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ORIGINAL ARTICLE

The origin and geochemical characteristics of Permian chert in the Eastern Sichuan Basin, China

Liangbiao Lin[1,2] · Yu Yu[2] · Jian Gao[2] · Wei Hong[2]

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Abstract Chert is widespread in Permian Maokou Formation and Wujiaping Formation of the eastern Sichuan Basin, China. Field observations in conjunction with major element, REE, and isotope analysis suggest that the chert is both biogenic and hydrothermal in origin. Further analysis indicates that hydrothermal features are more prominent in chert of the Maokou Formation, whereas chert of the Wujiaping Formation contains stronger evidence of biogenic origin. The SiO_2 content of chert of the Maokou and Wujiaping formations are 80.09–97.91 and 65.52–97.76 wt%, respectively. The average Al/(Al + Fe + Mn) values are 0.35 (Maokou Formation) and 0.38 (Wujiaping Formation), and most samples are plotted in the Fe-rich section of the Al–Fe–Mn diagram. SiO_2 abundance and Al/(Al + Fe + Mn) ratio analysis of chert of the Maokou and Wujiaping formations suggest a hydrothermal origin, although several samples were more indicative of biogenic origin. The average REE content of chert in both formations is low, and average REE is lower in chert of the Maokou Formation than in chert of the Wujiaping Formation. The Ce anomaly is weakly negative in the chert of the Maokou Formation (0.62) and Wujiaping Formation (0.71), whereas the average Eu value is greater in chert of the Maokou Formation than in chert of the Wujiaping Formation. The $\delta^{30}Si$ values of chert are 0.4–1.2‰ in the Maokou Formation and 0.7–1.4‰ in the Wujiaping Formation, and these values are close to the $\delta^{30}Si$ values of modern radiolarians. The average palaeoseawater temperatures under which the chert formed were calculated as 66 °C for chert of the Maokou Formation and 62 °C for chert of the Wujiaping Formation. These calculated temperatures are significantly higher than estimated ancient sea temperatures. These data and interpretations suggest that the chert of the Permian Maokou and Wujiaping formations were affected by volcanism and fracturing during the Permian. Seawater seeped through fractures and interacted with upwelling hot magma along basement faults, resulting in silica dissolution and the enrichment of waters from hot spots along fractures as well as the enrichment of seawater. This enrichment resulted in the mass reproduction of siliceous organisms, such as radiolarians and sponges, which were eventually deposited to form biosiliceous rocks.

Keywords Chert · Eastern Sichuan Basin, China · REE analysis · Isotope analysis · Hydrothermal origin · Biogenic origin

Introduction

Chert may be an important rock type for various economic purposes. For example, in some chert the pyrite content and organic carbon content may exceed 10% abundance. Some chert examples can be enriched in elements such as Ba, V, P, Mo, U, Th, Au, and Se (Wang 1994). Yet other chert examples are considered indicators of mineral deposits, because they are closely associated with polymetallic ores such as Cu, Pb, Zn either as alternating layers within the ore body or at the ore body boundaries, or as mineralized ore in individual layers (Li et al. 2007). Because chert

✉ Liangbiao Lin
linliangbiao08@cdut.cn

[1] State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Chengdu University of Technology, Chengdu 610059, Sichuan, China

[2] Institute of Sedimentary Geology, Chengdu University of Technology, Chengdu 610059, Sichuan, China

forms under specific geological and geochemical conditions, the rock can provide important information on the geological evolution of an area (Murray 1994). The formation of chert requires appropriate and abundant silica sources, as well as favourable geochemical conditions for the accumulation, preservation, saturation, and deposition of silica. Although chert may have a unitary texture and relatively simple mineral composition, the formational process may be extremely complex. At present, there are at least five models of chert formation: (1) biogenetic or biochemical deposits (Thurston 1972; Beauchamp and Bound 2002); (2) volcanic deposits (Sugisaki et al. 1982); (3) hydrothermal metasomatic deposits (Xia et al. 1995); (4) hydrothermal deposits (Adachi et al. 1986; Yamamoto 1987; Chen et al. 2006; Van den Boorn et al. 2010); and (5) sedimentary accumulation and remobilization of air-borne dust (Cecil 2004, 2012, 2015).

Permian chert is widely distributed in south China. In some situations the Permian chert is in the form of laminated beds, whereas in other situations the chert is in the form of nodules. It is believed that the Middle Permian laminated cherts of the Gufeng Formation in central and southern Hunan province are of hydrothermal origin (Fu et al. 2004) even though the chert is mixed with materials of non-hydrothermal origin (Xia et al. 1995). However, the Permian chert occurring as laminated beds of the Gufeng Formation in the north-eastern Yangzi platform is interpreted as biogenetic origin being accumulated under reducing conditions (Kametaka et al. 2005). In Guangyuan, Permian chert occurring as laminated beds, nodules of the Qixia, Maokou, Dalong Formation is interpreted as deposits of biological origin. The Permian chert occurring as laminated beds in southern Guizhou is interpreted as mainly of hydrothermal origin (Li et al. 2009). The majority of previous chert studies have focused on the Middle and Lower Yangzi region, whereas little has been studied on chert in the Upper Yangzi region. In order to reconcile the different models for the genesis of Permian chert rocks in southern China, this study focuses on the petrology, geochemical characteristics, and formation environment of laminated chert of the Middle Permian Maokou Formation (P_2m) and Upper Permian Wujiaping Formation (P_3w) in the Lengshuixi section in Shizhu, Chongqing (Fig. 1a).

Geological setting and chert features

The Permian period is associated with strong volcanic activity in South China. Volcanic activity began during the late Maokou stage of the Middle Permian and ceased at the end of the Late Permian. Volcanic activity peaked at the turn of the Middle Permian and at the beginning of the Late Permian in the Upper Yangzi area (Wang et al. 1994), where the 'Emeishan basalt' erupted along either side of contemporaneous faults (Fig. 1). Permian extensional tectonics in South China formed grabens and horsts, which resulted in the formation of deep-water siliceous mudstone platform-to-basin facies and shallow-water carbonate platform facies (Luo 1981). The paleogeography developed a pattern of platforms alternating with basins, inner-platform basins, and inner-basin platforms (Feng et al. 1996). The sedimentary system of the eastern Sichuan Basin was in the cratonic basin of the Upper Yangzi region with open and gentle topography in relatively shallow waters. The main contemporaneous faults in the area occurred between the Huayingshan fault and Qiyaoshan fault. Sedimentation, facies distribution, and volcanic activity of the area were controlled by these faults (Fig. 1c).

The Lengshuixi section in Shizhu, Chongqing located west of the Qiyaoshan fault. Permian strata are well developed in Shizhu County and are well exposed in the Lengshuixi section alongside the road connecting the county seat with the town of Mawu. Chert beds are present in the Upper Maokou Formation and the Middle and Upper Wujiaping Formation. At this location, the Upper Maokou Formation is about 50 m thick (Fig. 2) and consists of alternating units of dark, thinly bedded chert and dark-grey micrite (Figs. 2, 3), dark carbonaceous argillic limestone with dark thinly bedded chert (Fig. 4), and dark grey moderately thick bedded bio-micrite with dark thinly bedded chert. In Section 27 (Fig. 2), the dark, thinly bedded chert laminae are 3–4 cm thick, its thickness ratio to the carbonaceous argillic limestone is up to 1:20. Slump deformation and biogenic debris occured in the carbonaceous, argillic limestone and include sponges, brachiopods (Fig. 5), corals, and ammonites. Limestone gravels are also present in some chert beds, suggesting formation in a deep water basin (Lin et al. 2008). The Middle and Upper Wujiaping Formation at this location is approximately 62 m thick (Fig. 2) and consists of alternating layers of dark thinly bedded chert and dark carbonaceous shale, chert interbedded with grey lenticular limestone, and alternating layers of dark thinly bedded chert and dark-grey micrite. In this formation, the chert occurs as nodules, banded formations, and laminae. The Wujiaping Formation cherts consist mainly of radiolarian chert (Fig. 6), biodetrital micritic chert, and calcitic chert. The majority of the samples contain fossils (5–15%) and the fossil content in some units is greater than 25% abundance. Observed fossils include radiolarians (Fig. 6), sponge spicules, thin-shelled brachiopods, foraminifera, and ostracodes. Sections 35 and 36 (Fig. 2) are rich in organic remains such as radiolarians. Section 35 is mainly comprised of alternating beds of radiolarian chert and dark carbonaceous shale. The thickness of a single chert bed is 2–4 cm. The beds are well developed and rust-coloured, as they contain pyrite.

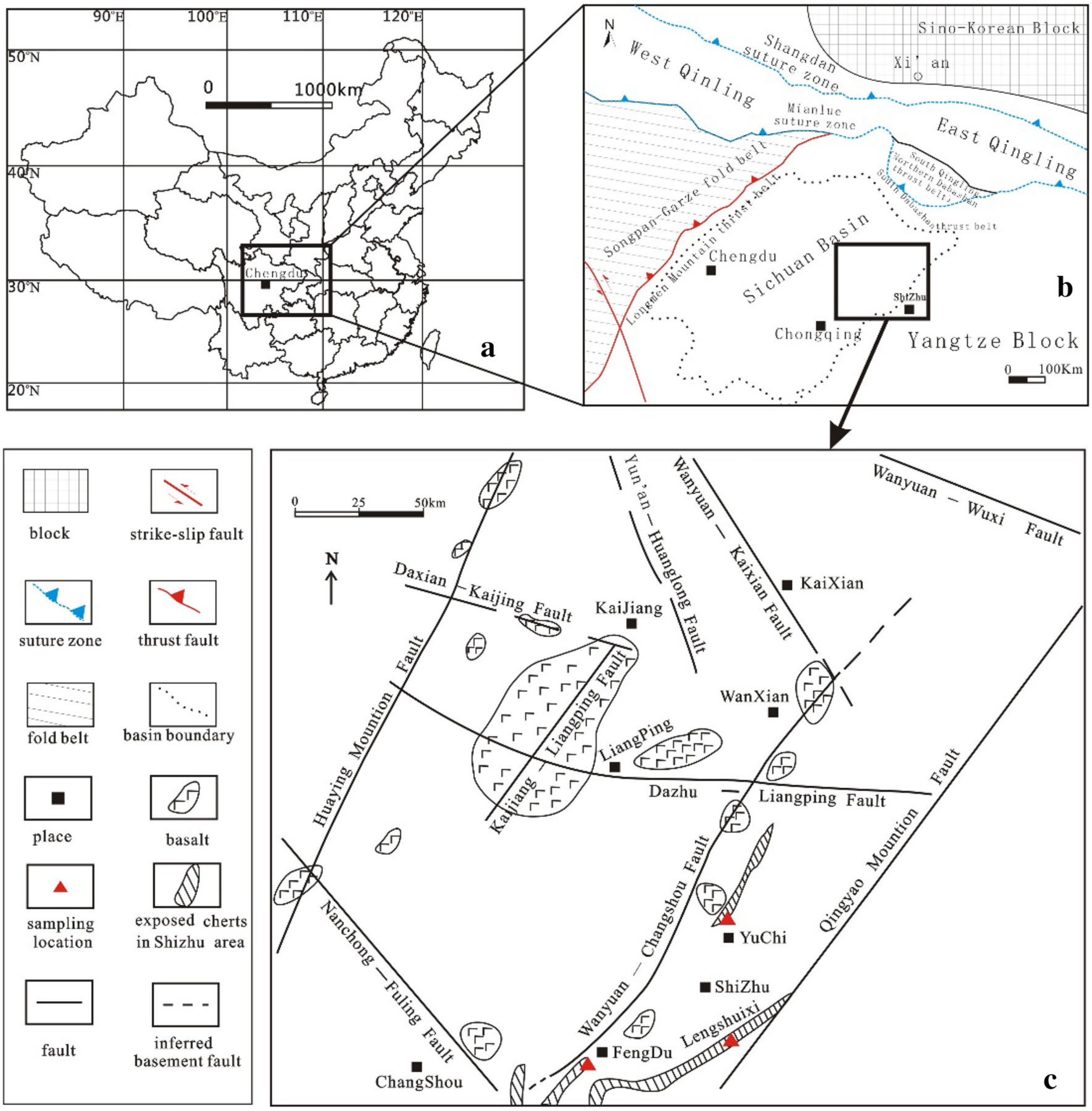

Fig. 1 Location and geological setting of the study area. **a** Location of the Upper Yangtze area. **b** Geological setting of study area and periphery. **c** Basement fault distribution map of the Permian strata in the eastern Sichuan basin, China

Section 36 consists of alternating beds of thin to moderately thick limestone and dark, thinly bedded chert. The limestone is flat with internal parallel stratification and 15% calcified radiolarian content.

Geochemical characteristics of cherts

Samples and analytical methods

Samples were collected from chert of the Maokou Formation and the laminated chert of the Wujiaping Formation. Thin sections were subsequently prepared and studied under the petrographic microscope. The original chert samples were selected for major elements, rare earth elements (REE), silicon, and oxygen isotope analysis. The major element composition was analysed using a Sequence Fluorescent X-ray Spectrometer (XRF-1500). REE were analysed by Inductive Coupling Plasma–Mass Spectrum (ICP–MS). The relative precision for the major and rare-earth element analysis is greater than 5%. Silicon and oxygen isotopes were analysed at the Institute of Mineral Resources Chinese Academy of Geological Sciences. The samples were first dissolved in HCl to remove carbonates and sulphides, then heated to remove organic matter, and finally oxidized by BrF_5 to remove O_2 and SiF_4. Finally, a MAT 251 EM spectrometer was used to analyse the oxygen and silicon isotopes with a relative precision of ±0.2 and ±0.1‰, respectively.

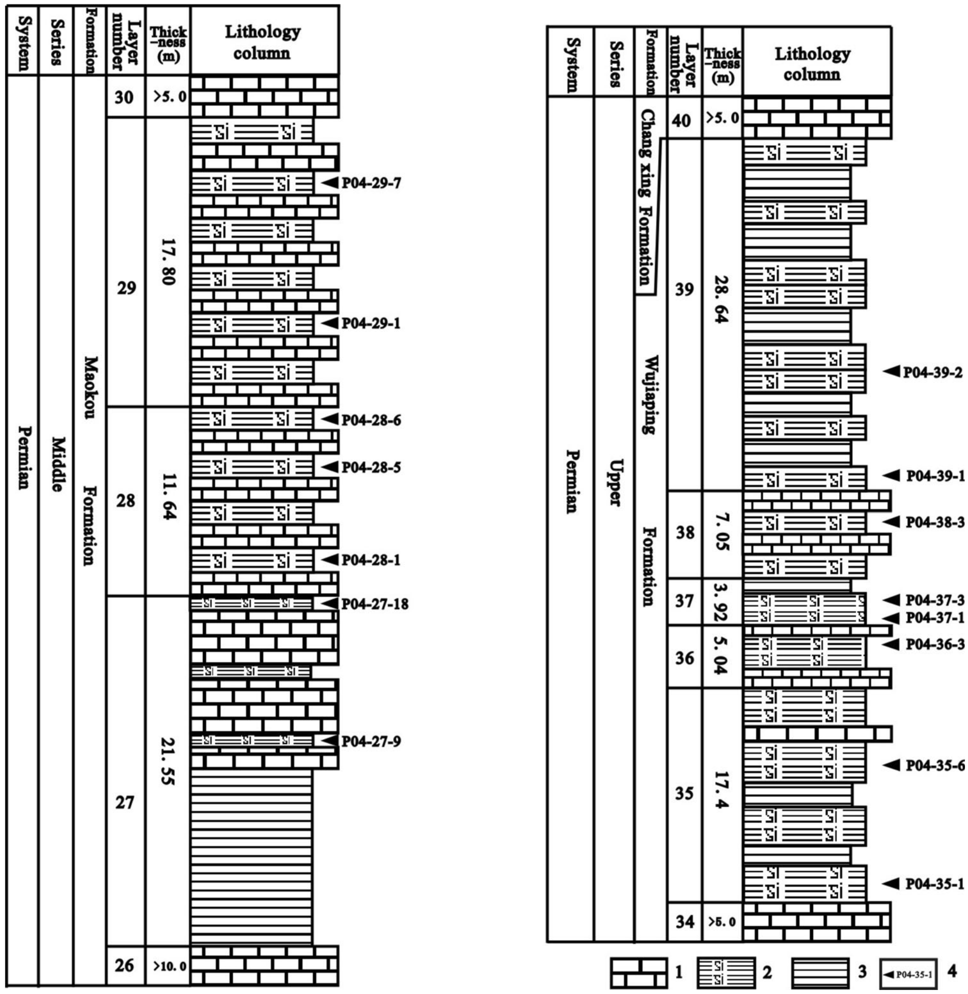

Fig. 2 Permian litho-stratigraphy of Shizhu, Chongqing. *1* Limestone, *2* Chert, *3* Carbonaceous shale, *4* sampling location and number

Fig. 3 *Dark grey* micritic limestone alternating with black thinly bedded-cherts of the Maokou Formation in Shizhu, Chongqing

Fig. 4 *Black* limestone with thinly bedded cherts of the Maokou Formation in Shizhu, Chongqing

Major Elements

Major element results (Table 1) show that the major chemical component in chert of the Maokou Formation is silica (SiO_2) with a relative weight percentage of 80.09–97.91%. Other major elements include CaO, Al_2O_3, and Fe_2O_3 with ranges of 0.24–8.54, 0.06–1.64, and 0.03–0.87 wt%, respectively. The remaining elements have

Fig. 5 Calcareous thin-shelled brachiopoda in chert of the Maokou Formation in Shizhu, Chongqing. Single polar

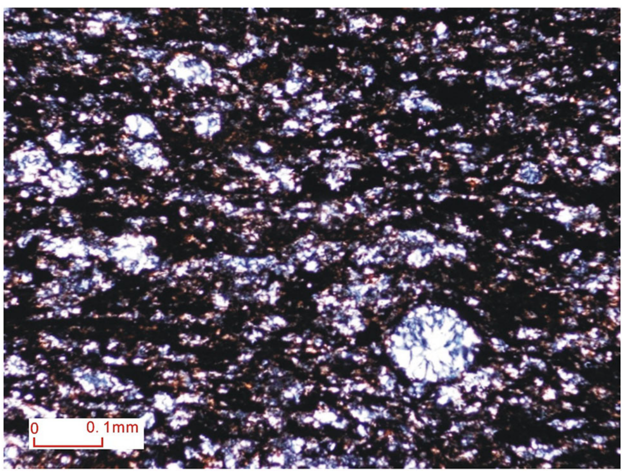

Fig. 6 Microphotograph of chert with radiolarians of the Wujiaping Formation in Bed 35 in Shizhu, Chongqing. Crossed polars

very low abundance. Silica (SiO_2) is also the major chemical component in chert of the Wujiaping Formation (65.52–97.76 wt%). The other major components are CaO, Al_2O_3, and Fe_2O_3 with ranges of 0.06–14.82, 0.12–5.70 wt%, and 0.14–4.12 wt%, respectively. The remaining minor elements have negligible abundance.

Elements such as Fe, Mn, Al, and Ti are important indicators for identifying chert genesis. Adachi et al. (1986) and Yamamoto (1987) studied hydrothermal chert and associated siliceous rocks from the northern Pacific Ocean and pointed out that the Al/(Al + Fe + Mn) ratio ranged from 0.01 (hydrothermal) to 0.60 (pelagic biogenesis). In the ternary Al–Fe–Mn diagram, the hydrothermal deposits lie in the Fe-rich corner, whereas the non-hydrothermal deposits are plotted on the Al-rich section. The Al/(Al + Fe + Mn) values of seven Maokou Formation samples are 0.44, 0.31, 0.50, 0.14, 0.11, 0.35, and 0.58 (Table 1) with an overall average of 0.35. In the Al–Fe–Mn diagram, all samples are plotted in area I except for samples P04-28-5 and Yuchi 2, which are plotted in the intersection of areas I and II (Fig. 7). This position on the plots suggests a strong hydrothermal signature for chert of the Maokou Formation.

The Al/(Al + Fe + Mn) values for the six Wujiaping Formation samples are 0.41, 0.69, 0.51, 0.17, 0.19, and 0.33 (Table 1). The average ratio of samples P04-35-1, P04-35-6, and P04-36-3 is 0.54, which is close to the value of biogenetic chert (Adachi et al. 1986; Yamamoto 1987). This interpretation is also supported by the presence of radiolarians and sponge spicules in bed 35 (>25%, Fig. 6) and bed 36 (~15%). The average of P04-37-1, P04-39-1, and P04-39-2 is 0.23, which is close to the ratios of Cretaceous hydrothermal chert of North Pacific (0.24) and California (0.22), as reported by Yamamoto (1987) and Liu (1991). The average Al/(Al + Fe + Mn) value for the whole Wujiaping Formation is 0.38. Thus, Fig. 8 suggests that all samples are plotted in area I (hydrothermal chert) except for samples P04-35-6 and P04-36-3, which are plotted in area II (biogenetic chert). Therefore, the chert of the Wujiaping Formation probably has both hydrothermal and biogenetic origins.

REE characteristics

REEs are used to distinguish between hydrothermal and non-hydrothermal deposits (Kato and Nakamura 2003; Bolhar et al. 2005). Shimizu and Masuda (1977) studied the Ce content in hydrothermal chert collected from abyssal drilling and three non-hydrothermal samples from Japan and Canada. They found that the hydrothermal chert exhibited a negative Ce anomaly with an average δCe value of 0.29, whereas the non-hydrothermal samples had an average δCe value of 1.2 and a positive Ce anomaly. Fleet (1983) studied the aqueous and sedimentary geochemistry of rare earth elements worldwide. He concluded that the total REE content in hydrothermal deposits is low, the Ce anomaly is negative, and there is a tendency for heavy rare earth element (HREE) enrichment. In contrast, non-hydrothermal deposits have high total REE content, positive Ce anomaly, and show no HREE enrichment. North American Shale Composite (NASC)-normalized REE patterns can also be used to identify the proportion of hydrothermal to non-hydrothermal deposits (Marchig et al. 1982). These features develop as a result of hydrothermal solutions that have mixed with seawater that has seeped through fractures and has become enriched in silica. Precipitated silica-rich minerals tend to have seawater characteristics, low REE content, and a negative Ce anomaly (Marchig et al. 1982).

Table 1 Major elements (wt%) of Permian chert from Maokou and Wujiaping formations in Shizhu, Chongqing

No.	Samples	Formation	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	TOTAL	FeO	Al/(Al + Fe + Mn)
1	P04-27-9	P_2m	84.98	0.62	0.03	0.32	0.002	0.36	5.89	0.07	0.07	0.03	7.10	99.47	<0.20	–
2	P04-27-18	P_2m	94.71	0.47	0.02	0.23	0.003	0.03	1.17	0.08	0.06	0.02	2.64	99.43	0.2	0.44
3	P04-28-1	P_2m	95.30	0.40	0.05	0.43	0.007	0.26	0.24	0.09	0.16	0.25	2.59	99.78	0.21	0.31
4	P04-28-5	P_2m	80.09	0.75	0.04	0.31	0.002	0.87	8.54	0.06	0.15	0.02	8.71	99.54	0.24	0.50
5	P04-28-6	P_2m	97.91	0.11	0.01	0.28	0.003	0.12	0.52	0.02	0	0.01	0.46	99.44	0.2	0.14
6	P04-29-1	P_2m	96.16	0.06	0.02	0.06	0.014	0.85	0.91	0.05	0.04	0.15	1.32	99.63	0.27	0.11
7	P04-29-7	P_2m	94.71	0.60	0.02	0.30	0.002	0.27	1.22	0.07	0.07	0.01	2.18	99.45	<0.20	–
8	Fengdu (1)	P_2m	93.94	0.38	0.02	0.31	0.002	0.07	2.12	0.07	0.02	0.01	2.54	99.47	0.20	0.35
9	Yuchi (2)	P_2m	94.94	1.64	0.03	0.49	0.004	0.11	0.63	0.03	0.37	0.03	1.14	99.40	0.36	0.58
10	P04-35-1	P_3w	75.64	4.36	0.25	4.12	0.016	1.05	1.53	0.47	1.08	0.58	9.74	98.84	0.52	0.41
11	P04-35-6	P_3w	72.41	5.70	0.24	1.01	0.002	0.39	0.31	0.09	2.04	0.42	17.68	100.29	0.85	0.69
12	P04-36-3	P_3w	65.52	1.66	0.08	0.64	0.006	0.33	14.82	0.08	0.38	0.05	16.21	99.77	0.52	0.51
13	P04-37-1	P_3w	96.60	0.18	0.03	0.40	0.008	0.72	0.22	0.07	0.07	0.14	1.32	99.76	0.21	0.17
14	P04-37-3	P_3w	95.96	0.58	0.03	0.20	0.003	0.16	0.64	0.04	0.06	0.02	1.74	99.42	<0.20	–
15	P04-38-3	P_3w	94.66	0.33	0.01	0.19	0.002	0.03	1.61	0.05	0.02	0.01	2.50	99.41	<0.20	–
16	P04-39-1	P_3w	97.76	0.12	0.03	0.14	0.007	0.26	0.20	0.05	0.04	0.03	1.21	99.85	0.21	0.19
17	P04-39-2	P_3w	97.57	0.38	0.02	0.30	0.002	0.01	0.06	0.06	0.03	0.01	1.04	99.48	0.26	0.33

Note Samples were analysed by Li He of the Institute of Geology and Geophysics, Chinese Academy of Sciences

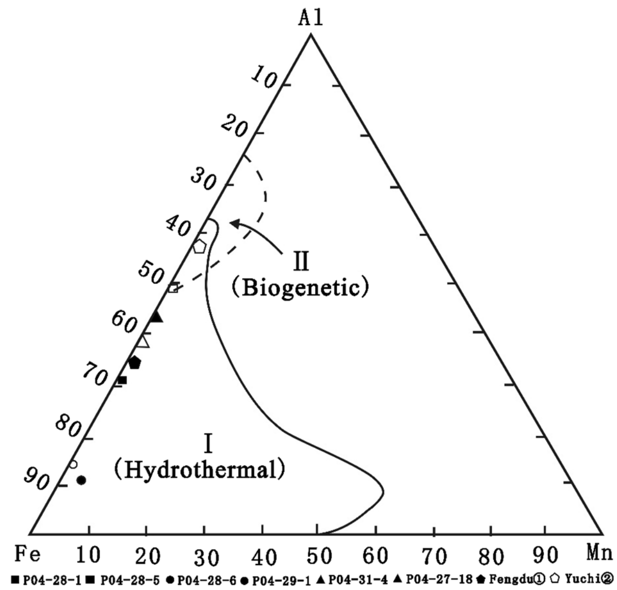

Fig. 7 Al–Fe–Mn diagram of chert of the Maokou Formation in the eastern Sichuan basin, China

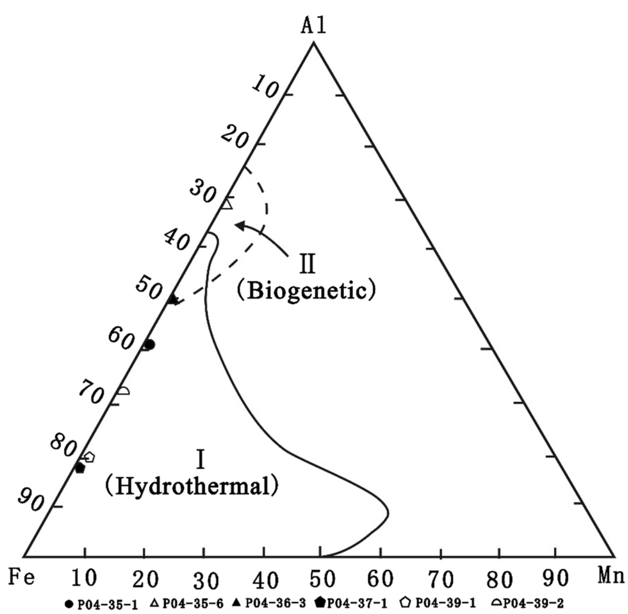

Fig. 8 Al–Fe–Mn diagram of chert of the Wujiaping Formation in the eastern Sichuan basin, China

The REE data (Table 2) for chert of the Maokou Formation show that the total REE content is low with an average value of 8.50 ppm. The ratio of light to heavy REEs (LREE/HREE) ranges from 2.69 to 9.37 with an average of 6.05. δCe for chert of the Maokou Formation ranges from 0.39 to 0.81 with an average of 0.62, and δEu ranges from 0.65 to 5.85 with an average of 1.39. The Eu anomaly is negative to positive, but most of samples do not show a clear Eu anomaly. The NASC-normalized REEs (Fig. 9) have HREE patterns that are slightly slanted to the

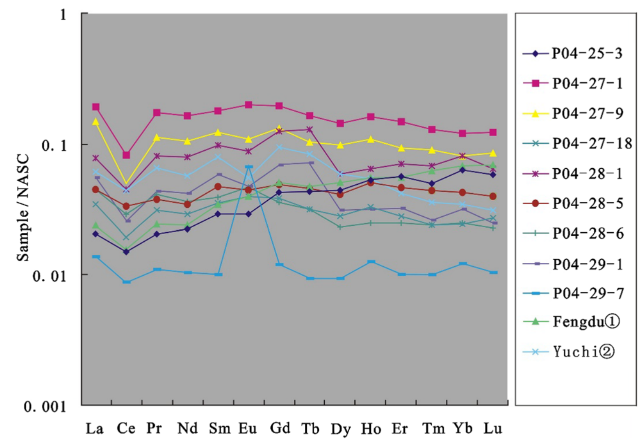

Fig. 9 NASC-normalized REE patterns of chert of the Maokou Formation

left or flat. All samples are moderately HREE-enriched with moderately negative Ce anomalies, which do not suggest entirely hydrothermal origin (Marchig et al. 1982; Fleet 1983). Obvious Eu anomalies were not observed in most samples with the exception of sample P04-29-7, which shows a positive Eu anomaly. According to Fleet (1983) and Shimizu and Masuda (1977), the chert of the Maokou Formation is primarily hydrothermal in origin with some non-hydrothermal components, which are responsible for the negative Ce anomaly and lack of clear Eu anomaly in most samples.

The REE analysis (Table 2) of chert from the Wujiaping Formation indicates that the average total REE is 38.55 ppm, the ratio of light to heavy REEs (LREE/HREE) ranges from 4.14 to 7.68, and the samples are moderately HREE-enriched. δCe ranges from 0.48 to 0.93 with an average of 0.71 and the Ce anomaly is moderate to weakly negative. δEu ranges from 0.70 to 1.12 without any obvious Eu anomaly. These patterns suggest that chert of the Wujiaping Formation is hydrothermal in origin, but not entirely. The NASC-normalized REE patterns of chert (Fig. 10) are relatively flat, with a slight left leaning tendency, which may not suggest entirely hydrothermal origin. These experimental results indicate that chert of the Wujiaping Formation has both hydrothermal and non-hydrothermal features in origin. The weakly negative Ce anomaly and absent Eu anomaly were the result of the mixing of non-hydrothermal components.

Silicon and oxygen isotopes

Silicon isotopes

The isotopic signature (δ^{30}Si) of silica minerals reflects their origins (Douthitt 1982; Ziegler et al. 2005). The δ^{30}Si value ranges from 1.1 to 1.4‰ for authigenic quartz in low-

Table 2 REE content (ppm) of Permian chert from Maokou and Wujiaping formations in Shizhu, Chongqing

No.	Samples	Formation	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑LREE	∑HREE	∑LREE/∑HREE	∑REE	δCe	δEu
1	P04-25-3	P_2m	0.66	1.09	0.16	0.74	0.16	0.04	0.22	0.04	0.26	0.06	0.19	0.06	0.2	0.03	2.85	1.06	2.69	3.91	0.73	0.92
2	P04-27-1	P_2m	6.2	6.00	1.38	5.44	1.02	0.25	1.02	0.14	0.83	0.17	0.50	0.07	0.37	0.06	20.29	3.16	6.43	23.45	0.45	1.05
3	P04-27-9	P_2m	4.72	3.72	0.89	3.43	0.69	0.14	0.69	0.09	0.56	0.11	0.32	0.05	0.25	0.04	13.59	2.11	6.44	15.7	0.39	0.89
4	P04-27-18	P_2m	1.10	1.42	0.25	0.96	0.20	0.05	0.20	0.03	0.16	0.03	0.10	0.01	0.08	0.01	3.98	0.62	6.41	4.60	0.59	1.10
5	P04-28-1	P_2m	2.48	3.26	0.64	2.63	0.56	0.11	0.65	0.11	0.34	0.07	0.24	0.03	0.25	0.03	9.68	1.72	5.63	11.40	0.56	0.80
6	P04-28-5	P_2m	1.43	2.43	0.30	1.13	0.27	0.06	0.25	0.04	0.24	0.05	0.16	0.02	0.13	0.02	5.62	0.91	6.18	6.53	0.81	1.01
7	P04-28-6	P_2m	1.42	2.12	0.32	1.20	0.22	0.06	0.19	0.03	0.14	0.03	0.08	0.01	0.08	0.01	5.34	0.57	9.37	5.91	0.68	1.29
8	P04-29-1	P_2m	1.76	1.86	0.34	1.38	0.33	0.06	0.36	0.06	0.18	0.03	0.11	0.01	0.10	0.01	5.73	0.86	6.66	6.59	0.52	0.76
9	P04-29-7	P_2m	0.44	0.64	0.09	0.34	0.06	0.08	0.06	0.01	0.05	0.01	0.03	0.01	0.04	0.01	1.65	0.22	7.50	1.87	0.70	5.85
10	P_2m(5)	P_2m	0.77	1.14	0.19	0.79	0.20	0.05	0.26	0.04	0.29	0.06	0.19	0.03	0.21	0.03	3.14	1.11	2.83	4.25	0.65	0.95
11	Yuchi(2)	P_2m	1.95	3.22	0.52	1.87	0.45	0.07	0.49	0.07	0.35	0.06	0.14	0.02	0.11	0.02	8.08	1.26	6.41	9.34	0.7	0.65
12	P04-35-1	P_3w	19.00	35.90	5.79	22.10	5.61	0.90	5.71	1.23	4.90	0.96	3.09	0.50	3.58	0.48	89.30	20.45	4.37	109.75	0.74	0.70
13	P04-35-6	P_3w	21.30	32.30	4.44	16.70	2.74	0.57	2.51	0.35	2.22	0.51	1.68	0.30	2.24	0.35	78.05	10.16	7.68	88.21	0.72	0.95
14	P04-36-3	P_3w	10.50	17.20	2.43	9.23	1.97	0.39	2.10	0.32	2.05	0.43	1.25	0.17	1.21	0.17	41.72	7.7	5.42	49.42	0.74	0.84
15	P04-37-1	P_3w	1.70	1.88	0.43	1.76	0.50	0.10	0.47	0.10	0.36	0.07	0.23	0.03	0.25	0.03	6.37	1.54	4.14	7.91	0.48	0.91
16	P04-37-3	P_3w	0.89	1.45	0.22	0.86	0.18	0.05	0.21	0.03	0.17	0.04	0.12	0.02	0.10	0.01	3.65	0.70	5.21	4.35	0.71	1.12
17	P04-38-3	P_3w	3.12	6.72	0.79	2.99	0.70	0.19	0.830	0.13	0.79	0.17	0.48	0.07	0.46	0.06	14.51	2.99	4.85	17.50	0.93	1.09
18	P04-39-1	P_3w	2.67	3.58	0.66	2.56	0.64	0.12	0.70	0.14	0.41	0.07	0.25	0.03	0.24	0.03	10.23	1.87	5.47	12.10	0.59	0.78
19	P04-39-2	P_3w	3.39	6.33	0.92	3.83	0.94	0.24	0.98	0.14	0.90	0.18	0.54	0.08	0.57	0.08	15.65	3.47	4.51	19.12	0.78	1.10
20	NASC	–	32	73	7.9	33	5.7	1.24	5.2	0.85	5.8	1.04	3.4	0.5	3.1	0.48	152.84	20.37	7.503	173.21	1	1

Note Samples were analysed by Zhang Yanhui of Analytical Laboratory of CNNC Beijing Research Institute of Uranium Geology

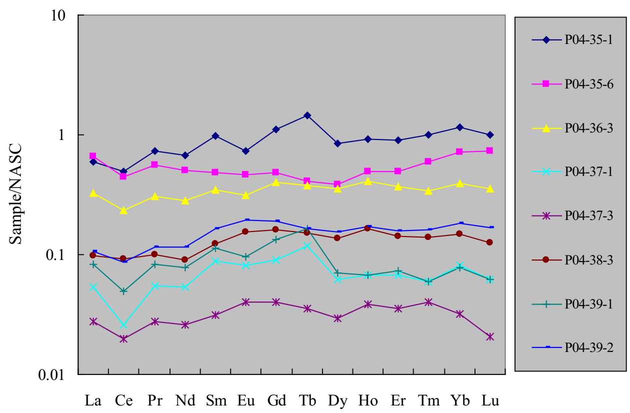

Fig. 10 NASC-normalized REE patterns of chert of the Wujiaping Formation

temperature waters. Hydrothermal quartz has a relatively small δ^{30}Si value which ranges between −1.5 and 0.8‰. The δ^{30}Si for secondary diagenetic quartz falls between the δ^{30}Si ranges of hydrothermal and authigenic quartz. The δ^{30}Si for metasomatic chert ranges from 2.4 to 3.4‰ (Ding et al. 1994). The average δ^{30}Si gradually increased from ranges typical of abyssal chert (−0.6 to 0.8‰) to semi-abyssal and offshore shallow sea chert (0.3–1.3‰), according to interpretations of δ^{30}Si values by Douthitt (1982), Song and Ding (1989), and Van den Boorn et al. (2010). The study of Chinese chert from different periods shows that δ^{30}Si is primarily concentrated in two ranges. The first range is from 0.1 to 0.5‰, which is identical with the δ^{30}Si range of volcanic and abyssal radiolarian cherts. The second range is from 0.3 to 1.3‰, which is identical with the δ^{30}Si range of shallow-water and semi-abyssal radiolarian chert. The second δ^{30}Si range is associated with shallow submarine carbonates (Ding et al. 1994).

The δ^{30}Si of chert of the Maokou Formation ranges from 0.4 to 1.2‰ with an average of 0.87‰ (Table 3). These values are close to those of hydrothermal quartz and similar to the values of shallow-water or semi-abyssal radiolarian chert in China (Ding et al. 1994). The hydrothermal and biogenic features of chert of the Maokou Formation suggest a semi-abyssal to offshore origin (Lin et al. 2008).

The δ^{30}Si of chert of the Wujiaping Formaiton ranges from 0.7 to 1.4‰ with an average of 1.02‰ (Table 3). Sample P04-35-6 has the lowest value of 0.7‰, whereas the remaining samples have δ^{30}Si values greater than or equal to 0.9‰. The δ^{30}Si values of chert of the Wujiaping Formation are obviously greater than that of silica minerals in modern hot springs (−3.4 to 0.2‰; Ding et al. 1994) and silica-bearing minerals in abyssal black smokers (−3.1 to −0.4%; Ding et al. 1994). Furthermore, δ^{30}Si values from chert of the Wujiaping Formation are similar to the δ^{30}Si values reported for shallow-water or semi-abyssal radiolarian chert of other periods in China (Ding et al. 1994). These features suggest that chert of the Wujiaping Formation is predominantly of a biogenetic origin rather than a hydrothermal origin, and that the chert formed in the transition zone between semi-abyssal and offshore shallow waters.

Oxygen isotopes

Oxygen isotopes in chert can be used to study their origin. The analysed samples are relatively pure because they consist predominantly of quartz. As a result, the δ^{18}O of quartz was used in the subsequent analysis and discussion (Clayton 1986). δ^{18}O ranges from 8.3 to 11.2‰ for igneous quartz with an average of 9‰; 11.2–16.4‰ for metamorphic quartz with an average of 13–14‰; 12.2–23.6‰ for hot-spring quartz; 13–36‰ for diagenetic quartz with an average of 22%; and 10.3–12.5‰ for modern beach sand with an average of 12‰. During diagenesis, δ^{18}O ranges from 19.3 to 21.8‰ with an average of 20.45‰ because quartz recrystallizes to poikilitic quartz (Clayton 1986). The δ^{18}O values in the chert of the Maokou Formation range from 20.3 to 29.4‰ with an average of 23.92‰, which fall within the range of diagenetic quartz. The δ^{18}O in chert of the Wujiaping Formation range from 19.7 to 27.6‰ with an average value of 24.74‰, which also falls within the range of diagenetic quartz.

The formation temperature of chert can be estimated by using the oxygen isotope fractionation equation of chert–water (Knauth and Epstein 1976),

$$1000 \times \ln\alpha_{\text{chert-water}} = 3.09 \times 10^6 \times T^{-2} - 3.29$$

where $\alpha_{\text{chert-water}} = (1000 + \delta^{18}O_{\text{chert}})/(1000 + \delta^{18}O_{H_2O})$ and T is the absolute temperature of the formation of chert. Assuming $\delta^{18}O_{H_2O} = 0‰$ in the above equation, the palaeoseawater temperature under which chert of the Maokou Formation formed was computed between 34 and 89 °C with an average of 66 °C. The paleoseawater temperature under which chert of Wujiaping Formation formed was computed between 45 and 95 °C with an average of 62 °C (Table 3). The computed palaeoseawater temperatures are clearly greater than the 20–25 °C palaeoseawater temperatures estimated for the Devonian–Permian period (20–25 °C) (Lu 1986).

Discussion

The general consensus is that SiO_2 is derived from continental (Yamamoto 1987), deep (Adachi et al. 1986; Yamamoto 1987; Xia et al. 1995; Chen et al. 2006), and biological sources (Beauchamp and Bound 2002;

Table 3 Silicon and oxygen isotopes of Permian chert from Maokou and Wujiaping formations in Shizhu, Chongqing

No.	Samples	Formation	$\delta^{30}Si_{NBS-28}$ ‰	$\delta^{18}O_{V-SMOW}$ ‰	*T* (°C)
1	P04-25-3	P_2m	0.4	20.3	89
2	P04-27-1	P_2m	1.2	21.4	81
3	P04-27-9	P_2m	0.8	25.9	52
4	P04-27-18	P_2m	0.9	25.1	57
5	P04-28-6	P_2m	1.2	29.4	34
6	P04-29-7	P_2m	0.7	21.4	81
7	P04-35-6	P_3w	0.7	19.7	95
8	P04-36-3	P_3w	1.4	27.6	45
9	P04-37-3	P_3w	1.0	25.5	56
10	P04-38-3	P_3w	1.1	26.8	49
11	P04-39-2	P_3w	0.9	24.1	65
12	The average value of P_2m cherts		0.87	23.92	66
13	The average value of P_3w cherts		1.02	24.74	62

Note The samples were analysed by Wan Defang at the Institute of Mineral Resources, Chinese Academy of Geological Sciences

Kametaka et al. 2005). Continental sources include chemically decomposed silicate minerals under warm and humid conditions in peneplains with unobstructed drainage. Deep sources are related to volcanic eruptions, the decomposition of volcanic materials, or marine hot spots. Biological sources include the siliceous remains of organisms that have directly absorbed SiO_2 from seawater. Nevertheless, biological sources are far more complicated because they include continental and deep sources.

Strong volcanic activity at the turn of the Middle–Late Permian in South China resulted in magma ascent and eruption along large, deep fractures or syndepositional fractures. The 'Emeishan basalt' (Fig. 1), a typical large igneous province (LIP) attributed to mantle–plume uplift (Li et al. 2003; He et al. 2006), also intruded along these fractures. The Al, Fe, and Mn contents of Permian chert in the eastern Sichuan Basin suggest that SiO_2 was derived from deep sources. However, the chert was probably affected by hydrothermal fluids as well. Most chert samples are plotted in the Fe-rich section of the Al–Fe–Mn diagram. The computed palaeoseawater temperature during which chert formed is higher than that of common seawater. The average calculated palaeoseawater temperature is 66 °C for chert of Maokou Formation and 62 °C for chert of the Wujiaping Formation. The Ce anomaly is moderate to weak (0.62 for chert of the Maokou Formation, and 0.71 for chert of the Wujiaping Formation), and the NASC-normalized patterns are relatively flat or slant slightly to the left.

Conversely, the $Al/(Al + Fe + Mn)$ ratios for the samples suggest biogenetic sources. The $\delta^{30}Si$ values for the chert samples are greater than the values of silica in modern hot spots, abyssal black smokers, and near or higher than the $\delta^{30}Si$ values of modern radiolarians. The $\delta^{18}O$ values of chert fall within the range of diagenetic quartz, which is markedly different from hot-spring quartz.

Generally, deep magmatic hydrothermal solution rise along deep fractures and mix with seeping seawater. As seawater temperature increases, the seawater begins to dissolve large amounts of SiO_2. Upwelling was widespread during the Permian (Hui et al. 2012), causing hot waters to dissolve large amounts of SiO_2 and migrate to relatively shallow areas. These conditions favoured the mass reproduction of siliceous organisms such as radiolarians and sponges, which eventually formed biogenic chert. Therefore, the Permian chert of the eastern Sichuan Basin is both hydrothermal and biogenic in origin. Hydrothermal features are more prominent in chert of the Maokou Formation compared with chert of the Wujiaping Formation, whereas the chert of the Wujiaping Formation has stronger biogenic characteristics.

Biogenic silica or chert is of great significance to the exploration and development of shale gas. Silica or chert indicates the deep water sedimentary environment, which is in favour of biota preservation and formation of rich-organic shale. Furthermore, brittleness of the shale increases as the content of silica increases. A higher content of the silica enables the shale to form natural fractures or makes the hydraulic fracturing easier to be successful in producing economic shale gas. This is the key factor of enrichment and high production of shale gas in Sichuan Basin (Wang et al. 2014; Zhao et al. 2016; Liu et al. 2017).

Conclusions

1. Silica (SiO_2) is the primary component of chert of both the Permian Maokou and Wujiaping formations, and

ranges in abundance from 80.09 to 97.91 wt% (Maokou Formation) and 65.52 to 97.76 wt% (Wujiaping Formation). The chert in both formations exhibits Fe and Mn enrichment. The average Al/(Al + Fe + Mn) ratios are 0.35 (Maokou Formation) and 0.38 (Wujiaping Formation), and most samples are plotted in the Fe-rich section of the Al–Fe–Mn diagram, which suggests a hydrothermal origin. Nevertheless, some samples have Al/(Al + Fe + Mn) ratios that suggest a biogenic origin.

2. The total REE content is low in chert of both the Permian Maokou and Wujiaping formations. The average values for the chert are 8.50 ppm (Maokou Formation) and 38.55 ppm (Wujiaping Formation). Heavy REEs show moderate enrichment, the NASC-normalized patterns are relatively flat or slant slightly to the left, and the Ce anomaly is moderate to weak (0.62 for chert of the Maokou Formation, and 0.71 for chert of the Wujiaping Formation). The Eu anomaly is more pronounced in chert of the Maokou Formation than in chert of the Wujiaping Formation. This observation suggests chert of the Maokou Formation experienced greater hydrothermal contributions compared to chert of the Wujiaping Formation.
3. The δ^{30}Si values of chert of the Maokou Formation range from 0.4 to 1.2‰ with an average of 0.87‰, which is close to the δ^{30}Si values of hydrothermal quartz and similar to the values of modern radiolarians. The δ^{30}Si values of chert of the Wujiaping Formation range from 0.7 to 1.4‰ with an average of 1.02‰, which is also near or greater than those of modern radiolarians. The average computed palaeotemperatures for the formation of the chert of the Maokou Formation (66 °C) and chert of the Wujiaping Formation (62 °C) are significantly greater than that of seawater.
4. The Permian chert of the eastern Sichuan Basin is both hydrothermal and biogenic in origin, and is closely related to Permian volcanic activity and fracturing. The chert of the Maokou Formation has more prominent hydrothermal features than the chert of the Wujiaping Formation, whereas the chert of the Wujiaping Formation is more biogenic in origin.

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