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Fluid inclusion and geochemical evidence for the origin of sparry calcite cements in Upper Permian Changxing reefal limestones, eastern Sichuan Basin (SW China)

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ABSTRACT

Gas reservoirs in the Upper Permian Changxing Formation in eastern Sichuan Basin are found mostly in dolostones, rather than the contemporaneous reefal limestones that had most of their porosity occluded by pervasive calcite cementation. The sparry calcite, which was the latest but most abundant type of cement, was responsible for major porosity loss. Hence, this study focuses attention on the origin of sparry calcite by employing petrography (e.g. microscope, cathodoluminescence), geochemistry (carbon, oxygen and strontium isotopes, trace elements, and clumped isotope thermometry) and fluid inclusion analysis. The sparry calcite cements are interpreted to be of burial origin as shown by their enclosement of radiaxial calcite and host rock fragments, the presence of two-phase (liquid and vapor) fluid inclusions with higher homogenization temperatures, and relatively lower oxygen isotopic values. Sparry calcites show none to very dull cathodoluminescence, preserve similar carbon and strontium isotopic signatures to other chemical components of host rocks, and have low concentrations of Fe and Mn. These facts indicate that the source for precipitation of sparry calcites was most probably derived from chemical compaction of host rocks and/or adjacent limestone strata. The contrast in porosity and sparry calcite abundance between the reefal limestones and dolostones imply that pervasive dolomitization of carbonates in the Changxing Formation probably occurred prior to chemical compaction, rather than deep-burial dolomitization proposed in previous studies. Early dolomitization enhanced preservation of porosity because the dolostones were more resistant to chemical compaction than the limestones. Reefal limestones in the Changxing Formation gradually lost their porosity during progressive burial because of chemical compaction and the resultant sparry calcite cementation. This study emphasizes the importance of chemical compaction in carbonate cement precipitation and the resultant porosity occlusion in deep burial carbonate successions.

1. Introduction

Sparry calcite cements, which are common porosity-occluding components in ancient carbonate successions, can be formed in various diagenetic environments that include near-surface freshwater settings (e.g. Bourque et al., 2001), shallow-burial, intermediate to deep burial settings (e.g. Choquette and James, 1987; Tobin et al., 1997; Bourque et al., 2001; Machel, 2005), and karst settings (e.g. Liu et al., 2010).

In the eastern Sichuan Basin, reef complexes in the Upper Permian Changxing Formation commonly host natural gas. In these deep-buried carbonates, however, porosity is found largely in dolomitized intervals of back-reef facies, whereas reef facies with high depositional porosity but little dolomitization are tight because of pervasive carbonate cementation. Among those carbonate cements, sparry calcites are volumetrically the most significant, occur throughout the massive reef facies, and fill most of the depositional porosity. The origin of the sparry calcite cements is, however, poorly understood.

This study, based on an integration of petrography, fluid inclusions, carbon, oxygen and strontium isotopes, trace element analysis, and clumped isotope thermometry, establishes the diagenetic environments in which these cements formed. Special attention is focused on the temperature and depth, the characteristics of diagenetic fluid, and the source of $CaCO_3$ that led to the precipitation of sparry calcite cements in the reefal limestones of the Changxing Formation.

2. Geological background

The Sichuan Basin, located in the eastern part of Sichuan Province, southwest China, is a foreland basin that evolved from an intracratonic basin with an area of approximately 230,000 km^2. The diamond-shaped Sichuan Basin (Fig. 1A) is surrounded 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 the Emeishan–Liangshan Fold Belt in the southwest.

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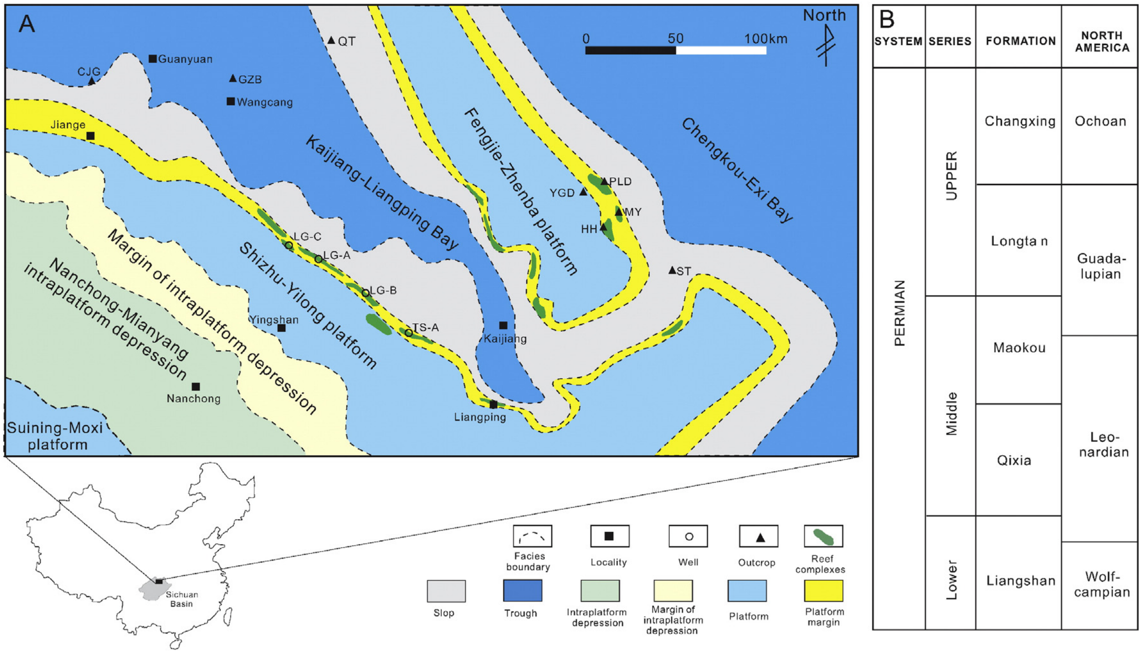

Fig. 1. A) Distribution of facies belts and reef complexes during late Permian of the study area (modified after Zhang et al., 2011 and Zou et al., 2011); B) Permian formations in Eastern Sichuan Basin and their equivalents in North America.

The sediments in the Sichuan Basin are up to 12 km thick. Marine sedimentation dominated in the basin from Precambrian to the Middle Triassic. In the late Permian, the Sichuan Basin experienced cratonic rifting and basement faulting during the Emei Taphrogeneis (Luo, 1991), and a paleogeomorphology configuration of *three topographic highs and three topographic lows* developed (Fig. 1A; Zhang et al., 2011; Zou et al., 2011). The three topographic highs are the Fengjie–Zhenba Platform, the Shizhu–Yilong Platform, and the Suining–Moxi Platform; and the three paleo-lows are the Chengkou–Exi Bay, the Kaijiang–Liangping Bay, and the Nanchong–Mianyang intraplatform depression. During deposition of the sediments that now form the Changxing Formation (equivalent to the Ochoan in North America, Fig. 1B), platform margin patch reef complexes were developed in the transitional areas between platforms and bays (Fig. 1A).

3. Material and methods

The data and samples used in this study were collected from the Longgang area in the eastern Sichuan Basin, where carbonates of the Upper Permian Changxing Formation are located at depths of 6000 to 6500 m in the subsurface. Cores from wells LG-A, LG-B (mainly limestones) and LG-C (mainly dolostones) were investigated (see Fig. 1A for their locations), and 80 samples including reefal limestones and dolostones were collected.

Forty large thin sections (5 cm × 4 cm) of reefal limestones and ten standard thin sections of dolostones, stained with Alizarin red S and potassium ferricyanide (Dickson, 1965), were examined using optical and cathodoluminescence (CL) microscopy. CL microscopy was performed on a CL8200MK5 cold cathode apparatus attached to a Leica 4500 microscope that was operated at 10–15 kV voltage and 400–500 mA beam current.

Fluid inclusion analyses were conducted on double polished thick (~100 μm) sections prepared using a cold technique (Goldstein and Reynolds, 1994) in order to prevent reequilibration of inclusions. Fluid inclusion petrography was carried out using a Zeiss microscope equipped with transmitted and UV light. Microthermometry was undertaken with a Linkam THMSG 600 cooling–heating stage. Calibration was performed using synthetic fluid inclusions at −56.6 (CO_2), 0.0 and 374.0 °C (H_2O). Homogenization measurements were performed before freezing runs to avoid stretching of the fluid inclusions. A LABRAM HR 800 Raman spectroscopy was adopted to assess the presence of gases in the inclusions, using a 375 nm Ar ion laser.

Carbon, oxygen and strontium isotope measurements were obtained from powders that had been collected from the host rock and their diagenetic phases using a micro-drill. For stable carbon and oxygen isotopes, ~10 mg of powders was reacted with 100% phosphoric acid for 4 h at 50 °C. The resultant CO_2 was measured for oxygen and carbon isotopic ratios on a DELTA V Advantage mass spectrometer. Isotopic values are presented in δ-notation and reported relative to the Vienna Peedee Belemnite (VPDB) standard. The accuracy of the $\delta^{13}C$ and $\delta^{18}O$ values is ±0.1‰ and ±0.2‰, respectively. For strontium isotope analysis, 100–150 mg sample powders were dissolved using a mixture of anhydrous 1 ml HNO_3 and 1 ml HF in a crucible at 190 °C for 48 h. Strontium was extracted using conventional exchange procedures (Baadsgard, 1987). The $^{87}Sr/^{86}Sr$ ratios were measured on a Triton Plus thermal ionization mass spectrometer and corrected relative to the NBS987 standard. The analytical mean error (2 sigma) is $\pm 0.5 \times 10^{-5}$ for $^{87}Sr/^{86}Sr$ ratios.

Trace element analysis were conducted on double polished thick (~120 μm) sections by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS), following the procedures of Fan et al. (2013).

Clumped isotope thermometry was done for two samples of sparry calcite at the University of California, Los Angeles, using the analytical methods described in Passey et al. (2010).

4. Results

4.1. Petrography

4.1.1. The Changxing reefal limestones

The reefal limestones of the Changxing Formation in the Sichuan Basin are composed largely of reef-building sponges and bryozoans, with lesser numbers of gastropods, brachiopods and foraminifers. Reefal limestones in the study area had high depositional porosity, which was subsequently occluded by multiple generations of carbonate cements, including radiaxial calcite, dolomite, and sparry calcite (Fig. 2 and Fig. 3). Pyrobitumen, which is common in some of the pores, postdated the radiaxial calcite and dolomite cements (Fig. 3A and B). The relative

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