

Article

Source and U-Pb Chronology of Diagenetic Fluids in the Permian Maokou Formation Dolomite Reservoir, Eastern Sichuan Basin, China

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Abstract: The hydrothermal dolomitization, facilitated by basement fault activities, had an important impact on the Permian Maokou Formation dolomite in the Sichuan Basin, which experienced complex diagenesis and presented strong reservoir heterogeneity. The source and age of diagenetic fluids in this succession remain controversial. In this study, various analyses were implemented on samples collected from outcrops and wells near the No. 15 fault in the eastern Sichuan Basin to reconstruct the multi-stage fluid activity and analyze the impact on reservoir development, including petrology, micro-domain isotopes, rare earth elements, homogenization temperature of fluid inclusions, and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) U-Pb dating. The homogenization temperature of primary brine inclusions in fine-grained matrix dolomite and saddle dolomite is concentrated between 100 and 150 °C, which indicates that the impacts of abnormally high temperatures of other geological bodies. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ value and low $^{87}\text{Sr}/^{86}\text{Sr}$ value indicate that the diagenetic fluid of fine-grained matrix dolomite is mainly Permian seawater. The U-Pb ages of fine-grained matrix dolomite are ~260 Ma, which coincides with the age of the main magmatism of Emeishan Large Igneous Province (ELIP), and hydrothermal fluid provided a favorable high-temperature environment in the penecontemporaneous stage. While highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ compositions suggests those of saddle dolomite, the high-temperature Sr-rich formation fluid. The U-Pb ages of saddle dolomite are 245–250 Ma, which coincides with the age of the 255–251 Ma magmatism of ELIP. This indicates that those should be the diagenetic products of the ELIP hydrothermal fluid in the shallow burial stage. The U-Pb age of coarse-grained calcite is 190–220 Ma, and it should be the diagenetic product of the deep burial stage. Brine inclusions associated with primary methane inclusions were developed in coarse-grained calcite, with a homogenization temperature range of 140.8–199.8 °C, which indicates that the formation fluid activities were related to hydrocarbon charging. The Permian Maokou Formation dolomite was firstly formed in the penecontemporaneous shallow burial stage, and then it was subjected to further hydrothermal dolomitization due to the basement faulting and the abnormally high heat flow during the active period of ELIP. Hydrothermal dolomitization contributed to the formation and maintenance of intercrystalline and dissolution pores, whereas it also formed saddle dolomite to fill the pores, and reduce the pore space. The influence of deep fluid activities on reservoir evolution is further distinguished.

Keywords: Sichuan Basin; Permian Maokou Formation; hydrothermal dolomitization; U-Pb chronology; Emeishan Large Igneous Province



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1. Introduction

During past decades, karst fracture-vuggy reservoirs have been important exploration targets in the Permian Maokou Formation, Sichuan Basin, South China [1]. After more than 60 years of exploration, nearly 100 natural gas reservoirs have been discovered, mainly in the southern Sichuan Basin, contributing to a cumulative proven reserve of $852 \times 10^8 \text{ m}^3$ [2,3]. High-yield gas flow has been recently reported in central and eastern Sichuan Basin (e.g., Wells GT-2, NC-1, and TL-6), demonstrating the presence of the dolomite reservoirs affected by deep hydrothermal fluids along basement faults in the Maokou Formation [4,5]. Due to the strongly heterogeneous spatial distributions, the dolomite reservoir is difficult to predict [6–8]. Therefore, it is critically important to explore the impact of hydrothermal alteration in this dolomite reservoir.

The Permian dolomites were widely distributed in the world [9], which contain chemical geological information about the seawaters and attracts many scholars' attentions. Several mechanisms have been proposed to explain the origin of dolomitization in the Maokou Formation, including basalt-related leaching dolomitization [10], burial dolomitization [11], hydrothermal dolomitization [12], superimposition of penecontemporaneous seawater-evaporating dolomitization and hydrothermal alteration [13], and tectonically-related hydrothermal dolomitization [14–17]. However, it remains controversial when it comes to the source and formation time of dolomitization fluids. The dolomite is supposed to be closely related to the Permian Emeishan Large Igneous Province (ELIP) based on analyses of its stratigraphic position and diagenetic sequences [18,19]. However, recent U-Pb dating indicates that these strata experienced multiple stages of dolomitization [20,21], with the earliest occurring at $240 \pm 12 \text{ Ma}$ to $233.8 \pm 6.4 \text{ Ma}$ and the latest at $16.40 \pm 0.74 \text{ Ma}$ to $12.3 \pm 1.2 \text{ Ma}$. These ages are much later than the ELIP, and the dolomitization of the Maokou Formation may occur in the burial period. Therefore, the tectonically-related hydrothermal fluids are related to the multi-stage activities of the Longmenshan thrust and nappe [22]. Hydrothermally-altered dolomite is also found along the basement faults in the central-eastern Sichuan Basin, and these basement faults are not much affected by the nappe structure of the Longmen Mountains. In this context, three questions need further research and clarification: (i) Is the dolomite developed along the faults formed in the penecontemporaneous period or the burial period? (ii) Is its formation related to ELIP? (iii) Does the alteration by multi-stage and multi-source fluids have constructive influences on the Maokou Formation reservoir?

It is common to determine the sequence of mineral formation through the cutting relationship between minerals or the homogenization temperature measurement of primary inclusions. However, these methods cannot obtain the precise geological age of diagenetic fluid activities. In recent years, the success and popularization of in-situ micro-domain U-Pb chronology have brought opportunities for accurately determining the age of carbonate rock deposition and diagenesis [23–32]. Accordingly, this study implemented a series of analyses to clarify the source and formation time of hydrothermal diagenetic fluids that influenced the Maokou Formation dolomite reservoirs in the eastern Sichuan Basin, including systematic U-Pb dating of carbonate minerals, micro-domain isotopes of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $^{86}\text{Sr}/^{87}\text{Sr}$, rare earth elements (REEs), and homogenization temperature of fluid inclusions. Furthermore, we evaluated the influence of multi-stage tectonic movements and deep fluids in the Maokou Formation reservoirs since the Permian and established a dolomite reservoir development model to provide a theoretical basis for the prediction of dolomite reservoir distribution.

2. Geological Background

During the early Late Permian, the Sichuan Basin was in an extensional environment [33,34]. Affected by mantle plume activities, voluminous basalts were accumulated in the western Sichuan Basin. Meanwhile, the ELIP led to an increase in the heat flow, which had an important impact on the sedimentation and hydrocarbon accumulation during this period [35]. During the depositional period of the Maokou Formation, the crust was

relatively stable, with prevalent carbonate platform deposits on gentle slopes. The Maokou Formation is 50–600 m thick, and the main lithologies are gray, light gray thick-bedded micritic bioclastic limestone, micritic limestone, and chert concretion-containing or siliceous thin layers [1,36,37]. The Maokou Formation is divided into four members based on the lithology and depositional environment. The first member, hereinafter referred to as Mao-1 Member, is dominated by black argillaceous bioclastic limestone and argillaceous micrite algal limestone, with eyeball-shaped structures, siliceous bands, and siliceous agglomerates. Mao-2 Member is characterized by gray-brown micrite bioclastic limestone, sparry bioclastic limestone, partially dolomitized limestone, and grain dolomite. Mao-3 Member consists of light gray sparry fusulina limestone, sparry bioclastic limestone, partially dolomitized limestone, and grain dolomite. Mao-4 Member is incompletely preserved and comprised of dark gray-black gray bioclastic micritic limestone, with parallel unconformity between itself and the overlying Longtan Formation (Figure 1a).

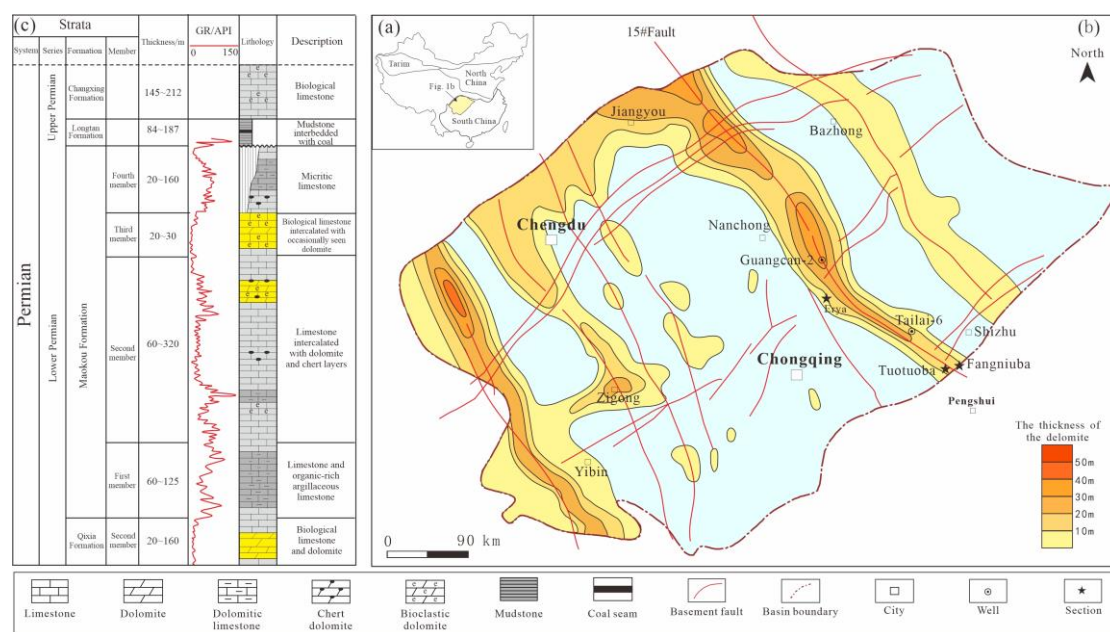


Figure 1. (a) Tectonic sketch map of China and location of the Sichuan Basin. (b) Distributions and thickness of the Maokou Formation dolomite and basement faults. (c) Stratigraphy of the Maokou Formation in the Sichuan Basin. The yellow colour is dolomite reservoir, GR = natural gamma-ray logging.

Vertically, the Maokou Formation dolomite is mainly developed in the upper part of the Mao-2 Member and the middle and lower parts of the Mao-3 Member (Figure 2).

In the map view, the Maokou Formation dolomite exhibits “layer-like” banded distributions along the basement faults [38]. The basement faults are mainly distributed in the NW-SE direction, among which the No. 15 extensional fault is relatively large in scale and has a strong control on the dolomite distribution (Figure 1b). In addition to controlling the dolomite reservoirs, basement faults also controlled the formation and distribution of oil and gas reservoirs in the Maokou Formation. In general, the contribution of the underlying Silurian source rocks to the Maokou Formation becomes larger at locations that are closer to the basement faults, resulting in higher gas contents and test productions [5,6].

In this study, our focus is on the eastern part of the No. 15 fault, including two outcrops (i.e., Fangniuba and Tuotuoba) and two wells (i.e., GT-2 and TL-6) (Figures 1 and 2).

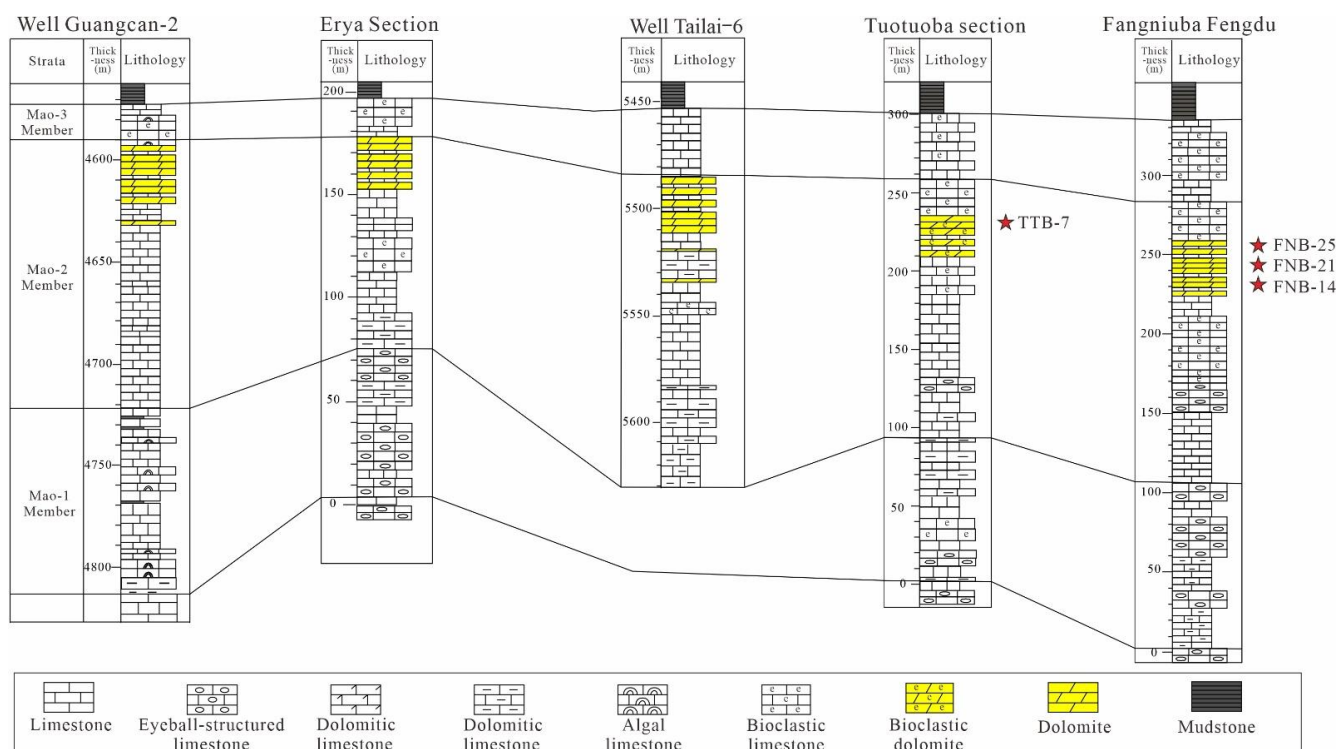


Figure 2. Correlation between wells drilled around the No. 15 basement fault in the eastern Sichuan Basin and outcropped Maokou Formation. The yellow colour is the reservoir, and the five-pointed star is the samples.

3. Sampling and Testing Methods

A total of 62 samples were obtained from two outcrops (i.e., Fangniuba and Tuotuba) and one well (i.e., TL-6) to prepare for sections. Detailed petrographic analysis was carried out under a Leica 4500 optical microscope (Leica, Wetzlar, Germany) and a CL8200MK5 (Cambridge Image, UK) cathodoluminescence (CL) microscope, which helped determine the diagenetic sequence. Representative samples were selected for analyses of C, O, and Sr isotopes, REEs, U-Pb dating, and homogenization temperature of fluid inclusions in micro-domains.

Measurements of C, O, and Sr isotopes and REEs were achieved at the Beijing Research Institute of Uranium Geology. Specifically, C and O isotopes were measured following the standard of DZ/T 0184.17–1997, “Determination of carbon and oxygen isotopic composition in carbonate minerals or rocks by the phosphoric acid method”. Dental drills were first used to obtain powder samples of different rock fabrics in micro-domains. Then, 20 mg of calcite or dolomite powder samples (200 mesh) were added with phosphoric acid for 24 h or 72 h at 25 °C, respectively. CO₂ released by the reaction was measured by a Finnigan MAT-252 mass spectrometer (Finnigan MAT, Bremen, Germany) to obtain isotope ratio results. The obtained values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were calibrated against the Vienna Pee Dee Belemnite (VPDB) standard. The Sr isotope was measured following the standard of GB/T 17672-1999, “Determination of isotopes of lead, strontium, and neodymium in rocks”. First, 100 mg of calcite or dolomite powder samples (200 mesh) were dissolved in 2 mL 6N HCl, followed by reactions at 100–110 °C for 24 h. Then, the solution was processed by an AG50WX12200–400 mesh ion exchange resin chromatography column to extract the Sr isotope. Eventually, a Finnigan MAT Triton TI surface thermal ionization mass spectrometer (Finnigan MAT, Bremen, Germany) was used to obtain the ratio of $^{86}\text{Sr}/^{87}\text{Sr}$. REEs were analyzed using a Thermo Scientific Element XR (Thermo, Waltham, MA, USA) inductively coupled plasma mass spectrometer. During the analysis, Rh was used as an online internal standard, and the laboratory rock standard sample (GBW-07312)

was repeatedly measured to control the analysis accuracy, which was demonstrated to be better than 10%. To eliminate the odd-even effect, the Australian Post-Archean Average Shale (PAAS) was used as the reference for REE standardization.

U-Pb dating was completed at the Institute of Geology and Geophysics, Chinese Academy of Sciences. First, handmade samples were cut into centimeter-sized pieces, cast into standard epoxy mounts (2.5 cm in diameter and 4–5 mm in thickness), and polished to the state with a roughness < 1 micron. The analytical dolomite was selected in an euhedral shape to avoid inclusions and microcracks. Then, U-Pb isotope analysis was carried out by the LA-SF-ICP-MS system, which combined the Photo Machine Analyst G2 (Photon Machines, Redmond, WA, USA) laser ablation system and Element XR (Thermo, Waltham, MA, USA). The experiment was carried out in a fully automated mode, with 60–80 ablation points as an analysis group. Two NIST SRM 614, two ARM-3, and three calcite standard substances (WC-1) were inserted at every ten analysis points. Each unknown sample was implemented with a 30–40 point analysis [30]. Data processing follows previous studies [24,25,39], using IsoplotR software for data plotting [40], and the success rate is 85%.

Fluid inclusion analysis was completed at the China University of Geosciences (Wuhan) using a NIKON-LV100 (Nikon, Tokyo, Japan) dual-channel fluorescence-transmitted light microscope and a Linkam THMSG 600 (Linkam, Salfords, UK) cold and hot stage. The temperature measurement error was ± 0.1 °C. The heating rate was set at 5 °C/min when measuring the homogenization temperature of the gas-liquid two-phase brine inclusions, and it was adjusted to 0.5 °C/min before the phase boundary line disappeared. Then, the temperature was kept constant for 2 min while recording the homogenization temperature at which the inclusions were completely homogeneous. Subsequently, the temperature was lowered to observe the appearance of bubbles. Again, the temperature was increased to measure the homogenization temperature for consistency confirmation.

4. Results

4.1. Lithological Features

The Permian Maokou Formation dolomite in the eastern Sichuan Basin is macroscopically layered or patchy in the field (Figure 3a,b), and the cracks, zebra stripes, and caves are very developed.

The cracks and caves are mostly filled with dolomite and calcite cement in sequence, and some are semi-filled, which results in some residual pore space remaining. The dolomite is associated with fracture systems in the core (Figure 4). These cracks are usually small in width and have limited extension length and are associated with karst caves and crystal caves. In addition, the cracks are mainly filled with dolomite and calcite cement. Silicon nodules can be seen coexisting with matrix dolomite, and both are cut by later fractures.

In the Erya section of the Huaying Mountain, layered dolomite is dominant and gradually changes into limestone; fine-medium-grained dolomite is distributed in a patchy form within silty-fine-grained matrix dolomite, with obvious anisocrystalline structures. In Well TL-6, Fangniuba, and Tuotuoba sections, patchy dolomite is dominant (Figure 5), and it coexists with micritic limestone, silty-fine-grained matrix dolomite, porous vuggy coarse-grained dolomite, and calcite; these lithologies macroscopically appear in the shape of “snowflakes” with alternating light and dark colors. Two types of pore spaces are developed: intercrystalline pores in matrix dolomite and residual fractures and vugs due to hydrothermal dolomitization. There are various hydrothermal mineral assemblages (e.g., saddle dolomite, quartz, sphalerite, and pyrite), forming complex diagenetic sequences (Figure 6a), which reflects multi-stage and multi-property fluid activities. The main mineral filling sequence in dolomite fractures and vugs is identified to be fine-grained matrix dolomite (MD)-saddle dolomite (SD)-coarse-grained calcite (CC)-quartz (Qt). MD is dominated by euhedral crystals and exhibits dull red luminescence (Figure 5f). SD develops ring structures and exhibits alternating light-dull-red luminescence. CC and Qt are formed later than SD, filling dissolution pores or veins and exhibiting dull or no luminescence.

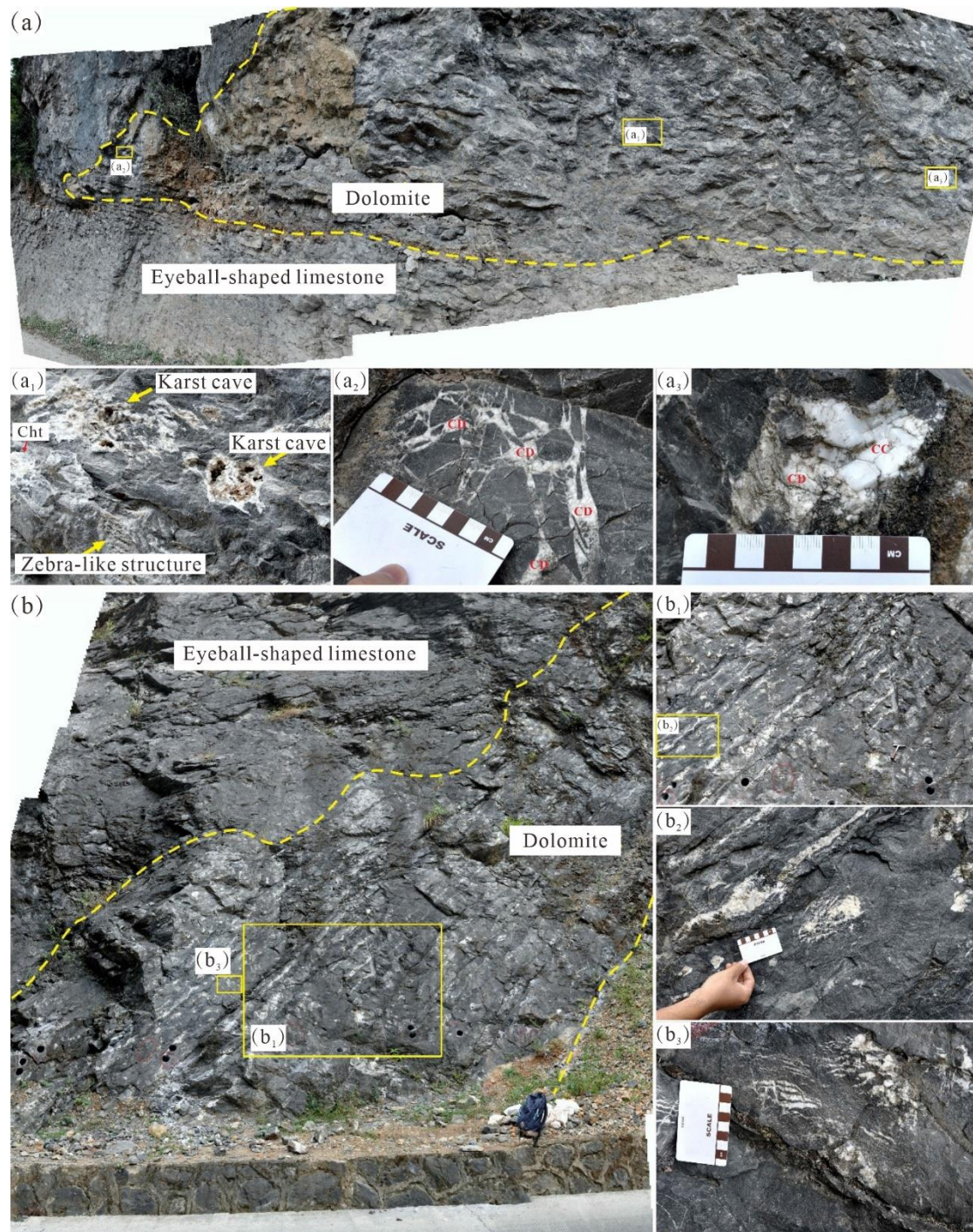


Figure 3. Field photographs showing the Permian Maokou Formation dolomite reservoirs in the eastern Sichuan Basin. (a) Maokou Formation dolomite is macroscopically layered and patchy in Tuo-tuoba section ((a₁) zebra-like structures, caves, and chert nodule (Cht) in the dolomite; (a₂) Fissures are filled with dolomite content (CD); (a₃) Caves are filled with dolomite and calcite content (CC). (b) Maokou Formation dolomite is macroscopically either layered or patchy in Fangniuba section ((b₁) CD is parallel distributed in the dolomite; (b₂,b₃) CD is in the crumby and zebra-like structures).

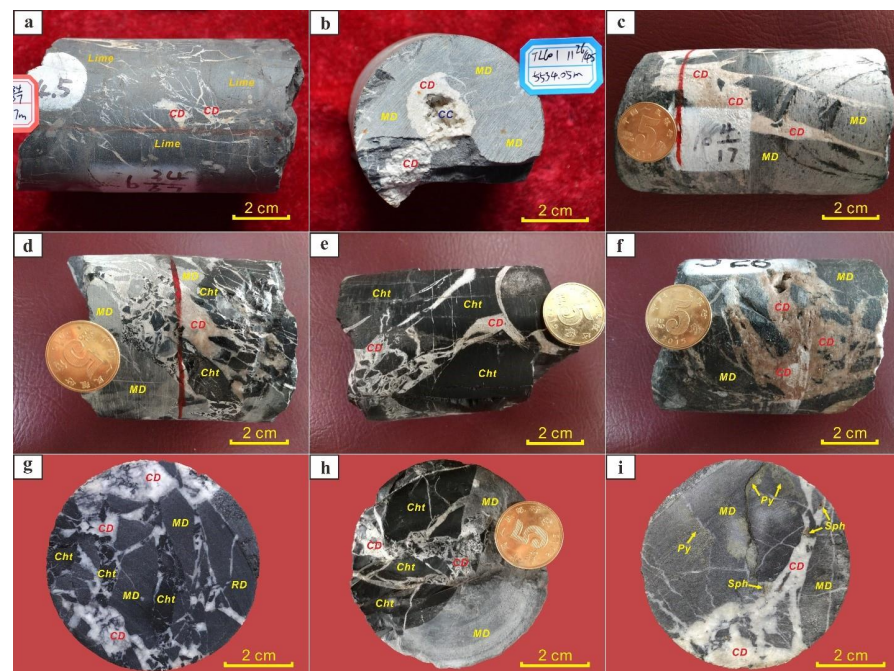


Figure 4. Core characteristics of Permian Maokou Formation dolomite reservoirs in the eastern Sichuan Basin. (a) Micro-cracks developed in dense limestone (Lime) and were filled with CD, TL7, 5106.6 m; (b) Karst caves associated with cracks were both developed in gray MD; the caves were filled with CD and CC in sequence, TL601, 5534.1 m; (c) Cracks were developed in gray MD and filled with CD, TL601, 5530.3 m; (d) Cht were developed in gray MD, and floating MD, chert breccia, and CD are seen in veins. TL601, 5528.4 m; (e) Cht were cut by network cracks, and the cracks were filled with CD. TL601, 5528.4 m; (f) Echelon fractures are developed in gray MD and partially filled with CD, with a small number of residual pores developed. TL6, 5490.3 m; (g) The cross-section of the rock core of d, floating matrix dolomite, and chert breccia can be seen in the network cracks; (h) The cross-section of the rock core of e, MD, was associated with flint nodules; (i) In the cross-section of the rock core of f, the pyrite crystals (Py) precipitate in the MD, and a small amount of sphalerite (Sph) and CD were developed in the fracture veins.

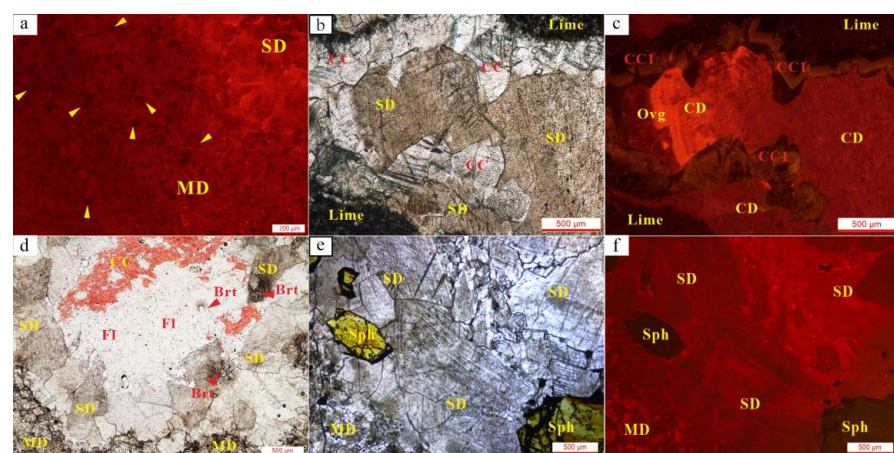


Figure 5. Cathodoluminescence characteristics of the Permian Maokou Formation dolomite in the eastern Sichuan Basin. (a) fine-grained matrix dolomite (MD) exhibits dull red luminescence; (b) Cave is filled with calcite (CC) and saddle dolomite (SD), surrounding rock is limestone (Lime), and the CC is cut through by later SD, TL7; (c) Cathode luminescence of (b), the CC is dark red and dolomite content (CD) is shiny red; (d) Cave is filled with CD, barite (Brt), fluorite (Fl), and CC in sequence, TL601; (e) Cave is sequentially filled with sphalerite (Sph) SD, the surrounding rock is MD, TL6; (f) Cathode luminescence of (e).

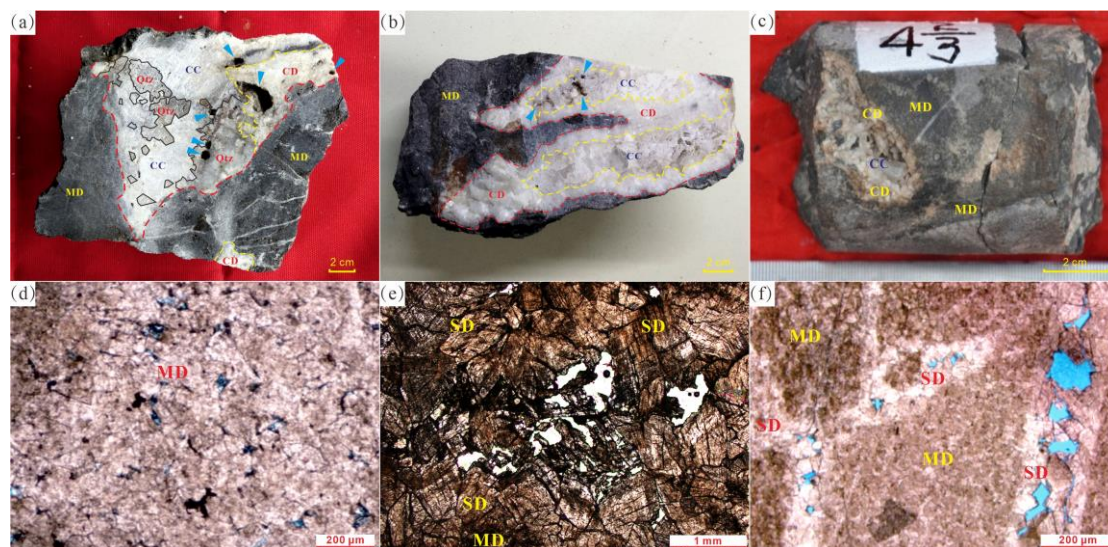


Figure 6. Pore space characteristics of the Permian Maokou Formation dolomite in the eastern Sichuan Basin. (a) Caves associated with fractures are developed in dolomite, filled with Qt, CD, and CC, with a small number of residual caves and pores which have not been fully filled (blue arrow), Tuotuoba section; (b) Zebra-like structures and residual caves and pores (blue arrow), Tuotuoba section; (c) Karst caves associated with fractures were developed in dolomite, with a cemented dolomite rim and coarse calcite visible. Most of the space in the caves is not filled; TL6, 5503.8 m [5]; (d) A small number of intergranular pores were developed in the MD; TL6, 5510.0 m [5]; (e) The karst caves in the MD were mainly filled with SD, with a small amount of residual karst pores developed. TL6, 5490.3 m; (f) Multiple sets of fractures are developed within the MD, which have not been fully filled by the SD, and a small number of residual pores are also developed.

The main types of dolomite reservoirs in the Maokou Formation in the eastern Sichuan Basin are fractured and pore space/karst cave reservoir. The types of pore spaces are mainly residual pores, solution pores, and fractures, with poor development of intergranular pores (Figure 6), and the development of the pore spaces is related to the hydrothermal solution.

4.2. C, O, and Sr Isotopes and REEs

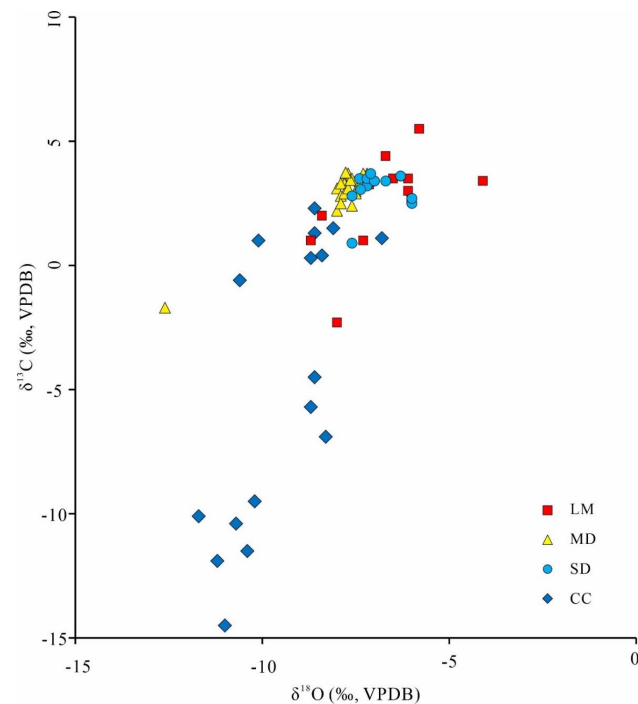
A total of fifty-eight C and O isotopic analyses of different diagenetic phases and limestone were measured, including nine limestone (LM) samples from the surrounding rock, twenty MD samples, ten SD samples, and fifteen CC samples (Table 1; Supplementary S1).

LM samples have a $\delta^{13}\text{C}$ range of -2.3‰ to 5.5‰ and a $\delta^{18}\text{O}$ range of -8.7‰ to -4.1‰ ; MD samples have a $\delta^{13}\text{C}$ range of -1.7‰ to 3.7‰ and a $\delta^{18}\text{O}$ range of -12.6‰ to -6.8‰ ; SD samples have a $\delta^{13}\text{C}$ range of 0.9‰ to 3.6‰ and a $\delta^{18}\text{O}$ range of -7.6‰ to -6.0‰ ; CC samples have a $\delta^{13}\text{C}$ range of -21.2‰ to 2.3‰ and a $\delta^{18}\text{O}$ range of -15.8‰ to -6.8‰ . In addition, 51 pieces of data were collected from previous studies. Compared with LM, MD, and SD samples, CC samples have wider distribution ranges of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, both of them are negative. MD and SD samples have relatively narrow distribution ranges of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, with obviously negative $\delta^{18}\text{O}$. LM samples have wide distribution ranges of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, partially overlapping with those of MD and SD; some $\delta^{18}\text{O}$ values of LM samples are positive (Figure 7; Table 1).

Totally, 59 $^{87}\text{Sr}/^{86}\text{Sr}$ data of different diagenetic phases (MD, SD, CC) and host limestone (LM) were measured, including 10 LM samples (0.706997 to 0.707822), 18 MD samples (0.707289 to 0.70864), 10 SD samples (0.707947 to 0.708466), and 15 CC samples (0.707617 to 0.713836) (Table 1; Supplementary S2). In addition, 6 pieces of data were collected from previous studies. Compared with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Permian seawater (0.70662–0.70774) [41], LM samples have similar values, while the others have slightly higher values, and CC has a particularly wider range of variation (Figure 8).

Table 1. Statistics of isotopic geochemistry of different diagenetic phases and limestone from the Permian Maouko Formation, Sichuan Basin. S.D. = Standard deviation.

Rock Fabric	$\delta^{13}\text{C}$ (‰, VPDB)		$\delta^{18}\text{O}$ (‰, VPDB)		$^{86}\text{Sr}/^{87}\text{Sr}$
	<i>n</i>			<i>n</i>	
LM		9	9		10
	Max	5.5	−4.1	Max	0.707822
	Min	−2.3	−8.7	Min	0.706997
	Mean	2.4	−6.8	Mean	0.707256
MD	S.D.	2.3	1.5	S.D.	0.000253
	<i>n</i>	20	20	<i>n</i>	18
	Max	3.7	−6.8	Max	0.708640
	Min	−1.7	−12.6	Min	0.707289
SD	Mean	2.8	−7.9	Mean	0.707949
	S.D.	1.2	1.2	S.D.	0.000305
	<i>n</i>	10	10	<i>n</i>	12
	Max	3.6	−6.0	Max	0.708466
CC	Min	0.9	−7.6	Min	0.707947
	Mean	3.0	−7.0	Mean	0.708263
	S.D.	0.8	0.5	S.D.	0.000171
	<i>n</i>	19	19	<i>n</i>	15
CC	Max	2.3	−6.8	Max	0.713836
	Min	−21.2	−15.8	Min	0.707617
	Mean	−5.7	−9.7	Mean	0.709362
	S.D.	6.6	1.9	S.D.	0.002165

**Figure 7.** C and O isotopes of different diagenetic phases and limestone in the Permian Maokou Formation.

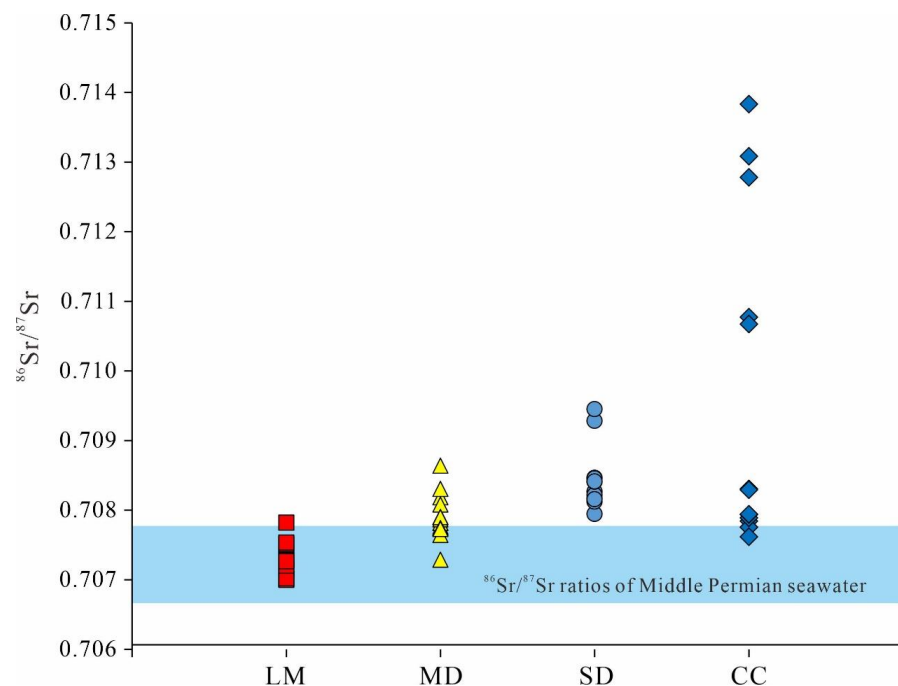


Figure 8. $^{87}\text{Sr}/^{86}\text{Sr}$ values of different diagenetic phases and limestone in the Permian Maokou Formation (the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Permian seawater (0.70662–0.70774, [40]) were marked for comparison).

$\Sigma\text{REE} + \text{Y}$ values of different diagenetic phases and limestone were measured, with an average of 6.91 ppm for LM, 6.05 ppm for MD, 10.78 ppm for SD, and 8.14 ppm for CC (Table 2).

In general, SD and CC have higher $\Sigma\text{REE} + \text{Y}$ values, revealing the facilitation of the burial diagenesis and the enrichment of REEs as the influence of seawater weakens. The normalized REE + Y data against the Post-Archean Australian Shale (PAAS) shows that all diagenetic phases and limestone show similar partition patterns, including right-leaned LREEs and gentle HREEs, which are similar to the features of modern seawater [42] (Figure 9). LM, MD, SD, and CC samples all show negative Ce anomalies and positive Y anomalies, while MD samples exhibit slight positive Eu anomalies.

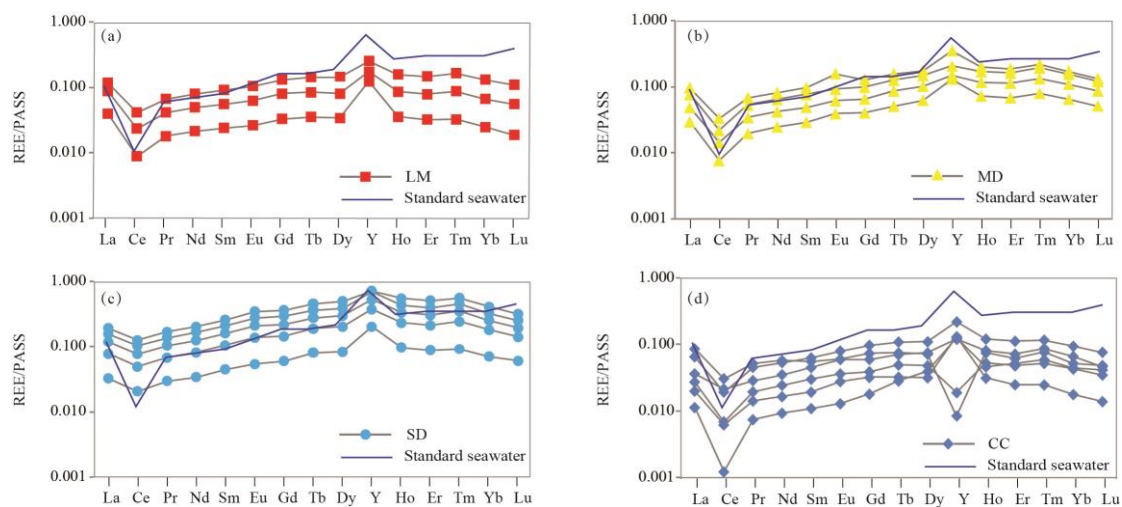


Figure 9. REEs in different diagenetic phases and limestone of the Permian Maokou Formation. (a) LM (b) MD (c) SD (d) CC.

Table 2. The rare earth element concentrations of different diagenetic phases and limestone in the Permian Maokou Formation, Sichuan Basin.

Sample No.	Rock Fabric	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	REE + Y	Ce/Ce*	Eu/Eu*
		µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g		
FNB-14-Lime	LM	1.50	0.696	0.158	0.716	0.131	0.028	0.152	0.027	0.157	3.32	0.035	0.091	0.013	0.069	0.008	7.10	0.306	0.922
FNB-18-Lime	LM	1.81	1.16	0.207	0.954	0.176	0.039	0.219	0.038	0.215	1.34	0.05	0.133	0.022	0.118	0.018	6.50	0.412	0.918
TTB-20-3 Lime	LM	1.09	1.39	0.212	1.01	0.193	0.045	0.232	0.046	0.302	2.13	0.068	0.190	0.031	0.181	0.021	7.14	0.665	0.985
FNB-12-MD	MD	1.12	0.607	0.173	0.834	0.161	0.042	0.187	0.039	0.290	3.49	0.071	0.192	0.032	0.181	0.002	7.42	0.312	1.125
TTB-5-1-MD	MD	0.719	0.526	0.127	0.572	0.108	0.024	0.115	0.027	0.183	0.495	0.044	0.127	0.021	0.124	0.019	3.23	0.398	1.007
TTB-15-MD	MD	1.06	0.595	0.168	0.762	0.152	0.033	0.157	0.031	0.221	1.59	0.053	0.141	0.025	0.132	0.021	5.14	0.320	1.001
TTB-16-MD	MD	1.12	0.684	0.167	0.75	0.157	0.030	0.169	0.031	0.192	4.74	0.052	0.129	0.020	0.131	0.020	8.39	0.356	0.861
TTB-22-SD	SD	1.24	1.63	0.259	1.15	0.247	0.058	0.279	0.062	0.387	5.43	0.095	0.25	0.037	0.198	0.023	11.35	0.663	1.029
TTB-24-SD	SD	1.72	2.30	0.334	1.62	0.337	0.091	0.383	0.082	0.563	4.57	0.135	0.353	0.060	0.309	0.020	12.88	0.697	1.179
TTB-25-SD	SD	1.76	2.51	0.359	1.66	0.355	0.077	0.420	0.086	0.585	2.43	0.138	0.364	0.059	0.271	0.015	11.09	0.727	0.925
TTB-27-SD	SD	1.44	2.06	0.298	1.44	0.268	0.066	0.342	0.066	0.425	4.63	0.100	0.263	0.042	0.203	0.015	11.66	0.724	1.004
TTB-28-SD	SD	1.33	1.75	0.270	1.21	0.275	0.080	0.328	0.069	0.477	0.433	0.110	0.302	0.044	0.238	0.014	6.93	0.672	1.235
FNB-12-Cal	CC	1.04	0.547	0.171	0.824	0.166	0.039	0.181	0.038	0.224	0.508	0.052	0.136	0.021	0.12	0.015	4.08	0.295	1.050
FNB-16-Cal	CC	2.49	1.53	0.399	1.81	0.348	0.086	0.452	0.084	0.512	5.88	0.119	0.318	0.047	0.264	0.046	14.39	0.348	0.997
FNB-20-Cal	CC	0.763	0.494	0.125	0.558	0.107	0.030	0.149	0.025	0.148	3.54	0.031	0.071	0.010	0.050	0.033	6.13	0.364	1.084
TTB-6-2-Cal	CC	0.434	0.098	0.066	0.317	0.061	0.014	0.084	0.022	0.184	3.40	0.046	0.149	0.024	0.126	0.006	5.03	0.131	0.893
TTB-8-Cal	CC	3.29	2.44	0.459	1.96	0.31	0.065	0.343	0.058	0.335	0.227	0.074	0.175	0.031	0.147	0.020	9.93	0.444	0.930
TTB-21-Cal	CC	1.38	1.71	0.253	1.19	0.249	0.064	0.277	0.054	0.349	3.22	0.080	0.203	0.035	0.186	0.018	9.27	0.663	1.136

4.3. U-Pb Chronology

6 U-Pb chronological data of different diagenetic phases and limestone were obtained, including two for MD, two for SD, and two for CC (Supplementary S3). These carbonate minerals have extremely low concentrations of U (4–4509 ppb) and Pb (0.1–1131 ppb). Although the U concentration is low, the U/Pb value has wide variations that can form $^{238}\text{U}/^{206}\text{Pb}$ – $^{207}\text{Pb}/^{206}\text{Pb}$ isochrons. Then, the crystallization age of the mineral can be determined by identifying the lower intersection points between the isochrons and the Tera-Wasserburg concordant line, yielding two MD ages (261.0 ± 11 Ma and 259.5 ± 3.0 Ma), two SD ages (244.7 ± 2.7 Ma and 250.0 ± 22 Ma), and two CC ages (218.9 ± 9.4 Ma and 191 ± 11 Ma) (Figure 10). The Mean Squared Weighted Deviates (MSWD) of these age data are all below 5, and three of them are below 2.5. Therefore, it is safe to conclude that the chronological data are harmonious, and that the data deviation is caused by experimental analysis errors [43].

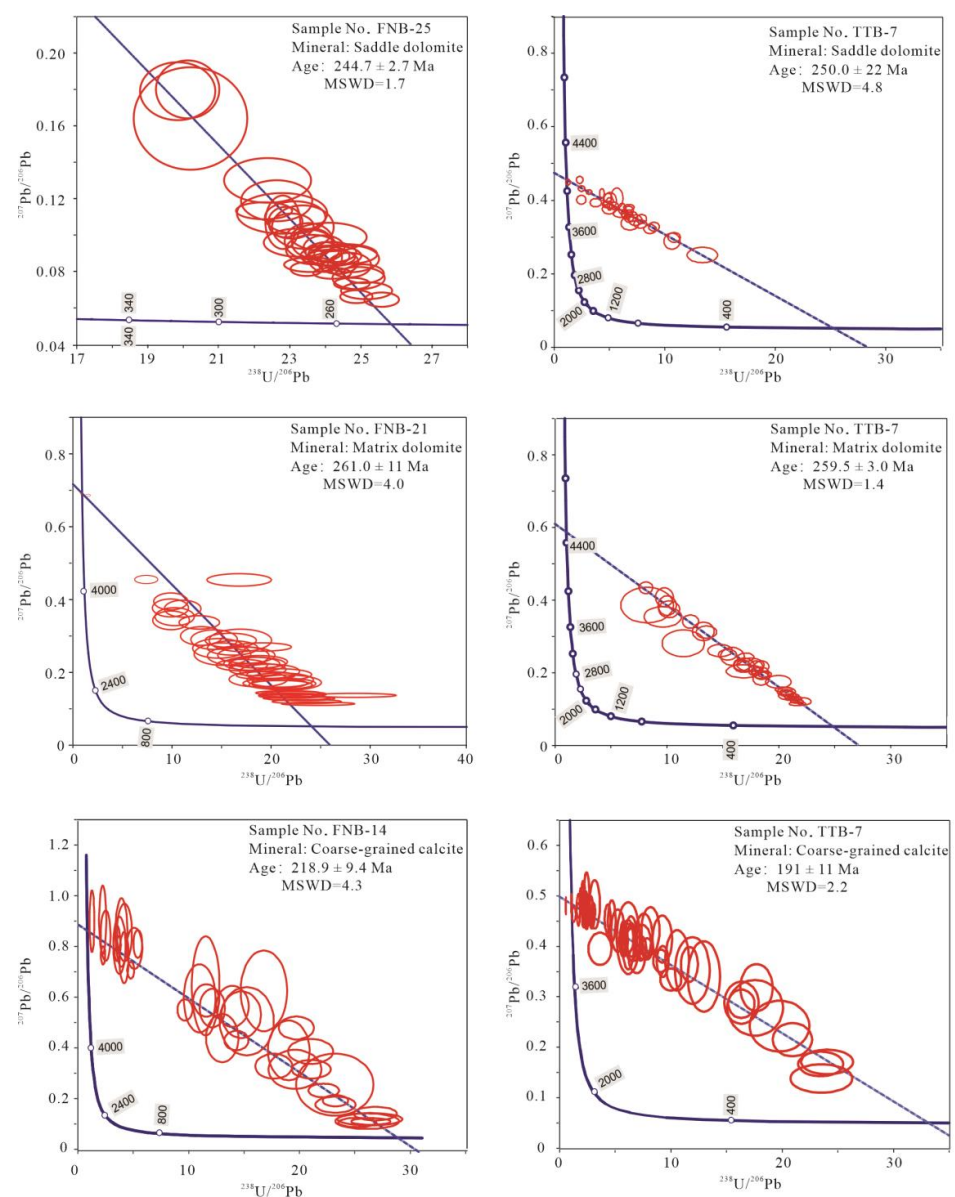


Figure 10. In situ U-Pb ages of different diagenetic phases in the Permian Maokou Formation.

4.4. Homogenization Temperature of Fluid Inclusions

The primary brine inclusions in MD are mainly distributed in relatively transparent dolomite grains, in oval, polygonal, and irregular forms. They have varying dimensions of 1–3 μm (Figure 11a), and they can be oriented, clustered, or isolated. Primary brine inclusions in SD are more regular in shape and relatively larger in size (3 to 8 μm ; Figure 11b) than those in MD.

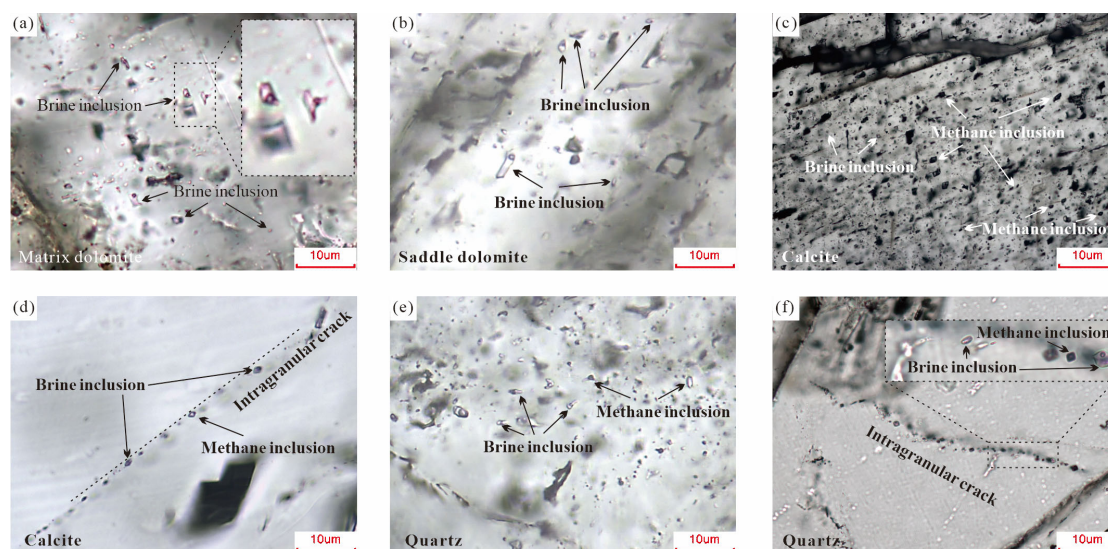


Figure 11. Photographs of fluid inclusions within different diagenetic phases in the Permian Maokou Formation. (a) Matrix dolomite (b) Saddle dolomite (c) Calcite 1 (d) Calcite 2 (e) Quartz 1 (f) Quartz 2.

Both gas-liquid two-phase brine inclusions and single-phase gas inclusions are seen in CC and Qt, with the former type dominant (Figure 11c–f). Primary methane inclusions (Figure 11c,e), secondary methane inclusions distributed along intracrystalline fractures (Figure 9d,f), and brine inclusions associated with methane inclusions are seen in CC and Qt. Gas inclusions captured in CC are relatively small (2 to 10 μm), while the associated gas-liquid two-phase brine inclusions are mostly regular quadrilaterals and polygons in shape (Figure 11c–d). The fluid inclusions captured in Qt are more regular than those in CC, exhibiting shapes of ellipses, subcircles, and irregular polygons (Figure 11e–f). The major axes of methane inclusions and brine inclusions range from 5 to 12 μm .

In order to determine the fluid activity stages and formation temperatures of different diagenetic phases and limestone, we measured the homogenization temperature and salinity of primary brine inclusions as well as the brine inclusions associated with gas inclusions in MD, SD, and CC (Supplementary S4). The primary brine inclusions in MD have a homogenization temperature range of 86.6–166.3 $^{\circ}\text{C}$ (concentrated between 110.5 and 146.8 $^{\circ}\text{C}$) and a salinity range of 13.3%–20.8%. In contrast, primary brine inclusions in SD have a homogenization temperature range of 94.1–168.3 $^{\circ}\text{C}$ (concentrated between 101.6 and 149.7 $^{\circ}\text{C}$) and a salinity range of 14.5%–22.7%. The brine inclusions associated with primary methane inclusions in CC have a homogenization temperature range of 140.8–199.8 $^{\circ}\text{C}$ and a salinity range of 14.3%–21.8%, while those associated with secondary methane inclusions have a homogenization temperature range of 100.3–174.8 $^{\circ}\text{C}$ (Figure 12a). There are no significant differences between the homogenization temperature of fluid inclusions in MD and SD, while that of later-filled CC is higher. The fluid salinities of MD, SD, and CC are comparable to those of hydrothermal dolomite fluids calculated by [44] (5–30 wt% NaCl eq.) (Figure 12b), which are much higher than that of the Permian seawater (4.4 wt% NaCl eq. [10]).

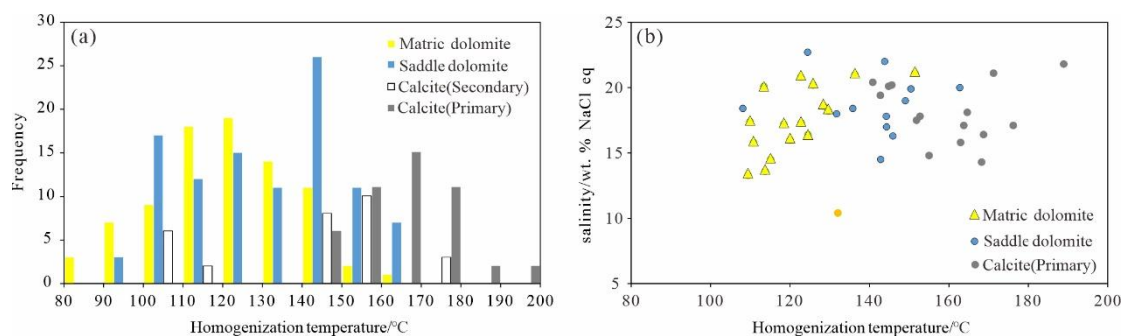


Figure 12. Homogenization temperature (a) and salinity of fluid inclusions (b) in different diagenetic phases and limestone of the Permian Maokou Formation.

5. Discussion

5.1. Dolomitization Time, Fluid Source, and Process

Due to the feature that the hydrothermal dolomite layer with irregular semi-filled structures is cut through by low-angle sutures, the hydrothermal activity was speculated to occur shortly after deposition, and the dolomite was supposed to be the diagenetic product of shallow burial [16]. The dolomitization time was determined quantitatively as the Wujiaping-Changxing period (259–252 Ma) by implementing in situ U-Pb dating on the MD and SD of the Maokou Formation in the Fangniuba and Tuotuoba sections in the eastern Sichuan Basin. The corresponding burial depth is less than 500 m [45], which is consistent with the shallow-burial diagenesis revealed by the suture structure. Previous study and our data have an age of 260–250 Ma, which has a certain link to the ELIP (261–257 Ma) [45–48]. Particularly, the formation time of MD coincided with the peak period of ELIP, revealing the significant impact of regional deep thermal activity on the Permian hydrothermal dolomitization in the eastern Sichuan Basin. The dolomitization time of SD was 240–250 Ma, which is slightly later than the ELIP. According to the reconstructed paleo-heat flow, the thermal effect of ELIP lasted for a long period, exerting significant influences during the Middle-Late Permian-Early Triassic, with the highest paleo-heat flow reaching 75–80 mW/m² in the eastern Sichuan Basin [49]. The sustained high heat flow provided a favorable environment for long-term dolomitization. It has been experimentally demonstrated that fluids with normal seawater salinity and Mg²⁺/Ca²⁺ can form dolomite with a high degree of order under high-temperature conditions (>100 °C) [50]. High temperatures can effectively overcome the resistance of dolomite crystallization and facilitate dolomitization.

MD in the Maokou Formation is characterized by the well-preserved original structure, similar $\delta^{13}\text{C}$ to LM, homogenization temperature of 110–150 °C for primary inclusions, recrystallization age of 260 Ma, and burial temperature of 60–120 °C (Figure 13).

These features, together with the slightly positive Y anomaly, the negative Ce anomaly, and the mostly low $^{87}\text{Sr}/^{86}\text{Sr}$ value, indicate the dolomitization fluid of MD is the Permian seawater [51]. Under the microscope, SD is seen with crystal plane bending and wavy extinction; its $\delta^{18}\text{O}$ value can reach −10‰, and its homogenization temperature is 102–150 °C, which is significantly higher than the normal formation burial temperature [39]. The positive Eu anomaly is a typical indicator of hydrothermal dolomitization [52]. During the process of hydrothermal fluid passed through the underlying clastic rocks, radioactive Sr elements from the clastic rock will enter the hydrothermal fluid [45]. The $^{87}\text{Sr}/^{86}\text{Sr}$ value is relatively high, also indicating that the dolomitization fluid came from hydrothermal fluid [11,16]. The salinities of fluids in SD are much higher than those of the Permian seawater (4.4 wt% NaCl eq.), which indicates that the dolomitization fluid may be a high-salinity thermal fluid related to ELIP.

Dolomitization of the Permian Maokou Formation can be divided into three stages according to the diagenetic sequence, U-Pb dating results, regional volcanism, and sedimentary environment evolution (Figure 14).

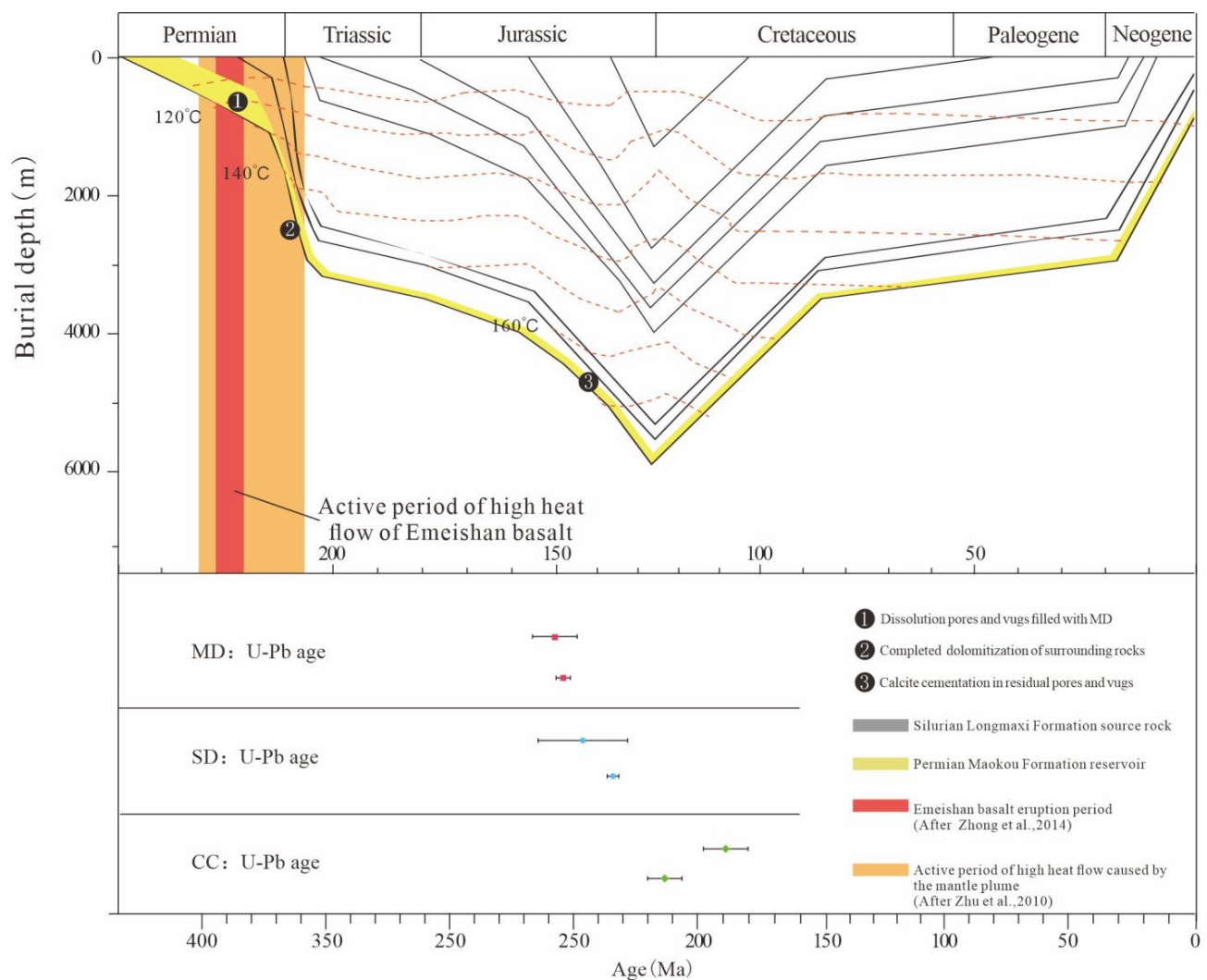


Figure 13. Relationship between burial history and diagenetic events of Permian strata in Fangniuba area, eastern Sichuan Basin [44] and the U-Pb ages of the MD, SD, and CC.

(1) The REE characteristics of LM are similar to those of seawater, with negative Ce anomalies and positive Y anomalies [51]. During the depositional stage, the Maokou Formation in the eastern Sichuan Basin was deposited on an open platform on a gentle slope, where the hydrodynamics were weak and micritic limestone and micritic bioclastic limestone were developed. High-energy bioclastic calcarenite was occasionally developed at local paleogeomorphic highs, while micritic silty dolomite was formed by penecontemporaneous evaporation pumping in areas where seawater circulation was limited.

(2) The term “penecontemporaneous stage” generally refers to shallow marine deposits that are exposed above sea level soon after their sediment. During this stage (Longtan Formation, the Late Permian), basalt eruption reached its climax, resulting in hydrothermal fluid flow. These fluids baked and heated the surrounding rock formations. Differential dolomitization occurred under the control of the dominant migration pathways between the high-energy facies belt and the loose filling of the karst. Seawater provided magnesium ions for the formation of dolomite, high heat flow facilitated the long-lasting dolomitization, and the Longtan Formation mudstones acted as cap rocks to prevent temperature loss. The long-lasting high paleo-heat flow, which was affected by ELIP, provided a favorable high-temperature environment for the further expansion of matrix dolomite. Matrix dolomite was mostly formed during 261–259 Ma, which was consistent with the peak period of the

mantle plume activity [53], indicating that the dolomitization by thermal fluids rising along faults was short and rapid.

(3) During the shallow burial stage, deep faults provided the migration pathways for dolomitization. The U-Pb age of MD is 250–244 Ma, which corresponds to the 255–251 Ma magmatism of ELIP [54]. The magnesium-rich fluid from the deep source rose along the fault and entered the fractures and vugs, forming saddle dolomite. The impact of strong faulting activity and abnormally high heat flow on the reservoir was relatively limited because the intense activity of the mantle plume of ELIP only lasted for 1–3 Ma. Consequently, hydrothermal dolomitization fluids in most areas were deep hydrothermal brine, with little participation of fluids from the deep mantle.

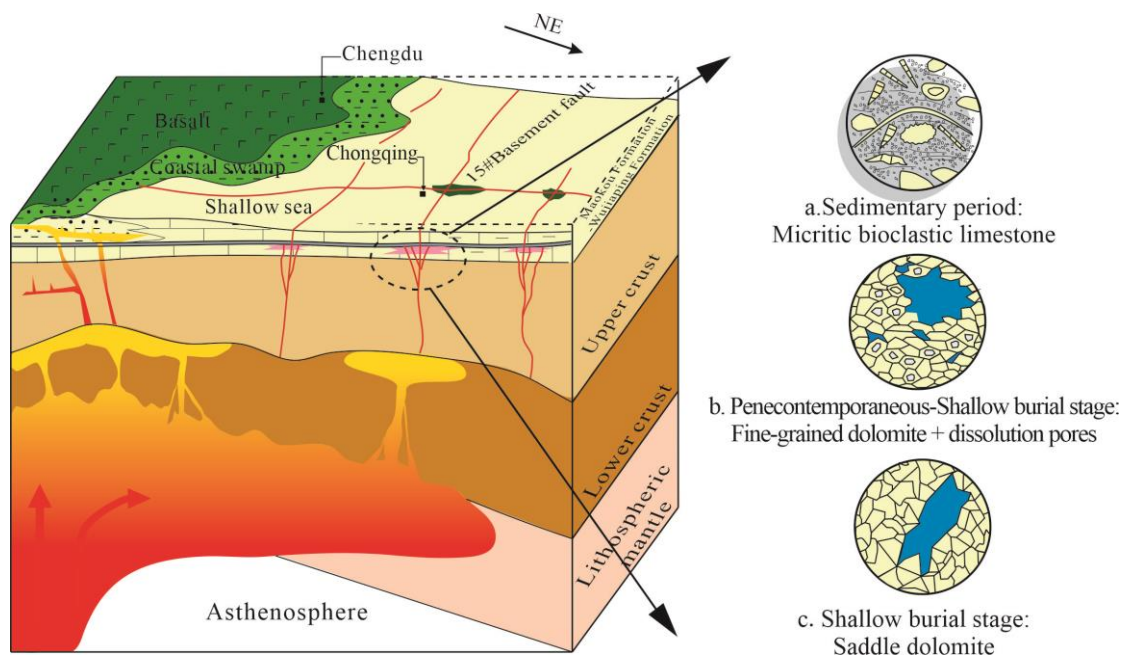


Figure 14. Schematic model illustrating hydrothermal dolomitization in the Permian Maokou Formation [32]. Dolomitization of the Permian Maokou Formation can be divided into three stages: micritic limestone and micritic bioclastic limestone were developed in an open platform during the sedimentary period; high heat flow facilitated the long-lasting dolomitization, which resulted to the formation of fine-grained dolomite in the penecontemporaneous stage. The magnesium-rich fluid from the deep source rose along the fault and entered the gractures and vugs, forming asddle dolomite.

5.2. Relationship between Multi-Stage Diagenetic Fluid Activities and Reservoir Development

The Maokou Formation dolomite reservoir first underwent alterations by seawater during the penecontemporaneous stage and deep thermal fluids during the shallow-burial stage. Then, it was subjected to hydrocarbon charging and diagenesis during the burial period. Consequently, a large number of calcite cements and bitumen were observed in the pores. Moreover, abundant oil and gas inclusions were observed in fractures of calcite (CC), MD, and SD. According to the results of U-Pb dating, CC was formed in the Late Triassic-Early Jurassic (220–190 Ma), which coincides with the rapid and deep burial period of the Maokou Formation (Figure 13). $\delta^{13}\text{C}$ values of partial CC can reach -15 to -10‰ , which is abnormally negative compared with the Permian-Triassic seawater. This is a typical indicator of the presence of organic sediments, suggesting a close relationship between calcite and organic shale [55,56]. At the same time, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of CC is higher than that of Permian formation water, indicating that the diagenetic fluid came from clastic rocks. The homogenization temperature of fluid inclusions ranges between 140.8 and 199.8 °C , which coincides with the oil window of Silurian source rocks. Therefore, it

can be inferred that the formation of CC occurs during the hydrocarbon charging when Sr-rich fluid in source rocks entered CC.

The multi-stage, multi-source diagenetic fluids have both constructive and destructive effects on the Maokou Formation reservoirs. The cracks are associated with caves in dolomite, which are filled with quartz, dolomite, and calcite in sequence. A small amount of residual caves and pores, which have not been fully filled, are also developed (Figure 6a). The effective pore space of the Maokou Formation dolomite mainly consists of intercrystalline pores, dissolution pores, residual pores, and micro-fractures. During the depositional and penecontemporaneous stages, high-energy shoal bodies were intermittently exposed to form dissolution pores or mold pores. In contrast, during the shallow burial stage, hydrothermal fluid upwelled and migrated laterally along the fractures and early-formed vugs, resulting in hydrothermal dissolution that connected vugs. Subsequently, as hydrothermal fluids intruded, saddle dolomite was precipitated, destructed the pores of the dissolution vugs. The long-lasting dolomitization of the surrounding rocks during the Late Permian formed layered or patchy dolomite, which promoted the development of intercrystalline pores and increased the permeability and porosity of the reservoir. Moreover, dolomite is more resistant to compaction than limestone, which can maintain porosity. During the deep burial stage, the formation fluid became active again due to the charging of oil and gas. In this condition, high-salinity brine caused the precipitation of calcite in the residual pores, which reduced the porosity.

As shown in the exploration practice, the Maokou Formation dolomite was subjected to the influences of multi-stage diagenetic fluids, and various types of authigenic minerals were formed in the reservoir pores, thereby resulting in highly heterogeneous reservoirs with low porosity and low permeability. However, compared with limestone, dolomite near the faults has better physical properties, and almost all the drilled high-quality reservoir intervals are in the dolomite. For instance, Well TL-6 in the Fuling area of the eastern Sichuan Basin is 4.5 km away from the basement fault, and the Maokou Formation dolomite reservoir in this well is 22.5 m thick, with porosities ranging from 2.23%–4.34%, with an average value of 3.34%, as well as permeabilities ranging from 0.00011–2.73 mD, with an average value of 0.0143 mD, and a test production of natural gas of 111,000 m³/day. The later-drilled Well TL-7 is 10.7 km away from the basement fault, and the Maokou Formation dolomite reservoir in this well is 14 m thick, with a test production of natural gas of 22,000 m³/day [45]. Therefore, it is safe to conclude that the deep fluid activity near the fault promoted the dolomitization of surrounding rocks, while the dolomitization of tight reservoirs increased the physical properties of the host rocks; hence, dolomite reservoirs were higher-quality reservoirs. However, the constructive effects of hydrothermal dolomitization on reservoirs in the Sichuan Basin is limited, which obviously shows the development of reservoir in the eastern Sichuan Basin and limited reservoir reformation in the central Sichuan [16].

6. Conclusions

Based on the results of systematic U-Pb dating of carbonate minerals, micro-domain isotopes, rare earth elements, and homogenization temperature of fluid inclusions presented in this study, we draw the following conclusions:

- (1) The diagenetic fluids of matrix dolomite were mainly Permian seawater, while those of saddle dolomite were derived from deep, high-temperature formation brine.
- (2) The U-Pb ages of fine-grained matrix dolomite and saddle dolomite yield a dominated age of 245–260 Ma. The timing of hydrothermal dolomitization is consistent with the active period of the ELIP. The deep geological processes not only provided dolomitization fluids but also provided the necessary thermal energy for the formation of the dolomite.
- (3) Hydrothermal dolomitization was conducive to the formation and maintenance of intercrystalline pores and dissolution pores, but it also formed saddle dolomite in pores, which destructed the physical properties of the reservoir. Therefore, the effects

of deep fluid activity on the carbonate reservoirs were twofold, being both constructive and destructive. During the deep burial stage, the formation fluid associated with hydrocarbon expulsion became active again, forming calcite cement to fill the early residual pores and vugs, further reducing the physical properties of the reservoir.

- (4) The Maokou Formation dolomite reservoirs in the eastern Sichuan Basin experienced multiple diagenetic processes, including penecontemporaneous-shallow burial tectonic rupturing, hydrothermal dolomitization, and deep burial cementation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14080803/s1>, Supplementary S1: The C and O isotopic composition of different diagenetic phases and limestone in the Permian Maokou Formation, Sichuan Basin. Supplementary S2: The Sr isotopic composition of different diagenetic phases and limestone in the Permian Maokou Formation, Sichuan Basin. Supplementary S3: Raw ratios and metadata for LA-ICP-MS U-Pb dating. Supplementary S4: Fluid inclusion microthermometry of different diagenetic phases and limestone in the Permian Maokou Formation, Sichuan Basin.

Author Contributions: Writing—original draft preparation, S.L., J.G. and T.Y.; Software, T.L. (Tianyi Li) and T.L. (Tianjia Liu); Methodology, Z.H., Investigation, E.L. and Y.H. All authors have read and agreed to the published version of the manuscript.

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