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GEOCHEMISTRY

Oxygen and Carbon Isotopic Composition of Carbonate Rocks of the Permian Qixia Formation, Sichuan Basin: Thermal Effects of Emeishan Basalt

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ABSTRACT

The late Permian thermal events related to Emeishan Basalt has made a great impact on the underlying carbonate rock properties in the western margin of the Yangtze Platform. In this paper, we investigate the carbon and oxygen isotopic composition of the Qixia Formation carbonates from two sections: the Qiaoting Section in the northeastern part of the Sichuan Basin and the Changjianggou Section at the northwestern edge of the Basin. The data reveal that: (i) Samples from Qiaoting section show a relatively narrow range of $\delta^{13}C$ and $\delta^{18}O$, varying from 2.7‰ to 5.2‰ with an average of 4.2‰, and -3.8‰ to -7.8‰ with an average of -5.4‰, respectively. In contrast, Samples from Changjianggou section exhibit larger magnitude of variation in $\delta^{13}C$ and $\delta^{18}O$, ranging from -1‰ to 3.8‰ with an average of 1.5‰, and -2.1 to -9.2‰, with an average of -6.0‰ respectively; (ii) $\delta^{13}C$ and $\delta^{18}O$ records in carbonates from Qiaoting section are similar to those of Middle Permian seawater whereas carbonates from the Changjianggou section are depleted in ^{13}C and ^{18}O compared to contemporary seawater; (iii) On the basis of combined petrographic and paleo-heat flow evidence, the lower carbon and oxygen isotopic composition of the carbonates from the Changjianggou section are interpreted to be the results of thermal effects of Emeishan Basalt because of its proximity to the eruption center of the basalt. The high temperature reduced the $\delta^{18}O$ values of the carbonates and forced the organic matter to mature at an early stage, thus producing ^{13}C-enriched carbon dioxide to participate in the formation of carbonates.

Keywords: Sichuan Basin, Qixia Formation, Carbon and Oxygen Isotopic Composition, Thermal Effect

Composición Isotópica de Oxígeno y Carbón en Rocas de Carbonato de la Formación de Edad Pérmica Qixia, en la Cuenca de Sichuan: Efectos Térmicos del Basalto Emeishan

RESUMEN

Los eventos térmicos del Pérmico tardío relacionados con el Basalto Emeishan han tenido un gran impacto en las propiedades de las rocas de carbonato subyacentes en el margen occidental de la plataforma Yangtze. En este artículo se investiga la composición isotópica de carbonatos de la formación Qixia en dos secciones: la sección de Qiaoting en la parte nororiental de la cuenca Sichuan y la sección Changjianggou, en el noroccidente de la cuenca. La información evidencia que, (i) las muestras de la sección Qiaoting tienen un espectro más angosto que va de $\delta^{13}C$ a $\delta^{18}O$, con variación de 2.7 ‰ a 5,2 ‰, con un promedio de 4.2 ‰, y -3.8 ‰ a -7.8 ‰, con una media de -5.4 ‰, respectivamente. En contraste, las muestras de la sección Changjianggou tienen una variación de mayor magnitud en $\delta^{13}C$ a $\delta^{18}O$ que va desde -1 ‰ hasta 3.8 ‰, con un promedio de 1.5 ‰, y de -2.1 a -9.2 ‰, con una media de -6.0 ‰, respectivamente; (ii) los registros de $\delta^{13}C$ y $\delta^{18}O$ en carbonatos son similares a los de agua marina del pérmico medio, mientras que los carbonatos de la sección Changjianggou se ven empobrecidos en 13C y 18O comparados al agua marina de esta edad; con base en la petrografía combinada y la evidencia del flujo paleotérmico, la baja composición isotópica de oxígeno y carbón de los carbonatos en la sección de Changjianggou se interpretó como resultado de los efectos térmicos del Basalto Emeishan debido a la proximidad con el centro de erupción. La alta temperatura redujo los valores de $\delta^{18}O$ de los carbonatos y llevó a la maduración temprana de la materia orgánica, lo que produjo dióxido de carbono enriquecido en ^{13}C durante la formación de los carbonatos.

Palabras clave: Cuenca de Sichuan, Formación Qixia, Composición isotópica de Carbón y Oxígeno, Efecto térmico.

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1. Introduction

The Middle Permian Qixia Formation is widely exposed on the margin of the Sichuan Basin. As a typical lithostratigraphic unit of the upper Paleozoic marine strata, this Formation can be used for stratigraphic correlation. The carbonate rocks of the Qixia Formation gradually change from "black Qixia" to "white Qixia" from the east to the west of the Sichuan Basin. The black Qixia is mainly comprised of medium-thick strata of dark grey limestone interbedded with shale and siliceous rocks, and it generally has dark colors and high contents of organic carbon. It is considered to be one of the four sets of marine source rocks in South China (Chen et al., 2010; Lv et al., 2010; Chen et al., 2012; Liu et al., 2014). The white Qixia is comprised of light grey blocks of limestone containing dolomitic limestone and dolomite, and it is mainly distributed throughout the northern sections of the Micang Mountain and the Longmen Mountain (Sichuan Provincial Bureau of Geology and Mineral Resources, 1991). This finding may reduce the significance of the traditional opinion that "the Qixia Formation is black and the Maokou Formation is while" in the case of western Sichuan Basin. For example, the Qixia Formation in the Qiaoting section in Nanjiang area, northeastern Sichuan, is made of overall grey-black limestone strata (Fig. 1a). Moreover, the Qixia Formation in the Changjianggou section in Jian'ge area, northwestern Sichuan, is generally of dark grey limestone, with grey dolomitic limestone forming the upper part (Fig. 1b). It is widely thought that the black Qixia was deposited in a deep water environment while the white Qixia was deposited in shallow water within a carbon platform (Hu et al., 2010; Chen, 2009). Previous work has shown Qixia Formation has the potential to become a hydrocarbon reservoir rock (Zeng et al., 2010; Hao et al., 2013; Tian et al., 2014). Thus, this regional variation of lithological features have elicited strong academic interest for deciphering the nature and development mechanism of this Formation.

Several studies have noticed abundant saddle dolomite and other types of dolomite that are characterized by curved-face and xenomorphic crystals with high homogenization temperatures (max. > 200°C) were found to be associated with dissolution pores, vugs and factures in the western part of the Sichuan Basin. The impact of geothermal activity has been invoked to explain the dolomitization mechanism (He and Feng, 1996; Wang and Jin, 1997; Chen et al., 2012; Hao et al., 2012; Li et al., 2012; Shu et al., 2012; Huang et al., 2013; Tian et al., 2014). In this paper, we focus on the influence of the related thermal events on the carbon and oxygen isotopic compositions of the marine carbonates of the Qixia Formation.

The global Permian carbonate rocks have stable and relatively high carbon isotopic compositions (Hermann et al., 2010; Saltzman and Thomas, 2012; Laya et al., 2013). In the carbon isotope curve of the Phanerozoic carbonates (Veizer et al., 1999), the central values of $\delta^{13}C$ of the Permian rocks were concentrated in the range of 2.5-4.5‰. In the carbon isotope record of China's Upper Yangtze Permian, which had a higher resolution than that of the curve reported by Veizer et al. (1999), the $\delta^{13}C$ values were also mostly in this range (Fig. 2a, Huang, 1997). A decline in $\delta^{13}C$, resulting from extinctions and replacements of life, was found near the Permian-Triassic boundary (Hiete et al., 2013;Tohver et al., 2013), indicating a high content and rapid burial of organic carbon in the global Permian.

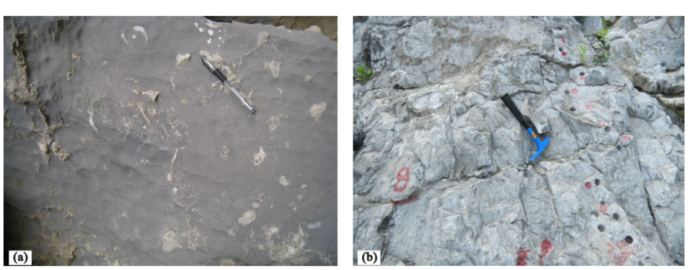

Figure 1. Outcrop photos of carbonates of Qixia Formation in in Sichuan Basin in (a) the Qiaoting section and (b) the Changjianggou section.

The $\delta^{18}O$ values of the global Permian carbonate rocks are mostly in the range of -3~6.5‰, and the corresponding curve is lower than that of the Carboniferous and Triassic (Veizer et al., 1999). This could have occurred because the Permian seawater had a relatively high temperature, or because the thermal events after the depositional stage had an impact on the Permian carbonate rocks. The oxygen isotopic composition of the Upper Yangtze Permian (Huang, 1997) was lower than that of the same period in the curve reported by Veizer et al. (1999). There are two possible reasons for this. One, the samples used by Veizer et al. were more representative of seawater, as carbon isotopes are more easily preserved in carbonates than oxygen isotopes. The other possible reason is that the carbon isotope curve of China's Upper Yangtze Permian had a higher resolution than that of the curve reported by Veizer et al. (1999). As shown in the previously reported curve, the lower $\delta^{18}O$ values of the Permian strata from Upper Yangtze were mainly occurred in: (1) the upper part of the Qixia Formation, (2) the top of the Maokou Formation, and (3) the top of the Permian. These three excursion may be associated with the thermal events related to Emeishan basalt eruption, the karstification related to the Dongwu Movement, and the increase in seawater temperature during the late Permian, respectively (Sun et al., 2012).

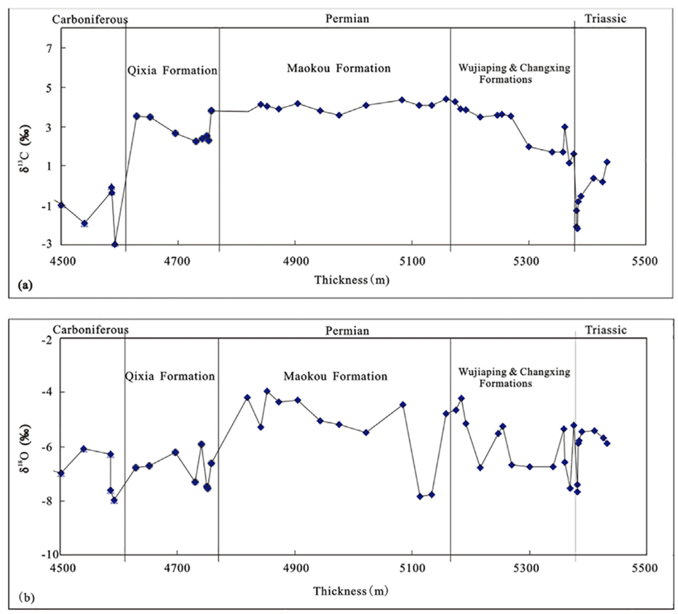

Figure 2. Curve of carbon isotope of marine carbonate rock in Upper Yangtze Permian. The curve was based on the related data in Oxygen Isotope Data (Huang, 1997) and Carbon Isotope Data (Huang, 1997).

Though the curve of carbon isotope in China's Upper Yangtze Permian had a relatively high resolution, only 8 samples of the Qixia Formation were used in the research (Fig. 2a). For further understanding of the composition and variation in carbon and oxygen isotopes in the Qixia Formation, the research group conducted a study on the carbonate rocks of this Formation in two sections, which were located in the northeast and northwest of the Sichuan Basin. A total of 94 groups of carbon and oxygen isotope data were collected and studied through a comparative analysis. Moreover, the impact of the thermal events related to the Emeishan basalt erruption on the carbon and oxygen isotopic compositions of this Formation was discussed.

2. Geological Setting and Sampling

Samples were collected from the Qiaoting section in the northeast of the Sichuan Basin (Nanjiang County) and from the Changjianggou section in the northwest of the basin (Jian-ge County). According to the tectonic division of the Sichuan Basin (Liu et al., 2000), the two sections are parts of the fault zones of the Micang—Daba the Longmen Mountain—Panxi, respectively (Fig. 3). Currently, the linear distance between the two sections is about 130 km in a north-west direction. The initial distance between the sections was supposed to be significantly greater than 130 km, because the tectonic activities following the depositional stage, especially those related to the Himalayan orogeny, could affect the distance between the sections. For instance, the nappe belt on the front edge of the Longmen Mountain, where the Changjianggou section is located, might decrease this distance.

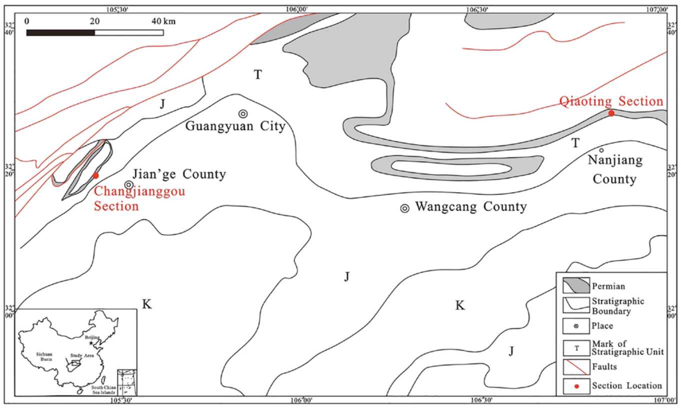

Figure 3. Geological scheme of the study area, modified after the 1:1,000,000 geological map of Sichuan Province, Sichuan Geology and Mineral Bureau, 1991. The map shows the locations of the two sections studied in the research, which are respectively parts of the Micang-Daba Mountains fault zone and the Longmen Mountain-Panxi fault zone.

The Qixia Formation occurs in the western and northern edges of the Sichuan Basin. The triple division of the Permian has been widely used in stratigraphic studies in China and other countries (e.g. Li et al., 2005; Shen et al., 2005). In this paper, the Qixia and Maokou Formations were included in the Middle Permian in accordance with the triple divisions of the Permian marine facies in the Sichuan Basin (Jin et al.,1999; Li et al.,2005) as well as the stratigraphic classification in International Stratigraphic Chart (2008) (Zhang et al., 2009). In these division plans, however, the lower Permian was poorly developed or even absent in Sichuan basin. The lower Permian, comprised of the Liangshan Formation, is about 1m thick in the Changjianggou section and less than 1m in the Qiaoting section. Due to very thin-bedded layers, this Formation was not marked in the maps in this paper.

The large area of Late Paleozoic basalt (Emeishan basalt) sits along the western margin of the Yangtze Block (Huang and Opdyke,1998) and is supposed to have thermal effect on its underlying carbonate rocks. Zhu et al., (2010) has demonstrated that the paleo-heat flow in the west of the Sichuan Basin reached a maximum at the end of the middle Permian at about 259 Ma (Fig. 4a). In this period, the paleo-heat flows measured in most wells were 60-80 mW/m^2, while the values in a few wells exceeded 100 mW/m^2. The paleo-heat flow characteristics reflected the thermal effect of the Emeishan basalt eruption during the late Paleozoic. When the paleo-heat flow peaked, the Permian Qixia Formation was at the shallow burial stage (Fig. 4b).

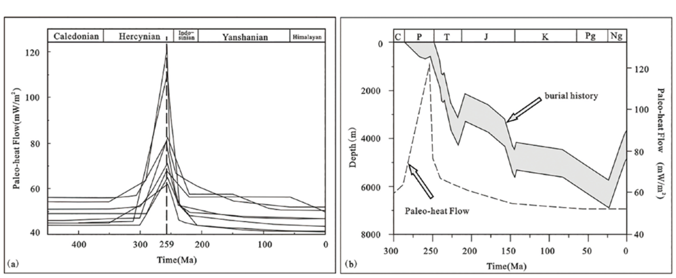

Figure 4. (a) A synthetic map of burial history and paleo-heat flow distribution for Well HS1 in western Sichuan Basin; (b) A paleo-heat flow distribution map for representative wells in the Sichuan Basin (modified after Zhu et al., 2009, 2010)

3. Methods

Samples used in the carbon and oxygen isotopic analysis were taken from the limestone matrix and dolomite matrix, avoiding the vug- or vein-filling calcite and dolomite crystals. Previous research indicated that the carbon and oxygen isotopic compositions of calcite and dolomite in vugs are lower than those of carbonate matrix (Huang et al., 2014). This research mainly involved the use of some geochemical methods, including carbon and oxygen isotopic analysis, as well as elemental analysis of some samples. The carbon and oxygen isotopic analysis was carried out at Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences, and the CNNC Beijing Research Institute of Uranium Geology, with the use of MAT-252 Mass Spectrometry. The latter was responsible for conducting the test in accordance with the standard of Application of Phosphoric Acid Method to the Measurement of Carbon and Oxygen Isotopic Compositions of Carbonate Minerals or Rocks (DZ/T 0184.17-1997). The former was responsible for analyzing the accuracy of the test results using the Kiel IV Carbonate Device sampling system in accordance with the GBW-04405 standard. The standard deviations of the $\delta^{13}C$ (PDB) and $\delta^{18}O$ (PDB) values were smaller than 0.040 and 0.080, respectively.

The analysis of the contents of CaO, MgO, Mn, Sr, and Fe contents was performed at the Geological and Mineralogical Testing Center of Huayang in Sichuan province. The CaO and MgO contents were measured using normal chemical analysis, with the limit of detection set at 1%. The relative errors of CaO and MgO measurements were 2% and 5%, respectively. The contents of Mn and Sr were determined by atomic absorption spectrometry, with the limits of detection set at 5×10^{-6} and 42×10^{-6}, respectively. The relative errors of the measurements were 13% and 14%, respectively. The Fe content was determined by colorimetry, with the limit of detection set at 0.01%. The relative error of the result was less than 8%

4. Results and Discussion

Table 1 exhibits the analysis results pertaining to the carbon and oxygen isotopes in 94 carbonate samples from the Qixia Formation in Qiaoting, Nanjiang, and Changjianggou, Jian'ge. The data of 22 samples marked with 'Δ' in table 1 have been published by Lv (2013). In addition to the isotopic data, the contents of Ca, Mg, Sr, Mn, and Fe and the corresponding Mn/Sr ratios of 69 of the 94 samples are also given for an understanding of the mineral compositions (relative contents of calcite and dolomite), representativeness, and diagenetic alteration of the samples.

4.1 Elemental compositions and their implication for diagenetic alteration

According to the elemental analysis, the average values of Mn, Fe, and Sr contents in the 69 samples were 48.8 ppm, 729.1 ppm, and 331.5ppm, respectively. Kaufman et al. (1992; 1993) employed Mn/Sr ratio<2~3 as criterion for selecting carbonate samples in which the isotopic values are considered to be proxy for those of seawater. Most of our samples have rather low Mn and Fe contents and relatively high Sr content and the average Mn/Sr ratio was very low, of only 0.31. However, among the aforementioned 69 samples, there were four samples with Mn content higher than 200ppm, having values at 818 ppm, 278 ppm, 406 ppm and 326ppm. Three of these four samples had very high Fe content as well, having values at 10442 ppm, 2724 ppm, and 14987 ppm, corresponding to the first three high Mn values listed above. The curves of carbon and oxygen isotopes in the subsequent discussion indicated that, among the three samples with both high Mn and Fe contents, two samples exhibited very low $\delta^{13}C$ and $\delta^{18}O$ values, which deviated from the overall trend. These two samples were collected from the bottom of the Qixia Formation in the Qiaoting section, which was adjacent to the Liangshan Formation. It was speculated that these samples were affected by some ^{12}C- and ^{16}O-rich fluids that were associated with the clastic rock strata.

Table 1. Carbon and oxygen isotopic compositions of carbonates of the Qixia Formation in Qiaoting, Nanjiang and Changjianggou, Jian'ge, and contents of Ca, Mg, Sr, Mn and Fe in the samples and corresponding Mn/Sr ratio

Changjianggou, Jian'ge, and contents of Ca, Mg, Sr, Mn and Fe in the samples and corresponding Mn/Sr ratios

Section	Sample No.	Sample type	Thickness (m)	$\delta^{13}C$ PDB(‰)	$\delta^{18}O$ PDB(‰)	CaO (%)	MgO (%)	Sr (ppm)	Mn (ppm)	Mn/Sr	Fe (ppm)	Remark
Changjianggou	JG1	limestone	0	-0.48	-4.08	54.91	0.17	84	25	0.29	1147	Δ
Changjianggou	JG6	limestone	3.74	1.4	-4.4							
Changjianggou	JG7	limestone	4.37	2.2	-3.7							
Changjianggou	JG8	limestone	4.84	2.3	-4.7							
Changjianggou	JG9	limestone	5.53	1.9	-6.2							
Changjianggou	JG10	limestone	6.22	1.9	-4.1							
Changjianggou	JG11	limestone	8.09	2.7	-3.58	53.84	0.94	279	29	0.1	186	Δ
Changjianggou	JG12	limestone	9.8	1.4	-5.9							
Changjianggou	JG13	limestone	10.8	2.4	-7.7							
Changjianggou	JG15	limestone	12.5	2.9	-4.8							
Changjianggou	JG16	limestone	13.12	3.3	-7.1							
Changjianggou	JG18	limestone	15.98	2.8	-5.1							
Changjianggou	JG22	limestone	24.51	3.84	-7.22	54.08	0.09	553	7	0.01	202	Δ
Changjianggou	JG23	limestone	27.22	-1	-6.2							
Changjianggou	JG25	limestone	31.57	0.5	-6.5							
Changjianggou	JG26	dolomitized limestone	32.66	1.8	-4.5							
Changjianggou	JG27	limestone	34.36	0.8	-6							
Changjianggou	JG28	limestone	35.04	0.3	-5.9							
Changjianggou	JG29	limestone	35.76	0.9	-6.5							
Changjianggou	JG30	limestone	36.15	0.7	-5.9							
Changjianggou	JG31	limestone	38.1	0.1	-6.6							
Changjianggou	JG32	limestone	39.49	-0.18	-8.37	51	3.83	68	102	1.5	337	Δ
Changjianggou	JG34	limestone	42.64	0.4	-7							
Changjianggou	JG35	limestone	43.19	-0.66	-9.11	54.98	0.39	56	49	0.88	135	Δ
Changjianggou	JG36	limestone	44.58	-0.4	-6.6							
Changjianggou	JG37	limestone	45.88	-1	-6.7							
Changjianggou	JG39-2	limestone	48.32	0.1	-7.51	55.5	0.09	76	32	0.43	186	Δ
Changjianggou	JG41	limestone	49.92	-0.4	-6.6							
Changjianggou	JG43	limestone	51.58	0.16	-7.03	55.5	0.26	67	22	0.33	202	Δ
Changjianggou	JG44	limestone	53.5	0.7	-6.5							
Changjianggou	JG45-1	limestone	54.33	0.77	-7.29	55.76	0.13	76	30	0.4	354	Δ
Changjianggou	JG47	dolomitized limestone	58.06	2.51	-6.14	31.6	5.19	86	64	0.74	152	Δ
Changjianggou	JG48	dolomitized limestone	59.2	2.74	-6.91	30.93	9.35	28	47	1.68	261	Δ
Changjianggou	JG49	calcitic dolomite	60.13	1.89	-9.16	29.94	10.89	23	40	1.74	337	Δ
Changjianggou	JG50	dolomitized limestone	62.03	2.99	-6.11	31.83	9.27	75	49	0.65	455	Δ
Changjianggou	JG51-1	dolomitized limestone	63.29	2.89	-6.68	31.12	10.29	69	326	4.72	590	Δ
Changjianggou	JG52	calcitic dolomite	66.57	2.24	-8.04	30.84	11.08	606	70	0.12	NG	Δ
Changjianggou	JG53	dolomitized limestone	69.09	2.35	-6	32.78	9.61	68	83	1.21	253	Δ
Changjianggou	JG54-1	dolomitized limestone	69.78	1.59	-7.35	52.54	8.85	101	38	0.38	186	Δ
Changjianggou	JG55-1	limestone	72.75	2.06	-6.2	55.03	0.26	95	19	0.2	152	Δ
Changjianggou	JG56	limestone	79.06	2.09	-5.42	55.74	0.09	149	20	0.13	219	Δ
Changjianggou	JG57	dolomitized limestone	79.95	3.28	-3.96	35.66	7.45	92	36	0.4	599	Δ
Changjianggou	JG58	limestone	80.46	2.05	-5.72	55.3	0.35	150	21	0.14	202	Δ
Changjianggou	JG59	dolomitized limestone	80.67	2.41	-5.04	48.07	6.32	168	23	0.14	472	Δ
Changjianggou	JG60	limestone	82.46	2.78	-5.37	51.14	3.68	117	14	0.12	599	Δ
Changjianggou	JG61	dolomitized limestone	83.7	3.3	-2.1							
Changjianggou	JG62	limestone	83.7	2	-3.8							

Qiaoting	LJ-A	limestone	1.67	-0.02	-9.86	49.61	0.4	426	818	1.92	10442	*
Qiaoting	LJ-B	limestone	3.35	1.67	-9.11	52.96	0.48	1007	278	0.28	2724	*
Qiaoting	LJ-D	limestone	16.74	2.67	-7.35	54.97	0.32	1206	38	0.03	374	
Qiaoting	LJ-F	limestone	19.69	3.65	-5.29	50.61	3.93	606	15	0.02	757	
Qiaoting	LJ-B2	limestone	22.72	4.21	-7.17	55.63	0.08	308	10	0.03	92	
Qiaoting	LJ-B4	limestone	24.9	4.13	-5.78	55.52	0.08	301	9	0.03	82	
Qiaoting	LJ-B5-1	dolomitized limestone	25.34	4.12	-4.58	42.23	10.28	823	15	0.02	983	
Qiaoting	LJ-B6	limestone	25.86	3.71	-3.65	54.6	0.99	517	9	0.02	212	
Qiaoting	LJ6	limestone	27.45	3.8	-6.32	55.29	0.25	470	7	0.02	128	
Qiaoting	LJ7-1	calcitic dolomite	28.33	4.86	-5.5	42.12	16.3	290	13	0.05	242	
Qiaoting	LJ7	dolomitized limestone	28.33	4.11	-7.34	49.88	4.46	322	7	0.02	109	
Qiaoting	LJ8A-1	dolomite	28.49	5.22	-4.27	32.51	19.27	328	13	0.04	293	
Qiaoting	LJ8A	calcitic dolomite	28.49	4.47	-6.32	36.55	16.19	290	12	0.04	149	
Qiaoting	LJ08	limestone	28.49	4.16	-7.5	53.56	1.82	419	8	0.02	424	
Qiaoting	LJ09	limestone	28.64	4	-7.79	54.94	0.33	410	8	0.02	212	
Qiaoting	LJ10	limestone	28.72	4.19	-6.33	54.71	0.74	550	7	0.01	144	
Qiaoting	LJ11	limestone	28.92	4.16	-6.29	55.17	0.33	430	8	0.02	101	
Qiaoting	LJ12	limestone	29.12	4.12	-6.37	55.63	0.08	355	9	0.02	86	
Qiaoting	LJ13-1	dolomite	29.36	4.94	-4.69	33.52	18.47	430	32	0.07	463	
Qiaoting	LJ13	limestone	29.36	4.14	-6.67	54.71	0.66	503	9	0.02	155	
Qiaoting	LJ14-1	dolomite	31.03	4.47	-4.44	34.97	18.15	382	36	0.1	677	
Qiaoting	LJ14	limestone	31.03	4.17	-5.96	54.25	0.83	474	8	0.02	143	
Qiaoting	LJ15-1	dolomite	32.23	5.21	-4.42	32.4	18.23	297	19	0.06	712	
Qiaoting	LJ15	limestone	32.23	4.12	-5.32	55.63	0.08	339	7	0.02	93	
Qiaoting	LJ16-2	dolomite	33.42	4.42	-6.28	32.4	18.79	142	20	0.14	123	
Qiaoting	LJ18	limestone	36.42	4	-3.97	55.29	0.08	171	8	0.05	20	
Qiaoting	LJ20	limestone	37.44	4.05	-5.3	54.1	0.79	793	406	0.51	14987	*
Qiaoting	LJ22	limestone	39.53	4.17	-5.04	54.83	0.74	265	11	0.04	636	
Qiaoting	LJ24	limestone	42.86	4.27	-5.35	55.29	0.33	418	15	0.03	255	
Qiaoting	LJ26	limestone	44.56	4.29	-5.7	55.06	0.33	234	7	0.03	76	
Qiaoting	LJ28	limestone	45.88	4.42	-5.32	54.83	0.41	333	10	0.03	196	
Qiaoting	LJ30	limestone	47.6	4.23	-5.41	55.4	0.08	192	9	0.05	160	
Qiaoting	LJ32	limestone	48.75	4.35	-4.96	55.75	0.08	334	10	0.03	286	
Qiaoting	LJ34	limestone	51.15	4.36	-4.47	54.83	0.41	346	9	0.03	160	
Qiaoting	LJ35-1	calcitic dolomite	51.9	4.62	-4.81	36.87	15.1	214	26	0.12	602	
Qiaoting	LJ35	calcitic dolomite	51.9	3.84	-5.61	40	13.55	219	28	0.13	309	
Qiaoting	LJ38-1	calcitic dolomite	53.79	3.97	-4.73	37.99	13.65	377	19	0.05	516	
Qiaoting	LJ38	calcitic dolomite	53.79	3.81	-4.8	39.77	12.97	234	26	0.11	365	
Qiaoting	LJ41	limestone	57.06	4.39	-4.58	54.6	1.16	321	11	0.03	506	
Qiaoting	LJ43	limestone	59.06	4.52	-3.88	55.29	0.25	366	10	0.03	124	
Qiaoting	LJ45	limestone	61.38	4.89	-4.88	55.52	0.08	523	12	0.02	220	
Qiaoting	LJ46	limestone	66.48	4.84	-4.78	54.71	0.66	857	18	0.02	276	
Qiaoting	LJ48	limestone	69.93	4.41	-3.96	54.48	0.74	382	9	0.02	304	
Qiaoting	LJ50	limestone	76.37	4.74	-5.24	55.63	0.08	462	12	0.03	284	
Qiaoting	LJ51	limestone	78.83	4.83	-3.79	54.83	0.66	381	13	0.03	197	
Qiaoting	LJ52	limestone	81.76	3.52	-4.59	54.25	0.91	346	37	0.11	458	
Qiaoting	LJ54-1	dolomite	83.98	3.12	-3.87	32.51	17.26	395	101	0.25	1490	

Note: Blank cells in the table represent without detection; NG=below the limit of detection; 22 samples marked with ‘Δ’ have been published by Lv, 2013; 3 samples marked with * have both high Mn content (>200ppm) and high Fe content (>2000ppm).

The carbonates of the Qixia Formation in the Qiaoting section and the Changjianggou section did not vary substantially in Fe and Mn contents, except for the aforementioned three samples with high Mn and Fe contents. The average Mn contents of the two sections were 47.3 ppm and 52.1 ppm, and their average Fe contents were 322.7 ppm and 344.2 ppm, respectively. The Sr content in the Qixia Formation was significantly higher in the Qiaoting section than in the Changjianggou section. Their average Sr contents were 421.0 ppm and 140.2 ppm, respectively. The Mn/Sr ratio of the Qixia Formation in the Qiaoting section was 0.05, which is much lower than the ratio of 0.74 in the Changjianggou section. Overall, it can be concluded that geochemical information of these samples are not significantly affected by non-seawater-like fluids such as meteoric fluids, which would lead to enrichment of Mn, Fe and higher Mn/Sr ratio.

4.2 Carbon and oxygen isotopes

Though the carbonates of the Qixia Formation in the two sections did not vary substantially in terms of elemental composition, their carbon and oxygen isotopic compositions varied greatly from one another (Table 1, Fig. 5, and Fig. 6). Selecting the boundary of Carboniferous-Permian and boundary of Qixia and Maokou Formation as joint, by which the $\delta^{13}C$ and $\delta^{18}O$ profile of sections in this research and previous study could be compiled. The carbon isotopic compositions of carbonates of the Qixia Formation in the Qiaoting section were relatively stable, except for two samples from the bottom that were affected by the clastic rocks of terrigenous origin in the Liangshan Formation. The $\delta^{13}C$ values of the samples ranged from 2.7‰ to 5.2‰, with the average being 4.2‰. This carbon isotopic composition was close to that of the global seawater of the period (Veizer et al., 1999). The high and stable $\delta^{13}C$ values of the marine carbonates in the Qixia Formation reflected a good ecological status of the Earth, stable species and populations of marine invertebrates with calcareous shells, and fast and continuous burial of organic carbon during this period.

In contrast, the Qixia Formation in the Changjianggou section exhibited significant variations and negative excursions in $\delta^{13}C$ and $\delta^{18}O$ records. The $\delta^{13}C$ values were between -1‰ and 3.8‰, and the average was 1.5‰, which was significantly lower than that of the Qixia Formation in the Qiaoting section and the global seawater of the same period (Veizer et al., 1999). The low $\delta^{13}C$ values were mainly distributed throughout the middle part of the Qixia Formation (the bottom of the second member of the Formation); the $\delta^{13}C$ values of samples from this part were mostly between -1‰ and 1‰. Despite Qixia Formation in the Changjianggou section and Qiaoting section was deposited in a shallow-water platform facies and an open platform facies, respectively (Huang et al., 2004), such difference could not lead to the observed variation in $\delta^{13}C$ values due to its insensitive to spatial factor.

It is more difficult to measure the oxygen isotopic compositions of carbonates that can represent seawater in geologic history. In the curve of oxygen isotope in Phanerozoic carbonates reported by Veizer et al. (1999), the oxygen isotopic compositions of marine carbonates showed an overall upward trend over time in the geologic history. In the Qiaoting section, however, the oxygen isotopic compositions of the carbonates of the Qixia Formation were relatively stable overall, ranging from -3.8‰ to 7.8‰ with an average of -5.4‰. This was slightly lower than that of the global seawater of the same period (Veizer et al., 1999). In contrast, the carbonates of the Qixia Formation in the Changjianggou section showed a significant variation and a negative excursion in oxygen isotopic composition. The $\delta^{18}O$ values mostly ranged from -2.1‰ to -9.2‰, and the average was -6.0‰, which is significantly lower than that of both the Qixia Formation in the Qiaoting section and the global seawater of this period reported by Veizer et al. (1999).

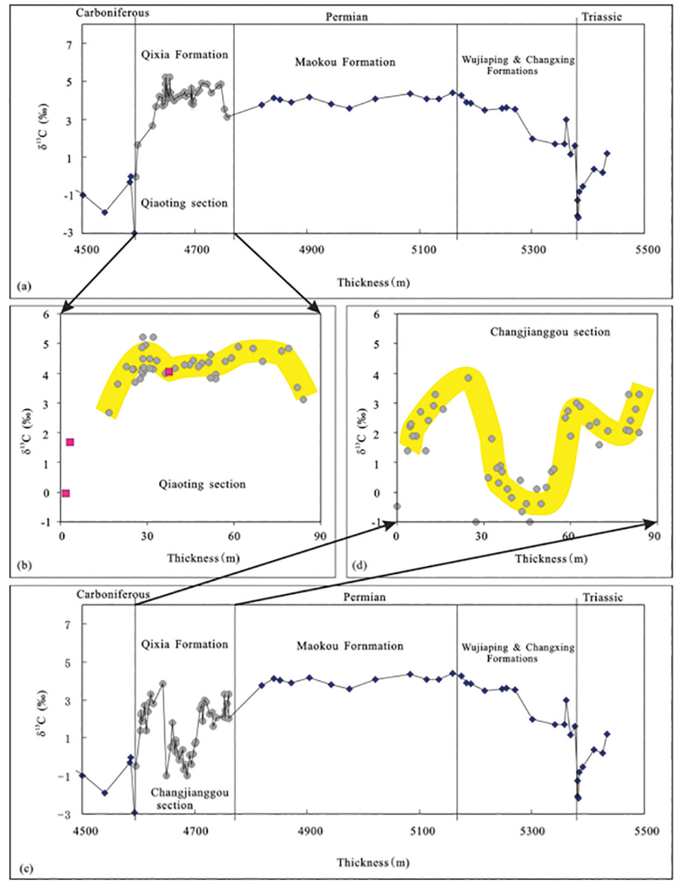

Figure 5. The cross-plots of carbon isotopic compositions and the thicknesses of carbonate rocks of Qixia Formation in Qiaoting and Changjianggou sections. The carbon isotopic compositions of the Permian and adjacent Formation are given. The data sources are the same as in Fig. 2. The grey circles and dark-blue rhombus are symbols for data from this study and Huang (1997). The red squares in Fig. 5b refer to the three samples marked with * in Table 1. The Liangshan Formation of the Lower Permian in the Changjianggou and Qiaoting sections are not shown in the figure due to their negligible thickness (<1m).

Marine carbonates are the largest inorganic carbon pool in nature. The carbon contents of most diagenetic fluids are relatively low compared to carbonate rock itself, indicating that carbon sources are buffered by the carbonates rather than fluid during diagenesis. As a result, the information about carbon isotope in seawater can be well preserved in carbonate rocks, especially the micritic carbonates that are characterized by low porosity and permeability. Because the possibility of meteoric influence has been ruled out during the sampling and data selecting process, The distinctly low $\delta^{13}C$ values of the carbonates of the Qixia Formation in the Changjianggou section indicated that carbon sources with low $\delta^{13}C$ values participated in carbonate formation when the rocks still had relatively high porosity and permeability, which lead to high water/rock ratio. Such process could not be involved in the normal thermal evolution of burial diagenesis sequence, because the rock would be highly compacted after high volumes of CO_2 have been released by the organic matter. In this case, the water/rock ratios were relatively low thus organic carbon's input was not available. Davies (2004) proposed the term ‘‘forced maturation’’ for the alteration of kerogen in host limestones during transient thermal anomalies. Davies and Smith Jr. (2006) pointed out that this process precedes regional burial maturation of organic material. Therefore, we suggested certain unusual thermal events took place in the early stage of diagenesis and caused early forced maturation of organic matter, subsequently decreasing the $\delta^{13}C$ values of carbonates by the entrance of carbon sources with low $\delta^{13}C$ values. In summary, the lower carbon & isotopic composition of the carbonates of Qixia Formation in the Changjianggou section suggested that the thermal events in the early stage of diagenesis had a greater influence on the Changjianggou section.

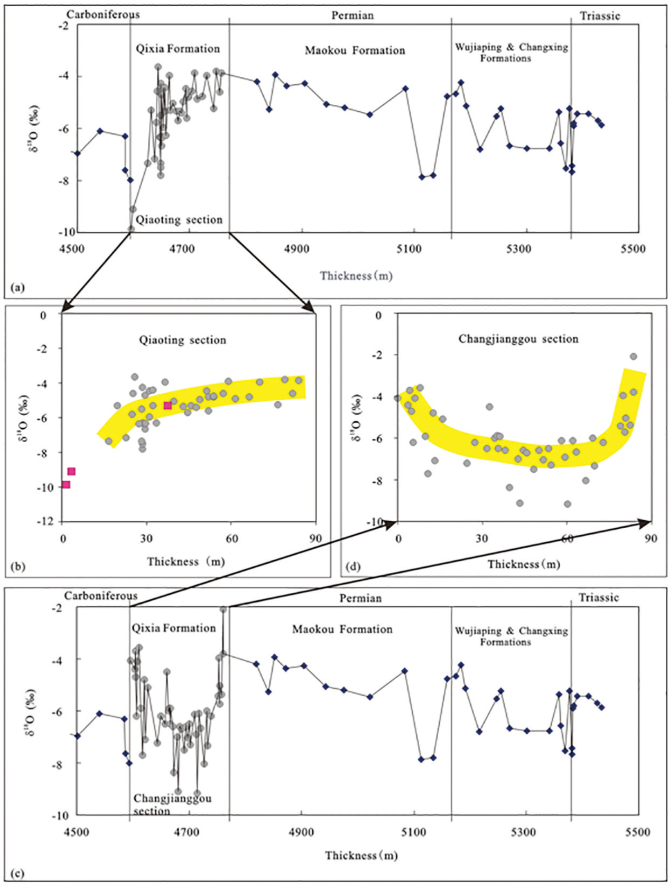

Figure 6. Cross-plots of oxygen isotopic compositions and thicknesses of carbonate rocks of Qixia Formation in Qiaoting and Changjianggou sections. The oxygen isotopic compositions of the Permian and adjacent Formation are shown. The data sources are the same as in Fig. 2. The grey circles and dark-blue rhombus are symbols for data from this study and Huang (1997).The red boxes in Fig. 6b refer to the three samples marked with * in Table 1. The Liangshan Formation of the Lower Permian in the Changjianggou and Qiaoting sections are not shown in the figure due to their negligible thickness (<1m).

The oxygen isotopic composition of carbonates is quite sensitive to temperature, and the decrease in the δ18O values of carbonates is usually caused by isotope fractionation resulting from rising temperature. The lower oxygen isotopic composition of the carbonates of the Qixia Formation in the Changjianggou section suggested that the Qixia Formation in this section had experienced higher temperatures during diagenesis. Due to the influence of the thermal events related to the eruption of the Emeishan basalt, the paleoheat flow in the western Sichuan Basin reached the highest level during the end of the middle Permian. The maximum paleo heat flows experienced by most wells were between 60 and 80 mW/m^2, and a few wells have exhibited maximum paleo heat flows higher than 100 mW/m^2 (Zhu et al., 2010). During this period, the Qixia Formation was at the stage of shallow burial (depth=500~100m) (Fig. 1b). The thermal events associated with the Emeishan basalt eruption could reduce the oxygen isotopic composition of the carbonates in the areas affected by the events and cause forced evolution and maturation of the organic matter. This was especially important to the Qixia Formation because of the extremely rapid burial of organic carbon in this Formation. Moreover, the release of CO_2 by organic carbon sources during the process can further change the carbon isotopic composition of the affected carbonates. Therefore, the Qiaoting section in Nanjiang, which is farther from the basalt area, was less affected by basalt eruption. This could be the major reason for the lower carbon and oxygen isotopic compositions of the carbonates of the Qixia Formation in the Changjianggou section in the west of the Sichuan Basin.

Numerous studies suggest that dolomite formed from seawater would have higher δ18O than calcite (eg. Fouke,1994). Several experimental determinations have been carried out for measuring carbonate-water oxygen isotopes fractionation factor and concluded that the fractionation factor of Oxygen will increase during Ca substitution by Mg (eg. Tarutani et al., 1969; Jiménez-López et al., 2004). The rate of change between the $\delta^{18}O$ of dolomite and Mg content has been estimated from the difference in $\delta^{18}O$ between coprecipitated dolomite and calcite (Vahrenkamp and Swart, 1994). Such estimates for $\Delta\delta^{18}O_{dolo\text{-}cal}$ at 25°C, based on experiments and theoretical calculations, include 4 to 7‰ (Northrop and Clayton, 1966; O'Neil et al., 1969; Matthews and Katz, 1977; Clayton et al., 1989), 2.6 to 4‰ (Fritz and Smith, 1970; Vahrenkamp and Swart, 1994; Schmidt et al., 2005; Vasconcelos et al., 2005;Chacko and Deines, 2008), 3‰ (Land, 1980). Although such values can be translated to 0.05–0.14‰ increase in $\delta^{18}O$ per 1%Mg increase, the magnitude of that increase for dolomite is poorly constrained for different temperature condition. Therefore, dolomitization effect are not likely to have significantly contributed to the overall patterns of oxygen isotopic records thus it is not quantified in the current discussion. In addition, given the fact that dolomitization degree in carbonates from Changjianggou section is generally higher than that from Qiaoting section (Li et al., 2015), the difference of temperature effects between these two sections would be higher if we take the effect of $\Delta\delta^{18}O$ between dolomite and calcite into account.

The discussion above should lead to the conclusion that, in the areas heavily influenced by the eruption of Emeishan basalt, such as the western part of the Sichuan Basin and some regions in Yunnan and Guizhou Provinces, the organic carbon has experienced forced maturation and oxidation in the early stage of diagenesis due to the thermal effects of the basalt eruption. This might have an adverse impact on hydrocarbon generation in the later stage. Huang and Wang (2008) have noticed that the thermal maturity of bitumen veins in the Kuangshanliang area in Northwestern Sichuan, which is near the Changjianggou section, had high thermal maturities. They proposed that this was caused by thermal alteration and diffusion during deep burial rather than by biodegradation. The thermal events associated with the Emeishan basalt eruption could be another cause of the high thermal maturities of the bitumen veins. Furthermore, the hydrocarbon exploration potential of the areas under the influence of the thermal events may have been reduced due to the early forced maturation and oxidation of organic matter.

5. Conclusions

The marine carbonates of the global Permian Qixia Formation have very high carbon isotopic composition, indicating an ecological prosperous status, and fast and continuous burial of organic carbon during this period. However, Qixia Formation in two sections, the Qiaoting section in the northeast and the Changjianggou section in the northwest of the Sichuan Basin, varied significantly in carbon and oxygen isotopic compositions.

The carbon and oxygen isotopic compositions of the carbonates of the Qixia Formation in the Qiaoting section vary relatively stable; the $\delta^{13}C$ values ranged from 2.7‰ to 5.2‰ (mostly around 4‰), with an average of 4.2‰, and the $\delta^{18}O$ values ranged from -3.8‰ to -7.8‰, with an average of -5.4‰. Both the carbon and oxygen isotopic compositions of the carbonates were close to those of the global seawater of this period.

The carbonates of the Qixia Formation in the Changjianggou section exhibited significant variations and negative excursions in $\delta^{13}C$ and $\delta^{18}O$ records. The $\delta^{13}C$ values were between -1‰ and 3.8‰, and the average was 1.5‰, which is significantly lower than that of the global seawater of the period. The $\delta^{18}O$ values were mostly in the -2.1 to -9.2‰ range, and the average was -6.0‰, which is also significantly lower than that of the global seawater of the period.

Most of the carbonate samples from the Changjianggou and Qiaoting sections had very low Mn and Fe contents and a relatively high Sr content. The elemental composition characteristics indicated that the samples from both sections have been diagenetically altered to a small degree and thus were representative of seawater of that period. Therefore, it is unreasonable to attribute the differences between the carbon and isotopic compositions in the two sections of the Qixia Formation to only diagenetic alteration.

The low carbon and oxygen isotopic compositions of the samples from the Changjianggou section were associated with the proximity to the eruption center of the Emeishan basalt. The thermal effect of the related thermal events reduced the oxygen isotopic composition of the carbonates. The high temperature forced the organic matter to mature rapidly, and the CO_2 released by organic carbon sources during the thermal evolution entered the carbonates, thus resulting in a decline in the $\delta^{13}C$ values.

The early forced maturation and oxidation of organic matter may have reduced the hydrocarbon exploration potential of the areas heavily influenced by the eruption of Emeishan basalt, such as western Sichuan Basin and some regions in Yunnan and Guizhou Provinces.

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