# COMPOSITIONS OF $\delta^{18}$ O AND $\delta^{13}$ C IN VARIOUS CARBONATES OF CORE RM IN THE ZOIGÊ BASIN AND CLIMATIC SIGNIFICANCE

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**ABSTRACT:** The hole RM, the deepest one fully obtained core in the Qinghai-Xizang Plateau, situated in the depositional center of the Zoigê Basin (33°57′N; 102° 21′E) in the northeastern Qinghai-Xizang Plateau with a depth of 310.46 m. From <sup>14</sup>C dating and paleomagnetic stratigraphic study, the core RM can date back to 900 ka B.P.. In this paper we analyzed the compositions of  $\delta^{18}$ O and  $\delta^{13}$ C in various carbonates can date (snail, obstrode, chemical carbonate) in core RM and discussed preferably the paleoclimatic record by the proxies of  $\delta^{18}$ O and  $\delta^{13}$ C of chemical carbonate (authicarbonate) from core RM in the past 140 ka. The results showed that the values of  $\delta^{18}$ O in various carbonates are generally identical, and the values of  $\delta^{13}$ C in it are inconsistent, while there exist better relativity. The studies also demonstrated that there was a negative correlation between  $\delta^{18}$ O and  $\delta^{13}$ C of authicarbonate in core RM in the past 140 ka, showing that the changes of  $\delta^{18}$ O values were mainly relative to the water temperature. According to above, the climatic evolutionary sequence were rebuilt in the past 140 ka in the region.

KEY WORDS: Zoige Basin, authicarbonate, stable isotope, paleoclimate

The hole RM, the deepest one fully obtained core in the Qinghai-Xizang Plateau, situated in the depositional center of the Zoigê Basin (33° 57′N; 102° 21′E) in the northeastern Qinghai-Xizang Plateau with a depth of 310.46 m. From <sup>14</sup>C dating and paleomagnetic stratigraphic study, the core RM can date back to 900 ka B.P..

The Zoigê Basin is situated in the east of the Qinghai-Xizang Plateau with the height of 3400 m a. s. l. and belongs to a plateau subfrigid zone, where there is herb peat mire. The Huanghe (Yellow) River flowed through the basin no more than 20 ka and the sediments of paleolake contained high authicarbonate. Therefore, this is an ideal region to research the change of paleoclimate. Here we analyzed the compositions of  $\delta^{18}$ O and  $\delta^{13}$ C in various carbonates (snail, obstrode, chemical carbonate) in core RM and discussed preferably the paleoclimatic record by  $\delta^{18}$ O and  $\delta^{13}$ C of authicarbonate from core RM in the past 140 ka.

### I. EXPERIMENTAL METHODS

The determination of stable isotope in snail is finished as follows:

- (1) Shells are cleaned with supersonic vibration in distilled water, dried and ground into powder.
  - (2) The samples are baked at 475°C to remove organic matter.
- (3) The pretreated samples are dissolved in 100%  $H_3PO_4$  at 25°C for 6–8 hours under a vacuum state. The released  $CO_2$  was separated and purified by liquid nitrogen, then  $\delta^{18}O$  and  $\delta^{13}C$  are measured in a Finingen Model 251 mass spectrometer expressed in the conventional  $\delta^{13}C$  with the standard PDB.

The determination of stable isotope in chemical carbonate is finished as follows:

First, the right amount samples are weighted and solved with water. Second, the liquid is filtered by sieve with 0.005 mm diameter core and centrifugalized. Then, the treated samples are dried and ground. The last process is similar to (3) mentioned above.

The analytical precision of the  $\delta^{18}\,\text{O}$  and  $\delta^{13}\,\text{C}$  for carbonate samples is  $\pm\,0.\,2\%$  and  $\pm\,0.\,1\%$  respectively.

#### II. EXPERIMENTAL RESULTS AND PALEOCLIMATIC ANALYSES

## 1. Experimental Results

Table 1 is the result of the determination of  $\delta^{18}O$  and  $\delta^{13}C$  of the snails in 30 strata and that of the authiocarbonate in the respective strata, it also contains  $\delta^{18}O$  and  $\delta^{13}C$  of snails, obstrodes and shells in the same strata as well as different sections of the same snail.

Table 1 shows that the composition of  $\delta^{18}O$  in lake authicarbonates is closely corresponding to that of snails, the difference is within  $\pm$  %. The difference in the values of  $\delta^{13}C$  between snails and authicarbonates is obvious, and the latter is richer heavy carbon isotope. The main reason is that their mineral composition is different, and so does the mechanism of stable isotope separation, but the change of their values of  $\delta^{13}C$  has a good well correlation. Comparison of the composition of  $\delta^{18}O$  and  $\delta^{13}C$  of snails and obstrodes in the same strata, the latter enriched heavy carbon isotope, but their composition of  $\delta^{18}O$  was identical (Table 1). The same results are drawn by analyzing various sections of a snail. The main reasons are as follows. (1) Various minerals have the different mechanism of stable isotope separation, snails consist of calcite, obstrodes are aragonite, calciteen enriches heavy carbon isotope(Rubinson *et al.*, 1969). (2) Various organisms or organism at different living period has different metabolism pattern or intensity, in other words, the amount of  $CO_2$  produced by organism during metabolism process is different, which influence the composition of shell carbon isotope, but the influence was little to their values of  $\delta^{18}O$ . The change of  $\delta^{18}O$  in shells are complex, and the mineral compositions

Table 1 The results of  $\delta^{18}\mathrm{O}$  and  $\delta^{13}\mathrm{C}$  in vaqrious carbonates in core RM

Depth		Snails		Authicarbonates	
(m)	δ <sup>13</sup> C	$\delta^{18}{ m O}$	$\delta^{13}\mathrm{C}$	$\delta^{18}{ m O}$	
14.08	-7.3	-14.654	- 10.771	- 4.968	
22.8	-9.558	-10.627	-9.896	-6.637	
31.9	-9.127	-8.749	- 10.387	-5.806	
43.21	-4.849	-9.262	-8.565	-3.201	
82.15*	-4.694	-12.224			
82.15	-6.611	-11.71	- 12.458	-0.911	
82.15 * *	-6.485	-11.904			
83.06	-6.668	-11.84	-12.081	-1.366	
86.47	7.414	-12.667	-11.608	-1.081	
87.47	0.261	-10.62	-10.431	4.279	
97.07	-5.724	-10.524	-12.094	-2.375	
131.6	-2.221	-10.876	-9.965	0.336	
134.11	-6.766	-12.711	-13.693	1.237	
136.06	-1.267	-8.517	-7.764	0.362	
166.27	-0.269	-8.626	-9.324	0.405	
181.79	-4.449	- 10.961	-11.26	-1.515	
201.42	-4.215	-11.006	- 10.295	-0.327	
218.92	-4.412	- 13.698	- 14.967	-0.417	
219.49	5.523	-9.32	-12.649	3.799	
232.62	-2.121	- 12.023	- 12.647	3.79	
232.98	7.411	-7.832	-8.801	11.618	
247.67	-3.24	- 10.601	- 10.693	-0.918	
253.67*	-3.669	- 10. 263			
253.67	-4.883	-9.933	- 10.01	-1.498	
253.67**	-5.122	- 9.986			
259.96	-7.422	-18.302	- 11.733	2.403	
261.83	-6.716	-7.833	-9.358	-2.385	
270.02	-3.353	-12.028	- 12. 194	1.988	
283.5	-4.677	-6.094	-7.813	-0.62	
287.15	-9.124	-8.651	-9.098	-5.543	
299.29	-5.829	-8.503	- 10.593	-3.724	
301.47	-4.486	-13.754	-14.738	-1.738	
305.82	-6.934	-7.967	-7.993	-1.644	
Depth	Snails		Obstrodes		
(m)	$\delta^{13}$ C	$\delta^{18}{ m O}$	$\delta^{13}\mathrm{C}$	8 <sup>18</sup> O	
195.06	-6.242	-12.655	-3.177	-11.669	
257.96	-5.792	-11.422	-3.745	- 11.05	
305.98	-6.152	-6.21	-0.851	-7.088	
Depth	Snail		Shell		
(m)	$\delta^{13}$ C	δ <sup>18</sup> O	δ <sup>13</sup> C	δ <sup>18</sup> O	
209.92	-5.603	- 10. 161	-7.523	-11.302	

<sup>\*</sup> bottom section of snail, \* \* top section of snail

of shells are unidentifiable (Stuiver, 1970). So the composition of stable isotope in shells is not ideal proxy of paleoclimate.

The above analysis shows that the values of  $\delta^{18}O$  in various carbonates are generally identical and the difference between them is rather small. Therefore, we could regard  $\delta^{18}O$  and  $\delta^{13}C$  in lake carbonates in core RM as climatic proxy to rebuild paleoclimate in the Zoigê Basin. But, because of the discontinuous distribution of snails and the little amount of snail in samples, it is difficult to obtain high resolution paleoclimatic sequences. We thus chose  $\delta^{18}O$  and  $\delta^{13}C$  of authicarbonate as proxy of climate to study the features of paleoclimate evolution.

# 2. Paleoclimatic Proxies of δ<sup>18</sup>O and δ<sup>13</sup>C in Lake Authicarbonate

The values of  $\delta^{18}$ O in lake authicarbonate are controlled by water temperature and water oxygen isotope, and the latter is relative to the  $\delta^{18}$ O of precipitation, evaporation and residence time of lake water (Bowen, 1990). When the isotope composition of lake water is constant, the various values of  $\delta^{18}$ O in lake authicarbonate reflects the fluctuation of respective water temperature, and the higher the temperature is, the heavier the oxygen isotope of lake authicarbonate is (Savin, 1977; Burcharott, 1980; Abell, 1985). But in some conditions, the isotope composition of lake water in which lake authicarbonate is deposited has a evident effect on it, for instance, when lake water is rich in heavy oxygen isotope due to intensive evaporation, consequently, the  $\delta^{18}$ O value of authicarbonate happen to change. And it also relates to the hydrological regime and icy water with light oxygen isotope around the particular basin. However, the information of the paleotemperature contained by oxygen isotope proxy can still be qualitatively obtained referring to the analyses of the carbon isotope of authicarbonate (Wu, 1997).

The values of  $\delta^{13}$ C in lake authicarbonate is connected to the exchange between carbon dioxide in the atmosphere and aquatic carbon, the hardness of the lake water and aquatic biological productivity etc. . But the changes of the  $\delta^{13}$ C values are mainly governed by the hardness of lake water(Mook, 1980; Emrich *et al.*, 1970; Rubinson *et al.*, 1969), and it is rich in heavy carbon isotope with respect to the high hardness of lake water. When a lake is evolving at the stage, in which only carbonate is deposited, the variations in the hardness of lake water indicate the degree of the condensation of water body. Therefore, the high salinity is response to the high values of carbon isotope and has an advantage of enrichment of the heavy oxygen. The changes in  $\delta^{18}$ O are thus mainly controlled by water temperature responsibly if the  $\delta^{18}$ O value correlate negatively with  $\delta^{13}$ C, namely, the higher  $\delta^{18}$ O value responding to Thermochron, on the contrary, the lower  $\delta^{18}$ O value to Kryochron. The fluctuation of the  $\delta^{18}$ O values in authicarbonate mainly reflects that  $\delta^{18}$ O values correlate definitely with  $\delta^{13}$ C, and the high values of  $\delta^{18}$ O indicates the high hardness of lake water, suggesting that lake evaluates the stage of the condensation of water body. On the contrary, lake is the refreshing stage(Wu, 1997).

## 3.1 The chronological sequence establishment

Based on the consolidation model of lake sediment (Rubinson, 1969), together with <sup>14</sup>C dating and paleomagnetic stratigraphy (Table 2), the ages of each stage and responsible sample depth have been obtained (Fig. 1).

Depth (m)	Ages (a B.P.)	Dating methods	
2.6	3324 ± 145	<sup>14</sup> C	
. 2.8	$3428 \pm 124$	<sup>14</sup> C	
4.1	6167 ± 155	<sup>14</sup> C	
6.3	$21600 \pm 1500$	<sup>14</sup> C	
8.2	$33140\pm2305$	<sup>14</sup> C	
25.0	110000(Blake Event)	paleomagnetic	

Table 2 Dating ages of various layers in core RM

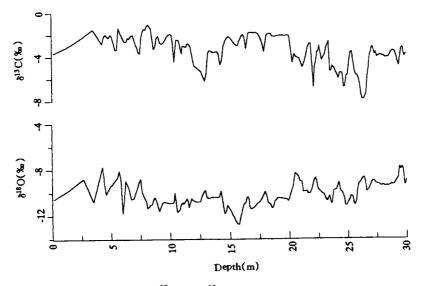


Fig. 1 Curves of δ<sup>18</sup>O and δ<sup>13</sup>C in authicarbonate of core RM

# 3.2 Climatic features in the past 140ka

The  $\delta^{18}$ O values of carbonate in the past 140ka changed from -7.7% to -12.8% (PDB) with the maximum magnitude of 5%, and the subordinate fluctuations are very obvious. All these basically reflect the characteristics of paleoclimate change. Moreover, in response to the sections of high values of oxygen isotope, the values of carbon isotope fluctuate intensively, the maximum magnitude of 5% (from -7.7% to -12.8%), indicating that the factors controlling the carbon isotope are more complicated in the warm periods. But oxygen isotope correlate negatively with carbon isotope, suggesting that the changes in  $\delta^{18}$ O are mainly controlled by wa-

ter temperature. According to the changes of the paleoclimatic proxies of  $\delta^{18}O$  and  $\delta^{13}C$  (Fig. 1), the several evolutionary stages in the past 140 ka may be distinguished as follows:

Unit 1: 31-20 m (140-80 ka B.P.) The sediments mainly consist of muddy silts contained organic remains and shell, with horizontal and wavy bedding. High  $\delta^{18}$ O with an average of -9.8% and low  $\delta^{13}$ C with the average of -4.52%, indicating a warm climate. But there are internally obvious subordinate fluctuations of  $\delta^{18}$ O and  $\delta^{13}$ C, reflecting an unstable climate. Low carbonate content and lower  $\delta^{13}$ C show the stronger exchange of  $CO_2$  between lake water and atmosphere, abundant biomass and intensive organic geochemical process. Therefore, the stage has an optimum heating and moisture association representing the warm and humid climate. According to the characters of the change of  $\delta^{18}$ O, this period can be compared to the oxygen isotope stage 5 recorded in the Greenland Ice Core Project(GRIP)(1993), among which two rapid cooling events existed in the substage 5e, one cold event occurred in the substage 5a, while 5c represents a relatively weak warm period, reflecting during the stage the climate was unstable.

Unit 2: 20-14 m (80-60 ka B.P.) The gray muddy silts are predominant, alternating silty mud, occasionally siderite nodules and patches. The lowest  $\delta^{18}O(-11.8\%)$  and highest  $\delta^{13}C$  of the section suggest that the cold climate and the peak content of carbonate reflect high hardness of the lake water, implying a cold and dry climatic period.

Unit 3: 14-8 m(60-30 ka B. P.) The sediments mainly consist of muddy silt, silt, silty mud as well as thin peat layers and fossil gastropod shell. The value of  $^{18}\text{O}$  has a increasing trend, reflecting that the temperature began to rise. The low content of carbonate, lower  $\delta^{13}\text{C}$  and higher organic matter content show a temperate and wet climatic conditions.

Unit 4: 8-0 m (30-1 ka B. P.) The sediments are mainly yellow, grayish yellow thick-layered sands with some lenticular bedding, a scour surface and disturbing structure at the bottom, showing that the fast filling sediments were caused by rivers. The Zoige paleolake was captured by the Huanghe River in the period, and the upper sand layer was formed by the Heihe River sediment after the Heihe River delta extended to the lake until the lake disappearance (Wang, 1995). Because of the dominant fluvial sediments,  $\delta^{18}$ O and  $\delta^{13}$ C of carbonate were positively correlated each other, and, because of the action of land carbonate, the values of  $\delta^{18}$ O were high, representing that the water environment was instable. Therefore, the information about paleoclimate failed to be drawn clearly from it. As the core was located in the first terrace of the Heihe River, the sediment over the past 1ka was lack.

## III. CONCLUSIONS AND DISCUSSION

By analyzing the compositions of  $\delta^{18}O$  and  $\delta^{13}C$  in various carbonates (snail, obstrode, chemical carbonate) in core RM, we can conclude that the values of  $\delta^{18}O$  in various carbonates deposited in the same period in the Zoigê basin are generally identical, and that the changes of stable isotope have a close correlation to water temperature. The studies of stable isotope of au-

thicarbonate in the past 140 ka suggest that 140-80 ka B.P., the climate condition was warm and wet, with obvious subordinate fluctuations, In this period, the condition of heat and moisture was optimum, causing the high lake biomass. The period is equivalent to stage 5 described in the deep-sea oxygen isotope. The stage 80-60 ka B.P., was equivalent to a cold and dry climate period. The period of 60-30 ka B.P. was mild and wet. After 30 ka B.P., the paleo-lake disappeared and the lacustrine sediments were replaced by fluvial sediments. Meanwhile, the climatic significance of oxygen isotope became indistinct, just reflecting the rapid environmental shift with the lake disappearance.

#### REFERENCES

- Abell P., 1985. Oxygen isotope ratios in modern African gastroped shells: a data base for paleoclimatology. *Chem. Geol.*, *Isotope Geosci.*, 58:183-93.
- Burcharott B., Fritz P., 1980. Environmental isotopes as environmental and climatological indicators. In: *Handbook of Envi*ronmental Isotope Geochemistry, Part I. eds P. Fritz and J. C. Fontes. Amsterdam, London, New York: Elsevier Scientific Publishers, 75 – 140.
- Bowen R. 1990. Isotopes and Climates. Elsevier Applied Science.
- Emrich K. et al., 1970. Carbon isotope fractionation during the precipitation of calcium carbonate. Earth planet. Sci. Letts., 8:363-71
- GRIP members, 1993. Climate instability during the last interglacial period recorded in the GRIP ice core. *Nature*, 364:203 207.
- Mook W., 1980. Carbon 13 in hydrogeological studies. In: Handbook of Environmental Isotope Geochemistry, part I. eds P. Fritz and J. C. Fontes. Amsterdam; Elsevier Scientific Publishers.
- Rubinson M., Clayton N., 1969. Carbon 13 fractionation between aragonite and calcite. Geochim. Cosmochim. Acta., 33: 997.
- Rubinson M., Clayton R. N., 1969. Carbon 13 fraction between aragonite and calcite. Geochim. Cosmochim. Acta, 33:997 – 1002
- Stuiver M., 1970. Oxygen and carbon isotope ratios of fresh water carbonates as climatic indicators. *J. Geophy. Res.*, 75: 5247-57.
- Savin S., 1977. The history of the earth's surface temperature during the past 100 million years. Ann. Rev. Earth Planet. Sci. 5:319-35
- Wu Jinglu, Wang Sumin, 1977. Climatic variation during the last interglacial period recorded in the lake carbonate deposit, east Qinghai-Xizang Plateau. Chinese Science Bulletin, 42(12). (in Chinese)
- Wang Yunfei, Wang Sumin, Xue Bin et al., 1995. Sedimentological evidence of the piracy of fossil Zoigê lake by the Yellow River, Chinese Science Bulletin, 40(18):1539. (in Chinese)