The Origin of Paleokarst in the Huanglong Formation of the Eastern Sichuan Basin: Evidence from δ¹³C, δ¹⁸O and ⁸⁷Sr/⁸⁶Sr

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Abstract: Karst rocks from the Huanglong Formation exposed at the margin of the Eastern Sichuan Basin can be divided into four types: slightly corroded, moderately corroded porous, intensely corroded brecciated and intensely corroded and replaced secondary calcic karstic rocks. The carbon, oxygen and strontium isotope compositions of the various karst rocks are analyzed systematically and compared to rocks without karst corrosion. The results indicate that (1) the Huanglong Formation in the eastern Sichuan Basin was a restricted bay supplied and controlled by freshwater in which mud-micrite and mud-dolomite exhibit low δ¹³C and δ¹⁸O values and high ⁸⁷Sr/⁸⁶Sr ratios; (2) all types of karstic rocks in the paleokarst reservoirs of the Huanglong Formation in the research area are affected by atmospheric freshwater with the δ¹³C and δ¹⁸O values and ⁸⁷Sr/⁸⁶Sr ratios in the original formation approaching those of atmospheric freshwater, which reflects ancient hydrological conditions, fluid properties, isotopic source and the fractionation effect; (3) the intensely corroded and replaced secondary limestone is affected by a variety of diagenetic fluids, often reflected by δ¹³C and δ¹⁸O values, while the ⁸⁷Sr/⁸⁶Sr ratios exhibit the strong degree of the corrosion; (4) after comparing the ⁸⁷Sr/⁸⁶Sr ratios of each type of karst rock, the diagenetic fluids are determined to be mainly atmospheric freshwater, and depending on the strength of corrosion, and the low ⁸⁷Sr/⁸⁶Sr ratio fluids in the layer will participate in the karst process. The carbon, oxygen, and strontium isotopes of different karstic reservoirs can provide meaningful geochemical information for forecasting and evaluating the development and distribution rules of the Huanglong Formation at the margin of the eastern Sichuan Basin in time and space.

Key words: paleokarst reservoirs, carbon and oxygen isotope, strontium isotope, geochemistry, Huanglong Formation, eastern Sichuan area

1 Introduction

Globally, paleokarst reservoirs are among the most important reservoirs for oil and gas exploration and development (Choquette and James, 1988; Guo, 1993; Chen et al, 2004; Richard et al., 2005; Xu and Du, 2005; Xia et al., 2006). The marine carbonate reservoirs found in China include the Wumishan Formation of the Sinian near the depression of western Liaoning (Zheng et al., 2009), the Majiagou Formation of the Ordovician in the Tarim Basin (Gu et al., 2002; Zhang and Wang, 2004; Hu et al., 2012) and the Ordos Basin (Wang and Al-Aasm, 2002, Chen et al, 2007; Ni et al., 2009; Zhang et al., 2012), the Dengying Formation of the Sinian (Zhang and Liu, 2009; Chen, 2010; Sun and Liu, 2013; Wei et al., 2013) and the Huanglong Formation of the Carboniferous (Wang et al., 1996; Zheng et al., 2003; Wen et al., 2009; Chen et al, 2011) and the Leikoupo Formation of the Triassic (Wang et al., 2012; Song et al., 2012), both in the Sichuan Basin. All these areas are linked to ancient karstification developed regionally in the surface of non-conformity, which reveals the importance of ancient karstification in oil and gas exploration and development (Wang and Al-Aasm,
2 Geological Setting

The study area is located in the eastern Sichuan Basin, bordered by Fangdou Mountain in the east, Huaying Mountain in the west, Daba Mountain in the north and Chongqing in the south. The entire area is approximately 5.5×10^7 km^2 and is part of the high and steep fold belt in the eastern Sichuan Basin. There are 6 secondary tectonic belts running from northwest to southeast: the Tieshanpo, Qilixia, Wenganjiang, Daitianchi, Nanmenchang and Dachigan belts (Fig. 1).

The late Carboniferous Huanglong Formation in the eastern Sichuan Basin mainly developed in a sabkha and bay-shelf environment (Chen et al., 2011) and its sedimentary evolution can be divided into 3 stages: (1) the early stage (formation of the first member of the Huanglong Formation: C_2hl^1), when a cream salt lake and evaporative tidal flat formed the sabkha environment with gypsum, microlite dolomite and secondary limestone remaining after degypsisification and dedolomitization; (2) the middle stage (formation of the second member of the Huanglong Formation: C_2hl^2) stretching from the edge of basin to its inner portion, when the lagoon, grain beach and restricted continental shelf developed after marine life invaded the region from the Exi-Chengkou and Ganzhi troughs, controlled by paleostrand on the edge of basin and palaeo-high in the basin and characterized by particle dolomite, grain dolomite, and microlite dolomite interbedded; and (3) the late stage (formation of the third member of the Huanglong Formation: C_2hl^3), marked by the development of the open continental shelf after the marine invasion, characterized by micrite, particle micrite dolomite with spar grainstone in the interlayer and a little dolomictite.

After the Yunnan movement in the late Carboniferous, the Huanglong Formation of the eastern Sichuan Basin experienced a shallow-middle burial diagenetic effect, at which point the region was largely exposed by a wide margin tectonic uplift (Zheng et al., 1995, 2003; Wen et al., 2009) and suffered from corrosion of atmospheric water. At this time, the third member of the Huanglong Formation was corroded and eaten away, resulting in a relics part of the roof Huanglong Formation karstic landform rolling and swelling, the development of paleokarstic rocks across a wide swath of the layer, and the formation of paleokarstic carbonate reservoirs. Until the early Permian, Lower Permian coal seams and Permian-Triassic thick carbonates in the Lianshan Formation were redeposited. As a result, the study area gradually entered an deepening reburial diagenetic stage and oil and gas accumulation period (Zhang et al., 2011).

Fig. 1. The tectonic map and section map of the Huanglong Formation in the eastern Sichuan Basin.
3 Sample Collection, Classification and Petrological Characteristics

3.1 Sample collection and classification

Samples for systematic testing and analysis were taken from 20 well cores, among which 76 samples were for carbon-oxygen isotope and 75 for strontium isotope. We classified these samples into 3 basic types based on their petrological features: karstic rocks, cements in the karstic rocks, and non-karstic rocks. Additionally, we avoided tectonic fracture zones and hydrothermal alteration zones during sampling. Slice identification was conducted for every sample to ensure precise classification. Carbon-oxygen isotope test analysis was performed at the Research Institute of Exploration and Development, Southwest Oil and Gas Field Company, China National Petroleum Corporation, using a MAT252 gas isotope mass spectrometer. The analytic standard was SY/T 6039-94. Sr isotope testing was performed at the State Key Laboratory of Oil & Gas Reservoir Geology and Exploitation using a MAT262 solid isotope mass spectrophotograph, and the measured error (2σ) of 87Sr/86Sr was less than 0.002%.

3.2 Petrological characteristics

3.2.1 Non-karstic rocks

Non-karstic rocks include micrites and penecontemporaneous dolomicrosparites from the sabkha (Fig. 2A) and grainstones (or grain dolomite) formed from burial dolomitization (Fig. 2B). Analyzing these three types of samples allows us to find the background value of the dissolution processes to compare them to the geochemical characteristics of the karstic rocks.

3.2.2 Karstic rocks

Karstic rocks can be divided into four types based on the intensity of corrosion and other identifying characteristics.

(1) Slightly corroded rocks

With microlite-powder crystal dolomites as the main rock (Fig. 2C), a small amount of solutional pores and seams exist in slightly corroded rocks, which are distributed across the entire Huanglong Formation. These rocks seem to have been formed from their mother rocks, compact microlite-powder crystal dolomites, in the early stage of the karst by atmospheric water in the vertical vadose zone of the upper karst section. Because they have poor physical properties (low porosity: 4%–8%, low permeability: 0.1×10^{-3}–1×10^{-3} \mu m^2), most of these rocks belong to the “Pore-Fracture” reservoir with low porosity and permeability.

(2) Moderately corroded porous rocks

With particle and crystalline grain dolomite as the main rock (Fig. 2D), many solution pores, cavities and seams exist in moderately corroded porous rocks, which are mainly distributed across the second member of the Huanglong Formation. These rocks seem to have been formed from their mother rocks, compact particle and crystalline grain dolomites, in the early/middle stage of the karst by meteoric water in the vertical vadose zone of the upper karst section (Zheng et al., 2003). Additionally, the pores, cavities and seams seem to be connected by dissolved or structural fractures. They have good physical properties (mid-porosity: 5%–12%, mid-permeability: 1×10^{-3}–10×10^{-3} \mu m^2), and most of these rocks therefore belong to the “Pore-Fracture” reservoir with middle-low porosity and permeability, and form the main reservoirs of the Huanglong Formation.

(3) Intensely corroded breccia

With breccias composed of various matrix sources (Zheng et al., 2003), many corroded caves and seams exist in intensely corroded breccias, which are distributed at various levels across the entire Huanglong Formation although they are concentrated in its second member. These rocks seem to have been formed in the middle-late stage of karst by meteoric water in active undercurrent zones of the middle karst section (Zheng et al., 2003) (Fig. 2F, Fig. 2F, Fig. 2G, Fig. 2H), and the caves and seams seem to be more frequently seen in dolomite breccias. These rocks have good physical properties (mid-porosity: 6%–15%, mid-permeability: 1×10^{-3}–10×10^{-3} \mu m^2), and most of these rocks therefore belong to the “Pore-Fracture” reservoir with middle-low porosity and permeability. These rocks form the main reservoirs of the Huanglong Formation.

(4) Intensely corroded and replaced secondary calcic karstic rocks

The intensely corroded and replaced secondary calcic karstic rocks can be divided into 2 types: secondary limestone (Fig. 2I), formed after dedolomitization and degypsumization, and secondary calcic breccias (Fig. 2J), formed after corrosion and collapse in caves. Both types of rocks were mainly distributed across the first member of the Huanglong Formation and seem to have been formed in the early-middle stage of the karst by meteoric water in the still undercurrent zone of the lower karst section; they further seem to have been influenced by evaporite in a sabkha environment. They have poor physical properties (low-porosity: 1%–4%, low-permeability: ≤0.1×10^{-3} \mu m^2) and therefore formed no reservoir.

3.2.3 Cements between the breccias

The main cements include freshwater calcite and dolomite. The freshwater calcite appearing in fine pores between breccias is composed of drusy or equiaxial
Fig. 2. Pictures of karstic rocks in the Huanglong Formation of the eastern Sichuan Basin.
A. Dolomite, QL47, -4935.4 m, normal stained slice (-); B. powder crystal dolomite, F3-2, -4937.1 m, stained slice (-); C. middle grain dolomite, corroded intergranular core developed, with carbonization tar in-fill; Td14, -4929.1 m, stained slice (-); D. biotritias dolomite, corroded intragranular core developed, Td14, -4929.1 m, stained slice (-); E. matrix support dolomite karstic breccia, Td51, -5003.4 m, rock core; F. dust+matrix support dolomite karstic breccia, Td72, -5103.4 m, rock core; G. dolomite karstic breccia, develop corrosion, Td87, -4846.7 m, stained slice (-); H. reticulate silt mosaic dolomite karstic breccia, spar calcite developed in between the breccias, Bld1, -3297.6 m, stained slice (-); I. the secondary limestone, the secondary calcite-owe dolomite crystal, F12, -4929.7 m, stained slice (-); J. stained slice (-); K. freshwater calcite, Td69, -5010.3 m, stained slice (-); L. freshwater dolomite, Ya12-2, -5019.3 m, stained slice (-).

granular aggregates that filled in large corrosion holes, cavies and seams and formed in the vadose zone-active undercurrent zone, while the massive crystal stock aggregates (Fig. 2K) were formed in a still undercurrent zone. Freshwater dolomite, on the other hand, is composed of bright euhedral diamond crystal as centripetal dusty (Fig. 2L) and rim cements on the margin of large corrosion holes, cavies and seams and was formed by meteoric water in a vadose zone. Comparing the two cements, freshwater dolomite may be formed slightly earlier than freshwater calcite, or they may both be formed through intergrowth with dolomite at the same time.

4 Geochemical Characteristics

4.1 δ13C and δ18O isotopes

Results of the analysis of the carbon-oxygen isotopes (Table 1) and component characteristics from 76 pieces of
Table 1 Carbon and oxygen isotopes for carbonates, karst rocks and cements in the Huanglong Formation of the eastern Sichuan Basin

<table>
<thead>
<tr>
<th>Intensity of karst</th>
<th>Lithology</th>
<th>Number of samples</th>
<th>δ13C/‰ (PDB)</th>
<th>Range of variation</th>
<th>Mean value</th>
<th>δ18O/‰ (PDB)</th>
<th>Range of variation</th>
<th>Mean value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-karstic</td>
<td>Micrite</td>
<td>3</td>
<td>-2.13 to -0.09</td>
<td>-1.35</td>
<td>-8.84 to -8.08</td>
<td>-8.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Microlite dolomite</td>
<td>7</td>
<td>1.83 to 4.18</td>
<td>3.10</td>
<td>-3.80 to -0.34</td>
<td>-1.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Grain dolomite</td>
<td>10</td>
<td>-2.15 to -3.70</td>
<td>1.31</td>
<td>-5.54 to -1.67</td>
<td>-2.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slightly-corroded</td>
<td>Particle-grain dolomite in corroded pore</td>
<td>12</td>
<td>-1.90 to -3.96</td>
<td>1.68</td>
<td>-5.67 to -0.12</td>
<td>-2.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moderately-corroded</td>
<td>Particle-grain dolomite in corroded pore</td>
<td>14</td>
<td>-1.52 to -3.82</td>
<td>2.01</td>
<td>-7.78 to -1.32</td>
<td>-3.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intensely-corroded</td>
<td>Dust in dolomite karst breccias</td>
<td>7</td>
<td>1.40 to 2.79</td>
<td>2.2</td>
<td>-4.20 to -1.08</td>
<td>-3.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intensely-corroded and altered</td>
<td>Matrix in dolomite karst breccias</td>
<td>4</td>
<td>-1.82 to -2.78</td>
<td>0.20</td>
<td>-9.54 to -2.44</td>
<td>-5.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cements</td>
<td>Freshwater calcite</td>
<td>3</td>
<td>-4.37 to 0.02</td>
<td>-1.96</td>
<td>-9.69 to -5.80</td>
<td>-8.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Freshwater dolomite</td>
<td>5</td>
<td>-0.25 to 1.62</td>
<td>0.82</td>
<td>-6.27 to -8.87</td>
<td>-7.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brachiopods from Bochun and Ottawa (Veizer, 1999)</td>
<td></td>
<td></td>
<td>-3.81 to 8.98</td>
<td>-15.38 to -0.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

various carbonates and karst rocks are described below.

4.1.1 Non-karstic rocks

The small range (Table 1) and the mean value of the δ13C and δ18O in marine carbonates (micrite) in the study area are both within the range of marine carbonate from the Carboniferous period (Veizer et al., 1999), so it is possible that the marine carbonates (micrite) here retain the characteristics of the original formation. The range (Table 1) of the δ13C and δ18O in the sbbaka micrites is also small, which is related to metasomatism in penecontemporaneous stages and has a higher mean value for δ13C (4.45‰) and δ18O (6.74‰) than marine carbonate (micrite). While the range of very fine-crystalline dolomite is small and the mean value is lower than that of microlite dolomite, analysis shows that it experienced metasomatism of hydrothermal fluids (with low δ13C and δ18O) in the buried diagenetic stage.

4.1.2 Karstic rocks

Karstic rocks in the Huanglong Formation of the eastern Sichuan Basin can be divided into four types based on the intensity of corrosion by meteoric water: slightly corroded, moderately corroded porous, intensely corroded breccia and intensely corroded, and replaced secondary calcite karstic rocks.

(1) The slightly corroded particle (or grain) dolomites have almost the same δ13C and δ18O values as the non-karstic grain dolomites and exhibit a few dissolved pores between grains and intercrystalline solution pores. This may indicate that they experienced slight corrosion by atmospheric water in the vadose zone.

(2) Although they have almost the same δ13C values as the slightly corroded karstic rocks, the moderately corroded particle (or grain) dolomites have a wide range of δ18O values, while the mean value is negative. They also exhibit a large amount of dissolved pores, holes, and seams in addition to sparry calcites and crystal dolomites that may indicate that they experienced moderate corrosion in the vadose zone.

(3) Like the moderately corroded rocks, the intensely corroded dolomite karst breccias have relatively negative δ13C (2.8‰) and δ18O (2.46‰) values in dust and matrix, which may indicate that the matrix experienced more corrosion from dust than from atmospheric water.

(4) The intensely corroded and replaced secondary limestone have almost the same δ13C and δ18O values as the matrix of the intensely corroded dolomite karst breccias, which may indicate that they experienced intense corrosion of atmospheric water.

4.1.3 Freshwater cements

The freshwater calcites have nearly the lowest δ13C values and the second lowest δ18O values of all the samples, while the freshwater dolomites have relatively high δ13C values (~2.78‰) compared to the freshwater calcites. Further, the mean value (0.82‰) is close to that of the matrix (0.919‰), and has somewhat higher δ18O values (~0.54‰), which are higher than those of other karstic rocks.

4.2 Strontium isotope

The results of the analysis of the strontium isotopes (Table 2) and their component characteristics based on the examination of 75 pieces of paleokarst reservoirs are described below.

4.2.1 Non-karstic rocks

(1) The range of the ⁸⁷Sr/⁸⁶Sr ratios in the marine carbonates (micrite) of the Huanglong Formation in the eastern Sichuan Basin, which may retain the characteristics of the original formation, is 0.706947–0.710150, which is obviously larger than the range of ⁸⁷Sr/⁸⁶Sr of the marine limestone in the globe during the late Carboniferous period (0.707585–0.708566) (Veizer et al., 1999) and the range of the marine limestone in southern China (0.70732–0.70757). At the same time, the mean values of the ratios are as high as 0.708263.
<table>
<thead>
<tr>
<th>Intensity of karst</th>
<th>Lithology</th>
<th>Number of samples</th>
<th>(^{87}\text{Sr}/^{86}\text{Sr}) range of variation</th>
<th>Mean value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-karst</td>
<td>Micrite</td>
<td>5</td>
<td>0.706947–0.710150</td>
<td>0.708263</td>
</tr>
<tr>
<td></td>
<td>Microlite dolomite</td>
<td>7</td>
<td>0.709443–0.718779</td>
<td>0.712154</td>
</tr>
<tr>
<td></td>
<td>Grain dolomite</td>
<td>10</td>
<td>0.706763–0.714777</td>
<td>0.711779</td>
</tr>
<tr>
<td>Slightly-corroded</td>
<td>Particle-grain dolomite in corroded pore</td>
<td>12</td>
<td>0.705209–0.718571</td>
<td>0.711059</td>
</tr>
<tr>
<td>Moderately-corroded</td>
<td>Particle-grain dolomite in corroded pore</td>
<td>14</td>
<td>0.705261–0.716675</td>
<td>0.710988</td>
</tr>
<tr>
<td>Intensely-corroded</td>
<td>Dust in dolomite karst breccias</td>
<td>7</td>
<td>0.705840–0.715378</td>
<td>0.710410</td>
</tr>
<tr>
<td></td>
<td>Matrix in dolomite karst breccias</td>
<td>4</td>
<td>0.705368–0.713548</td>
<td>0.709790</td>
</tr>
<tr>
<td>Intensely-corroded and altered</td>
<td>Secondary limestone</td>
<td>11</td>
<td>0.70527–0.714291</td>
<td>0.709298</td>
</tr>
<tr>
<td>Cements</td>
<td>Freshwater calcite</td>
<td>3</td>
<td>0.707233–0.716564</td>
<td>0.710754</td>
</tr>
<tr>
<td></td>
<td>Freshwater dolomite</td>
<td>4</td>
<td>0.707152–0.718850</td>
<td>0.713512</td>
</tr>
</tbody>
</table>

Brachiopods from Beichuan and Ottawa (Veizer, 1999).

\[^{87}\text{Sr}/^{86}\text{Sr}\] diagrams can be explained as follows:

1. Carbon and oxygen isotopes of micrite distributed in the range of Carboniferous marine carbonate (Veizer et al., 1999) may stand for the normal marine sedimentary rocks of that time. We used Keith and Weber's (1964) computational formula \(Z = 2.048 \times (\delta^{13}C - 50) + 0.498 \times (\delta^{18}O - 50)\) for paleosalinity (\(Z\): PDB standardization; “\(Z = 120\)”: the boundary of marine and freshwater; higher \(Z\) values reflecting higher salinity of the fluids) to evaluate the mud-micrite and dolomircite in the study area, and found that \(Z = 124.09\) in the Huaglong Formation of the late Carboniferous period in the eastern Sichuan Basin. This result was lower than the value (\(Z = 135.48\), Yang et al., 2011) found for southern China in the same period, which may be evidence of the influence of freshwater on the sediments in the Huaglong Formation during the late Carboniferous period in the eastern Sichuan Basin and correspond to a restricted bay in the rich supply of freshwater.

2. The carbon and oxygen isotopes of non-karst microlite dolomites were more prevalent than those of micrite, showing that micrite was subject to powerful evaporation and that CO₂ (rich in \(^{12}\text{C}\)) appeared first (Liu et al., 2001), resulting in higher levels of \(^{13}\text{C}\) in salt water; meanwhile, the \(^{13}\text{C}\) of dolomite increased. This suggests that high salinity brine makes up the diagenetic fluids, a theory that is consistent with the sabkha environment, with the result that dolomite exhibits higher \(^{13}\text{C}\) and \(^{18}\text{O}\) ratios than calcite in brine fluids subject to the same temperature and pressure.

3. The burial dolomites (Fig. 3-III) (the non-karstic crystal grain dolomite and particle dolomite) exhibit almost identical, slightly negative \(^{13}\text{C}\) and \(^{18}\text{O}\) values as the micrite (Fig. 3-II), which may indicate that the buried formation brine of the early sabkha resulted in dolomitization of the burial dolomites, with the isotope recording the recrystallization of the microlite dolomite (Zheng et al., 2008). The slightly negative \(^{13}\text{C}\) and \(^{18}\text{O}\)

4.2.2 Karstic rocks

The karstic dolomites have higher \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios than those of the micrites in the Huaglong Formation and lower ratios than those of the microlite dolomites (Table 2). In order from the highest to the lowest with the increasing intensity of corrosion, they are the slightly corroded particle-grain dolomites, the moderately corroded particle-grain dolomite, the intensely corroded dolomite karstic breccias (dust has a higher value than matrix), and the intensely corroded and replaced secondary limestone.

4.2.3 Freshwater cements

The range and the mean values of the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios in freshwater calcite are lower than those of microlite dolomite and slightly corroded particle-grain dolomite and higher than those of moderately corroded particle-grain dolomite, secondary limestone and micrite, but close to those of moderately corroded particle-grain dolomite in the corroded pore. At the same time, the freshwater dolomites exhibit a wide range of \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios and the highest mean value of all the samples.

5 Discussion

5.1 Explanation for \(^{13}\text{C}\) and \(^{18}\text{O}\) isotopes

The distribution of non-karst rocks, karst rocks and cements distributed in their unique regions in the \(^{13}\text{C}\) and \(^{18}\text{O}\) range.
values may show the isotope reduction of the non-karstic crystal grain dolomite and particle dolomite as the temperature and pressure increased after the reduction of the isotope fractionation in the water-rock reaction (Huang et al., 2009).

(4) The cements (the freshwater calcite and dolomite) have the lowest δ¹³C and δ¹⁸O values of all the samples (Fig. 3-VIII), of which the negative δ¹⁸O values greatly exceed the range of CO₂⁻ in the original formation in particular. For this reason, we argue that the cements were formed by the atmospheric water (rich in Ca²⁺, Mg²⁺) after the corrosion of the dust, resulting in cements rich in δ¹³C and δ¹⁸O.

(5) The δ¹³C and δ¹⁸O values of the karstic rocks, including slightly corroded rocks (Fig. 3-IV), moderately corroded rocks (Fig. 3-V) and intensely corroded rocks (Fig. 3-VI), are all located in the regions between the crystal grain-particle dolomites (Fig. 3-II) and the cements (Fig. 3-VIII); with the increase of corrosion intensity of atmospheric water, the δ¹³C and δ¹⁸O values would become lower and more negative. We also found that the range of the δ¹³C values is wider than that of the δ¹⁸O narrow, which may be related to the fractionation factor of the oxygen isotope (approximately 3.6‰) and the carbon isotope (approximately 1.2‰) in the water-rock reaction in low temperature (Veizer, 1975; Wei and Wang, 1988).

(6) The matrix of the intensely corroded dolomite breccias exhibits a wider negative range of δ¹³C and δ¹⁸O values (Table 1) than dust, which may be related to specific surface areas over which the corrosion of the atmospheric water is stronger.

(7) The δ¹³C and δ¹⁸O values of the intensely corroded and replaced secondary limestones, located in the regions between the slightly corroded rocks (Fig. 3-IV) and the intensely corroded rocks (Fig. 3-VI), have slightly negative δ¹³C values and clearly negative δ¹⁸O values. Owing to the similarity of these characteristics to the matrix of the intensely corroded dolomite breccias and the obviously negative δ¹⁸O values, we argue that the secondary limestones were formed by intense corrosion and alteration (Zhai et al., 1997; Rameil, 2008). Additionally, the lack of clarity surrounding the regions of the secondary limestones may be due to combined influence of atmospheric water (Schole et al., 2003), pore water (Fu et al., 2008), fluids after gypsum dissolution (Choi et al., 2012), and so on; in other words, we argue that the secondary limestones are influenced by a variety of fluids.

5.2 Explanation for strontium isotope
Considering also the paleogeographic setting and the characteristics of carbon and oxygen isotopes, the characteristics of the strontium isotopes (Fig. 4) can be explained as follows:

(1) The Huanglong Formation in the NE Sichuan Basin belongs to a “restricted-half restricted” bay on the continental margin. The old land around the sedimentary basin was rich in ⁸⁷Sr and the Sr isotopes in the ocean could not easily reach the “restricted-half restricted” bay, and thus the normal marine sediments in the Huanglong Formation (micrite) show high ⁸⁷Sr/⁸⁶Sr ratios (mean value

![Figure 4](https://via.placeholder.com/150)
is 0.708263) and various karstic rocks and cements that influenced the corrosion of the surface water show higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. These findings also provide support for Professor Zheng’s argument (1997, 2010) that “The continental crust Sr (rich in $^{87}\text{Sr}$) invaded the eastern Sichuan Basin resulting in high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Huanglong Formation there.”

(2) The marine carbonates (micrite) have the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the sabkha microlite dolomite formed by the evaporation pump has the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, which coincides with the phenomenon that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of modern sabkha carbonates are clearly higher than those of normal marine carbonates (Müller et al., 1990). Viewed in this light, the dolomite in the Huanglong Formation of the penecontemporaneous period was formed after the sabkha brine replaced the normal marine carbonates.

(3) Having only experienced hydrothermal metasomatism, the grain dolomite exhibits higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than microlite limestone and slightly lower ratios than microlite dolomite. Viewed in this light, we found that dolomitization hydrothermal fluids are closer to salt water in the eastern Sichuan region and may be derived from sabkha brine trapped in holes in layers of the Penecontemporaneous period (Zheng et al., 2010).

(4) The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios decrease their levels in microlite dolomite to those in the slightly corroded particle (or grain) dolomite, moderately corroded particle (or grain) dolomite, intensely corroded karst breccias, and secondary limestone, which reveals that the karst fluids display lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than dolomitization fluids. As the balance effect in isotope qualities, the $^{86}\text{Sr}$ in atmospheric freshwater would replace the $^{87}\text{Sr}$ in dolomite. For this reason, with the reinforcement of corrosion, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the dolomite would tend to decrease.

(5) The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the matrix of dolomite karstic breccias are lower than those in dust, which may indicate that as the grain size decreases, the qualities of the isotope tend to be in balance, and both the specific surface area of the particle and the recrystallization control the intensity of the water-rock reaction (Wen et al., 2009).

(6) The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in freshwater calcite fall between the moderately corroded particle (or grain) dolomite and the intensely corroded karst breccias, although they are closer to the former. This suggests that the rocks were influenced in the early stages of corrosion by atmospheric water (low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio), and as corrosion continued, the limestone was corroded (She et al., 2013; Fan et al., 2007) and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of fluids decreased (Frumkin and Stein, 2004; Zhou, 2007). As the reaction continued, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio shrunk further and further, resulting in dolomite karstic breccias and secondary limestone ultimately displaying the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

5.3 Distribution patterns of geochemical characteristics in paleokarst reservoirs

At the beginning of the late Carboniferous epoch, the ocean invaded the eastern Sichuan region, resulting in the Huanglong Formation (carbonate rocks) overlapping the Hanjadian Formation (dark mudstone) of the middle Silurian unconformably. Evaporation lagoon and tidal flat resulted in the deposit of sabkha sediments, such as very fine-fine crystalline secondary limestone, gypsum, microlite limestone, and microlite dolomite in the low system tract, which formed the first member of the Huanglong Formation.

At the same time, normal marine carbonates (micrite) in the Huanglong Formation were influenced by atmospheric water and fluids from the crust in a restricted environment, resulting in low $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. On this basis, after the diagenetic fluids in the sabkha environment experienced significant evaporation and concentration, the injection of crustal Sr, microlite dolomite in the penecontemporaneous stage exhibited higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

The ocean continued to invade the area in a stair-step pattern from NE to SW, flowing all the way into the middle of the Huanglong Formation, while the barrier coast and the half-restricted shelf formed the second member of the Huanglong Formation, with grainstone, microlite grainstone, micrite, and microlite dolomite in the rhythm interbed group until the surface reached its maximum flood point.

The third member of the Huanglong Formation was mainly characterized by microlite grainstone and micrite.

Then, in the shallow to mid-depth burial diagenetic stage, dolomitization occurred and the fluids were largely highly concentrated marine pore water trapped in the formation (Zheng et al., 2010). Thus, the particle and grain dolomite exhibit good porosity and permeability with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are higher than those of normal marine carbonates (micrite) and lower than those of sabkha dolomite (microlite dolomite) (Zheng et al., 2009).

The entire Huanglong Formation was exposed and suffered 15-20 Ma ancient hypergenesis after the Yunnan uplift in addition to significant corrosion until the end of the late Carboniferous period. Due to different hydrologic conditions, rock systems, and isotopic characteristics in various karstic geomorphic units, we inferred 3 distribution patterns (Fig. 5):

(1) In the upper karstic section, the slightly and moderately corroded grain and crystal dolomite developed in a vertical vadose zone. In this pattern, atmospheric water quickly flowed through the vertical vadose zone to the undercurrent zone, resulting in limited $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and a slight decline in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.
(2) The intensely corroded dolomite karstic breccias developed in undercurrent zones in the middle of the karstic section. In this pattern, the atmospheric water continued to corrode rocks with a result that the δ13C and δ18O values continued to decline in freshwater calcites, while the 87Sr/86Sr ratios of the dolomite karstic breccias became lower than freshwater calcites because the fluids came from limestone of the original formation (low 87Sr/86Sr ratios).

(3) In the lower portion of the karstic section, the intensely corroded secondary limestone developed in a still undercurrent zone. In this pattern, the karstic water (including atmospheric water, pore water, and fluids after gypsum dissolution) strongly corroded the rocks, resulting in uncertain δ13C and δ18O values and declining 87Sr/86Sr ratios that approach the levels of normal marine limestones.

6 Conclusions

(1) The Huanglong Formation in the late Carboniferous period of the Eastern Sichuan Basin was formed in a restricted bay. Additionally, the original sediments exhibit low δ13C and δ18O values and high 87Sr/86Sr ratios in micrite and dolomicroite mud, which may be greatly influenced by the abundant supply of freshwater in the environment.

(2) All types of karst rocks in the paleokarst reservoirs of the Huanglong Formation in the study area are affected by atmospheric freshwater, and the δ13C and δ18O numbers and 87Sr/86Sr ratios in the original formation approach those of atmospheric freshwater, reflecting its ancient hydrological conditions, fluid properties, isotopic sources and fractionation effects.

(3) The intensely corroded and replaced secondary limestones were repeatedly affected by a variety of diagenetic fluids as reflected by their δ13C and δ18O numbers, while the 87Sr/86Sr ratios show the strength of the corrosion.

(4) After comparing the 87Sr/86Sr ratios of each type of karst rock, we found that the diagenetic fluids were mainly atmospheric freshwater. Furthermore, as corrosion continues, the low 87Sr/86Sr ratio fluids in the layer will participate in the karst process.

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References


Rameil, N., 2008. Early diagenetic dolomitization and dedolomitization of Late Jurassic and earliest Cretaceous platform carbonates: A case study from the Jura Mountains (NW Switzerland, E France). Sedimentary Geol., 70–85.


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