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The Diagenetic Alteration of the Carbonate Rocks from the Permian Qixia Formation as Response to Two Periods of Hydrothermal Fluids Charging in the Central Uplift of Sichuan Basin, SW China

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Abstract: The hydrothermal fluid–carbonate rock reaction is frequently regarded to occur in deep-burial diagenesis, and the hydrothermal dissolution is usually distributed and takes place along the faults. Previous studies have suggested that there was hydrothermal fluid activity locally in the Permian Qixia Formation in Sichuan Basin, likely related to the Emeishan basalt eruption. However, the effect of hydrothermal fluids on the carbonate rocks of the Qixia Formation in the central uplift of Sichuan Basin is still unclear. Based on the characteristics and geochemical parameters of the diagenetic minerals, this study aims to reveal the diagenetic alteration related to the hydrothermal fluid–rock reaction in the Qixia Formation and reestablish the diagenetic evolution by using the timing of diagenetic mineral precipitation. The methods include petrographic observation; trace and rare earth element (REE) analysis; C, O and Sr isotope measurement; fluid inclusion temperature measurement and cathodoluminescence analysis. According to the petrographic characteristics, the dolostones are mainly of crystalline structure, namely fine-medium crystalline dolostone, meso-coarse crystalline dolostone, and coarse crystalline dolostone, with the cathodoluminescence color becoming brighter in that order. The limestones from the Qixia Formation are of the bioclastic limestone type, with no cathodoluminescence color. Compared with dolostones, limestones have higher Sr content, lower Mn content, and heavier oxygen isotopes. With the crystalline size of dolostone becoming coarser, the oxygen isotopes of dolostones tend to become lighter. The meso-coarse crystalline dolostone has the highest Mn content and negative carbon isotope. Both limestones and dolostones have an obvious positive Eu anomaly in the Qixia Formation. However, the REE patterns of fine-medium crystalline dolostones are very different from those of meso-coarse crystalline dolostones. It is credible that there were two periods of hydrothermal fluid charging, with different chemical compositions. The first period of hydrothermal fluids could laterally migrate along the sequence boundary. Fine-medium crystalline dolostones were almost completely distributed below the sequence boundary and were dolomitized during the shallow burial period. As products of the hydrothermal fluid–dolostone reaction, the saddle-shaped dolomites in the meso-coarse crystalline dolostones were the evidence of the second period of hydrothermal fluids. As a result, the dolomitization model was established according to the timing of diagenetic mineral precipitation, which can improve that the geological understanding of the effect of hydrothermal fluid activities on the carbonate rocks in the Qixia Formation.

Keywords: Sichuan Basin; Permian; elements; isotope; dolostones; hydrothermal dolomitization

1. Introduction

The genesis of dolostone is always the focus of carbonate reservoir research. Dolostone reservoirs are widely distributed in the Permian Qixia Formation of the paleo-uplift in the central Sichuan Basin, China. Formation of the dolostone in the Maokou Formation overlying the Qixia Formation in the central Sichuan Basin was thought to relate to hydrothermal activity, as evidenced by abnormally high fluid inclusion homogenization temperature, positive Eu anomaly, abnormal isotope of limestone, and saddle-shaped dolomites [1–3]. Hydrothermal dolomitization in the Permian period was mainly affected by the activity of the Emei mantle plume, induced by magma eruption at about 259 Ma [4]. As a result, the dolomitization occurred with the hydrothermal fluid charging at this period [5–8]. However, previous studies were mostly concentrated on the northwest areas of Sichuan Basin, the relationship between the formation of dolostone and hydrothermal activity of the Qixia Formation in the central uplift of Sichuan Basin is still unclear.

Recently, the great exploitation potential of the Permian natural gas in Sichuan Basin has been shown. By the end of 2017, the accumulative proved reserves of natural gas in the Middle Permian in Sichuan Basin reached $881 \times 10^8 \text{ m}^3$ [9]. The Middle Permian Qixia Formation experienced early diagenesis during the most intensive basalt eruption [10]. The influence of the hydrothermal activities on the dolostone in the early diagenetic stage has not been well known. Based on the observation of thin sections; scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis; C, O, Sr isotopes measurement; cathode luminescence; and fluid inclusion homogenization temperature detection, this study aims to reveal the influence of hydrothermal activities on the formation and evolution of the dolostones in the Qixia Formation in the central uplift of the Sichuan Basin.

2. Geological Setting

The study area is located in the flank of the giant nose-shaped structure of Leshan-Longnusi paleo-uplift (Figure 1b). The tectonic evolution in the study area was mainly affected by the central uplift of the Sichuan Basin [11,12]. The central uplift developed in the Caledonian period and finally formed in the Early Permian after multiple tectonic movements [13–16]. During the Middle Permian period, the uplift of the basin basement resulted in differential denudation at the top of the Middle Permian in the study area [17] (Figure 1c). Due to the Emei ground fissuring movement, a large amount of basalt erupted in the early stage of the Late Permian, with the basement fault's reactivation and hydrothermal fluid activity [9,17,18]. There are four stages of the Emei mantle plume activities [17]. In the first stage of the Emei, basalt began to erupt and the relative sea level fall occurred in the late Qixia period. The second stage was characterized by the extensional rifting from the early restricted platform to the basin facies in the middle and late Maokou period. In the third stage, the pervasive karstification with the significant fall of relative sea level, occurred in the end of the Maokou period. In the fourth stage of the basalt eruption, faults were activated, and hydrothermal fluid charged into reservoirs in the early period of the Late Permian [17].

In the study area, the strata from the Sinian to the Jurassic periods could be identified, while the Devonian is generally absent. The Ordovician to Carboniferous sediments can be found occasionally at the edge of the study area. As a result, the Permian strata directly overlaid the Cambrian one in most area. The Upper Permian strata is composed of the Longtan and the Changxing formations, and the Middle Permian could be divided into the Qixia Formation and the Maokou Formation. The Lower Permian consists of the Liangshan Formation [18–21]. The Qixia Formation has a conformable contact relationship with the Lower Permian Liangshan Formation and the Maokou Formation [21–23]. However, the parallel unconformity between the Qixia Formation and the Maokou Formation could be observed in the northwest Sichuan Basin [24,25].

During the Middle Permian, the Qixia Formation deposited on the shallow open marine setting, including shoal and back-shoal [26]. The Qixia Formation has a thickness

of 80–110 m and can be divided into two members, e.g., the first member and the second member of the Qixia Formation. The first member of the Qixia Formation (Q1 Member) can be divided into two lithologic sections. The lower part of the Q1 Member is composed of the micritic limestones deposited in the deep marine, and the upper part consists of the bioclastic limestones and dolostones deposited on the shoals. The second member of the Qixia Formation (Q2 Member) mainly consists of bioclastic limestones, microsparry pelletal limestones, sparry intraclastic limestones, dolomitic limestones, and crystalline dolostones, with a small amount of marlstones. The skeletal grains in bioclastic limestones include foraminifera, algae, sponges, and bivalves [19,22].

Figure 1. Geological setting of the study area. (a) The location of Sichuan Basin in southwestern China. (b) The study area is located in the red frame of (b). (c) Stratigraphic column and tectonic movements. (d) Vertical distribution of two types of dolostones.

3. Methods

The geological information of the Qixia Formation in this study covers 3 drilling wells with cores and 15 drilling wells with rock debris. The samples for petrographic observation and geochemical measurement were collected from two wells, MX108 (13 samples) from a depth between 4657.5 and 4690.78 m and MX42 (7 samples) from a depth between 4649.3 and 4655.62 m. Overall, 17 samples were studied by means of cathode luminescence, one sample was observed by a scanning electron microscope, 15 samples were tested for the composition of rare earth elements, 13 samples were measured for the composition of microelements, 13 samples were tested for the composition of light isotopes and Sr isotope, 10 samples were measured for the fluid inclusion within dolomites and calcite cements, 7 samples were subjected to X-ray diffraction. These experiments were performed in the State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation in the Chengdu University of Technology, China.

Petrographic investigation of thin sections was performed on a microscope (Leica 4500p, Wetzlar, Germany). Blue epoxy resin was used for casting, and alizarin red was used for dyeing. The cathode luminescence of dolostones was observed by the CL8200 MK5-2 (made in Britain) cold cathode instrument. The working voltage was 14 kW, the current was 380 μ A, and the vacuum degree was 0.003 mbar. Exposure time was adjusted to 12 s. The scanning electron microscope instruments were a Quanta 250 FEG + Inca

X-max20 (FEI Company, Hillsboro, OR, USA) and an INCA x-max20 (Energy Disperse Spectroscopy, Oxford Instruments, High Wycombe, UK). The samples were coated with gold, and the electron images were taken with an acceleration voltage of 20 kV, a filament current of 240 μ A, and a beam diameter of 4 μ m.

The composition of elements was analyzed, using ICP-MS (inductively coupled plasma mass spectrometer, Agilent 7900, Santa Clara, CA, USA), with a test temperature of 20 °C and a relative humidity of 30%. Before testing, the samples were sliced and ground into a 200 mesh.

Carbon and oxygen stable isotopes were measured by the mass spectrometer (MAT253plus, Hillsboro, OR, USA), with an analysis error of $\pm 0.1\%$. Samples were processed through phosphoric acid method. The sample was dissolved with anhydrous phosphoric acid at 25 °C for 24 h. The δ values of C and O were reported relative to the V-PDB standard. The Z value was calculated using the formula: $Z = 2.048(\delta^{13}\text{C} + 50) + 0.498(\delta^{18}\text{O} + 50)$ [27–29].

Sr isotope was determined by a multi-receiving inductively coupled plasma mass spectrometer (Neptune Plus, Waltham, MA, USA). The error of strontium isotope measurement was represented by $2\sigma \pm$.

For the measurement of fluid inclusions, dolomites were selected. The homogenization temperature of fluid inclusions was measured on a THMS600 Cooling-Heating Stage (Linkam Scientific, Epsom, UK). The rate of temperature increase can be controlled to within 1 °C/min when approaching the critical point.

The order degrees of dolomite were determined by X-ray diffraction (XRD) using a Rigaku DMAX-3C equipped with Cu K α radiation (40 kV, 20 mA). The order degrees of dolomite were calculated by the ratio of two diffraction peaks $d(015)/d(110)$.

4. Results

4.1. Lithology

The lithologies of the Qixia Formation in the study area are mainly composed of dolostone, dolomitic limestone, and limestone. According to the classification of dolomites [30], the dolostones are composed of fine-medium crystalline dolostones and meso-coarse crystalline dolostones.

4.1.1. Fine-Medium Crystalline Dolostone

The crystal morphology of most fine-medium crystalline dolostones is subhedral. The crystal size of dolostone was mostly between 0.10 and 0.40 mm, and there was a mosaic contact relationship between crystals. The color of these dolostones under cathode luminescence was dark red (Figure 2a). The order degrees of fine-medium crystalline dolomites were from 0.69 to 0.79, with an average of 0.75. The cell parameters of these dolomites were different from that of the ideal dolomites. Suspected asphalt or heavy oil could be seen in the fine-medium crystalline dolostones under SEM (Figure 3). Energy spectrum analysis showed that the carbon content was as high as 80.3% (Table 1), which was identified as organic matter. Barite (BaSO_4) was also observed in the dolostone under SEM, identified by EDS. Through observation of a thin section, it was found that there were few visible pores in the fine-medium crystalline dolostone. The pores within the dolostone were mostly intercrystalline pores. These dolostones were prone to be distributed along the sequence boundary in the study area.

4.1.2. Meso-Coarse Crystalline Dolostone

Through core observation, the meso-coarse crystalline dolostones were found to be light gray to gray. The crystal sizes of meso-coarse crystalline dolostones ranged from 0.40 to 1.00 mm. The crystals of these dolostones were almost euhedral, with a straight edge. In some cases, the cloudy core and bright rim of dolomites could be observed. The order degrees of meso-coarse crystalline dolomites were higher than that of fine-medium crystalline dolomites, ranging from 0.82 to 0.93, with an average value of 0.87 (Table 2). The cell parameters of these dolomites were close to that of the ideal dolomite. The

color of these dolostones under cathode luminescence was orange (Figure 2b,d). The caves, dissolved pores, and dissolved fractures developed on the cores of the meso-coarse crystalline dolostones. The caves are usually filled with saddle-shaped dolomites, calcites and asphalts. The saddle-shaped dolomites were identified by sickle, curved crystal face, and wave extinction under the cross-polarized light (Figure 2E,e). The distribution of meso-coarse crystalline dolostones was massive and scattered in the Q1 and Q2 members.

Figure 2. The thin-section image and CL color of the carbonate rocks from the Qixia Formation. (A) MX42, 4659.68 m, fine-crystalline dolostone(-), (a) MX42, 4659.68 m, fine-crystalline dolostone, the color is dark red under cathode luminescence; (B) MX42, 4655.62 m, meso-coarse crystalline dolostone(-), (b) MX42, 4655.62 m, meso-coarse crystalline dolostone, the color is deep red under cathode luminescence; (C) MX108, 4671.8 m, fine-medium crystalline dolostone(-), (c) MX108, 4671.8 m, fine-medium crystalline dolostone, the color is red under cathode luminescence; (D) MX108, 4690.78 m, meso-coarse crystalline dolostone(-), (d) MX108, 4690.78 m, meso-coarse crystalline dolostone, the color is dark red under cathode luminescence; (E) MX108, 4690.78 m, meso-coarse crystalline dolostone, with some saddle-shaped dolomites(-), (e) MX108, 4690.78 m, meso-coarse crystalline dolostone, with some saddle-shaped dolomites(+); (F) MX42, 4652.18 m, dolomitic limestone(-), (f) MX42, 4652.18 m, dolomitic limestone, the color of the limestone part under cathode luminescence is null; (G) MX42, 4649.30 m, dolomitic limestone, fluorite(-), (g) MX42, 4649.30 m, dolomitic limestone, the color of the dolomites part under cathode luminescence is red. The arrow indicates fluorite; (H) MX42, 4659.10 m, bioclastic limestone(-), (h) MX42, 4659.10 m, the bioclastic limestone parts are dark under cathode luminescence.

Figure 3. SEM image of barite and core image of asphalt. (a) Barite under SEM. (b) Vug filling with asphalt.

Table 1. Elemental composition of asphalt and barite.

Well	Depth (m)	Lithologies	Magnification	Material	C/%	O/%	S/%	Cl/%	Ca/%	Au/%	Si/%	Al/%	Ba/%
MX42	4651.2	Fine-medium crystalline dolostone	600	Barite	9.95	28.45	10.33	0	0.44	8.55	0.34	0.45	41.49
MX42	4651.2	Fine-medium crystalline dolostone	600	Asphalt or oil trace	80.3	5.19	8.13	0.41	0.49	5.49	0	0	0

Table 2. The order degrees of various dolostones.

Well	Depth (m)	Lithologies	Order Degrees of Dolostones (δ)
MX42	4650.50	Meso-coarse crystalline dolostone	0.93
MX42	4651.20	Meso-coarse crystalline dolostone	0.82
MX42	4655.42	Fine-medium crystalline dolostone	0.69
MX42	4655.62	Meso-coarse crystalline dolostone	0.93
MX42	4659.68	Fine-medium crystalline dolostone	0.79
MX108	4671.8	Fine-medium crystalline dolostone	0.77
MX108	4689.46	Meso-coarse crystalline dolostone	0.84
MX108	4690.78	Meso-coarse crystalline dolostone	0.82

4.1.3. Dolomitic Limestone

The dolomitic limestone was partially dolomitized bioclastic limestone. The matrix between particles was mostly micrite calcite. The dolomitized particles were scattered in the matrix. For the dolomitic limestone part, the color of the limestone part under cathode luminescence was null (Figure 2F,f), and the dolostone part was dark red. These dolomitic limestones could be observed in the Q1 and Q2 member.

4.1.4. Limestone

Limestone is common in the Qixia Formation, dominated by bioclastic limestone (Figure 2H). The skeletal types and full organisms observed under the microscope included foraminifera, algae, *Fusulinella* sp., bivalves, brachiopods, and echinoderms. The intraclastic limestone and pelletoid limestone could also be observed in the Qixia Formation.

The bioclastic limestones and marlstones were interbedded in the lower part of the Q1 Member. The bioclastic limestone and intraclastic limestone developed in the upper part of Q1 Member. There was mainly sparry bioclastic limestone, micro-sparry pelletoid limestone, and sparry intraclastic limestone in the Q2 Member.

4.2. Elements

The composition of rare earth elements (REEs) of the carbonate rocks from the Qixia Formation in the study area is shown in Table 3. The total REE contents were in the range of 0.26–0.60 $\mu\text{g/g}$, in which the contents of heavy rare earth elements were 0.09–0.30 $\mu\text{g/g}$, and the contents of light rare earth elements ranged from 0.12 to 0.30 $\mu\text{g/g}$. The light rare earth/heavy rare earth ratios ranged from 0.66 to 1.81. The δEu values were 1.04–7.43, and the δCe values were 0.77–0.90 (Table 3). REE patterns of dolostones and limestones without diagenetic alteration are shown in Figure 4. The REE patterns of fine-medium crystalline and meso-coarse crystalline dolostone were characterized by positive Eu anomalies, compared with dolomitic limestone and limestone. In the REE pattern of meso-coarse crystalline dolostone, heavy rare earth elements were relatively enriched (Figure 4). At the same time, the δEu values of meso-coarse crystalline dolostone and fine-medium crystalline dolostone were different.

Table 3. Rare earth element composition of carbonate rocks from the Qixia Formation.

Well	Depth (m)	Lithologies	Rare Earth Element Concentration (µg/g)														Rare Earth Element Parameters					
			La	Ce	Pr	Nd	Sm	Eu	Tb	Gd	Dy	Ho	Er	Tm	Yb	Lu	Σ REE	Σ LREE	Σ HREE	Σ LREE/Σ HREE	δEu	δCe
MX108	4657.5	Limestone	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.01	0.02	0.03	0.02	0.26	0.12	0.15	0.79	1.11	0.86
MX108	4664.19	Limestone	0.05	0.03	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05	0.04	0.48	0.21	0.27	0.78	1.04	0.85
MX108	4671.16	Fine-medium crystalline dolostone	0.03	0.02	0.02	0.02	0.02	0.11	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.41	0.23	0.18	1.31	6.14	0.83
MX108	4675.9	Dolomitic limestone	0.02	0.02	0.02	0.01	0.01	0.04	0.02	0.02	0.02	0.02	0.02	0.03	0.04	0.03	0.33	0.13	0.2	0.66	2.73	0.83
MX108	4681.84	Dolomitic limestone	0.04	0.03	0.03	0.02	0.02	0.03	0.02	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.41	0.18	0.24	0.76	1.29	0.82
MX108	4686.49	Limestone	0.04	0.03	0.03	0.02	0.03	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.03	0.42	0.18	0.24	0.77	1.51	0.83
MX108	4689.46	Meso-coarse crystalline dolostone	0.03	0.02	0.02	0.02	0.03	0.08	0.02	0.03	0.02	0.03	0.02	0.03	0.04	0.03	0.44	0.21	0.23	0.94	3.17	0.84
MX108	4690.65	Limestone	0.04	0.02	0.02	0.02	0.02	0.04	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.31	0.15	0.16	0.97	1.95	0.82
MX42	4649.3	Dolomitic limestone	0.05	0.03	0.02	0.02	0.02	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.27	0.17	0.09	1.81	2.19	0.8
MX42	4650.5	Meso-coarse crystalline dolostone	0.09	0.05	0.04	0.03	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.01	0.03	0.02	0.41	0.26	0.15	1.71	1.29	0.78
MX42	4651.2	Meso-coarse crystalline dolostone	0.06	0.04	0.03	0.02	0.02	0.03	0.02	0.02	0.01	0.01	0.01	0.02	0.03	0.02	0.33	0.2	0.13	1.46	1.48	0.83
MX42	4652.18	Dolomitic limestone	0.08	0.05	0.05	0.04	0.04	0.05	0.03	0.03	0.03	0.03	0.03	0.04	0.05	0.05	0.6	0.3	0.3	1	1.35	0.81
MX42	4653.95	Limestone	0.04	0.03	0.02	0.02	0.01	0.04	0.01	0.01	0.01	0.02	0.01	0.02	0.03	0.02	0.3	0.17	0.14	1.22	3	0.9
MX42	4655.42	Fine-medium crystalline dolostone	0.03	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.3	0.14	0.17	0.84	1.86	0.81
MX42	4655.62	Meso-coarse crystalline dolostone	0.05	0.03	0.03	0.02	0.02	0.1	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.41	0.24	0.17	1.41	5.8	0.77
MX42	4659.1	Limestone	0.04	0.02	0.02	0.02	0.02	0.05	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.35	0.18	0.17	1.07	2.73	0.78
MX42	4659.68	Fine-medium crystalline dolostone	0.03	0.02	0.02	0.02	0.02	0.13	0.02	0.02	0.02	0.02	0.02	0.02	0.04	0.03	0.42	0.24	0.19	1.26	7.43	0.81

Note: ΣREE = SUM (La~Lu); ΣLREE = SUM(La~Eu); ΣHREE = SUM(Tb~Lu); δEu = Eu/((Sm + Gd)/2); δCe = Ce/((La + Pr)/2).

Figure 4. The REE patterns of carbonate rocks from the Qixia Formation (the normalizing values used were those of North-American shale).

The contents of trace elements are shown in Figure 5. It can be seen that the strontium content in limestone was from 349.48 to 699.00 ppm, with an average value of 476.05 ppm. The strontium content in dolomitic limestone ranged from 335.58 to 431.19 ppm with an average of 395.15 ppm. The strontium content of fine-medium crystalline dolostone was from 88.36 to 225.49 ppm, with an average value of 135.07 ppm. The strontium content of meso-coarse crystalline dolostone was from 80.02 to 132.87 ppm, with the average value of 104.34 ppm. The amount of manganese in dolomitic limestone was from 51.61 to 61.21 ppm, with the average value of 55.20 ppm. The amount of manganese of limestone was from 37.00 to 132.53 ppm, with an average value of 72.27 ppm. Manganese contents of the fine-medium crystalline dolostones ranged from 107.12 ppm to 166.52 ppm, with an average value of 136.97 ppm. Manganese contents of the meso-coarse crystalline dolostones ranged from 240.65 to 411.97 ppm, with an average value of 325.26 ppm.

Figure 5. Sr, Mn, and Ba value cross plots of different lithologies.

4.3. C, O, Sr Isotopes

The carbon and oxygen stable isotope values of limestone, fine-medium crystalline dolostone, and meso-coarse crystalline dolostone in the study area are shown in Table 4. The $\delta^{18}\text{O}$ of limestone was from -5.25‰ to -8.53‰ , with an average value of -6.92‰ . The $\delta^{13}\text{C}$ of limestone was from -2.62‰ to 4.35‰ . The $\delta^{18}\text{O}$ of fine-medium crystalline dolostone was from -7.18‰ to -8.53‰ , with an average value of -7.96‰ , and the $\delta^{13}\text{C}$ of fine-medium crystalline dolostone was from -1.21‰ to 4.99‰ , with an average value of 1.18‰ . The $\delta^{18}\text{O}$ of meso-coarse crystalline dolostone ranged from -7.26‰ to -8.35‰ , with an average value of -7.64‰ , and the $\delta^{13}\text{C}$ of meso-coarse crystalline dolostone ranged from -1.32‰ to 4.19‰ .

Table 4. Carbon, oxygen, and strontium isotope values of carbonate rocks in the Qixia Formation.

Well	Depth (m)	Lithologies	$\delta^{13}\text{C}_{\text{V-PDB}}\text{‰}$	$\delta^{18}\text{O}_{\text{V-PDB}}\text{‰}$	$^{87}\text{Sr}/^{86}\text{Sr}$
MX42	4649.3	Dolomitic limestone	−1.32	−7.26	0.707781
MX42	4650.5	Meso-coarse crystalline dolostone	−1.21	−7.3	0.708383
MX42	4651.2	Meso-coarse crystalline dolostone	−1.21	−7.23	0.70808
MX42	4652.18	Dolomitic limestone	−1.19	−8.08	0.707699
MX42	4655.42	Fine-medium crystalline dolostone	−1.35	−7.18	0.708412
MX42	4655.62	Meso-coarse crystalline dolostone	4.58	−8.52	0.708181
MX42	4659.68	Fine-medium crystalline dolostone	−1.41	−6.99	0.708089
MX108	4657.5	Limestone	4.35	−5.25	0.707121
MX108	4664.19	Limestone	−2.62	−8.53	0.70749
MX108	4671.16	Fine-medium crystalline dolostone	4.93	−8.53	0.70799
MX108	4671.8	Fine-medium crystalline dolostone	4.99	−8.06	0.708392
MX108	4681.84	Dolomitic limestone	3.61	−6.65	0.707894
MX108	4689.46	Meso-coarse crystalline dolostone	4.19	−8.35	0.708118
MX108	4690.78	Meso-coarse crystalline dolostone	3.73	−8.64	0.708526

Combined with the calculation method of ancient seawater temperature (T_s) proposed by Keith and Shackleton et al. [28,31], using the average value of $\delta^{18}\text{O}$ of Quaternary marine carbonate rocks of -1.2‰ as the standard for age correction, the T_s of the Qixia period could be calculated. The average $\delta^{18}\text{O}$ value of the Qixia Formation was -7.61‰ . The difference between the $\delta^{18}\text{O}$ value of the Quaternary marine carbonate rocks and that of the Qixia Formation was -6.41‰ . Then the actual test value was subtracted from the corrected value $\Delta\delta^{18}\text{O}$, and the corrected $\delta^{18}\text{O}_{\text{CaCO}_3}$ value was obtained.

$$T_s (^{\circ}\text{C}) = 15.976 - 4.2\delta^{18}\text{O}_{\text{CaCO}_3} + 0.13(\delta^{18}\text{O}_{\text{CaCO}_3} + 0.2)^2(\delta^{18}\text{O}_{\text{CaCO}_3}) = \delta^{18}\text{O}_{\text{V-PDB}}\text{‰} - \Delta\delta^{18}\text{O} \quad (1)$$

$$\Delta\delta^{18}\text{O} = \text{The average value of } \delta^{18}\text{O}_{\text{V-PDB}}\text{‰} - (-1.2\text{‰}), (-1.2\text{‰}) = \text{Average } \delta^{18}\text{O} \text{ of Quaternary marine carbonate rocks} \quad (2)$$

According to the Formulas (1) and (2) [27–29,32], the ancient seawater temperature of the Qixia period in the study area was calculated (Table 5). As shown in Table 5, the T_s of the Qixia period was between 11.35 and 25.87°C , with an average value of 21.26°C . At the same time, the oxygen isotope values could also be used to calculate the temperature of the precipitation of carbonate minerals (T_c) [33].

$$T_c (^{\circ}\text{C}) = 13.85 - 4.54\delta^{18}\text{O}_{\text{V-PDB}}\text{‰} + 0.04(\delta^{18}\text{O}_{\text{V-PDB}}\text{‰})^2 \quad (3)$$

As shown in Table 5, the diagenetic temperature of fine-medium crystalline dolostone was between 48.77 and 55.49°C . According to the geothermal gradient of $3^{\circ}\text{C}/100\text{ m}$ [34,35], the burial depth was about 1600 m .

The $^{87}\text{Sr}/^{86}\text{Sr}$ values of dolostones from the Qixia Formation were between 0.707121 and 0.708526 (Table 4). The $^{87}\text{Sr}/^{86}\text{Sr}$ values of limestones ranged from 0.707121 to 0.70749 , with an average value of 0.707306 . The $^{87}\text{Sr}/^{86}\text{Sr}$ values of dolomitic limestones were between 0.707699 and 0.707894 , with an average value of 0.707791 . The $^{87}\text{Sr}/^{86}\text{Sr}$ values of fine-medium crystalline dolostones were between 0.70799 and 0.708189 , with an average

value of 0.708113. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of meso-coarse crystalline dolostones were from 0.708383 to 0.708526, with an average value of 0.708455. It can be seen that the $^{87}\text{Sr}/^{86}\text{Sr}$ values of dolostone were heavier than those of dolomitic limestone and limestone, while the $^{87}\text{Sr}/^{86}\text{Sr}$ values of meso-coarse crystalline dolostone were heavier than that of fine-medium crystalline dolostone (Table 4).

Compared with the range of $^{87}\text{Sr}/^{86}\text{Sr}$ in seawater at the depositional period [36,37], the $^{87}\text{Sr}/^{86}\text{Sr}$ values of limestones, dolomitic limestones, and some fine crystalline dolostones in the Qixia Formation were mostly within the range of Sr isotope composition of contemporaneous seawater (Figure 6). The $^{87}\text{Sr}/^{86}\text{Sr}$ was prone to increase with the dolomitization. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of meso-coarse crystalline dolostones in the Qixia Formation were generally heavier than those of fine-crystalline dolostone, dolomitic limestone, and limestone (Figure 6).

Table 5. The calculated ancient seawater temperature and diagenetic temperature based on oxygen isotopes.

Well	Lithologies	Depth (m)	$\delta^{18}\text{O}_{\text{V-PDB}}\text{‰}$	$\delta^{18}\text{O}\text{-CaCO}_3$	Ancient Seawater Temperature ($^{\circ}\text{C}$)	Theoretical Diagenetic Temperature ($^{\circ}\text{C}$)
MX108	Meso-coarse crystalline dolostone	4690.78	−8.64	−2.23	25.88	56.06
MX42	Fine-medium crystalline dolostone	4659.68	−6.99	−0.58	18.43	47.54
MX108	Limestone	4657.5	−5.25	1.16	11.34	38.79
MX108	Limestone	4664.19	−8.53	−2.12	25.36	55.49
MX42	Fine-medium crystalline dolostone	4655.42	−7.18	−0.77	19.25	48.51
MX42	Meso-coarse crystalline dolostone	4651.2	−7.23	−0.82	19.47	48.77
MX42	Dolomitic limestone	4652.18	−8.08	−1.67	23.27	53.14
MX108	Fine-medium crystalline dolostone	4671.16	−8.53	−2.12	25.36	55.49
MX108	Fine-medium crystalline dolostone	4671.8	−8.06	−1.65	23.18	53.04
MX42	Meso-coarse crystalline dolostone	4655.62	−8.52	−2.11	25.31	55.43
MX108	Dolomitic limestone	4681.84	−6.65	−0.24	16.98	45.81
MX42	Dolomitic limestone	4649.3	−7.26	−0.85	19.60	48.92
MX42	Meso-coarse crystalline dolostone	4650.5	−7.3	−0.89	19.78	49.12
MX108	Meso-coarse crystalline dolostone	4689.46	−8.35	−1.94	24.52	54.55

Figure 6. The cross plot of oxygen isotope and strontium isotope.

Figure 7. Homogenization temperature of fluid inclusion. (a) Distribution histogram of the homogenization temperature of fluid inclusion within dolomites; (b) image of fluid inclusions in MX108 well 4689.46 m.

4.4. Homogenization Temperature of Fluid Inclusions

The homogenization temperatures (T_h) of fluid inclusions within dolomites of the Qixia Formation are shown in Figure 7a. The fluid inclusions within the dolomite crystal are shown in Figure 7b. It was found that there were two obvious T_h intervals, as shown in Figure 7a. The first interval was 95–125 °C, with an average T_h of 108 °C. The second interval was 135–165 °C, with an average T_h of 148 °C.

5. Discussion

5.1. Timing and Stages of Dolomitization

In the study area, fine-medium crystalline dolostones and meso-coarse crystalline dolostones were found in the Qixia Formation. The carbon isotope values of these two types of dolostones were close to those of limestones. The $\delta^{13}\text{C}$ of limestone was from -2.62‰ to 4.35‰ . The carbon isotope of Permian seawater was 2‰ – 5‰ [38]. It indicates that they have the same carbon source [39–41]. The $\delta^{13}\text{C}$ values of dolostones were mostly positive (Table 4), indicating that meteoric water or organic matter was rarely involved in the dolomitization [42,43].

Through the analysis of crystal morphology, the degrees of crystal automorphism of fine-medium crystalline dolostones were found to be relatively poor, with a subhedral texture. The order degrees of dolomites in the fine-medium crystalline dolostones were relatively low, ranging from 0.69 to 0.79. The color of fine-medium crystalline dolostone under cathode luminescence was dark red, showing low Mn concentration. There was a Eu positive anomaly observed in the fine-medium crystalline dolostone, indicating a reducing environment. Meanwhile, the calculated diagenetic temperature of the fine-medium crystalline dolostone was from 48.77 to 55.49 °C, using the oxygen isotope. These characteristics show that the fine-medium crystalline dolostones formed under a relatively low temperature, with incomplete dolomitization [44,45].

The crystal morphology of meso-coarse crystalline dolostone was euhedral, with a straight edge. There was also a cloudy center and a bright rim structure of these dolomites. The order degrees of these dolomites were relatively high, ranging from 0.82 to 0.93. The color of meso-coarse crystalline dolostone under cathode luminescence was orange. There was a distinct Eu positive anomaly observed in the meso-coarse crystalline dolostone. The content of strontium decreases with the dolomitization [36,46,47]. In terms of the strontium contents in the two types of dolostones (Figure 5), the strontium contents of the meso-coarse crystalline dolostones were higher than that of fine-medium crystalline dolostone, indicating that the dolomitized fluids of the two types of dolostones might be different. The Mn contents of meso-coarse crystalline dolostones were significantly higher than that of the fine-medium crystalline dolostones, dolomitic limestones, and limestones (Figures 5 and 8). The content of strontium in dolostone has a negative correlation with the content of magnesium [42,46,48]. This trend results because the ionic radius of strontium (the ionic radius of strontium is 0.113–0.132 nm) is relatively close to that of calcium (the ionic radius of calcium is 0.099–0.118 nm), while the ionic radius of magnesium is 0.065–0.087 nm [3]. Therefore, strontium ions will replace calcium ions

and leave magnesium ions. The relatively high Mn contents indicate a relatively reducing environment and strong diagenetic alteration. During the deposition process, the oxygen isotope values decrease with the increase of temperature [49], assuming that the salinity of ancient seawater is basically unchanged. The more negative $\delta^{18}\text{O}$ (Figure 6) and relatively high temperature of fluid inclusions enclosed in dolomites shows there was a diagenetic environment with a high temperature (Figure 7a). The relatively heavy $^{87}\text{Sr}/^{86}\text{Sr}$ values of meso-coarse crystalline dolostone might be related to the presence of exogenous ^{87}Sr input during dolomitization. These characteristics indicate that meso-coarse crystalline dolostone formed in a strong reducing environment with a relatively high temperature. The dolomitization of the meso-coarse crystalline dolostone was complete, and dolomite crystals of these dolostones were close to that of ideal dolomites.

Figure 8. Cross plot of carbon and oxygen isotopes.

Therefore, based on the analysis data, there were two phases of diagenetic fluid with different temperatures and geochemical composition in the diagenesis process of the Qixia Formation. The carbon and oxygen isotopes of the carbonate rocks from the Qixia Formation could be divided into two areas (Figure 8), showing the two phases of diagenetic fluid. The different Eu anomaly of the two populations of dolomites also indicates that there were two different diagenetic fluids (Figure 4) [41,42,50,51]. Meanwhile, the two intervals of homogenization temperatures of fluid inclusions could be seen in Figure 7a.

The paragenesis of dolostones from the Permian Qixia Formation in the central uplift of the Sichuan Basin can be determined by a diagenetic sequence. The asphalt filling fractures could be observed in the core and thin sections of the two types of dolostones (Table 1 and Figure 3), indicating that the timing of dolostone formation was earlier than that of oil and gas filling. Previous studies suggested that the hydrocarbons had charged into the Qixia Formation in the study area after Jurassic [51,52]. Therefore, the time of dolostone formation should be earlier than the Jurassic period.

Based on the above discussion, this study suggests that dolostone in the study area was formed in two stages during two periods. Fine-medium crystalline dolostone was formed in the shallow burial period. Meso-coarse crystalline dolostone was formed in the relatively deep burial environment before the Jurassic.

5.2. Dolomitization of Dolostone Formed by Hydrothermal Fluids

As discussed above, the dolostones in the Qixia Formation were dolomitized before the Jurassic period. The burial depth of the Qixia Formation in the study area during

the Jurassic was about 2500 m [46], assuming the average geothermal gradient was the maximum value of 4 °C/100 m [35]. The burial temperature of the Qixia Formation in this period was 100 °C. The homogenization temperatures of fluid inclusions within dolomites ranged from 95 to 165 °C (Figure 7), which is significantly higher than the burial temperature of 100 °C. The high homogenization temperature indicates that the formation of dolostone may be affected by local high-temperature conditions or thermal events [40,41,53,54]. At the same time, the oxygen isotope values of the two populations of dolomites were obviously negative. Excluding the meteoric water, the negative oxygen isotope may be affected by the hydrothermal fluid [40,41,47]. The oxygen isotope value of dolostones influenced by hydrothermal fluid usually was more negative than that of limestone and reflux-seepage dolostone, e.g., the hydrothermal dolostone with $\delta^{18}\text{O}$ of below -7‰ [55] and coarse crystalline dolomite with $\delta^{18}\text{O}$ of -7.82‰ [3] in the Maokou Formation in the central uplift of the Sichuan basin. The $\delta^{18}\text{O}$ of fine crystalline dolostone (-7.18‰ to -8.53‰) and meso-coarse crystalline dolostone (-7.26‰ to -8.35‰) in this study were more negative than that of limestone (average value of -6.92‰). However, the $\delta^{18}\text{O}$ of hydrothermal dolostones in other basins is usually below -10‰ [56,57], the relatively heavier $\delta^{18}\text{O}$ in the study might have been influenced by the high salinity. Strontium isotope could be used to identify the occurrence of hydrothermal fluids [8]. The Sr isotopes of meso-coarse crystalline dolostone were heavier than that of fine-medium crystalline dolostone and were beyond the range of Sr isotope of contemporaneous seawater (Figure 6). Barite was observed under a microscope. Meanwhile, there was the obvious Eu positive anomaly of the two types of dolostone and the heavy rare earth elements were relatively enriched in the meso-coarse crystalline dolostones, indicating a strong reducing environment probably caused by the hydrothermal fluids [32,58–60]. These characteristics indicate that the diagenesis of the two types of dolostones were influenced by hydrothermal fluids. According to the oxygen isotopes, with values beyond -10‰ , and distinct Eu positive anomaly of these dolomites, the hydrothermal fluid was of relatively high salinity and reducing capacity, with the source of sealed seawater in the strata.

Combined with the regional tectonic setting, Emeishan basalt erupted strongly from the late depositional period of the Early Permian Maokou Formation to the early stage of the Late Permian in the southwest area of the Sichuan Basin [34,61]. Therefore, the local high-temperature condition may be closely related to the eruption of Emeishan basalt. The high temperature of fluid inclusion with a range of 135–165 °C (Figure 7) and the relatively high order degrees of dolomites indicate that the formation of meso-coarse crystalline dolostone occurred in the period of hydrothermal fluid activity during the eruption of Emeishan basalt. However, based on the U-Pb isotope dating of dolomite, the age of the hydrothermal dolomite formation in the Qixia Formation in the southwest area of Sichuan basin was suggested at about 216–206 Ma [62], indicating the hydrothermal dolomite formation occurred after the eruption of Emeishan basalt. Therefore, in this study it was determined that the meso-coarse crystalline dolomites of the Qixia Formation might have formed in the relatively deep burial diagenesis, after the moment of Emeishan basalt eruption. At the same time, saddle-shaped dolostone and matrix dolostone were also formed [63,64].

Through the statistics of a large number of hydrothermal dolostones in the world, Davies and Smith (2006) found that nearly 80% of hydrothermal dolomitization occurs during early diagenesis or shallow burial [32,39,65]. The homogenization temperatures of fluid inclusions within fine-medium crystalline dolostone were mostly between 95 and 125 °C (Figure 7a), indicating that the formation of dolomite may be related to the early stage of hydrothermal fluid activity, before the timing of meso-coarse crystalline dolomite formation. According to the heat flow recovery results of some typical wells in the study area [66], the temperature in the study area began to increase rapidly from the Permian period. The regional heat flow value suddenly increased at about 259 Ma, and then began to decrease significantly [66]. The rapid increase of the heat flow value resulted from the Emei ground fissuring movement in the Sichuan Basin during the Late Permian–Late Triassic,

which was characterized by extensional fault activity [67]. The peak temperature of hydrothermal fluid in that period occurred at the moment of Emeishan basalt eruption. Some high-temperature fluid inclusions within calcite veins in the fine crystalline dolostones might have been captured in the period of this geological event. The relatively low Mn content of fine-medium crystalline dolostone and the low abnormal value of Eu positive anomaly (Figure 4) indicate that the diagenetic temperature of fine-medium crystalline dolostones was lower than that of meso-coarse crystalline dolostones. The formation of fine-medium crystalline dolostone might have occurred in the early stage of the Emeishan basalt eruption, during the stage of hydrothermal fluid rising from lower strata in the depositional period of the Q2 Member (calculated from the burial depth).

5.3. The Influence of Two Stages of Hydrothermal Fluid Activity on the Dolostone Formation

Through the well-to-well correlation using the well cuttings, the fine-medium crystalline dolostones were found to be distributed along the sequence boundary between Q1 and Q2 Members, with good lateral continuity (Figure 1d). During the deposition of the Q1 Member, a large-scale shoal was developed in the study area. The bioclastic limestones with good physical properties were developed at the top of the Q1 Member [26]. As the consequence of the Emei ground fissuring movement, the hydrothermal fluid related to the mantle plume continuously charged into the Qixia Formation through the faults [18,68]. In the early stage of hydrothermal fluid activity, the hydrothermal fluids flowed laterally in the bioclastic limestones along the sequence boundary, which prompted the dolomitization and led to the layered distribution of fine-medium crystalline dolostone.

During the hydrothermal fluid activity after the Permian, meso-coarse crystalline dolostone formed. It can be seen that the meso-coarse crystalline dolostones are not distributed laterally as fine-medium-grained dolostone but were massive and locally distributed (Figure 1d), mainly distributed along faults [18,40,54,65,69–71]. During the formation of the meso-coarse crystalline dolostones, the hydrothermal fluid moved upward rapidly through the fracture. When the hydrothermal fluid passing through the Q1 Member, because the porosity had been very low as the result of diagenesis, the hydrothermal fluid could not move rapidly laterally. The dolomitization induced by the second stage of hydrothermal fluid only occurred along the fault zone.

The dolomitization models of the dolostones from the Qixia Formation following the two stages of hydrothermal fluid activity were established in the study (Figures 9 and 10).

Figure 9. Genetic model of dolostone formation affected by the first stage of hydrothermal fluid.

Figure 10. Genetic model of dolostone formation affected by phase II fluid.

6. Conclusions

The dolostone of the Qixia Formation in the central uplift of Sichuan Basin formed in two stages. The fine-medium crystalline dolostone formed in the shallow burial environment. The meso-coarse crystalline dolostone formed in a relatively deep burial environment.

The genesis of the dolostones from the Qixia Formation in the central uplift of the Sichuan Basin was related to hydrothermal fluid activity.

The formation of dolostones from the Qixia Formation in the central uplift of the Sichuan Basin was affected by two-stages of hydrothermal fluid activity. In the first stage, diagenetic fluid entered into the Qixia Formation and flowed laterally along the sequence boundary at the top of the Q1 Member, resulting in the formation of fine-medium crystalline dolostone. In the late diagenesis, high-temperature diagenetic fluids passed through the Qixia Formation, leading to the formation of meso-coarse crystalline dolostones along the faults.

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