regions reflect the effects of climate, vegetation and human activity.

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