Microbial Participation in Formation of Lacustrine Dolomite of The Middle Permian Lucaogou Formation, Urumchi, Xinjiang, China

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INTRODUCTION

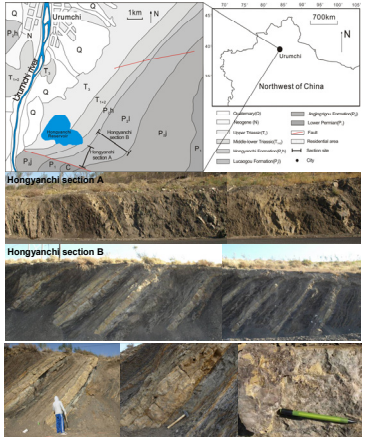
Studies on modern anaerobic and aerobic bacteria show that microbial activities are able to overcome kinetic barriers to the formation of low-temperature dolomite (<50℃, Mansfield, 1980; Vasconcelos *et al*., 1995; Vasconcelos & McKenzie, 1997; Roberts *et al*., 2004; Sánchez-Román *et al*., 2008). However, there is also a persistent controversy on whether those research findings provide reliable criteria for the interpretation of ancient analogues (Southam & Donald, 1999; Fernández-Díaz *et al*., 2006; Bailey *et al*., 2010).
Ancient lacustrine dolomites offer good opportunities to demonstrate the possible microbial dolomite in comparison with modern counterparts.
This report focus on the micromorphologies of the dolomite and the geochemistries of the dolostones and limestones in Middle Permian anoxic lacustrine Lucaogou Formation (Corresponding to Wordian Stage, Guadalupian Series) in Hongyanchi sections of Urumchi, Northern Xinjiang, NW China, to discuss the potential relationships between the organisms and the formation of dolomite.

MINERAL COMPOSITION

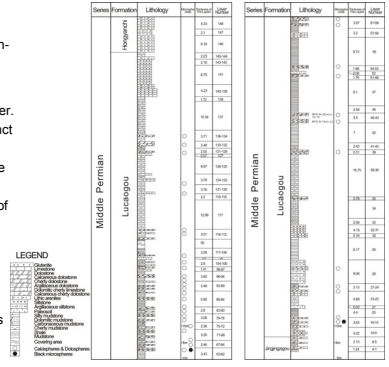
The Lucaogou Formation consists mainly of lacustrine dolostones interbedded with limestones, sandstones, mudstones, and oil shales. X-ray diffraction patterns indicate the dolostone composed of poorly ordered dolomite (60%-100%), quartz (2%-26.8%) and calcite (4%-23%). The degree of dolomite ordering ranged from 0.49 to 0.52. Over 50% of the dolomite was very fine-grained dolomite (<4 μm). Four types of carbonate micromorphologies were found: microspheres (Both calcispheres and dolospheres), nano-sized structures: nano-granules and nano-rods, and micron-sized subhedral and anhedral dolomite.

MICROSPHERES

Micron-scale spheroids ranged from 6 to 20 μm in diameter. They had simple shapes with crystalline lumens and distinct dark brown rims, and were scattered among the dolomite matrix together with fossil fragments. Some spheroids were surrounded by layers of organic matter.
EDS analyses showed the microspheres were composed of dolomite, ferro-dolomite, ferro-calcite, and Mg-Fe-calcite. Dolospheres (<10 μm) were usually smaller than calcispheres (10-20 μm).
Both dolospheres and calcispheres exhibit similar micro-structures: An outermost mineral coating composed of nanosize granules, nano-rods and fragments of contiguous crust over a smooth spheroid surface.
Other dolomite spheroids did not show such coating structures probably because they have endured some recrystallization.



Location of Hongyanchi sections (A and B) and the exhibition of Lucaogou Formation in Hongyanchi sections in Urumchi, China



The lacustrine sedimentary sequences of Lucaogou Formation in Hongyanchi section B

NANO-RODS AND NANO-GRANULES

Nano-rods are about 50 nm wide, ranging in length from 250 to 1000 nm. They were observed in two different conditions: (1)Those that are associated with micro-spheroids and oriented perpendicular to their surface form the crust at the interface between spheroids and matrix. (2) Those that are observed in the matrix. They were randomly oriented and associated with silica. EDS analysis indicates the composition was Si-rich dolomite.
The microsperoids and some anhedral dolomite were aggregated by numerous ovoid and spheroidal nano-sized granules, ranging from several tenth to 120 nanometers, which appeared to represent the very basic units to constitute such dolomite. EDS analysis indicates their composition were also dolomite.

MICRON-SIZED SUBHEDRAL AND ANHEDRAL DOLOMITE

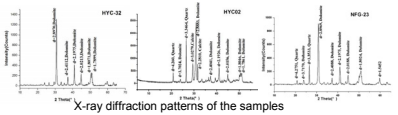
The microspheres were surrounded by a large amounts of micron-sized subhedral and anhedral dolomite (0.5 to 20 μm), while the rhombohedral dolomite is rare. EDS and major elements analysis indicate that some anhedral dolomite contains silicic impurities. X-ray diffraction analysis confirms that the phase composition of these impurities was clay-sized quartz, which may have originated from terrigenous clastics that were indistinguishable under the polarizing microscope.

INORGANIC EXPERIMENT RESULTS

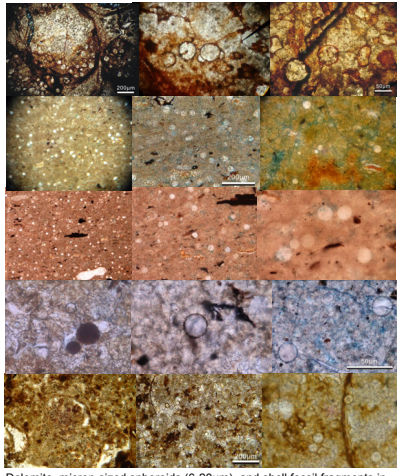
1. The inorganic spheroid lacks of the coatings and the nanotextures of the coatings.
2. The basic unites in inorganic calcispheroids mediated in agar are micro-sized rhombic crystals instead of nanogranulars or nano-rods.

GEOCHEMISTRY RESULTS

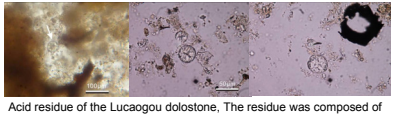
Whole rock analyses of major and trace elements reveal that some dolomite is rich in iron. Mg/Ca ratio of dolostones ranged from 0.38 to 0.61. The (Mg+Fe)/Ca ratio ranged from 0.53 to 0.69. The strontium of the dolostones ranged from 449.41 to 841.54, which was near to or higher than that of limestone. Sr/Ca ratios of the dolostones ranged from 22.77 to 42.33 were also higher than that of the limestone. The sodium of dolostones ranged from 2225.81 to 3338.71 which was 2.7 to 4.1 times higher than the limestone.



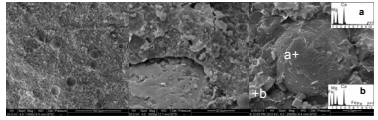
X-ray diffraction patterns of the samples



Dolomite, micron-sized spheroids (6-20μm), and shell fossil fragments in Lucaogou petrographic thin sections



Acid residue of the Lucaogou dolostone, The residue was composed of flocculated sludge and organic fragments. White arrow points to a microspheroid



SEM photomicrographs and EDS spot (+) analyses of microspheroids and the anhedral dolomite matrix

STABLE AND RADIO ISOTOPES GEOCHEMISTRY

The positive $\delta^{13}C$ indicates that bacterial methanogenesis may play an important role in carbonate precipitation because light ^{13}C entered into bacterial methane and the residual must be heavy due to the large carbon isotopic fractionation (Irwin et al., 1977; Games and Hayes, 1978; Mazzullo, 2000).
$^{87}Sr/^{86}Sr$ of the lacustrine carbonate rocks ranged from 0.705826 to 0.706292, lower than Permian Seawater (0.706854 to 0.707355, Korte et al., 2006). $^{143}Nd/^{144}Nd$ isotopes varied from 0.512380 to 0.512776, close to Bulk Silicate Earth (BSE, Rollison, 1993).

DISCUSSION AND CONCLUSION

1. The microspheroids including calcispheres and dolospheres mostly with crystals lumens and dark organic margins are still of unknown origins.
2. The contact zone between spheroids and matrix contained nano-sized textures of amorphous carbonate deposits (nanogranules) and transitional crystalline stages (nano-rods), which are most directly associated with known microbial activities and may have formed an early transition toward mineralization.
3. Subhedral and anhedral dolomite comprised the bulk of dolostones. Their poor degree of ordering, absence of replacement texture (e.g. from an earlier $CaCO_3$ phase), enrichment of strontium, sodium, iron and organic matter, heavily positive carbon isotopes, and the mixture with clay-sized quartz, suggest that the micron-sized subhedral and anhedral dolomites were likely precipitated by rapid crystallization from the bacterially mediated solution.

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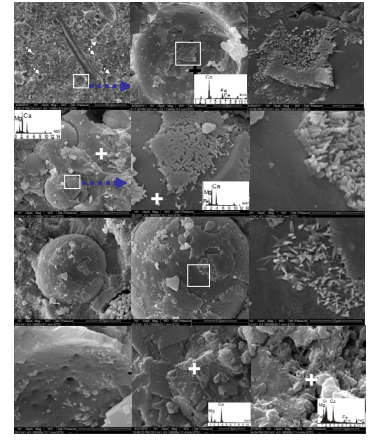
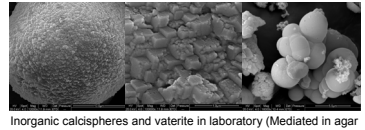
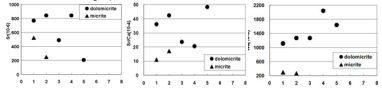


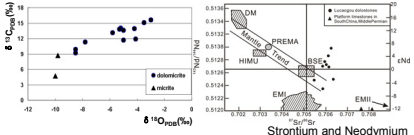
SEM photomicrographs and EDS spot (+) analyses of the calcispheres, dolospheres, nanogranules, nano-rods, and anhedral dolomite matrix



Inorganic calcispheres and vaterite in laboratory (Mediated in agar and without agar)



Strontium, Sr/Ca ratio and Sodium of the dolostones and limestones



Stable isotopes of Lucaogou carbonate rocks — Strontium and Neodymium isotopes pattern

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