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Review article

Indication of rare earth element characteristics to dolomite petrogenesis—A case study of the fifth member of Ordovician Majiagou Formation in the Ordos Basin, central China

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ABSTRACT

Rare earth elements (REEs), as important geochemical tracers, can well reflect the information carried by diagenetic fluids. In this paper, petrological and REE characteristics are studied to investigate diagenetic fluid information and dolomite petrogenesis using samples from the fifth member of Ordovician Majiagou Formation (Ma5) in the Ordos Basin based on the comprehensive analysis of C, O, and Sr isotopes. Three types of dolomites are identified in the study area, namely the dolomicrite, micrite-silty dolomite, and silty dolomite. Different types of dolomites have distinct total REE contents, among which the dolomicrite has the highest average total REE content and that could be possibly attributed to the abundant algal and argillaceous materials. All the three types of dolomites are featured by lower total contents of REEs than marine micrite, enriched light rare earth elements (LREEs) and deficit heavy rare earth elements (HREEs), which could result from the constant diffusion of REEs in the late diagenetic environment as well as the stronger complexing capacity of HREEs than LREEs. REE partition patterns in three types of dolomites are similar to those in marine micrite, which indicate the dolomitization fluids to be seawater or marine-origin fluids. In the dolomicrite, an obvious negative Eu anomaly (average value 0.63) and a faint negative Ce anomaly (average value 0.94) suggest that the sedimentary environment should be featured by low temperature and weak oxidation. Meanwhile, negative δ^{13} C excursion (average value - 1.23%), positive δ^{18} O excursion (average value -7.59%), and high mean 87 Sr/ 86 Sr ratios (average value 0.70992) along with petrological characteristics demonstrate the dolomicrite to originate from penecontemporaneous dolomitization. In the micrite-silty dolomite, the obvious negative Eu anomaly (average value 0.69) and the medium negative Ce anomaly (average value 0.72) indicate such kind of dolomites should be formed in the sedimentary environment characterized by low temperature and weak oxidation-weak reduction. The negative δ^{13} C excursion (average value -0.43%), positive δ^{18} O excursion (average value -7.29%), and relatively low mean ⁸⁷Sr/⁸⁶Sr ratios (average value 0.70955) identify the micrite-silty dolomite to be product of seepage reflux dolomitization in the supratidal zone. In the silty dolomite, the weakened negative Eu anomaly (average value 0.75) indicates relatively high temperature, and the obvious negative Ce anomaly (average value 0.66) implies reducing environment. Based on analysis of values of $\delta^{13}C$ (average value -0.65‰) and $\delta^{18}O$ (average value -6.46%) as well as ratios of 87 Sr/ 86 Sr (average value 0.70958), silty dolomite is regarded to form due to burial dolomitization.

1. Introduction

Middle Ordovician Majiagou Formation dolomite has been regarded as one of the most important targets for oil and gas exploration in the central Ordos Basin, the second largest petroliferous basin in China. Lots of works have been done on the dolomitization mechanism, Yang et al. (2012) proposed the formation mechanism of microbial dolomite using C and O isotope analysis; Li et al. (2005) put forward the mixed water dolomitization and locally existent hydrothermal dolomitization mechanisms based on combined analysis of C, O and Sr isotopes as well as trace elements. There are also dolomitization mechanisms proposed based on X-ray diffraction analysis, C and O isotopic characteristics, and

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trace element analysis, such as penecontemporaneous dolomitization, diagenetic dolomitization, burial dolomitization and local hydrothermal dolomitization (Liu et al., 2006; Wang et al., 2009; Huang et al., 2010; Zhao and Wang, 2011). However, the following problems still exist: (1) the origin of dolomite is still divergent according to works by different scholars; (2) the origin of dolomite is mostly discussed based on analysis of C, O and Sr isotope characteristics combined with trace element analysis, which is vulnerable to multiplicity of solution (Hu et al., 2010), and the analysis of rare earth elements is insufficient; (3) previous studies highlighted the origin of dolomites in the whole Majiagou Formation, with insufficient attention paid to the Ma-5 Member, and their conclusions were most inferred based on the sedimentary background.(4)these methods did not necessarily vield reliable results as trace elements or isotopic features in dolomites could be modified, overprinted, and even completely reversed due to heterochronouss inputs or subsequent diagenesis (Müller et al., 1990; Azmy et al., 2001; Eren et al., 2007).

Rare earth elements (REEs), as important geochemical tracers, have been widely used in the depositional environment, provenance and geochemical analysis (Haskin and Gehl, 1962; Piper, 1974; Henderson, 1984; Wang et al., 1986). Different fluids, such as seawater, meteoric water, and hydrothermal fluids, exhibit different REE signatures. Thus the sediments precipitated from them commonly inherit the REE signatures of their parent fluids (Lottermoser, 1992; Webb and Kamber, 2000). Previous studies suggested that marine calcites could well inherit the REE partition pattern of original seawater because they were not significantly influenced by the late diagenesis, and thus featured by enriched LREEs, deficit HREEs, and negative Eu anomaly (Banner et al., 1988; Qing and Mountjoy, 1994a,b; Miura and Kawabe, 2000; Kamber and Webb, 2001; Nothdurft et al., 2004). However, REE compositions and patterns can be dramatically altered if dolomites experience modifications in diagenetic systems with extremely high water-rock ratios, particularly in non-seawater-like diagenetic fluids, such as meteoric water and hydrothermal fluids (Murray et al., 1991; Webb and Kamber, 2000; Shields and Stille, 2001; Nothdurft et al., 2004; Webb et al., 2009). It has been gradually recognized that the characteristics of REEs in dolomites result from the redistribution and rebalance of REEs within diagenetic fluids and original carbonate deposits (Han et al., 2009). Thus, the REE signatures in dolomites provide important information to decipher origins of both sedimentary and diagenetic fluids. Therefore, in this study, REEs in three types of dolomites are comprehensively investigated based on the study of petrological characteristics and then compared to those in marine micrite. Moreover, C, O, and Sr isotopic characteristics are integrated to explore the origins of dolomitization fluids in Ma5 in the Ordos Basin, which can provide some reference for the future studies on dolomite petrogenesis. In addition, the presented results can serve as a reference for REE feature interpretations of ancient dolomites from other formations.

2. Geological setting

Ordos Basin is located in the western North China Platform, geographically covering the area bounded by Helan Mountain in the west, Lvliang Mountain in the east, Yin Mountain in the north, and Qinling Mountain in the south. It is a rectangular structural basin, linked with surrounding tectonic units by faults. There are a total of six tectonic units in the Ordos Basin according to its current structural characteristics, including Yimeng Uplift, Jinxi Fold Belt, Yishan Slope, Tianhuan Depression, Western Margin Thrust Belt and Weibei Uplift (Fig. 1). The Majiagou Formation carbonate reservoir rocks cover an area of 48,000 km², widely distributed but absent in the central paleohigh area. Majiagou Formation is a set of carbonate rocks interbedded with evaporite (Shi et al., 2009), consisting of six members. The first, third and fifth members are mainly composed of dolomicrite and micrite-silty dolomite and gypsiferous dolomite, respectively, which are formed in the dolomitic flat, gypsiferous flat, and dolomitic-gypsiferous flat,

respectively. The second, fourth and sixth members mainly consist of limestone (Li et al., 2005; Yang et al., 2011; Guo et al., 2012). To be specific, there are 10 sub-members in the fifth member (Dai and He, 2005; Wang et al., 2009), among which the fifth sub-member is the main reservoir and widely distributed in the middle and eastern part of the basin (Fig. 2). The studied area is located in the east of the central paleohigh region, and the depositional environment is dominated by the North China Sea depositional system. During the deposition, the overall rising North China Platform led to the relative sea level fall (Huang et al., 2012). Shallower water as well as dry and hot climate commonly resulted in the strong evaporation and thus the formation of evaporates (He et al., 2014). The sedimentary environment consists of multiple ring-shaped facies belts with the center in the eastern depression, and there are gypsiferous-halite basin facies, gypsiferous-dolomitic flat facies, and muddy-dolomitic flat facies from the center to the outside (Fig. 1).

3. Sample preparation and experimental method

All the samples are collected from Ma5 in 18 coring wells (Fig. 1). There are a total of 26 pieces of whole rock samples, sampling of which avoids dissolution pores and vugs as well as calcite veins to the largest degree to reduce the influence of late diagenesis on stable isotopic composition and thus reflect the original sedimentary characteristics. Among them, six samples are dolomicrite, six micrite-silty dolomite, eleven silty dolomite, and three micrite. In order to guarantee the accuracy, all casting thin sections are comprehensively observed and analysed under the normal microscope, cathodoluminescence, and scanning electron microscope to clarify their petrological characteristics. Because the contents of REEs in the marine authigenic minerals and silicate impurities are much higher than that of in the dolomite, a small amount of those materials that are mixed in the samples can largely influence the redistribution of REEs in the dolomite (Palmer, 1985; Banner et al., 1988; Murray et al., 1992; Webb and Kamber, 2000; Nothdurft et al., 2004). In order to reduce their influence on the analysis results, acetic acid was used to remove them.

A total of 26 thin sections are doubly polished and half-stained with Alizarin Red S to distinguish dolomite and calcite. The petrographic analysis is performed using DM2500 leica microscope at Southwest Petroleum University. Cathodoluminescence microscopy is conducted using a CITL 8220 MK3 instrument (operating conditions: 20 kV beam voltage and 200 µA beam current) at Hangzhou Supervision and Testing Center, Ministry of Land and Mineral Resources, China. Morphological analyses of the studied samples are examined by a Jeol 5600 Scanning Electron Microscope (SEM) equipped with an electron back-scattering CENTAURUS system at the Key Laboratory of Carbonate Reservoirs, CNPC. X-ray diffraction (XRD) analyses are performed with a Bruker D8 Advance X-ray diffractometer (Cu Ka X-ray source) at Hangzhou Supervision and Testing Center, Ministry of Land and Mineral Resources, China. Analysis of REEs is implemented at the Central South Mineral Resources Supervision and Testing Center of the Ministry of Land and Resources of China. Analysis method and process follows the general of inductively coupled plasma mass spectrometry (ICP-MS) with Thermo X Series II inductively coupled plasma mass spectrometry instrument. The instrumental detection limit is 10^{-12} and the measurement error can be controlled at 5%, which meets the requirements. Selected samples are then crushed to 75 µm in the agate mortar, and then put into paper sample bags for the later use. Specific workflow is as follows: first, put 40 mg of powder samples in the crucible; then add 5 mL of acetic acid with concentration of 1 mol/L into the crucible for 10-h dissolution; implement centrifugation and transfer the upper clear liquid containers for drying by distillation; add 1 mL of concentrated nitric acid to dissolve impurities; dry the solution again to remove residual acetic acid solution; add 5 mL of nitric acid with concentration of 1 mol/L; after the complete dissolution, add 1 mL of scaling liquid with mass fraction of 100×10^{-9} , and fix the volume 10 mL; and shake the

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