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Contents

Origin of dolomite-evaporite paragenesis sequence and its hydrocarbon exploration implications: A case study from Lower-Middle Cambrian in Sichuan Basin (South China)

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Abstract

Dolomite-evaporite paragenesis sequences (DEPS) are found in many hydrocarbon-rich basins worldwide, but their origin remains uncertain. To understand the genesis and hydrocarbon potential of DEPS, a multi-technique approach involving petrography, sedimentology, and geochemistry was used. The study examined two types of evaporite and four types of dolomite in DEPS using C-, O-, and S-isotopes, as well as major and trace elements. Based on the relationship between evaporite and dolomite thickness and spatial superposition, five lithofacies associations (LAs) were identified in DEPS, representing different sedimentary processes. Among these, LA1, characterized by interbedding of dolostone and evaporite, was the most developed, while LA2 had the lowest degree of development. DEPS showed a dual-cores distribution pattern in the Sichuan Basin, with higher development observed in the lagoon perimeter. The formation of DEPS in the Lower-Middle Cambrian was influenced by factors such as paleogeography, tectonic conditions, paleoclimate, lagoon migration, and sea level fluctuations. A sedimentary model was developed to understand the sedimentological characteristics and depositional processes under different conditions. The study also revealed the potential for oil and gas exploration within DEPS, with LA2, LA3, and LA4 showing favorable reservoir properties, LA5 having optimal sealing conditions, and LA1 capable of forming reservoirs when stacked in layers. Based on reservoir and seal attributes, LA3 was identified as a high-quality reservoir-seal combination, and combining LA5 with LA2, LA3, and LA4 created a favorable reservoir-seal configuration. These findings provide insights into the genesis of DEPS and their hydrocarbon potential.

Keywords: Dolomite-evaporite paragenesis sequence; Sedimentary characteristics; Formation mechanism; Hydrocarbon exploration; Lower-Middle Cambrian; Sichuan Basin

Genesis mechanism and Mg isotope difference between the Sinian and Cambrian dolomites in Tarim Basin

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Abstract

Dolomite genesis is a century-old mystery in sedimentology. To reveal the mechanism of dolomite genesis, two core problems need to be addressed. The first is the origin and migration mechanism of Mg^{2+}-rich fluids during the dolomitization process. The second is the kinetic barrier caused by Mg^{2+} hydration during dolomite precipitation at low temperatures. To address these problems, our study, based on detailed petrological, sedimentological, geochemical (major and trace elements), and isotopic (C–O–Mg) analysis, clarified the source and migration of Mg^{2+}-rich fluids and the kinetic barrier mechanism of low-temperature dolomite precipitation in the Upper Sinian Qigebulake Formation and the Lower Cambrian Xiaoerbulake Formation in the Tarim Basin. First, we found that the Mg^{2+}-rich fluids required for the dolomitization of dolomite in the Xiaoerbulake Formation were primarily derived from the Early Cambrian marine fluid. At the interface of the sedimentary cycle, $\delta^{26}Mg$ values fluctuated considerably, indicating that the sequence interface was the starting point and channel for the migration of dolomitized fluids. Sea level variation plays a major role in controlling the dolomitization process of the Xiaoerbulake Formation. Second, the Qigebulake Formation contains low-temperature dolomite with Mg^{2+}-rich fluids supplied by seawater, microorganisms, and sedimentary organic matter. Comprehensive analysis shows that the dolomite of the Qigebulake Formation was formed by microbial induction by anaerobic methane bacteria. Finally, the properties and sources of dolomitization fluids and the formation process of dolomite were the reasons for the difference in the Mg isotope composition of dolomite during the Sinian–Cambrian transition. This study reveals the genetic mechanism of the Sinian–Cambrian dolomite in the Tarim Basin and establishes a new method to explain the genesis of microbial dolomite by C–O–Mg isotopes, providing a reference for the reconstruction of the formation and evolution of dolomites.

Key words: Dolomite genesis; Mg isotopes; Carbon and oxygen isotopes; Xiaoerbulake Formation, Qigebulake Formation; Tarim Basin

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Origin of Dolomites from the Maokou Formation of the Middle Permian in the Eastern Sichuan Basin: Evidence from Petrology, Mineralogy, and Geochemistry

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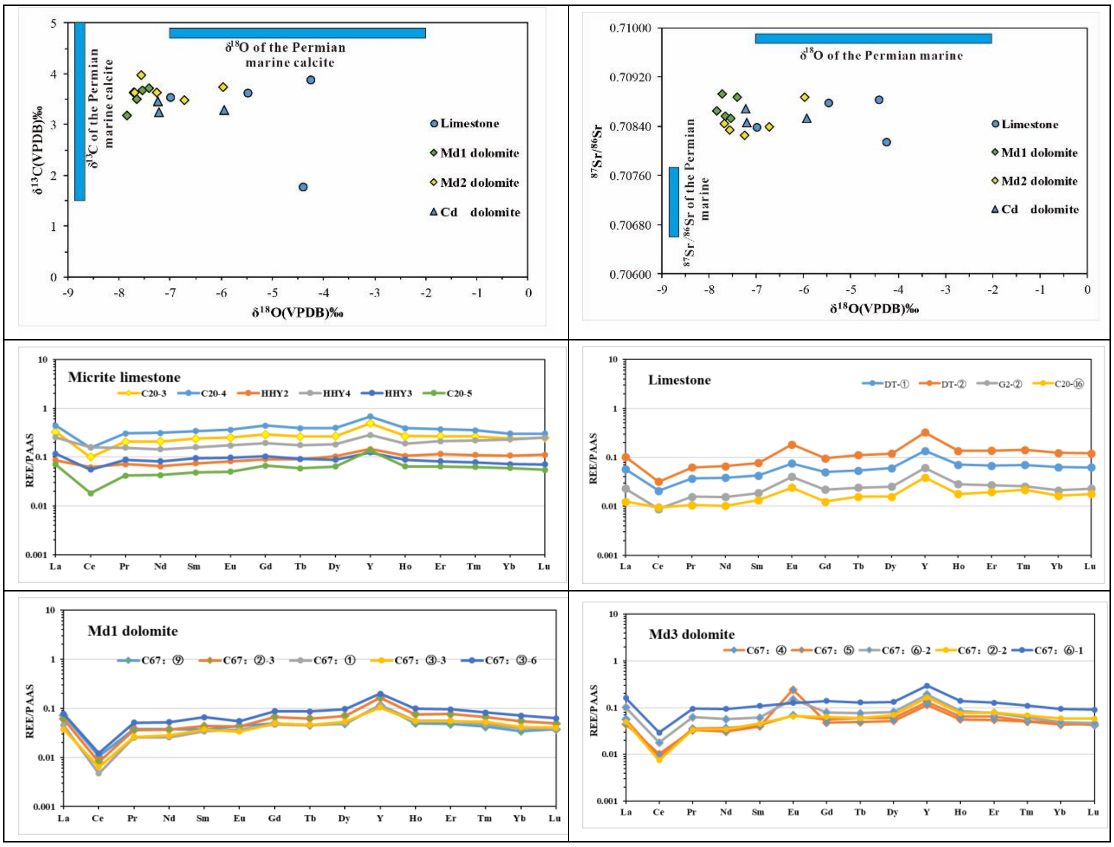
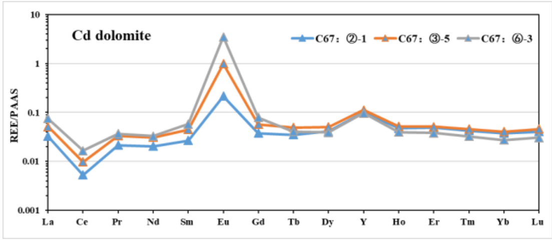
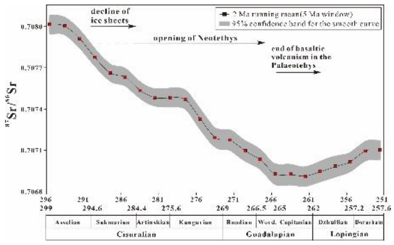
Abstract

Dolomite has always been a research topic of great concern in sedimentology due to its rich oil and natural gas resources, but the origin of dolomite has always been an unsolved mystery in sedimentology. In recent years, massive dolomite has been discovered along the 15 # basement fault in the Maokou Formation of the Middle Permian in the eastern Sichuan Basin. However, due to the hydrothermal influence of ELIP, the genesis of dolomite is often explained as tectonic hydrothermal dolomitization. There is almost no distribution of dolomite in the Qixia Formation in the eastern part of the Sichuan Basin, indicating that the distribution of dolomite does not possess interlayer permeability. This seems to be different from the mechanism of tectonic hydrothermal dolomitization. This article is based on some evidence from petrology, mineralogy, and geochemistry to study the dolomite of the Maokou Formation in the eastern Sichuan region. The results show that: 1) there are three types of dolomite in the study area (well preserved original structure of inlaid non straight crystal surface semi idiomorphic heteromorphic powder dolomite Md1, inlaid non straight crystal surface semi idiomorphic heteromorphic fine crystal dolomite Md2 with fog center bright edges, and saddle shaped non straight crystal surface heteromorphic coarse crystal dolomite Cd); 2) The petrological and geochemical characteristics show that Md1 dolomite exhibits a quasi contemporaneous seawater source, Md2 dolomite exhibits a mixed source of shallow burial seawater with a small amount of foreign hydrothermal fluid, and Cd dolomite exhibits a large amount of hydrothermal fluid mixed with a small amount of contemporaneous seawater source; 3) Based on the regional sedimentary tectonic background, it is believed that Md1 dolomite was formed by pre ELIP activity, quasi contemporaneous reflux infiltration dolomitization, Md2 dolomite was formed by ELIP activity, shallow burial thermal convection dolomitization, Cd saddle shaped dolomite was formed in the late stage of ELIP activity, and shallow burial tectonic hydrothermal dolomitization. Comparative analysis suggests that the thermal convection model can also be used to explain the formation causes of Md2 dolomite similar to the Qixia Formation and Maokou Formation in other regions of the Sichuan Basin. This provides a reference for the genesis of dolomite formed during other major igneous events in the province.

Key words: Sichuan Basin; Maokou Formation; Thermal convection dolomitization; Reflux infiltration dolomitization; Tectonic hydrothermal dolomitization; ELIP




Cd dolomite
C67：②-1
C67：③-5
C67：⑥-3
REE/PAAS
10
1
0.1
0.01
0.001
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Y
Ho
Er
Tm
Yb
Lu


decline of ice sheets
opening of Neotethys
end of basaltic volcanism in the Palaeotethys
2 Ma running mean(5 Ma window)
95% confidence band for the smooth curve
$^{87}Sr/^{86}Sr$
0.7080
0.7077
0.7074
0.7071
0.7068
296
291
286
281
276
271
266
261
256
251
299
294.6
284.4
275.6
269
266.5
265
262
257.2
257.6
Asselian
Sakmarian
Artinskian
Kungurian
Roadian
Word.
Capitanian
Dzhulfian
Dorashan
Cisuralian
Guadalupian
Lopingian

Dissolved Mn^{2+} promotes bacterially-induced protodolomite precipitation in brackish oxidized water

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Abstract

The origin of sedimentary primary dolomite is controversial and has been referred to as one aspect of “the dolomite problem”. The formation of microbial dolomite is strongly influenced by various environmental factors, such as salinity, Mg/Ca, clay minerals, and organic matter. Manganese is a common impurity element in dolomite, which can promote the ordering of dolomite under the action of microorganisms. However, the mechanism by how Mn^{2+} helps dolomite nucleate is not fully understood.

In this study, a strong mineralizing bacterium, *Bacillus licheniformis* Y1, was used to carry out experiments in the $MgCl_2$-$CaCl_2$-$MnCl_2$ brackish-water system. The characteristics of water chemistry, mineralogy of sediments and bacterial metabolites were analyzed and compared. The results show that when the content of Mg^{2+} in solution is low (Mg/Ca molar ratio<2), *B. licheniformis* Y1 in manganese-free solution can induce the formation of magnesia-free calcite and low-magnesium calcite, while the addition of 0.001 mol/L Mn^{2+} can lead to the precipitation of magnesium-rich calcite. When the content of Mg^{2+} in the solution is relatively high (Mg/Ca> 6), *B. licheniformis* Y1 in manganese-free solution can induce aragonite and dypingite, while the addition of 0.001 mol/L Mn^{2+} can lead to manganese dolomite in the precipitate. Manganese dolomite is a regular spherical aggregate, diameters range from 15 to 60 microns, (104) position of crystal face is close to dolomite. Manganese-oxygen chemical bonds, organic functional groups such as C=O, C-O-C, and organic elements such as N and P were detected on the mineral surface. The precipitation of manganese dolomite is related to the change of microbial extracellular polymeric substances (EPS) composition. Humic acids in EPS, especially fulvic acid, increased with Mn^{2+} concentration. Fulvic acid contains a large number of functional groups such as carboxyl groups, it can effectively promote the dehydration of magnesium-water complex. Trace amounts of manganese themselves combine readily with carbonates, and the addition of manganese stimulates changes in bacterial secretions. Mn^{2+} and *B. licheniformis* Y1 synergistically promote the formation of Mn-rich dolomite.

Key words: Manganese; *Bacillus licheniformis*; Kutnohorite; Fiuvic acid; Mn-dolomite

Properties of dolomitizing fluids indicated by rare earth elements: A case study of the Upper Miocene to Pliocene dolostone on the Xisha Islands, South China Sea

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Abstract

Rare earth elements and yttrium (REE+Y) are stable and predictable chemical markers used to study diagenetic fluids. However, the impact of dolomitization on the REE+Y signatures is still not well understood. To investigate the factors influencing REE+Y signatures, this study examines dolostone samples from the Xisha Islands in the South China Sea. The samples, taken from the Huangliu Formation (Upper Miocene) and the Yinggehai Formation (Pliocene) in well CK-2, exhibit low REE+Y concentrations (<10 ppm), LREE depletion, HREE enrichment, negative cerium (Ce) anomalies, and high Y/Ho values similar to modern seawater. The REE+Y profile of the dolostone does not correlate with sedimentary facies, suggesting that facies did not affect the fractionation and incorporation of REE+Y during dolomitization. Deviations from seawater Ce and praseodymium (Pr) anomalies in the Huangliu Formation indicate that the dolomitizing fluid was influenced by evaporation or fluid-rock interaction. Positive europium (Eu) anomalies may be attributed to higher dolomitization temperatures or the input of Eu-rich plagioclase into the South China Sea. Sequential digestion of dolomitic limestone from the Yinggehai Formation, including bulk rock and pure dolomite analysis, reveals that dolomitization has a minor yet evident effect on REE+Y concentrations, Y/Ho ratios, and Ce anomalies. The comparable REE+Y signatures of dolostone from the Xisha Islands, the Pacific Ocean, and the Caribbean Sea suggest a common seawater source for the dolomitizing fluid, indicating potential global paleoceanographic controls on dolomitization during the Cenozoic era. This study serves as a valuable reference for interpreting the paleoenvironmental significance of ancient dolostone in the geological record, particularly the REE+Y signatures of Cenozoic "island dolostone".

Early dolomitization of the Upper Ediacaran Qigebrak Formation in the northwestern Tarim Basin: Evidence from petrography, REE and clumped isotope

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Abstract

The research conducted on the Upper Ediacaran Qigebrak Formation in the Aksu area of the northwestern Tarim Basin focused on the mechanism of early dolomitization. Through comprehensive analyses of petrography, carbon and oxygen isotopes, strontium isotope, rare earth elements, and clumped isotope, three types of matrix dolomites were identified in the Qigebrak Formation: dolomicrite (MD-1), primary fabric preserving dolomite (MD-2), and primary fabric destructive dolomite (MD-3). MD-1 crystals are small, measuring less than 5 μm, and exhibit planar-s to nonplanar textures. MD-2 crystals range in size from 5 to 20 μm and display planar-s textures, showcasing primary microbial fabrics. On the other hand, MD-3 crystals vary between 50 μm and 200 μm and exhibit nonplanar textures, indicating the obliteration of primary depositional fabrics. The δ13C, 87Sr/86Sr values, and REE patterns of the dolomites are similar to those of seawater, suggesting a close relationship between the early-diagenetic dolomitization fluids and contemporaneous seawater. Combining the clumped isotope temperature (TΔ47≈60 °C) with the δ18O water range of dolomitization fluids, the study concludes that seepage-reflux dolomitization, involving mesosaline to penesaline seawater under strong evaporation conditions, is the primary mechanism responsible for the formation of large-scale dolomites in the Qigebrak Formation.

Key words: Northwestern Tarim Basin; Qigebrak Formation; Early dolomitization; Clumped isotope

The mechanism of Mg^{2+} inhibition in $CaCO_3$ crystallization

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Abstract

Magnesium ions have been found to inhibit the crystallization kinetics of calcium carbonate ($CaCO_3$). Previous studies have suggested several possible mechanisms for this inhibition: (1) magnesium ions entering the calcium carbonate lattice, leading to increased crystal solubility; (2) magnesium ions adsorbing onto the crystal surface, increasing surface energy and thus reducing nucleation rate; (3) magnesium ions inhibiting crystal dissolution-recrystallization processes. However, solid experimental evidence for these potential mechanisms is lacking. In this study, a solution turbidity monitoring device was constructed to monitor the changes in the crystal induction time of calcium carbonate crystallization in supersaturated solutions under different Mg/Ca ratios. The crystal induction time refers to the time from the formation of supersaturated solution to the occurrence of turbidity change. The results showed that the crystal induction time increased with higher Mg/Ca ratios. Furthermore, a mechanistic model of the crystal induction time was used to fit the experimental data, and the model fitting results indicated that the inhibitory effect of magnesium ions on the crystallization kinetics of calcium carbonate is primarily achieved by increasing the surface energy of calcium carbonate. Specifically, increasing the molar ratio of Mg/Ca in the solution from 0 to 6 resulted in an increase in the surface energy of the formed crystals from 0.042 J/m^2 to 0.053 J/m^2, leading to a significant increase in the crystal induction time. These findings have important implications for understanding how inorganic ions

impact the crystallization kinetics of $CaCO_3$.

Multiform proto-dolomite related to microbes of ultra-deep Early Cambrian in the Tarim Basin

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Abstract

There have been extensive discussions on the "dolomite problem", particularly regarding the microbial dolomite pattern. In this study, we present the discovery of proto-dolomite containing organic matter in the ultra-deep Lower Cambrian strata, specifically at a depth of approximately 7355-7358 m in the Tarim Basin. The dolomitic limestone samples were collected from the Wusongger Formation in WXH1, located in the western Tabei Uplift, and were deposited in a tidal flat environment. Macroscopically, the samples exhibit distinct light and dark interlayered laminae, with a thickness of about 1-2mm, which display characteristic features of stromatolites. Fluorescence microscopic analysis revealed a strong fluorescence effect in the dark laminae. Scanning electron microscope (SEM) imaging coupled with energy dispersive spectroscopy (EDS) analysis showed the presence of ring-shaped, rhombohedral, and clotted crystals, as well as mineral aggregates with the Mg/Ca ratio ranging from 0.7 to 1, distributed within the dark laminae. These crystals and aggregates are indicative of proto-dolomite formation. Based on macro and micro petrographic studies, the sample

is suggested to have been deposited in a hydrostatic environment near the redox zone. This is further supported by elemental geochemical proxies such as UEF (unknown element fraction) and MoEF (molybdenum enrichment factor). Additionally, the poorly crystallized proto-dolomite exhibits morphological and size distribution similarities to those observed in microbial culture experiments, suggesting that active microbes and/or organic matter might act as triggers for dolomite formation. These findings confirm the preservation of microbial structures in ancient dolomitic limestone, provide insights into the morphological evolution of dolomite growth, and validate their potential use as biosignatures. Future research can employ more precise techniques to study the microenvironment of these dolomite precipitations and further elucidate the influence of ancient organic matter on dolomite precipitation.

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Strontium isotope age and its implications of "background dolomite" on well CK-2 in the Xisha Islands, South China Sea

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Abstract

"Background dolomite" refers to the dolomite developed within dolomitized limestone, and typically, the dolomite content in the limestones is less than 50%. Given that "background dolomite" often coexists with calcite, there is a challenge to extracting pure dolomite from it, which is both laborious and time-consuming. Consequently, current research on "background dolomite" is relatively weak, which prevents the understanding of the overall appearance and genesis of island dolostones. Well CK-2 (927.85 m) drilled on the Chenhang Island in the Xisha Islands, South China Sea in 2013 revealed the complete stratigraphic sequence of island dolostones. The lower part (308.5~519 m) is the late Miocene massive dolostones of the Huangliu Formation, and the upper part (180~308.5 m) is the "background dolomite" of the Pliocene Yinggehai Formation, which provides high-quality materials for studying the overall picture of the development and evolution of island dolostones. Based on it, the strontium isotope age of "background dolomite" was analyzed in this paper, and simultaneously, the age evolution of dolomite chemistry in the Xisha Islands and its guiding significance to the origin of dolomite. The $^{87}Sr/^{86}Sr$ age shows that the "background dolomite" of the Yinggehai Formation formed from 4.5 to 0.5 Ma (million years) ago, and the whole rock of the Yinggehai Formation was formed before 4.5 to 1.6 Ma. The $^{87}Sr/^{86}Sr$ age ranges are almost similar, suggesting that the "background dolomite" of the Yinggehai Formation had been formed shortly after the depositional period and was the product of early dolomitization period. Since there isn't a significant correlation between the $^{87}Sr/^{86}Sr$ values and the Sr content in the "background dolomite", its Sr content resembles that of most islands and reefs (0-500 ppm). Moreover, the Mn/Sr ratio is less than 1, which indicates a specific phenomenon that the "background dolomite" of the Yinggehai Formation mainly formed in an open fluid environment that existed during its formation. The dolomitization time of the Well CK-2 in the Xisha Islands (10 to 0.5Ma) almost covers the development time (10 to <0.5Ma) of the global island dolostones, which almost records the whole process of development and evolution of island dolostones. The age of the dolomitization gradually becomes younger from the bottom to the top of the Yinggehai Formation, with insignificant discontinuities, which are difficult to use with the traditional "event dolomitization". This phenomenon can probably be explained by the process of (semi-) continuous "time-transgressive" dolomitization. The transformation time of the massive dolostones of the Huangliu Formation into the "background dolomite" of the Yinggehai Formation is about ~4 Ma, which corresponds to the Pliocene cooling period (e.g., expansion of the Arctic ice sheets), indicating that the low temperature diagenetic environment probably caused partial dolomitization of the Yinggehai Formation to form "background dolomite". On the other hand, since the original depositional environment of the Yinggehai Formation is the lagoonal environment in the center of the platform, it might be due to the seawater fluid for dolomitization flowed from the edge of the Xisha platform. During the seawater flowing to the center, with the gradual consumption of Mg^{2+} during the dolomitization process, the lagoon sediments locate in the center of the platform (location of well CK-2) have only partially been dolomitized to form "background dolomite".

Keywords: strontium isotope; background dolomite; Xisha Islands; Cenozoic