Reflux dolomitization of the Upper Permian Changxing Formation and the Lower Triassic Feixianguan Formation, NE Sichuan Basin, China

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ABSTRACT

Natural gas is found in Upper Permian and Lower Triassic dolomite reservoirs of the NE Sichuan Basin, China. Studying the mechanisms for porosity-modifying dolomitization and predicting its spatial distribution is of great importance for exploration and field appraisal. Subsurface core samples from the oolitic Lower Triassic Feixianguan Formation and outcrop samples reef carbonate Upper Permian Changxing Formation were studied using cathodoluminescence (CL), electron microprobe, fluid inclusion and isotope studies ($\delta^{18}$O, $\delta^{13}$C and $^{87}$Sr/$^{86}$Sr), in an attempt to determine the origin of the dolomitizing fluids. Trace element and isotope data show that Lower Triassic seawater was most likely responsible for dolomitization of both the Permian and Triassic rocks. Sr/Ca molar ratios, calculated for the diagenetic fluid, suggest seawater was involved in dolomitization. Strontium isotope data suggest that seawater $^{87}$Sr/$^{86}$Sr during the Jialingjiang (Lower Triassic) reached 0.7078; this ratio is recorded ubiquitously in both Lower Triassic oolitic dolomite and the underlying Lower Permian reef dolomite. In the Permian Changxing Formation, elevated Triassic $^{87}$Sr/$^{86}$Sr values have overprinted the significantly lower $^{87}$Sr/$^{86}$Sr ratio characteristic of Upper Permian seawater. Fluid inclusion analysis led to the conclusion that dolomitization must have commenced at a temperature lower than about 50°C. Integrating the sedimentology, petrology and geochemistry data, we conclude that coeval Lower Triassic (Feixianguan or slightly younger) seawater caused dolomitization by a reflux-seepage process for both the Lower Triassic and Upper Permian units. There is no evidence for deep burial or meteoric-marine mixing-zone dolomitization. It is likely that evaporating seawater initially flowed into the highly porous oolitic Feixianguan Formation in a sabkha/lagoonal setting and precipitated anhydrite nodules and beds. Concomitant dolomitization, in the underlying Permian reef carbonates, continued during seepage even after the supply of sulphate was exhausted, leading to an absence of anhydrite in Permian Changxing Formation.

Key words: anhydrite, calcite, carbonate reservoir, cement, diagenesis, dolomite, lagoon, sabkha

INTRODUCTION

Dolomite accounts for about 50% of all carbonate rocks (Zenger et al. 1980) and can hold significant volumes of petroleum. Studying the mechanisms for dolomitization, and therefore being able to predict its spatial distribution, is of great importance. Although numerous models for dolomitization exist, many dolomite reservoirs are associated with sediments initially deposited under evaporitic conditions and are interpreted as having a seawater reflux origin (Sun 1995; Jones & Xiao 2005).

Huge petroleum resources have been discovered in the Upper Permian Changxing Formation and Lower Triassic Feixianguan Formation carbonate reservoirs in NE Sichuan Basin, China. Significantly, good reservoir quality in East Sichuan Basin is associated with carbonates that have a high dolomite content (typically up to 80–90%) (Cai et al. 2004, 2010; Zhao et al. 2005; Ma et al. 2008). Several conflicting models have been proposed to explain the origin of the Feixianguan Formation oolitic dolomites, namely marine-meteoric mixing-zone dolomitization, burial dolomitization and seepage-reflux dolomitization (Zhao...
et al. 2005; Wang et al. 2007; Ma et al. 2008; Huang et al. 2009; Zheng et al. 2009). These various models have been supported by different types of geochemical and sedimentological data but there is no consensus about which mechanism was responsible for the generation of the Feixianguan ooid-replaced dolomites. Two recent studies have showed that reflux dolomitization may have been responsible for the majority of the Feixianguan Formation dolomites (Hu et al. 2012; Pan et al. 2012). The stratigraphically underlying Changxing Formation reef limestone is also extensively dolomitized although there are few geochemical data published on this unit, and little attention has been given to the origin of this dolomite (Hu et al. 2013).

In this paper, we present new data for subsurface core samples of the Lower Triassic Feixianguan Formation (T1f) ooid-replaced dolomite reservoirs and outcrop of Upper Permian Changxing Formation (P3ch) reef dolomites using light and CL petrology, electron microprobe analysis, as well as Sr, C and O isotope analyses, in an attempt to define the origin and characteristics of dolomitization fluids as well as the formation mechanisms of the oolitic and reef dolomites. Specially, we address of the following questions: (1) What are the petrological and geochemical characteristics of dolomites in the Upper Permian Changxing Formation and Lower Triassic Feixianguan Formation (P3ch-T1f) intervals? (2) Can geochemical parameters be used to constrain the origin and type of the fluid responsible for dolomitization? (3) What mechanisms were responsible for the formation of dolomites in P3ch-T1f intervals in the Sichuan Basin?

GEOLOGIC SETTING

The diamond shaped Sichuan Basin is located in the east of Sichuan Province, southwest China. It is a large intracratonic basin with an area of about 230 000 km² (Fig. 1A) and is surrounded by several mountain belts. The Sichuan Basin is tectonically enclosed by the Longmenshan fold belt in the northwest, the Micangshan uplift in the north, the Dabashan fold belt in the northeast, the Hubei-Hunan-Guizhou fold belt in the southeast and by the Emeishan-Liangshan fold belt in the southwest.

In the Middle Changxing (Upper Permian), the NE Sichuan Basin gradually evolved into a platform-edge bioclastic facies with accumulation of reef carbonates with well-developed primary framework porosity. Multicycle, reef-shoal combinations of bioclastic, bioherm framework and oolitic sediments (with abundant primary intergranular porosity) developed in the middle and late Changxing (Ma et al. 2008; Fig. 2). During the Feixianguan (early Triassic), an arid climate persisted in the northeast Sichuan Basin and a semi-isolated evaporate carbonate platform formed on the east side of Kajiang-Liangping Trough (Fig. 1A). Oolitic banks were present on the margins of the trough, which were intensely dolomitized and subsequently forming high-quality reservoir rocks holding substantial gas reserves (Fig. 1B). The total thickness of the Feixianguan Formation in the study area is between 300 m and 500 m and has been subdivided into four members in stratigraphic order: T1f1, T1f2, T1f3 and T1f4 using core and wireline log analysis (Cai et al. 2004). According to Ma et al. (2008), there are multiple gypsiferous layers in the Feixianguan Formation due to a combination of sea-level fluctuation and the arid climate. Purple shales and some anhydrite beds are interlayered with thin-bedded micritic limestones in the upper part of the Feixianguan Formation; these make up a good regional seal for the underlying P3ch-T1f carbonate reservoir (Zhao et al. 2005; Fig. 2).

SAMPLES AND METHODS

A total of 27 carbonate samples were collected from the Puguang, Maoba, Luoqiazhai, sour gas fields in the lower unit of the Triassic Feixianguan Formation (T1f). These are ooid-replaced dolomite reservoir samples. A further 13 samples were collected from Panlongdong outcrop of the upper unit of the Changxing Formation (P3ch), consisting of reef facies dolomites. All samples were subject to petrological study and geochemical analyses, including CL, microprobe, fluid inclusions and C/O/Sr isotopes.

For petrographic and a CL analyses, a cold cathode Relion III CL luminescence microscope was used with a beam voltage of 15 kV, a current of 500 μA and a beam diameter of 4 mm. Fluid inclusions were studied using a Linkam THMSG 600 thermometric stage fitted on a Zeiss Axioskop 40A Pol light microscope fitted with a UV lamp to determine whether they were oil or aqueous inclusions. Mineral composition was determined using a Cameca Camebax BX 50™ instrument equipped with three spectrometers and a backscattered electron (BSE) detector. Operating conditions for the electron microprobe were 20 kV accelerating voltage and 12 nA beam current with 10 μm beam size. Count times were 20 sec on peaks and 10 sec on each background. Natural and synthetic mineral standards were applied for correction. The raw data were processed using the online ZAF-type corrections.

The carbonates are locally composed of calcite and dolomite, as well as noncarbonate materials such as siliciclastics, oxide and sulphide. Samples for isotope analysis were broken into chips and subsequently picked for clean fragments, selected to be free of drilling mud contamination, using a binocular microscope. Fine powder samples were then extracted using a dentist’s drill and used for strontium isotopic measurement.
About 120 mg of drilled samples was used for strontium isotope analyses. Effort was made to exclude the influence of siliciclastics by sequential digestion. Calcite was leached in 0.5 M sub-boiling distilled acetic acid at room temperature for 4 h (after Zhao et al., 2009). Dolomite was leached in 3.4 M acetic acid at 60°C for 24 h. The aliquots for trace element determination were analysed by inductively coupled plasma mass spectrometry (ICP-MS). The strontium in each component was further separated by the conventional cation exchange techniques using ion exchange resin (packed with Bio-Rad AG50Wx8).

Strontium isotope analyses were performed on a Finnigan MAT-262 multicollector thermal ionization mass spectrometer (TIMS). The measured values for the NBS-987 standard were 87Sr/86Sr: 0.710256 ± 0.000014 (n = 8, 1 SD). The whole procedure Sr blank was lower than 200–300 pg.

For carbon and oxygen isotopes analyses, about 30–50 mg of drilled out sample was reacted overnight with 100% phosphoric acid at 25°C under vacuum to release CO2 from the carbonate minerals. The CO2 was then analysed for carbon and oxygen isotopes on a Finnigan MAT-262 mass spectrometer. The measured values for the NBS-18 standard were δ13C: -1.96% ± 0.05% (n = 8, 1 SD). The whole procedure C blank was lower than 200–300 pg.

Fig. 1. Palaeogeography of Feixianguan in NE Sichuan Basin: a semi-isolated evaporite–carbonate platform occupied the east of Kajiang-Liangping Trough (A); and the location of gas fields in Feixianguan Formation reservoirs in the NE Sichuan Basin (B). Modified from Zhao et al. (2005).
MAT251 mass, spectrometer standardized with NBS-18. All carbon and oxygen data are reported in units of per mil relative to the Vienna Peedee Belemnite (VPDB) standard. The precision for both $\delta^{13}C$ and $\delta^{18}O$ measurements is ±0.1.

RESULTS

Petrology

The dolomites in the P3Ch-T1f intervals are predominantly composed of reef and ooid-replaced dolomites. Ooid-replaced dolomites can be subdivided into sparry and residual types according to the degree of preservation of the original textures. The fluid inclusions in dolomite tend to be too small to be used for microthermometry although some single-phase aqueous inclusions were identified, trapped in residual ooid-replaced dolomites (Xie et al. 2006).

Ooid-replaced dolomites associated with reef facies in the Permian Changxing Formation (Fig. 3A–B) are typically composed of silt-sized crystals containing subhedral to euhedral dolomite crystals. The grain-supported primary fabric contains calcite cement in the intergranular pores with bitumen locally surrounding some grains. This kind of dolomite shows non- to dull-red luminescence while calcite cements have absolutely no luminescence under CL (Fig. 3A,B).

Reef facies dolomites in the Permian Changxing Formation are composed of sponge bafflestone dolomites, sponge framestone dolomites and dolomite veins. The size of the primary sponge stems is from 1 to 10 mm. Megacrystals of white calcite cement fill the spaces between the foramen of the sponge (Fig. 3C). Bitumen is commonly associated with late-stage calcite cements. The reef dolomite shows non- to dull-red luminescent character while calcite cements have absolutely no luminescence.

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Sparry ooid-replaced dolomites in the Feixianguan Formation are composed of silt-sized crystals containing a small proportion of finer, subhedral to euhedral dolomite crystals. Primary ooids range in size from 200 to 500 μm and show well-preserved concentric laminations and a grain-supported fabric with two-stage isopachous cement rims (Fig. 3D). Sparry ooid-replaced dolomite shows non- to dull-red luminescence under CL. Intergranular and intragranular pores are well developed, with bitumen and quartz cement locally infilling the pores.

Some dolostones in the Feixianguan Formation have signs of a primary oolitic fabric (ghost dolostones) due to intense dolomitization and recrystallization (known as residual dolomites). These are composed of euhedral to subhedral, very finely crystalline dolomite. The fine dolomite crystals inside the ooids are tightly packed. Euhedral dolomite is present at the margins of ooids. Most of the circum-grain cement cannot be differentiated. Calcite cement and bitumen have partially filled in the intergranular pores. Residual ooid-replaced dolomite shows dull-red luminescence while the associated later calcite is nonluminescent under CL (Fig. 3E,F).

Geochemistry results

Carbonate mineral compositions

The compositions of dolomite and calcite in the Upper Permian Changxing Formation and Lower Feixianguan Formation, obtained from wavelength dispersive electron microprobe (with a resolution of about 20 ppm for Sr, Fe and Mn), are listed in Table 1. The Sr concentration of dolomite ranges from 25 to 524 ppm. The Fe concentration of dolomite ranges from 39 to 373 ppm. The Mn concentration of dolomite ranges from 31 to 256 ppm. The Mg/Ca molar ratio for dolomite ranges between 0.87 and 0.94. The Sr concentration of calcite ranges from 25 to 524 ppm. The Fe concentration of calcite ranges from 39 to 373 ppm. The Mn concentration of calcite ranges from 31 to 256 ppm. The Mg/Ca molar ratio for calcite ranges between 0.87 and 0.94.
Strontium concentrations obtained from wet chemical analysis are listed in Table 2. The Sr concentration of calcite ranges from 304 to 4618 ppm, while the Sr concentration of dolomite lies between 49 and 240 ppm. These data corroborate the electron microprobe data.

C/O/Sr isotope data
Carbon and oxygen isotopic compositions of dolomite and calcite cements from the Upper Permian and Lower Triassic are presented in Fig. 4 and Table 2. Dolomite shows broadly uniform δ18O and δ13C values, falling within a narrow range between −3.4 and −5.2‰ (V-PDB) for δ18O and −2.9 and 2.3‰ (V-PDB) for δ13C. One early reef calcite cement has a lower δ18O value of −7.2‰ (V-PDB) and δ13C value of −0.2‰ (V-PDB).

The strontium isotopic compositions of the dolomite and calcite cements are presented in Fig. 5 and Table 2. The ooid-replaced dolomites in the T1f and the P3ch reef dolomites show a limited range of Sr isotope ratios. The Feixianguan Formation dolomite has 87Sr/86Sr ratios from 0.707356 to 0.707740. The Changxing Formation dolomite has 87Sr/86Sr ratios from 0.707732 to 0.707847. One early reef calcite cement sample in the Changxing Formation has a lower 87Sr/86Sr ratio of 0.707066 (Table 2). An early calcite cement in the Permian reef has a low 87Sr/86Sr ratio of 0.707066, characteristic of Upper Permian seawater.

DISCUSSION
Geochemical changes recorded in the dolomites

The interpretation of dolomite geochemistry and isotopes is here predicated on the assumption that the dolomite has not been recrystallized. Previous studies on a different well (Hu et al. 2012; Pan et al. 2012) have concluded that the majority of the T1f dolomites were reflux origin, but note that nothing has been previously reported on the Upper Permian dolomite. The dolomite samples collected in this study, and reported in the earlier studies, have very small crystal size, do not contain two (i.e. higher temperature) phase fluid inclusion and only present few single liquid
fluid inclusions. This suggests that the dolomite, discussed in this and the previous papers, has not undergone burial diagenetic recrystallization.

**Significance of strontium concentration data**

Strontium concentrations can be used to help understand the nature of the dolomitizing fluid. Previous studies of the Feixianguan Formation have shown that the Sr concentrations in dolomite (average 140 ppm) are significantly lower than the limestone counterpart (average 1080 ppm) (Huang et al. 2006, 2008a, 2009). Enrichment of strontium in limestone by the aragonite-calcite conversion process during early diagenesis has recently been proposed (Li et al. 2012). Because the large Sr ion is confined to the Ca sites in calcite and dolomite, there are typically much higher concentrations of Sr in calcite than in dolomite (Jacobson & Usdowski 1976; Kretz 1980). Remnant inclusions of precursor carbonate (calcite) and the equilibrium distribution coefficient of Sr between dolomite and diagenetic fluids (D$_{Sr}$) are considered to be the major factors controlling the reported Sr concentrations in dolomite (Budd 1997). Estimates of the Sr distribution coefficient (D$_{Sr}$) for dolomite vary from 0.015 to 0.025 (Veizer 1983; Vahrenkamp & Stewart 1990; Banner 1995; Budd 1997). SEM and microprobe data from dolomite in this study (with low Sr concentration of 25–524 ppm; Table 1) have not revealed remnant calcite inclusions. In addition, the Sr concentrations of dolomite from microprobe analysis are similar to the results of wet chemical analysis (with low Sr concentrations of 49–240 ppm). In this study, the dolomite compositions measured by microprobe can therefore be used to determine the nature of the dolomitizing fluid. The Sr/Ca molar ratio of the dolomitizing fluid can be calculated from the equation (Sr/Ca)$_{dolomite}$ = D$_{Sr}$ (Sr/Ca)$_{fluid}$. Such calculations yield Sr/Ca ratios for the
Triassic Feixianguan Formation dolomitizing fluid of 0.0012–0.0740 for $D_{\text{Sr}} = 0.015$, and 0.0007–0.0444 for $D_{\text{Sr}} = 0.025$. Similar calculations for the Permian Changxing Formation dolomitizing fluid give Sr/Ca ratios of 0.0059–0.0451 for $D_{\text{Sr}} = 0.015$, and 0.0035–0.0271 for $D_{\text{Sr}} = 0.025$. These molar ratio values span the range from (to significantly higher than) the Sr/Ca ratio of present day seawater (0.0086; Drever 1988) and so lead to the inference that seawater may have been responsible for dolomitization. The considerable range of $D_{\text{Sr}}$ value of dolomite argues, nonetheless, for some caution in this interpretation.

**Significance of Fe and Mn concentration data**

Manganese is the main activator, and Fe is the main quencher of luminescence in carbonate minerals so CL patterns allied to trace element data have been used to interpret the origin of the water from which the carbonate minerals grew (Marshall 1988; Machel & Burton 1991; Machel et al. 1991; Savard et al. 1995). Iron and Mn concentrations (Table 1), in contrast to Sr, reflect the redox state of the dolomitizing fluid and the diagenetic environment. Mn$^{2+}$ and Fe$^{2+}$ substitute for both Mg$^{2+}$ and Ca$^{2+}$ in calcite and dolomite. It has been reported that increasing influences of meteoric water during early diagenesis lead to enrichment of Mn$^{2+}$ and Fe$^{2+}$ during mineral growth (Veizer 1977, 1978; Brand & Veizer 1980; Driese & Mora 1993; Savard et al. 1995). Meteoric waters involved in carbonate diagenesis have been shown to result in Mn concentrations up to 34 000 ppm (Driese & Mora 1993) and Fe concentrations up to 14 500 ppm Fe (Popp et al., 1986).

Previous studies have shown that the Lower Triassic Feixianguan Formation carbonates had relatively low Mn and Fe contents, with average values about 27 ppm and 480.5 ppm, respectively (Huang et al. 2006). Cathodoluminescence and trace element data from both dolomites and calcite cements in P_3ch-T_1f intervals (Table 1, Figs 3 and 6) indicate that the compositions of dolomite and calcite cements are significantly different. Relative to the earlier non- to dull luminescent ooid-replaced dolomites, the completely nonluminescent late-stage calcite spar cements contain significantly more Fe and Sr but similar amounts of Mn. The minimum concentration of Mn required to initiate visibly Mn-activated luminescence in carbonates is 25 ppm, while the minimum Fe content for the quenching of luminescence is below 200 ppm (Budd et al. 2000). The Mn concentrations of dolomite and calcite samples are generally <200 ppm (Table 1 Fig. 6), and the Fe contents of these carbonates are generally more than 100 ppm.
Therefore, the luminescence colours of the dolomite and calcite samples are controlled by the quenching character associated with slightly elevated Fe concentrations. The fundamental CL character, with non-luminescent to dull luminescent dolomite and completely nonluminescent calcite spar cements, persists over the entire study area despite there being different structural domains resulting from several tectonic movements (Cai et al. 2003, 2004, 2010; Hao et al. 2008; Ma et al. 2008). The widespread distribution of uniformly nonluminescent dolomite and the composition of the dolomite suggests that dolomitization resulted from early diagenetic events and was unrelated to later-stage tectonic activities (Driese & Mora 1993).

The very low concentrations of Mn and Fe present in dolomite cements in both Upper Permian and Lower Triassic rocks suggest that invasion of meteoric water had negligible influence on dolomitization in either formation. Instead, it is possible to conclude that the slightly luminescent dolomite with its low Fe concentrations grew from oxidized marine waters. By contrast, late-stage calcite cements have Fe concentrations nearly twice those in ooid-replaced dolomites suggesting that they grew under reducing conditions during burial diagenesis (Veizer 1978).

Interpretation of isotope data

Origin and significance of oxygen isotope data

Dolomitization of carbonates needs large volumes of water to supply the required Mg so that identifying the source of the water can be a major indicator of the type of dolomitization. Oxygen isotopic compositions of the dolomite are controlled by temperature and the isotopic composition of the water that caused dolomitization (Land 1992). The $\delta^{18}O$ of the water that caused dolomitization can be calculated from the mineral $\delta^{18}O$ if the temperature of growth can be established, for example, from the homogenization temperature (Th) of aqueous fluids inclusion in dolomite.

In this study, all fluid inclusions in dolomite were found to be small and single phase. Single-phase inclusions have been reported to be diagnostic of the early stages of diagenesis at temperature significantly less than about 50°C (cf. Goldstein & Reynolds 1994). The single-phase aqueous inclusions trapped in dolomite therefore suggest that dolomitization commenced during early stages of diagenesis at temperature below 50°C. The abundance of reef and oolitic shoals and banks facies, as well as the occurrences of evaporite (Zhao et al. 2005; Ma et al. 2008), in the Permian and Triassic carbonate sequences in the Sichuan Basin suggests warm conditions and subtropical palaeo-latitude.

Note that a likely near-surface temperature in the arid, low latitude climate typical of the Upper Permian to Lower Triassic in the palaeo-Sichuan area would have been up to about 35°C (Zhao et al. 2005). Unfortunately, the single-phase fluid inclusions were too small to determine salinity of the dolomitizing fluid.

The $\delta^{18}O$ values of dolomite from the P 3ch-T1f reef-oolitic facies dolomites (Table 2) are between $-2.6$ and $-5.3\% V-PDB$ (Fig. 6). Accepting the above temperature constraints (using an estimate of 35°C for the temperature of dolomitization) and using the Land (1983) fractionation equation, then the $\delta^{18}O$ value of the dolomitizing water was between $-3.1$ and $-5.4\% V-SMOW$ (Fig. 7).

Following the example of Azmy et al. (2001), we have utilized the $\delta^{18}O$ values of marine calcite to constrain the $\delta^{18}O$ of coeval seawater (Land 1983; Budd 1997). The oolitic shoal and bank limestone as well as micrite in Feixianguan Formation show $\delta^{18}O$ values in a range predominantly between $-4\% V-PDB$ and $-7\% V-PDB$ (Zhu et al. 2005a; Zhao et al. 2005b). This range is entirely typical of oxygen isotope values from pristine marine bioclasts from the early Triassic (probably ranging between $-3.5$ and $-5.0\% V-PDB$ with limits from $-2$ to $-7\% V-PDB$, Veizer et al. 1999) and suggests that these values can be used to derive the oxygen isotope ratio of the contemporary seawater. Assuming a temperature of 20–25°C for the subtropical seawater present during the deposition of these marine carbonates in the Sichuan Basin (Zhao et al. 2005; Ma et al. 2008) and employing the Friedman & O’Neil (1977) calcite-water oxygen isotope fractionation equation, then the $\delta^{18}O$ of the seawater can be estimated to have been between $-1.7$ and $-5.9\% V-SMOW$ with a mean expected value of about $-3.5\% V-SMOW$. This range is consistent with the range of estimates for $\delta^{18}O$ of the water responsible for the replacive growth of dolomite (Fig. 7) suggesting that dolomitization may have occurred in coeval seawater. In summary, it is possible to conclude that dolomitization occurred at temperature below 50°C. Accepting the above temperature constraints, then the $\delta^{18}O$ of the dolomitizing water was between $-3.1$ and $-5.4\% V-SMOW$ (Fig. 7).

Fig. 7. Temperature versus $\delta^{18}O$ diagenetic fluid for various $\delta^{18}O$ dolomite values that were reconstructed from the equation $10^a \ln T = 3.2 \times 10^b T^{-2} - 3.3$ (Land 1983). The shaded areas mark the interpreted temperature range of dolomitization.
that the dolomite and calcite from the Upper Permian and Lower Triassic carbonates in the Sichuan Basin grew from much the same seawater.

Significance of carbon isotope data
Because there is typically low CO₂ concentrations in diagenetic waters and because the fractionation of ¹³C and ¹²C is relatively insensitive to temperature (Land 1992), mineral δ¹³C values can be used to reveal the source of the carbon in the carbonate (Veizer et al. 1999). Previous studies (Wang et al. 2002; Zhao et al. 2005; Zhu et al. 2005a) have suggested that Feixianguan Formation carbonates, including oolite limestone, micritic limestone and dolomite, show that the carbon isotopic composition of coeval sea water had an average carbon isotopic ratio of about 2‰ V-PDB. This is typical of early Triassic marine carbonate δ¹³C (Veizer et al. 1999).

The P₃ch-T₁f reef-oolitic facies dolomites show a narrow range of δ¹³C values (−2.9 to 4.2‰ V-PDB), similar to the results of previous studies (Wang et al. 2002; Zhao et al. 2005; Zhu et al. 2005b; Hu et al. 2013). The carbon in dolomites was thus most likely derived from contemporaneous, marine-derived carbonate, and there is no carbon isotope evidence of deep burial processes being responsible for dolomitization.

Origin and significance of strontium isotope data
The strontium isotope ratio of global seawater has evolved over geological time as a function of intensity of weathering and relative sea level (Veizer et al. 1999; McArthur & Howarth 2004); this signal can be recorded in marine carbonates. The evolution of the strontium isotope ratio of late Permian to early Triassic seawater has been reviewed by Korte et al. (2003) and McArthur & Howarth (2004) who showed that seawater strontium isotope values were <0.7072 during the late Permian but increased to 0.7082 in the first 10 Ma of the early Triassic. During the deposition of the Feixianguan Formation (Early Triassic), which spanned some five million years (Zhao et al. 2005), the ⁸⁷Sr/⁸⁶Sr ratios of coeval seawater have been previously reported to range from 0.70715 to 0.70772 (Huang et al. 2008a). Instead, we suggest that the early Triassic (possibly Jialingjiang) seawater strontium isotope ratio actually reached 0.70784 (Table 2; Fig. 5), a value independently supported by Martin & Macdougall (1995).

Banner et al. (1988) and Banner & Hanson (1990) argued that strontium isotope ratios could be altered by water–rock interaction during dolomitization if (i) there is a high water–rock ratio; (ii) the source of the strontium is significantly different in age to the rock being dolomitized or (iii) the source of the strontium was associated with potassium-bearing minerals such as illite or K-feldspar (e.g. the dolomitizing fluid came from clastic rocks). The original ⁸⁷Sr/⁸⁶Sr may remain unchanged, regardless of the composition and volumes of fluid that pass through the rock, if the water had strontium with a similar isotope ratio as the host carbonates (Denison et al. 1994). Hence, carbonate lithologies that have undergone profound water–rock interaction may still yield the original seawater ratio if an early diagenetic event was caused by contemporary seawater.

Dolomite and calcite cements (Li et al. 2012) from the Feixianguan show ⁸⁷Sr/⁸⁶Sr values range from 0.70735 to 0.70774. This suggests that dolomitization in T₁f oolites (and growth of calcite cements in T₁f intervals) occurred in coeval Feixianguan seawater-derived diagenetic fluids (Fig. 5). Of the data reported here in Table 2, one Permian Changxing Formation early reef calcite sample corresponds to a late Permian seawater Sr isotope ratio suggesting negligible diagenesis occurred to this sample. All dolomite and early reef calcite cement from the Changxing Formations show high ⁸⁷Sr/⁸⁶Sr values falling between 0.70771 and 0.70784, higher than expected coeval Permian seawater. Uniform ⁸⁷Sr/⁸⁶Sr values for the P₃ch reef facies dolomite and calcite cements are similar to, or slightly greater than, reported Feixianguan (early Triassic) seawater values (Fig. 5). This suggests that dolomitization in the P₃ch reef facies dolomite was due to Triassic Feixianguan or slightly younger (Jialingjiang) seawater. Thus, it is most likely that dolomitization in both Triassic and Permian rocks was caused by early Triassic seawater (and see Huang et al. 2006, 2008b, 2009; Zheng et al. 2009). Dolomitization of early Triassic carbonates by early Triassic seawater is perhaps not unexpected. Dolomitization of late Permian carbonates by early Triassic seawater suggests that there was downwards percolation of younger seawater into underlying sediments.

In summary, petrographic data, single-phase fluid inclusions, mineral chemical criteria and stable and radiogenic isotopes seem to reflect one major episode of early dolomitization for the P₃ch-T₁f carbonates. We conclude that evaporated, marine-derived brines were responsible for the dolomitization of P₃ch-T₁f carbonates, as there were multiple gypsiferous layers deposition and evidence of anhydrite precipitation in the oolitic dolomite reservoir in the Feixianguan Formation (Fig. 2; Ma et al. 2008) as well as the overlying Jialingjiang Formation (Cai et al. 2003, 2004).

Discussion of the dolomitization mechanism
Previous studies of the Feixianguan Formation in the NE Sichuan Basin, either using sedimentological, petrographic, or geochemical evidence, have suggested conflicting causes of dolomitization: (i) marine-meteoric mixing zone; (ii) burial dolomitization or (iii) seepage-reflux (Zhao et al. 2008b; Wang et al. 2007; Ma et al. 2008; Huang et al. 2009; Zheng et al. 2009; Hu et al. 2012; Pan et al. 2012).

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Zhao et al. (2005), Wang et al. (2007), Ma et al. 2008 and Huang et al. (2009) suggested that mixing-zone dolomitization occurred in the Feixianguan Formation using oxygen isotope data or sedimentary environment indicators. However, in the present study, there is no geochemical or petrographic evidence of meteoric water in the ooid-replaced dolomites of the Feixianguan Formation. The CL characteristics, the low Mn and Fe concentrations and the strontium isotope ratios of the ooid-replaced dolomites all count against meteoric water-influenced dolomitization. Thus, the ooid-replaced dolomite reservoirs in the Feixianguan Formation are unlikely to be the result of mixing-zone dolomitization.

Some have argued that burial dolomitization occurred in the Feixianguan Formation (Zhao et al. 2005; Huang et al. 2009; Zheng et al. 2009; Li et al. 2012). If intermediate to deep subsurface dolomitization was important in the study area, a mechanism would have been required to force large quantities of water through the precursor carbonate sediment. The principal mechanisms proposed for moving Mg-bearing waters through subsurface carbonates include (i) compaction-driven flow; (ii) topography-driven flow; and (iii) thermal convection (Machel 2004; Whitaker et al. 2004; Whitaker & Xiao 2010; Gabellone et al. 2013). Compaction-driven flow would presumably have pushed older brines through overlying younger strata and so left its isotopic (especially $^{87}$Sr/$^{86}$Sr) imprint. Topography-driven flow would likely have caused meteoric influx and signs of reduced Fe- and Mn-rich meteoric water with characteristic $\delta^{18}$O. In the case of the Sichuan basin, the dolomitizing water was apparently derived from seawater with low Fe and Mn concentration, marine $\delta^{18}$O and early Triassic $^{87}$Sr/$^{86}$Sr ratios suggesting that neither compaction-driven flow nor topography-driven flow could have been responsible for the formation of the dolomite. The presence of single-phase aqueous inclusions suggests that dolomitization must have commenced at a temperature significantly lower than about 50°C, which further discounts the possibilities of deep burial dolomitization and thermal convection-driven water movement.

During the Feixianguan and Jialingjiang (early Triassic), an arid climate persisted in the northeast Sichuan Basin and a semi-isolated evaporate carbonate platform formed on the east side of Kaijiang-Liangping Trough. Oolitic shoals began to develop and gradually formed a complex of barrier islands behind which lagoons formed and seawater evaporation resulting in elevated salinity (Zhao et al. 2005). Note that there are multiple gypsum-rich layers in the Feixianguan Formation (Ma et al. 2008). Previous studies (Wang et al. 2002, 2007; Zhu et al. 2005b; Du et al. 2007) reported that anhydrite cements and nodules are present in the ooid-replaced dolomites in Feixianguan Formation. Such anhydrites are notably absent in the underlying late Permian Changle Formation. Anhydrite is a common by-product of reflux dolomitization (Jones & Xiao 2005; Al-Helal et al. 2012). The progressive evaporation of refluxing seawater will first lead to dolomite growth and then gypsum growth. This reaction is favoured by slightly elevated temperature as this encourages evaporation of seawater inside the barrier islands and the landward flux of seawater through the near-surface carbonate sediments.

During the early Triassic, the primary oolitic limestones of the Feixianguan Formation were porous and probably allowed Feixianguan seawater to seep into the restricted lagoon as net evaporation led to a lower water surface in the lagoon than the mean sea level. Evaporated seawater then refluxed downwards and laterally into the porous

![Fig. 8. Reflux dolomitization model for the formation of dolomites in P3ch-T1f intervals.](image)
oolitic carbonates as well as the underlying Permian reef facies carbonates (Fig. 8). The movement of Feixianguan evaporated brine resulted in progressive dolomitization and locally precipitated anhydrite within the Feixianguan Formation, and the porous T1f carbonates were dolomitized (Zhao et al. 2005; Hu et al. 2012). We propose that Feixianguan seawater caused initial dolomitization of the Upper Permian Changxing Formation while slightly younger (and more radiogenic) Jialingjiang seawater resulted in further dolomitization of the Changxing Formation reef facies carbonates. We surmise that the salinity of the dolomitizing fluids decreased during reflux and by the time the water refluxed/penetrated into Changxing Formation, the salinity was below the point of gypsum precipitation thus accounting for the lack of anhydrite in the Changxing Formation reef dolomites.

CONCLUSIONS

(1) The Permian Changxing Formation reef dolomites and Lower Triassic Feixianguan Formation ooid-replaced dolomites in the Sichuan Basin have non- to dull-red luminescence and low Sr, Mn and Fe concentrations. The presence of single-phase fluid inclusions suggests that dolomitization was a low temperature (<50°C) process.

(2) Isotope data (87Sr/86Sr, δ18O and δ13C) from the Permian and Triassic dolomites and interpreted Sr/Ca molar ratio of the dolomitizing water suggest that seawater was responsible for dolomitization. 87Sr/86Sr values suggest that Lower Triassic seawater that caused dolomitization, even in the underlying Permian Changxing Formation.

(3) By integrating sedimentology, petrology and geochemistry, we conclude that coeval Feixianguan seawater caused dolomitization of the Feixianguan dolomites and minor dolomitization of the Changxing reef facies by a reflux-seepage process. Jialingjiang seawater (slightly younger than Feixianguan seawater) was responsible for the majority of the Changxing reef facies dolomitization also by a reflux-seepage process. The growth of anhydrite nodules and beds in the Feixianguan Formation supports the reflux-seepage model. The absence of anhydrite in the Changxing Formation suggests that concomitant dolomitization in the underlying Permian reef carbonates continued during seepage even after the supply of sulphate was exhausted.

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Hu ZW, Huang SJ, Li ZM, Zhang YY, Xu ES, Qi SH (2013)

Goldstein RH, Reynolds TJ (1994)

Systematics of Fluid Inclusions


Friedman I, O’Neil JR (1977) Compilation of stable isotope...
CONTENTS

Rudy Swennen, Francois Roure, Jacques Pironon, Fadi H. Nader and Mark Person

101 Synchrotron XRF and XANES investigation of uranium speciation and element distribution in fluid inclusions from unconformity-related uranium deposits

112 Age and genesis of the White Pine stratiform copper mineralization, northern Michigan, USA, from paleomagnetism
D.T.A. Symons, K. Kawasaki and J.F. Diehl

127 Modelling fault reactivation and fluid flow around a fault restraining step-over structure in the Laverton gold region, Yilgarn Craton, Western Australia
Y. Zhang, P.M. Schaub, H.A. Sheldon, T. Poulet and A. Karrech

140 Fluid channeling along thrust zones: the Lagonegro case history, southern Apennines, Italy

159 Diagenesis versus hydrothermalism and fluid–rock interaction within the Tuscan Nappe of the Monte Amiata CO2-rich geothermal area (Italy)
M. Gasparrini, G. Ruggieri and A. Brogi

180 Diagenetic evolution of a fractured evaporite deposit (Vilobi Gypsum Unit, Miocene, NE Spain)
M. Moragas, C. Martinez, V. Baqués, E. Playà, A. Travé, G. Alias and I. Cantarero

194 Geochemical simulations to assess the fluorine origin in Sierra de Gador groundwater (SE Spain)
L. Daniele, M. Corbella, A. Valles, M. Diaz-Puga and A. Pulido-Bosch

204 Quantification of diagenesis impact on the reservoir properties of the Jurassic Arab D and C members (Offshore, U.A.E.)

221 Dedolomitization and reservoir quality: insights from reactive transport modelling
L.-C. Escorcia, E. Gomez-Rivas, L. Daniele and M. Corbella

232 Reflux dolomitization of the Upper Permian Changxing Formation and the Lower Triassic Feixianguan Formation, NE Sichuan Basin, China
L. Xiang, C.F. Cai, R.H. Worden, K.-K. Li and L. Xiang

246 Petroleum system evolution in the inverted Lower Saxony Basin, northwest Germany: a 3D basin modeling study
B. Bruns, R. Di Primo, U. Berner and R. Littke