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Stable Carbon Isotope Geochemical and Hydrochemical Features in the System of Carbonate–H_2O–CO_2 and Their Implications —Evidence from Several Typical Karst Areas of China

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Abstract On the basis of hydrochemical observation and experimental calculation, the features of stable carbon isotope geochemistry in the karst dynamic systems of the Guilin Karst Experimental Site, Huanglong Ravine and Wujiangdu Dam Site are summarized in this study. Furthermore, an attempt has been made to solve several geochemical problems, such as the origin of CO_2 in the system, kinetic fractionation of carbon isotopes during calcite deposition, hydrochemistry and formation of tufa, and carbon–14 dating of tufa of hydrothermal origin. The results show that three kinds of karst dynamic system can be distinguished: (1) the shallow system, such as the Guilin Karst Experimental Site, in which soil CO_2 provides the an active agent for karst processes; (2) the geothermal system, such as the Huanglong Ravine, in which metamorphic or / and juvenile CO_2 is the source of activity for karst; (3) the anthropogenic system, such as the Wujiangdu Dam Site, in which the stable carbon isotope geochemical and hydrochemical features have been greatly affected by human activity.

Key words: karst dynamic system, stable carbon isotope, geochemistry, hydrochemistry, tufa formation, carbon source

Carbon, hydrogen and oxgen are three important and most active elements in the carbonate–H_2O–CO_2 system. The study on the isotopes of these elements is conducive to understanding the source of substances, the nature of the system (open or closed), the kinetic mechanism of calcite dissolution and deposition, and the forming processes of karst geochemistry.

In the past, many researches have been done on the characteristics of hydrogen and oxgen isotopes in the karst system. These researches focused on understanding the source of water (Chen et al, 1988; Liu, 1996), the age of water (Chen et al, 1988, Wang, 1991), and the palaeoclimate change (Qin, 1996). The research on the characteristics of stable carbon

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isotopes and particularly the source of carbon in the karst system, however, is limited in China (Wang, 1985; Zhu, 1990). Therefore some case studies of the carbon isotope characteristics and its geochemical implications in several typical karst areas of China are undertaken in this study.

1 Site Description

1.1 Guilin Karst Experimental Site

The site is situated near Yaji Village in the southeast suburb of Guilin, about 8 km away from Guilin City. It is at the boundary between a peak–cluster depression and a peak–forest plain. The area of the site is about 2 km^2. The strata of the experimental site are mainly pure limestone of the Upper Devonian Rongxian Formation, with a thin soil cover. The major vegetation includes bushes and grasses. The annual mean air temperature and precipitation are 19℃ and 1900 mm, respectively. Precipitation is the sole recharge source of groundwater in the site.

Three zones, i.e. the epikarst zone in the upper part, the aeration zone in the middle part and the saturation zone in the lower part, are distinguished vertically in the site (Fig. 1). Among them, solutional fissures are well developed and of even distribution in the epikarst zone, where part of water discharges into epikarst springs, such as Spr. 25 and Spr. 54, in peak–cluster depressions, and then goes into the aeration zone or/ and saturation zone via sinkholes in the depressions; while the other part is connected directly with the lower parts via fissures or/ and conduits. At last, all water except for evaportranspiration discharges mainly into spring Spr. 31 on the boundary of the peak–forest plain (Liu, 1992; Yuan et al, 1996).

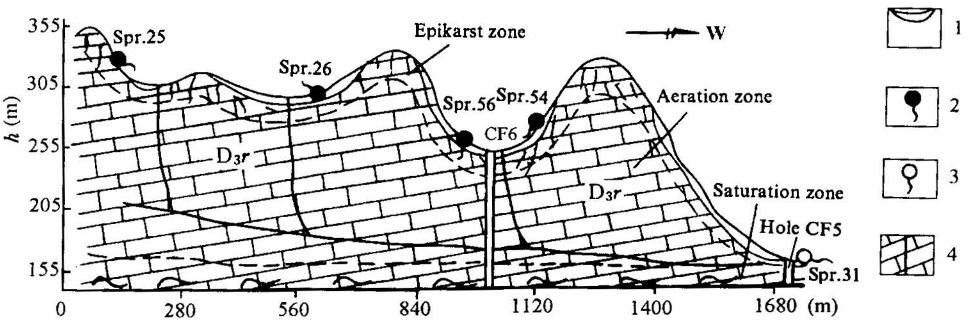

Fig. 1. Geological profile of the Guilin Karst Experimental Site.
1. Soil cover; 2. epikarst spring; 3. saturated spring; 4. limestone and conduit; D_{3r}–limestone of the Upper Devonian Rongxian Formation.

1.2 Huanglong Ravine of Sichuan

The ravine is located on the northwestern plateau of Sichuan Province in the central sector of the Minshan Mountains at an altitude of roughly 3400 m asl. The strata in the recharge area are mainly Devonian to Permian limestone. Hydrogen and oxygen isotope studies have shown that the groundwater is recharged by the infiltration of precipitation (Chen et al, 1988). Groundwater with rich CO_2 gas discharges in the form of springs at an altitude of

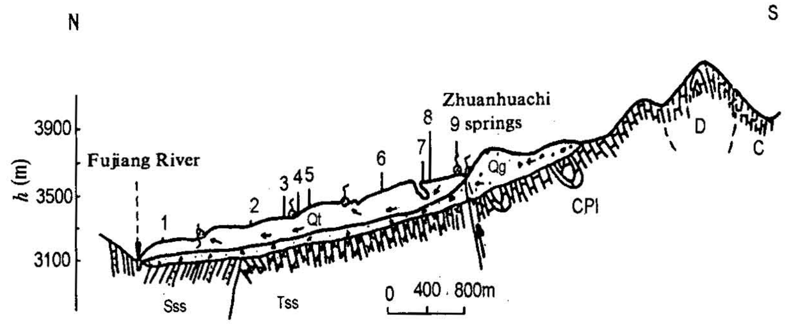

Fig. 2. Geological profile of the Huanglong Ravine (including field observation station Nos. 1 to 9).
Qt / Qg = Quaternary tufa / glacial sand and gravel; Tss = Triassic sandstone and slate;
CPl = Carboniferous–Permian limestone; C = Carboniferous limestone; D = Devonian slate and limestone;
Sss = Silurian slate interclated with sandstone.

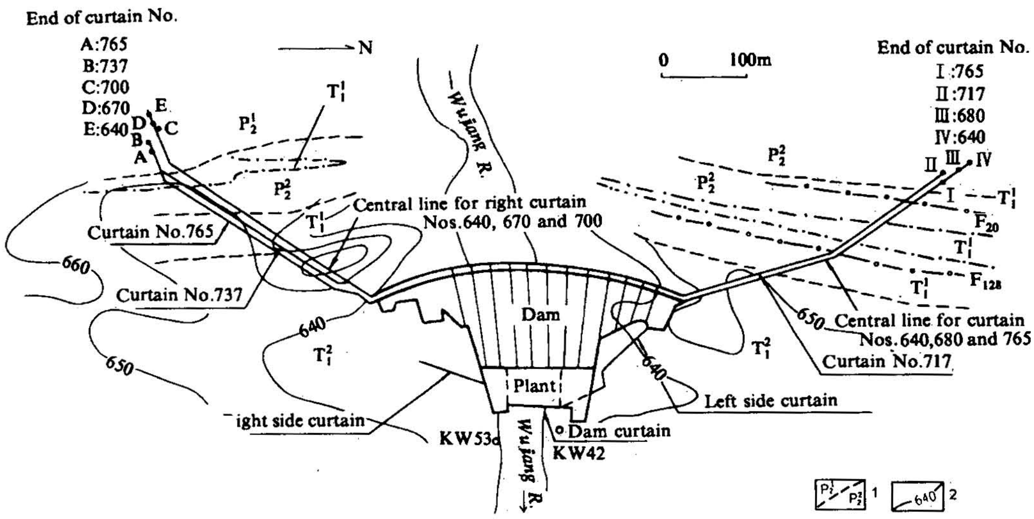

Fig. 3. Plan of grouting curtains for leakage control of the Wujiangdu Dam.
T_1^2 = Triassic limestone; T_1^1 = Triassic shale; P_2^2 = Permian limestone; P_2^1 = Permian coal formation.
1. Stratigraphy boundary; 2. groundwater contour (m) before reservoir construction. 765, 737, 717···denote the elevations (m) of the galleries for curtain grouting.

3578 m under the control of lithology and deep faults (Fig. 2). Along a valley, 3.5 km in length and 250 m in width, very thick tufa has been deposited (Liu et al, 1995). Because of the yellow colour of the tufa and its morphological resemblance to the shape of a dragon, the location is named the Huanglong (which means Yellow Dragon in Chinese) Ravine.

1.3 Wujiangdu Hydropower Station of Guizhou

The station is one of the biggest hydroelectric projects built in karst areas of China. Its dam

Table 1 Analytical data of $\delta^{13}C$ and hydrochemistry in the system of carbonate–H_2O–CO_2 of the Guilin Karst Experimental Site, Huanglong of Sichuan, and Wujiangdu Dam Site

System	Sample type	$\delta^{13}C$ (‰)	Water temp. (℃)	pH	HCO_3^- (mg / l)	CO_3^{2-} (mg / l)	OH^- (mg / l)	Ca^{2+} (mg / l)	P_{CO_2} (*Pa*)	SIc
Guilin Karst Exp. Site	D_{3r} limestone	0.9	–	–	–	–	–	–	–	–
	soil CO_2	−20.7	–	–	–	–	–	–	–	–
	S25 sinter	−8.0	–	–	–	–	–	–	–	–
	S54 sinter	−8.2	–	–	–	–	–	–	–	–
	S29 spr. water	−12.4	19.2	6.98	257.42	–	–	88.80	2491	−0.20
	S31 spr. water	−12.6	19.4	7.02	237.90	–	–	84.00	2110	−0.20
	S54 spr. water	−12.1	16.1	7.13	245.22	–	–	88.40	1651	−0.11
	S55 spr. water	−12.4	17.1	7.18	203.13	–	–	76.40	1233	−0.18
	S291 spr. water	−10.6	19.8	7.50	225.70	–	–	82.40	659	0.24
Huang–long Ravine	C–P limestone	3.0	–	–	–	–	–	–	–	–
	spr. CO_2 gas[1]	−6.8	–	–	–	–	–	–	–	–
	spring water	–	6.3	6.41	774.70	–	–	202.00	26000	−0.20
	water / tufa(8)	2.7 / 4.1	7.8	7.86	658.80	–	–	174.80	790	1.16
	water / tufa(7)	2.9 / 4.0	4.9	8.13	298.29	–	–	80.00	200	0.77
	water / tufa(6)	2.0 / 4.1	5.3	8.33	265.96	–	–	65.20	110	0.85
	water / tufa(5)	2.9 / 4.7	5.7	8.44	301.95	–	–	72.80	98	1.06
	water / tufa(4)	3.1 / 4.5	5.7	8.49	292.80	–	–	76.00	85	1.11
	water / tufa(3)	3.3 / 4.5	5.6	8.41	263.52	–	–	66.40	92	0.93
	water / tufa(2)	3.7 / 5.5	6.4	8.47	287.92	–	–	62.40	88	1.02
	water / tufa(1)	3.5 / 5.1	7.0	8.43	262.91	–	–	66.00	88	1.06
Wu–Jiangdu Dam Site	Permian lim.	3.0	–	–	–	–	–	–	–	–
	stalag. (L765)	−10.4	–	–	–	–	–	–	–	–
	soda str.(L717)[2]	−19.5	–	–	–	–	–	–	–	–
	stalag. (L717)[2]	−27.0	–	–	–	–	–	–	–	–
	stalag. (L765)[2]	−30.0	–	–	–	–	–	–	–	–
	seep. water (R640)[3]	−19.3	17.6	12.56	0.00	39.60	381.82	399.20	0	3.17
	drain. water (R700)[4]	−23.0	17.6	12.02	0.00	34.80	113.22	135.20	0	1.77
	seep. water (L765)	−12.7	17.3	7.57	289.75	0.00	0.00	99.20	700	0.44
	boreh. water (L640)	−11.3	18.5	7.17	282.43	0.00	0.00	91.20	1730	0.00
	spring water	−13.4	17.1	7.40	277.55	0.00	0.00	123.20	981	0.30

Notes: P_{CO_2} = CO_2 partial pressure of water; SIc = saturation index of calcite; S25, S54 and S55: epikarst springs and their numbers; S29 and S291: springs in aeration zone; S31: spring in saturation zone; water / tufa(8)-water / tufa(1): observation stations from the upper reaches to lower reaches of the Huanglong River (Fig. 2); R640 and R700: grouting galleries on the right side and their elevations; L640, L717 and L765: grouting galleries on the left side and their elevation.

1: $\delta^{13}C$ of total dissolved carbon in thermal spring waters in the Tengchong volcanic area and Erdaohai geothermal area are −9.8‰ and −4.8‰ respectively; 2: soda straw and stalagmite of concrete seepage water origin; 3: seepage water from concrete; 4: drainage water from borehole through curtain.

is as high as 165 m. In the station, huge curtains, located in the dam foundations and on both banks of the Wujiang River, were built by means of high–pressure cement grouting to prevent serious leakage (Fig. 3). These grout curtains are leakproof on the whole; however, tufa deposits such as soda straw and stalagmite appear in large amounts in the galleries for curtain grouting (Liu et al, 1994; Liu, 1996). Relevant study (Liu, 1996) has indicated that the leakage water in the galleries is mainly derived from groundwater.

2 Methods and Results

The following methods were adopted in the study: (1) Samples of limestone and tufa were collected from the study area. Water samples for $\delta^{13}C$ analysis were filled in a 2500 ml plastic bucket, and then the total dissolved inorganic carbon (TDIC) in water was deposited by adding saturated $BaCl_2$–KOH solution to water to produce $BaCO_3$ on the spot. The CO_2 gas samples for $\delta^{13}C$ analysis were collected in 600 ml plastic bottles with the air exhausting method. All these samples were analysed for $\delta^{13}C$ in the laboratory. (2) Water temperature, pH, HCO_3^-, Ca^{2+}, and CO_2 partial pressure in air and soil were measured in situ. (3) The saturation index of calcite (SIc) and CO_2 partial pressure P_{CO_2} of water were calculated with SOLMINEQ88 (Kharaka et al, 1988).

Table 1 and Fig.4 show some results of this study. For comparison and calculation, Table 1 also lists the $\delta^{13}C$ of CO_2 gas in the Tengchong volcanic area of Yunnan Province and the Erdaohai geothermal field of Sichuan Province.

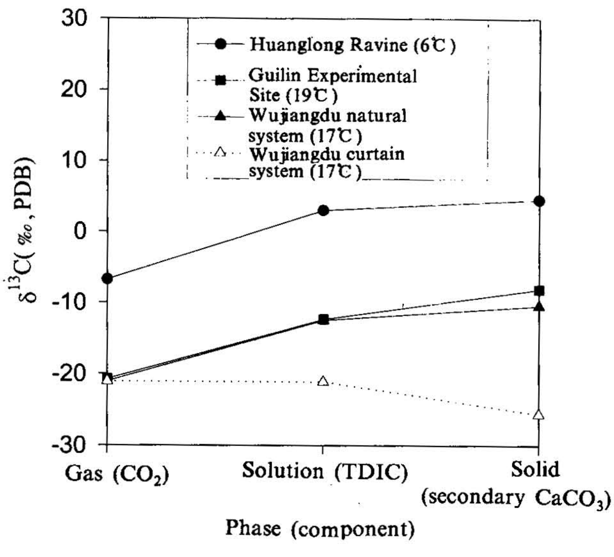

Fig. 4. Features of $\delta^{13}C$ in different carbonate–H_2O–CO_2 systems.

3 Discussion and Conclusion

3.1 Source of CO_2 in the systems

The solubility of carbonate is very low in pure water. The solubility and dissolution rate, however, increase markedly in the water with CO_2. (Liu, 1992). So it is very important to know the source of CO_2 in the study of karst processes. For this purpose, one can make use of information obtained from carbon isotope and hydrochemical studies.

It is known that the annual mean air temperature is 19℃ in the Guilin Karst Experimental Site; then, according to Deines (1974), the enrichment factor would be −8.4‰ when isotopic equilibrium between gaseous CO_2 and HCO_3^- is attained at this temperature under open system conditions. Given the mean value of −12.4‰ for $\delta^{13}C$ of HCO_3^- in spring waters (Table 1 and Fig.4, with the exception of S291, see below), then the $\delta^{13}C$ of CO_2 gas in the system is −20.8‰ [−8.4+(−12.4)]. This is in good agreement with the measured $\delta^{13}C$ value for soil CO_2 gas (−20.7‰, Table 1), which implies that the CO_2 supplied for calcite dissolution comes from soil in the site and also indicates a good relationship between the HCO_3^- concentration of epikarst spring and soil CO_2 partial pressure (Liu, 1992). Furthermore, these prove that the system is open to the air with CO_2.

In light of the same principle, we find that the $\delta^{13}C$ of CO_2 gas is −21.1‰ in the Wujiangdu natural karst system. This value falls into the range (−18-−28‰) of $\delta^{13}C$ of soil CO_2 gas given by Galimov (1966), which means that the CO_2 for karst processes in the system is also mainly derived from soil.

The $\delta^{13}C$ of CO_2 gas in springs of the Huanglong Ravine has been determined to be −6.8‰ (Table 1). This value falls in the range of $\delta^{13}C$ for CO_2 originating from the deep part of the earth or from the atmosphere (Craig, 1953). It is, however, different from that of biological soil CO_2. In addition, as the CO_2 partial pressure of the spring waters (>0.2 atm) is several hundred times as high as that of the atmosphere and dozens of times as large as that of soil gas, it is inferred that the CO_2 in the karst system of the Huanglong Ravine is not of atmospheric origin nor of soil origin, but juvenile or metamorphic. According to the geological conditions and the characteristics of $\delta^{13}C$, the CO_2 in the system may be the mixture of juvenile CO_2 and the CO_2 produced by decomposing of limestone ($CaCO_3 \rightarrow CO_2 + H_2O$). Taking the $\delta^{13}C$ of limestone at the Huanglong Ravine as 3.0‰ (Table 1) and assuming the decomposition of limestone is complete, then the $\delta^{13}C$ of CO_2 thus formed is also 3.0‰. On the other hand, the CO_2 in the Tengchong volcanic area of Yunnan Province could be considered to be mainly of juvenile origin due to the absence of limestone, so the value of $\delta^{13}C = -9.8‰$ (Table 1) can be regarded as a typical value for the CO_2. Suppose CO_2 resulting from limestone decomposition makes up x percent of the total CO_2 content in Huanglong springs, then the juvenile CO_2 accounts for (100−x) percent, so according to the mass balance of isotopes, we have

$$x \cdot \delta^{13}C_{limstone} + (100-x)\delta^{13}C_{juvenile} = 100 \cdot \delta^{13}C_{CO_2}$$

hence, $x \approx 23$, i.e. 23% of the total CO_2 content in Huanglong springs originated from decomposition of limestone, and the rest (77%) is juvenile.

Same kind of calculation shows that 39% of the total CO_2 content in the Erdaohai geothermal springs came from decomposition of limestone and that the rest (61%) is juvenile.

3.2 High $\delta^{13}C$ in Spring S291 of the Guilin Experimental Site

As shown in Table 1, spring S291 has the highest $\delta^{13}C$ in the springs of the Guilin Experimental Site. The spring is intermittent. It issues only after heavy rain, and becomes an open puddle usually. The water samples discussed here were taken from the puddle when no rain.

In the puddle, water is in a relatively static state, so the influence of the atmosphere is pronounced. This is reflected by the higher pH, low CO_2 partial pressure and positive calcite saturation index (Table 1) of spring S291. These hydrochemical features are related to degassing of CO_2 and deposition of $CaCO_3$, i.e.

$$Ca^{2+}+2HCO_3^- \rightarrow CaCO_3 \downarrow +CO_2\ (g) \uparrow +H_2O$$

Without doubt, the presence of this chemical reaction will influence the $\delta^{13}C$ of the total dissolved inorganic carbon of water. When isotopic equilibrium is reached, ^{12}C will be rich in the phase of CO_2 (g), and ^{13}C will be richer in $CaCO_3$ than in HCO_3^-. However, the isotopic fractionation between CO_2 (g) and HCO_3^- is much larger than that between $CaCO_3$ and HCO_3^-. According to the above reaction degassing of every 1 mole CO_2 will produce 1 mole of $CaCO_3$ deposits. So the carbon rich in ^{12}C is removed from water, and accordingly ^{13}C remains in HCO_3^-. This process results in the appearance of higher $\delta^{13}C$ in spring S291.

3.3 Formation of tufa in Wujiangdu galleries

Field observation found that there are two kinds of tufa in Wujiangdu galleries. One (type 1) is related to normal karst seepage water with pH< 8, and the other (type 2) is related to seepage water or / and drainage water with pH>>8 from concrete or / and cement grouting curtains. The deposition rate of type 2 is usually tens or hundreds of times as large as that of type 1. Moreover, the water that produces type 2 has not only a high pH value but also a high calcite saturation index, which contrasts with the water that produces type 1, which has a low pH value and a low calcite saturation index (Table 1).

There are also differences in features of $\delta^{13}C$ and carbon isotope evolution of the two systems that produce the two kinds of tufa. The Wujiandu natural karst system has similar $\delta^{13}C$ and isotopic evolution to those of the Guilin Karst Experimental Site. This shows that the tufa in both of them is formed under natural conditions, i.e., by carbonate dissolution in groundwater under the effect of soil CO_2 and redeposition due to the degassing of CO_2 from groundwater. According to Liu and He (1994) and Liu (1996), the tufa related to seepage water from concrete or drainage water from grouting curtains is formed by an entirely different mechanism and is the result of the following CO_2–absorbing reaction:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow +H_2O$$

where $Ca(OH)_2$ is a product of cement hydration and left in the concrete and curtains and CO_2 is mainly from soil. The CO_2–absorbing rate is very fast, and the carbon in water almost all comes from CO_2, so there occurs almost no fractionation between the total dissolved inorganic carbon and CO_2 gas (Fig. 4).

3.4 Kinetic fractionation of carbon isotope during calcite deposition

According to Deines (1974), during calcite deposition, when isotopic equilibrium is reached, isotopic enrichment factors between HCO_3^- and $CaCO_3$ ($\varepsilon_{HCO_3^- - CaCO_3}$) are −2.2‰, −2.1‰ and −2.0‰ at 5℃, 10℃ and 20℃, respectively. From Table 1 and Fig. 4, only the Wujiangdu natural karst system has similar values of $\varepsilon_{HCO_3^- - CaCO_3}$ (−2.07‰), i.e., isotopic exchange equilibrium has been reached. The values of $\varepsilon_{HCO_3^- - CaCO_3}$ in the Guilin Karst Experimental Site and Huanlong Ravine are −1.59‰ and −4.24‰, which are both deviated from the equilibrium fractionation value and show the occurrence of kinetic isotope fractionation during calcite deposition. According to Turner (1982), the enrichment of ^{13}C in calcite decreases with increasing deposition rate. In other words, the fractionation between HCO_3^- and $CaCO_3$ is unimportant. It is known that the calcite deposition rate is in the range of 1–5 mm / year in the Huanglong Ravine. This value is much higher than that in the Wujiangdu natural karst system, which may be the reason for the lower $\varepsilon_{HCO_3^- - CaCO_3}$ (absolute value) in the Huanglong Ravine. The high absolute $\varepsilon_{HCO_3^- - CaCO_3}$ value (−4.24‰) in the Guilin Experimental Site may be related to the lowest calcite deposition rate, which is most favourable to the enrichment of ^{13}C in $CaCO_3$ and thus the fractionation between HCO_3^- and $CaCO_3$.

3.5 Problem in carbon−14 dating of geothermal tufa

The principle of carbon−14 dating of tufa is as follows:

Before deposition of calcium carbonate, ^{14}C in water is active in the natural exchange cycle, i.e., the content of ^{14}C in water is the same as that in the exchangeable carbon reservoir. With the beginning of deposition, calcium carbonate has no longer exchange with surroundings (e.g. atmosphere and water). Because there is no replenishment of ^{14}C, primary radioactive ^{14}C decreases according to the decay law, and then timing begins. The formula for dating is:

$$t = 8035 \ln (A_0 / A_{sample})$$

where A_0 and A_{sample} are specific radioactivities of ^{14}C in the exchangeable reservoir and in the sample t years after stopping exchange, respectively.

Therefore the prerequisite for C−14 dating is that there is radioactive ^{14}C in the measured sample. However, for the tufa of geothermal origin, such as the tufa at Huanglong, there is almost no ^{14}C because the dissolution of old carbonate minerals prior to deposition was mainly driven by metamorphic and juvenile CO_2, which has no ^{14}C and belongs to "dead carbon". So, it is inappropriate to determine the age of such kind of tufa with the C−14 dating method. If there is ^{14}C in the tufa, it would be mainly obtained by means of the exchange with the atmosphere or / and biosphere after deposition. Thus the age of tufa determined by this kind of ^{14}C is unreasonable and doubtful.

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