Geochemical evidence for non-marine depositional environment of foraminiferal fossils from the Nihewan Basin, China

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Abstract From the first finding in 1970s, the findings of foraminiferal fossil assemblages in inland basins have been reported from time to time, especially in recent years. The debates on the depositional environment of foraminiferal fossils have become the hot spot of researches again in China. Based on the researches of trace element geochemistry and electron scanning microscope of shells of Quaternary foraminiferal fossils from the Xiaodukou section in the inland Nihewan basin, the original $^{87}Sr/^{86}Sr$ and other geochemical information of shells were believed to be preserved well and could be used to rebuild the geochemistry of contemporary waters where foraminifera deposited, although there existed some effects of burial diagenesis on the geochemistry of shells to a certain extent. The $^{87}Sr/^{86}Sr$ ratios of well-preserved Xiaodukou foraminiferal shells were measured, giving a range of 0.711190±25—0.712018±14, apparently higher than the value of contemporary seawater (0.709087—0.709147) and similar to that of the Sanggan River, proving that it represented the value of the ancient lacustrine water. The hyperbolic mixing models of $^{87}Sr/^{86}Sr$-palaeosalinity and $^{87}Sr/^{86}Sr$-Sr/Ca indicated that the contemporary waters where Xiaodukou foraminifera inhabited was an inland lake and there was no seawater input to the depositional environment.

Keywords: continental foraminiferal fossil, burial diagenesis, criteria of $^{87}Sr/^{86}Sr$-palaeosalinity hyperbolic mixing model, criteria of $^{87}Sr/^{86}Sr$-Sr/Ca hyperbolic mixing model, Xiaodukou section.

In the last thirty years, foraminiferal fossil assemblages were found in many typical Quaternary and Early Tertiary continental strata, such as the Tianshuihai Lake in Tibet Plateau[1], the Tarim Basin and the Luobupo Lake in Xinjiang[2], the Nihewan Basin, Hebei Province, the Yuncheng Basin, Shanxi Province, the Qianjiang Basin, Hubei Province, the Jiyang Depression, Shandong Province, and in Cretaceous strata in the Sichuan Basin[3]. There exist two kinds of viewpoints about the depositional environment of those foraminiferal fossil assemblages in academic circles: (i) the inhabitant environment for foraminiferal fossil assemblages has something to do with sea. Advocators of this viewpoint suggested that the strata containing foraminiferal fossil assemblages in the inland areas were formed as a result of transgression[4], or that after the basin containing foraminiferal fossil assemblages was formed it did not close totally and hence there existed "channelways" to connect with the sea and through which seawater could enter the basin irregularly[5], or that the strata represented the weak marine transitional deposits[6]. (ii) Opponents suggested that the inhabitant environment for foraminiferal fossil assemblages has nothing to do with sea. In the inland areas, those basins containing foraminiferal fossils were totally separated from the sea at the beginning of their formation. If the chemical condition of a lake evolved to that of sea, the appearance and development of foraminifera would be possible[7—9]. To sum up, the focus of the debates is on the different characters of contemporary waters where foraminifera deposited. It is well known that different kinds of waters have obviously different geochemical compositions and inorganic particles or biological bodies deposited from them have their geochemical "imprint" to a certain extent. For example, Sr deposited together with biological calcite minerals does not fractionate in any kinds of waters, and if they do not undergo chemical alteration after deposition, Sr-bearing biological calcite minerals will record $^{87}Sr/^{86}Sr$ ratio of contemporary waters where it deposited. So, the $^{87}Sr/^{86}Sr$ ratios of biological calcite minerals can be used to discriminate marine, transitional and continental depositional environments. In the last years, the non-marine genesis of foraminiferal fossil assemblages in the Nihewan Basin was reported briefly by the present authors[9,10]. In this paper, based on the previous work, through the analyses of the detailed geochemical data, the authors postulate the hydrogeochemical characteristics of the ancient Nihewan Lake, and explain the continental genesis of foraminiferal fossil assemblages and lacustrine deposit genesis of foraminiferal fossil assemblages-bearing strata.

1 Geological background of the working section

Xiaodukou, one of the depositional centers for the ancient Nihewan Lake, is located at Yangyuan County, Hebei Province, 300 km away from the modern coastal line and 500 m above sea level. Sanggan River and its tributary Huliu River flow over the Xiaodukou area. In the Xiaodukou section lacustrine and river sediments were intercrossed spatially and temporally from Neogene to Middle Pleistocene, where mammal animals, foraminiferal fossils and plentiful ostracoda and spore fossils were found. Foraminiferal fossils were preserved in the 28th bed[9,11]. The 27th bed consists of yellowish-brown sandy silt interbedded with thin-bedded clay. Interbedded sand and gravel, coarse sand and thin-bedded clay exist at the bottom of the 28th bed, and in descending order of grain size of sands and silts the yellowish-brown sands slowly become fine upwards. The 29th bed is composed of pale brown muddy silt and silt. In the total 10.8m thick strata of the 28th bed, one kind of foraminiferal species "*Nonion shansiensis*" with a great variety of unusually shaped shells among individuals was found, approximately 0.20 mm and 0.10 mm in shell diameter and height, respectively. The distribution density of lacustrine ostracoda in the strata is proportional to that of foraminifera and the amount of those two kinds of microfossils in the sand bed is higher than that in the clay bed on the average. Palaeomagnetic measurements on the Xiaodukou section showed that the Jaramillo palaeomagnetic event (0.90—0.97 Ma) began at the top of the 27th bed and ended at the bottom of the 29th bed[11], the depositional time of the 28th bed was from 970 to 910 thousand years with estimated averaging sedimentation rate being 15.71cm/ka. So, the living time of foraminiferal fossil assemblages in the Xiaodukou section was approximately from 0.99 Ma to 0.91 Ma.

2 Samples and analytical methods

Sedimentary samples for this study, at 25 cm intervals, were collected constantly from the 28th foraminiferal fossil assemblages-bearing bed in the Xiaodukou section of the Nihewan Basin. 1000 g sedimentary samples were soaked in distilled water for 24 h and scattered spontaneously. By using the standard sieve to grade in distilled water, grains, larger than 0.09 mm in diameter, were selected to evaporate till dryness at 80℃—90℃. Then, the dry samples were floated in CCl_4 and foraminiferal fossils were concentrated and hand-picked out carefully under a binoscope as an analytical test at one time. All fossil samples were immersed in H_2O_2 for 1 h, and then repeatedly washed (three times) by using deionized water and ethanol before isotope and trace-element measurement. In order to compare with foraminiferal fossils, continental ostracoda in 22th bed in the Xiaodukou section and 600 ml Sanggan River and the Huliu River water samples were obtained respectively. Water samples were filtered through minipore filter membrane (ϕ 0.45 μm) and evaporated to dryness for measurement.

Test samples were dissolved in 5%HAc. The solution was centrifuged and evaporated to dryness, followed by changing acetate into chloride in 1N HCl and being directly loaded onto the Dowex-50W×8 resin column(200—400 mesh). By using 1N HCl as washing liquid the first 30 ml liquid was discarded and the following 20 ml Sr-rich liquid was collected. The Sr-rich liquid was purified again by passing it through the Dowex-50W×8 resin column(100—200 mesh). The total Sr blank for this procedure was 5×10^{-9} and $^{87}Sr/^{86}Sr$ ratio measured for standard NBS 987 was 0.710296, 2σ mean for 0.0018%. All $^{87}Sr/^{86}Sr$ ratios were measured on Mat-261 mass spectrometer at the Open Laboratory of Isotope, Chinese Academy of Geological Sciences, China. All measured values of samples were corrected by using $^{88}Sr/^{86}Sr$ (8.37521).

Ten selected microfossil particles of each sample were put into small teflon beaker. 4 drops of purified water and 1 drop of nitric acid were loaded along the wall of the beaker successively. After effervescence another drop of nitric acid was added again, then the solution was evaporated to dryness. This procedure was repeated once again and finally 1 drop of nitric acid was added and evaporated to dryness. By using Rh-bearing inner standard solution as dilute liquid 1 ml solution was made for measurement of Ca, Sr, Mn and Rb contents on inductively coupled plasma mass spectrometer (ICP-MS) at Institute of Geochemistry, Chinese Academy of Sciences. In this whole procedure, the total Mn blank was 0.77×10^{-9}, and others were beyond the capacity of ICP-MS. Ca and Sr concentrations of water samples were measured using atomic absorption spectrometry at Institute of Geochemistry, Chinese Academy of Sciences.

3 Analytical results

Analytical results are listed in table 1. The $^{87}Sr/^{86}Sr$ ratios of foraminiferal shells of the Xiaodukou section were measured, giving a range of 0.711190±25—0.712018±14, 0.711515 in average, apparently higher than the value of contemporary seawater (0.709087—0.709147)[12] and similar to the value of the Sanggan River before and after concourse (0.711721±18 and 0.711508±8 respectively), the Huliu River (0.709960±16—0.709997±16) and lacustrine ostracode shells in the 22th bed (0.710564±14). It is obvious that $^{87}Sr/^{86}Sr$ value of ancient lacustrine water represented by ostracode in 22th bed is similar to the value of the modern Sanggan River. The Sanggan River is reasonably considered as representative supply source of lacustrine water in the ancient Nihewan Lake.

Table 1 $^{87}Sr/^{86}Sr$, trace-element contents and its ratios of foraminiferal shells at the Xiaodukou section and river waters

No.	Sample No.	$CaCO_3$(μg)	Mn(10^{-3})	Sr(10^{-6})	Sr/Ca(10^{-3})*	Sr/Mn*	$^{87}Sr/^{86}Sr$
1	28-2	17.91	1.210	1103.3	1.268	0.572	0.711351±14#
2	28-3	19.61	0.790	1087.9	1.250	0.864	
3	28-5	17.93	0.864	1014.1	1.166	0.736	0.711616±13
4	28-6	20.85	0.743	950.6	1.092	0.803	0.711594±15
5	28-7	28.29	0.767	960.3	1.104	0.786	
6	28-9	33.37	0.696	1055.1	1.213	0.951	0.711369±12
7	28-10	26.13	0.623	987.8	1.135	0.996	
8	28-11	51.25	1.012	951.1	1.093	0.589	0.711546±13
9	28-12	32.75	0.780	1028.0	1.182	0.826	0.711190±25
10	28-13	18.58	0.625	980.8	1.127	0.985	0.711502±15
11	28-15	36.64	1.162	1314.1	1.510	0.709	0.711667±10
12	28-16	26.87	1.297	1012.6	1.164	0.490	0.712018±14
13	28-17	24.12	0.610	1070.2	1.230	1.101	0.711296±14
14	22 (Ostracode)	18.41	0.463	1091.7	1.245	1.480	0.710564±14
Average value		27.26	0.860	1039.7	1.195	0.801	0.711515
The Sanggan River before concourse				0.93			0.711721±18
The Sanggan River after concourse		61.5 Ca10^{-6}		0.92	6.829		0.711508±8
The Huliu River							0.709960±16 0.709997±16

*, Atomic ratio; #, average standard error.

The trace element contents of foraminiferal shells at the Xiaodukou section were measured, giving Sr contents in the range of $(950.6—1314.1)\times10^{-6}$, 1039.7×10^{-6} in average, Sr/Ca (atomic ratio) for $(1.092—1.510)\times10^{-3}$, 1.195×10^{-3} in average, Sr/Mn for 0.490—1.101, 0.801 in average. According to the lowest standard of Sr/Mn >0.5 the foraminiferal fossils did not undergo burial diagenesis[13], however, the Mn contents (table 1) of foraminiferal fossils were greater than 300×10^{-6}, implying that it underwent burial diagenesis[13]. Rb and Fe contents are beyond the capacity of ICP-MS ($<10^{-9}$), hence, the effect of radioactive ^{87}Rb to ^{87}Sr can be ignored, especially for younger Quaternary biological shells. Sr content and Sr/Ca of the Sanggan River water are

0.92×10^{-6} and 6.829×10^{-3} respectively.

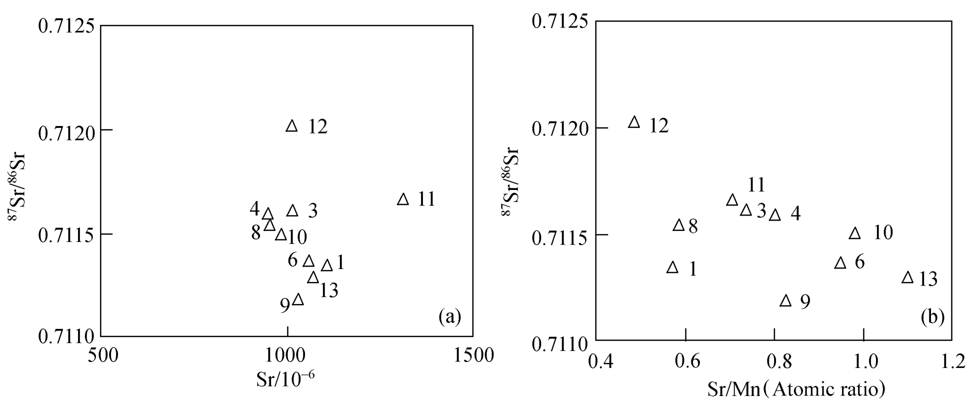
Systematic scanning electron microscopy (SEM) examination showed that most of test samples had clean surface and apparent pore structure in the interior chamber surface and good columnar structure in the chamber wall. However, some test samples with clean outer surface had recrystallization, secondary enlargement and dissolution in the interior chamber surface, and the other materials fill the pores and recrystallization exists in the chamber wall.

4 Discussion

4.1 Burial diagenesis

It was realized for a long time that the structure and texture, chemical components and isotopic compositions of biological shells could be changed by burial diagenesis when biological shells, accompanying with sediments, were deposited and buried[14—17]. A lot of research results[18—23] in recent years demonstrated that the change of structure and texture and appearance of recrystallization and dissolution of the test shells did not mean the change of Sr isotopic composition of the shell, meanwhile, the test shells with clean surface and well-preserved structure and texture determined by SEM did not mean to retain well the initial geochemical information either. So, the change and the change degree of chemical composition of fossil shell cannot be determined and evaluated directly by micro investigation or the sole analysis of trace element, but determined by the difference between the chemical composition of shell and fluid in the burial diagenesis[20].

To evaluate the effect of burial diagenesis on the test samples, $^{87}Sr/^{86}Sr$-Sr and $^{87}Sr/^{86}Sr$-Sr/Mn diagrams were made by using $^{87}Sr/^{86}Sr$, Sr and Sr/Mn data of test samples. $^{87}Sr/^{86}Sr$-Sr data of test samples disperse greatly (fig.1(a)) and do not display the hyperbolic trend which is characteristic indicator of effect of burial diagenesis on the change of Sr isotopic composition of fossil shell[21—23]. In the diagram of $^{87}Sr/^{86}Sr$-Sr/Mn (fig.1(b)), although $^{87}Sr/^{86}Sr$ and Sr/Mn data of test samples show linear relationship outwardly to a certain extent, it does not demonstrate



(The number for sample number) (The number for sample number)

Fig.1. $^{87}Sr/^{86}Sr$-Sr and $^{87}Sr/^{86}Sr$-Sr/Mn plot of foraminiferal fossils.

well-regulated change feature from the top to the bottom or from the middle to the end at the Xiaodukou section (fig.1). This is identical to the change feature of $^{87}Sr/^{86}Sr$ and Sr/Mn data of the modern and well-preserved biological shells and carbonate[23]. Based on the above, original $^{87}Sr/^{86}Sr$ and other geochemical information of foraminiferal shells at the Xiaodukou section was basically preserved and could be used to reconstruct $^{87}Sr/^{86}Sr$ ratio and other chemical composition of contemporary waters where foraminifera deposited.

4.2 Characteristics of contemporary waters where foraminifera deposited

Because the concentration of Sr in marine water is much higher than that in fresh water and there exists big difference of $^{87}Sr/^{86}Sr$ ratio between them, the $^{87}Sr/^{86}Sr$ ratio in the mixed waters between them, such as estuary, bay, is controlled by that of seawater[24—26], i.e. a small amount of seawater input can alter greatly the $^{87}Sr/^{86}Sr$ ratio of mixed water. Taking Sr content (0.93×10^{-6}) and $^{87}Sr/^{86}Sr$ ratio (0.711721) of the Sanggan River before concourse as the end-member of the ancient fresh water and Sr content (8.0×10^{-6}) and $^{87}Sr/^{86}Sr$ ratio (0.709114) of the contemporary seawater as the other end-member of seawater[12], the relationship between $^{87}Sr/^{86}Sr$ and palaeosalinity of mixed waters between seawater and the ancient fresh water could be calculated[26]. The results are shown by curve A in fig. 2. $^{87}Sr/^{86}Sr$ data of test samples are plotted in fig. 2 (because of $^{87}Sr/^{86}Sr$ ratios of part of samples higher than that of the ancient fresh waters it is not shown in fig.2 and their paleaosalinities are determined directly to be 0‰), except test samples 28-12 (0.711190±25) and 28-17 (0.711296±14) in the range of 0.7‰—1‰ in palaeosalinity, and the other samples are less than 0.35‰ in palaeosalinity. If the Sanggan River after concourse was used to replace the end-member of the ancient fresh water, a new hyperbolic mixing curve is obtained (curve B in fig. 2). Except test samples 28-12 and 28-17 in the range of 0.35‰—0.60‰ in palaeosalinity, all the samples were less than 0.35‰ in palaeosalinity and most of them were near to 0‰. If the Sanggan River was reasonably considered as representative supply source of lacustrine water in the ancient Nihewan Lake, according to the calculation of $^{87}Sr/^{86}Sr$-palaeosalinity model, the amount of seawater input in the mixed waters was less than 1%, almost near to 0%, indicating that the depositional environment of foraminiferal

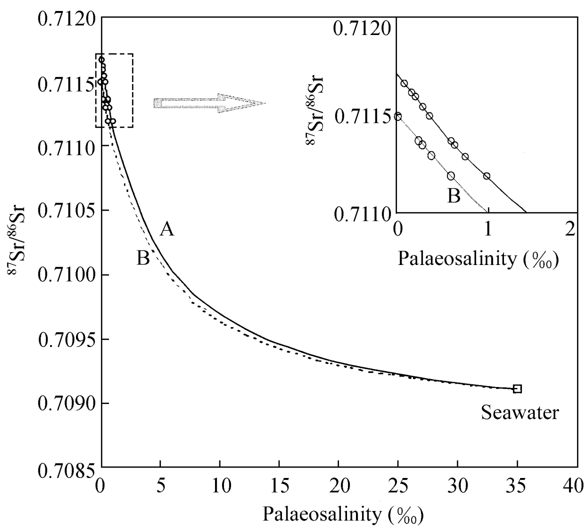


Fig. 2. Diagram of $^{87}Sr/^{86}Sr$-palaeosalinity of contemporary waters where foraminifera deposited. —, Sangganhe before concourse-seawater; ○, foraminiferal fossil; ······, Sangganhe after concourse-seawater.

fossils did not belong to the pure marine face. Can it be possibly the transitional depositional environment?

Proportion and component of the both end-members in the mixed waters could be determined by the hyperbolic mixing curve relationship between $^{87}Sr/^{86}Sr$ and Sr/Ca[27]. Using the average values of world fresh water[27] (Sr, 0.071×10^{-6}, Ca, 19.65×10^{-6}, Sr/Ca, 1.66, and $^{87}Sr/^{86}Sr$, 0.7119) or the Sanggan River (Sr, 0.92×10^{-6}, Ca, 61.5×10^{-6}, Sr/Ca, 6.83, and $^{87}Sr/^{86}Sr$, 0.711508) respectively as one end-member of fresh water and contemporary seawater as the other end-member of seawater (Sr, 8.0×10^{-6}, Ca, 415×10^{-6}[27], Sr/Ca, 8.86, and $^{87}Sr/^{86}Sr$, 0.709114), two $^{87}Sr/^{86}Sr$-Sr/Ca hyperbolic mixing curves are simulated in fig. 3. Sr/Ca ratio of contemporary water where foraminifera deposited could be restored by using the partition coefficient (D(Sr)) between foraminiferal shell and contemporary waters where foraminifera inhabited. Supposing the contemporary waters were fresh water and its Sr/Ca ratio was similar to that of the Sanggan River, D(Sr) was calculated to be 0.15—0.22, resembling D(Sr) (0.11—0.19)[28] of modern marine foraminifera. If plotting the $^{87}Sr/^{86}Sr$ and Sr/Ca data of the contemporary waters reestablished by using the different D(Sr) values on the simulated $^{87}Sr/^{86}Sr$-Sr/Ca diagram (fig. 3), those data did not locate in two hyperbolic mixing curves but concentrated in the end-member of fresh water. Fig. 3 clearly shows that no matter how the values of D(Sr) change, the Sr/Ca ratios of test samples would change in the horizontal line which consisted of the data in the fig. 3 and did not match the hyperbolic mixing curves, implying that the contemporary waters did not have any relationship with seawater. This was consistent with the results obtained by the previous regionally geologic tectonic and palaeohydrologic work, demonstrating that "channelways" did not exist between the ancient Nihewan Lake and seawater[29, 30].

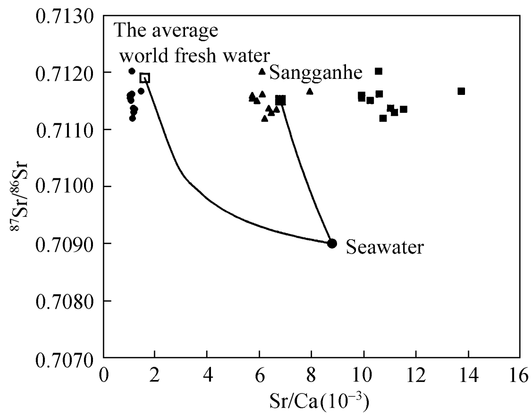


Fig. 3. Diagram of $^{87}Sr/^{86}Sr$-Sr/Ca of contemporary waters where foraminifera deposited. ●, Foraminiferal fossil; ■, contemporary waters where foraminifera deposited — D(Sr)=0.11; ▲, contemporary waters where foraminifera deposited—D(Sr)=0.19.

In the last decades, some findings about modern foraminiferal species existing in inland salt-water, brackish-water lakes without any relation to sea have been reported and demonstrated that it is highly possible that some foraminiferal species, which can tolerate the environment extremely deviating from the normal sea, can inhabit inland lakes.

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