

Paleoenvironmental Traces of Carbon and Oxygen Isotopes in Carbonate Rocks: An Example From Dengying Formation in Xichuan Area, Henan Province

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Abstract

The carbon and oxygen isotope composition of carbonate rocks is an important index for accurate analysis of the paleo-sea environment, which depends on Mn/Sr, $\delta^{18}\text{O} > -10\text{‰}$, correlativity of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ and “age effect” of $\delta^{18}\text{O}$. This study reports carbon and oxygen isotope data of carbonate rocks from the Dengying Formation in the Xichuan area. $\delta^{13}\text{C}$ values range -1.58‰ to 3.76‰ , with an average value of 1.55‰ , and $\delta^{18}\text{O}$ values are -14.91‰ to -1.88‰ , with an average value of -6.95‰ . The $\delta^{18}\text{O}$ values of three samples are less than -10‰ , so they are excluded and taken to be correlative with the cracking of the Rodinia supercontinent during the Neoproterozoic. The paleotemperature range 7.40°C to 35.05°C , with an average value of 21.09°C . Paleo-salinity range 8.38‰ to 19.30‰ , with an average value of 13.89‰ . Z values range 127.80 to 135.03 and thus all exceeded 120, with an average value of 131.25. These calculations indicate that the Xichuan area had deposited marine carbonate rocks, with the hot and dry tropical monsoon climate, and a transgressive process overall during the Dengying age.

Introduction

Composition of carbon and oxygen isotopes in carbonate rocks, which always indicates the composition of ancient oceans (Shao, 1994; Kaufman et al., 1997, 2006; Guo et al., 2003, 2007; Du et al., 2018), has also been applied in the context of oceanic paleoenvironmental tracing, such as of sea-level changes, paleotemperature, paleo-salinity, and biological vicissitudes (Kaufman et al., 1996; Zachos et al., 2001; Ghosh et al., 2006; Thiagarajan et al., 2011) and chemical stratigraphic approach (Calver, 2000; Amthor et al., 2003; Condon et al., 2005; Zhang et al., 2005; Kaufman et al., 2007). During geological periods, the carbon and oxygen isotopes composition from the geological mass changes as a result of isotopic fractionation, which is caused by diagenesis, or other factors. Accordingly, reliability analysis of carbon and oxygen isotope composition is the primary prerequisite for paleoenvironmental tracing (Derry et al., 1991; Pr at et al., 2011; Schobben et al., 2016; Reynolds et al., 2019). A report (Kuang et al., 2011) on carbon and oxygen isotope composition of carbonate rocks in Yanshan area of the north China, have used $\delta^{18}\text{O}\text{-Mg/Ca}$, $\delta^{18}\text{O}\text{-Sr}$, $\delta^{18}\text{O}\text{-Mn}$, $\delta^{18}\text{O}\text{-Fe}$ and Mn-Sr, and Fe-Mn as a baseline for estimating levels of diagenetic alteration—all of which emphasize correlation between oxygen isotope and major and trace elements. In the diagenetic process, the altered fluid has different degrees of influence on the carbon and oxygen isotopes, and has little effect on the carbon isotope, but it may cause the oxygen isotope to be fractionated again. To determine whether it is affected by the diagenesis, it is necessary to consider the correlation of carbon and oxygen isotopes. Furthermore, the oxygen isotope composition in ancient strata has often changed for a long time, it also needs to think about the “age effect”. Using as an example of Dengying carbonate rocks in the Xichuan area, Henan Province, analyze reliability of carbon and oxygen isotope composition, reconstruct the paleoenvironment of Dengying Formation in the Xichuan area, and uncover other information about the biological vicissitudes, paleoclimate, sea-level changed, paleo-salinity, paleotemperature and the like.

Carbon and Oxygen Isotopes and Paleoenvironmental Trace

$\delta^{13}\text{C}$ is described by the $^{13}\text{C}/^{12}\text{C}$ ratio because ^{14}C has radioactivity, which is usually characterized the carbon isotope composition in natural geological mass, the relative norm is PDB (Pee Dee Belemnite from Cretaceous in South Carolina, USA). Organic carbon (reductive carbon) and inorganic carbon (oxidative carbon) reserves are present, with a difference between average $\delta^{13}\text{C}$ values is 25‰ (Chen et al., 1995). Study have revealed (Zheng, 2000) that most organic carbon $\delta^{13}\text{C}$ values are highly differentiated, and characterized by negative $\delta^{13}\text{C}$ excursions in the different earth spheres and ecological elements. For example, $\delta^{13}\text{C}$ in lake water range -8‰ to -16‰, but in river water is -10‰— which compared with seawater ($\delta^{13}\text{C} = 0 \pm 2\text{‰}$), are negatively excused. $\delta^{13}\text{C}$ value is -24‰, -25‰, -40‰ in coal, petroleum and natural gas respectively, which are more negatively excused than others materials. Both terrestrial flora and fauna and marine flora also tend to be negative excursion ($\delta^{13}\text{C}_{\text{terrestrial}} = -22\text{‰}$, $\delta^{13}\text{C}_{\text{marine}} = -24\text{‰}$), perhaps relate to organisms' ability to absorb ^{12}C preferentially, the $\delta^{13}\text{C}$ value is less negatively excused than others' ($\delta^{13}\text{C}_{\text{lake}} = -5\text{‰}$, $\delta^{13}\text{C}_{\text{river}} = -12\text{‰}$, $\delta^{13}\text{C}_{\text{non-marine sedimentary rocks}} = -4\text{‰}$, $\delta^{13}\text{C}_{\text{metamorphic rocks}} = -2\text{‰}$, $\delta^{13}\text{C}_{\text{magmatic rocks}} = -6\text{‰}$, $\delta^{13}\text{C}_{\text{marine sedimentary rocks}} = 0\text{‰}$, $\delta^{13}\text{C}_{\text{flora}} = 0\text{‰}$; Fig. 1).

Because ^{17}O only occurs in the solar system, describe the oxygen isotope composition in natural materials by using $\delta^{18}\text{O}$, which equates to $^{18}\text{O}/^{16}\text{O}$, standardized as SMOW (Standard Mean Ocean Water). From Zheng's research (2000), compare with ocean water, oxygen isotope composition of atmospheric precipitation is more unstable, and it tend to concentrate light isotope ^{16}O oppositely. In the biosphere, mantle and crust, all $\delta^{18}\text{O}$ values tend to positive excursion, excluding eclogite ($\delta^{18}\text{O} = -10\text{‰} \sim 10\text{‰}$), $\delta^{18}\text{O}$ range 0‰ to 44‰. Sedimentary rocks and marine sediment are particularly concentrated heavy isotope ^{18}O .

Thus there are many differences between carbon and oxygen isotopes among earth's various spheres and geological masses. Sedimentary rocks are widely distributed, having a diversified diagenesis. Different sedimentary rocks have different isotope composition, and because they underwent less post-sedimentation change than magmatic rocks and metamorphic rocks, their carbon and oxygen isotope composition may still convey partial paleoenvironment information.

^{13}C With Biological Evolution, Climate, and Sea-Level Vicissitudes

It is necessary to research the carbon isotope composition of marine carbonate rocks for studying biological evolution, climate, and sea-level vicissitudes (Chappell and Shackleton, 1986; Joachimski et al., 2006). Carbon isotope composition is usually affected by biological activities, specifically atmosphere-sea exchange (Yan et al., 2005; Guo et al., 2013; Bauch et al., 2015; Ding et al., 2019):

(1) Biological evolution: In suitable conditions, $^{13}\text{C}_{\text{ocean water}}$ will increase when large quantities of flora absorb light isotopes ^{12}C , so that $\delta^{13}\text{C}$ value tends to positively excure in sedimentary carbonate rocks, whereas $\delta^{13}\text{C}$ value tends to negatively excure. Thus, positive $\delta^{13}\text{C}$ excursion indicates a high level of marine productivity.

(2) Climate change: The maximum temperature that an organism can withstand varies from 1 °C to 5 °C (Wang and Xia, 2000). During the glacial epoch, temperatures decreased rapidly, so that partially stenothermal organisms perished because of an inability to adapt the environment. The ^{12}C was increased accompany with decreased of marine productivity, so that $\delta^{13}\text{C}$ value showed negative excursion.

(3) Sea-level vicissitudes: When sea-level rises, paleo-land erosion and oxidation area decreases, and reductive organic carbon diminishes. Ocean water tends to concentrate ^{13}C , has positive $\delta^{13}\text{C}$ excursion.

The aforementioned biological evolution, climate, and sea-level changes not only affect organic carbon burial rates but also correspond to and influence one another. In glacial epoch, temperature and sea-level diminish, making organisms likely to perish; ^{12}C is released from organisms to seawater; ^{13}C content is lower than ^{12}C ; and negative $\delta^{13}\text{C}$ excursion is seen. As a result, negative $\delta^{13}\text{C}$ excursion indicates reductions of sea-level and temperature, declines of organisms, and decrescence of organic carbon burial rate, whereas positive $\delta^{13}\text{C}$ excursion means a raise in sea-level and temperature, prosperity of organisms, and growth of the organic carbon burial rate.

In the Jiangshan area, Zhengjiang Province, Dengying carbonate rocks' $\delta^{13}\text{C}$ are stable, showing a gradual decline, their $\delta^{13}\text{C}$ values range - 2.11‰ to 2.71‰. But both the lower and upper $\delta^{13}\text{C}$ values are negatively excursed, indicating that sea-level was lower in the early Dengying. With negative $\delta^{13}\text{C}$ excursion in the upper Dengying Formation, also demonstrates that the paleoenvironment experienced a dramatic change from the Sinian to the Cambrian (Peng et al., 2006).

$\delta^{18}\text{O}$ Value and Paleotemperature of Water

Compared with carbon isotope in carbonate rocks, the temperature has a sizable effect on oxygen isotope, creating a positive correlation between oxygen isotope and temperature (Zhang, 1997). It is thus possible to calculate the paleotemperature of water using $\delta^{18}\text{O}$ (Zhang, 1985).

After Urey's introduction of this concept in 1948, Epstein proposed an empirical formula for calculating temperature by oxygen isotope composition in 1953:

$$T (\text{°C}) = 16.45 - 4.31(\delta^{18}\text{O}_c - \delta^{18}\text{O}_w) + 0.14 (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w)^2 \quad (1)$$

Where $\delta^{18}\text{O}_c$ is testing data for carbonate rocks (PDB) and $\delta^{18}\text{O}_w$ is data for seawater in the geological period (SMOW).

Shackleton produced a corrected empirical formula in 1974 (Zhang, 1985; Du et al., 2018):

$$T (^{\circ}\text{C}) = 16.9 - 4.38 (\delta^{18}\text{O}_{\text{c}} - \delta^{18}\text{O}_{\text{w}}) + 0.10 (\delta^{18}\text{O}_{\text{c}} - \delta^{18}\text{O}_{\text{w}})^2 \quad (2)$$

Shao (1994) suggested an adjustment to Shackleton's formula:

$$\delta^{18}\text{O}_{\text{c}} - \delta^{18}\text{O}_{\text{w}} = (\delta^{18}\text{O}_{\text{CaCO}_3} - \delta^{18}\text{O}_{\text{H}_2\text{O}}) + 0.22 \quad (3)$$

where $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ means that $\delta^{18}\text{O}$ (SMOW) value in ancient seawater, which equals 0‰:

$$\delta^{18}\text{O}_{\text{c}} - \delta^{18}\text{O}_{\text{w}} = \delta^{18}\text{O}_{\text{CaCO}_3} + 0.22 \quad (4)$$

As a result, the empirical formula has to be adjusted:

$$T (^{\circ}\text{C}) = 16.9 - 4.38 (\delta^{18}\text{O}_{\text{CaCO}_3} + 0.22) + 0.10 (\delta^{18}\text{O}_{\text{CaCO}_3} + 0.22)^2 \quad (5)$$

Based on various research findings, the formula is more effective when used after the Jurassic, primarily for reasons associated with post-diagenesis and hydrothermal activity as well as tectonic activities. Such activities may lead to oxygen isotopic fractionation, so that oxygen isotope does not preserve original information about isotope composition.

Srinivasan et al. (1994) found that minimum temperature of saddle dolomite when mineralized can also be calculated based on hydrothermal replacement:

$$10^3 \ln \alpha_{\text{Dol-H}_2\text{O}} = 2.78 \times 10^6 T^{-2} (\text{K}) + 0.91 = \delta^{18}\text{O}_{\text{Dol}} - \delta^{18}\text{O}_{\text{H}_2\text{O}} (\text{SMOW})$$

The empirical formulas of Epstein and Shackleton emphasize what is known the $\delta^{18}\text{O}$ values of marine carbonate rocks, which affects paleotemperature in ancient ocean water. Most of the time, many statistical data are chosen to represent $\delta^{18}\text{O}$ values, or it is assumed to be equal ocean water nowadays ($\delta^{18}\text{O}_{\text{w}} = 0\text{‰}$), but such an approach neglects isotopic fractionation, the effects of density, ocean water salinity and diagenesis, and indeed whether the $\delta^{18}\text{O}$ value of ancient seawater was equal the nowadays. Thus, Shackleton's formula must be adjusted to weaken changeable level of oxygen isotope composition, which is affected by diagenesis and isotopic fractionation. Srinivasan's formula is based on $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ range 2‰ to 8‰ (SMOW), which may be described the minimum temperature when carbonate rocks' minerals are mineralized (Srinivasan et al., 1994). The several empirical formulas mentioned earlier have their advantages and disadvantages, so multiple confirmations are needed.

$\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Paleo-salinity

In 1953, Epstein and Mayeda published a scatter graph for $\delta^{18}\text{O}$ value and salinity (S) from the North Atlantic, finding a correlation between $\delta^{18}\text{O}$ value and salinity. Their data were adjusted by Craig and Gordon (G. Faure, 1983):

$$\delta^{18}\text{O} (\text{SMOW}) = -21.2 + 0.61S (\text{‰})$$

Other research has also found that $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values will increase with salinity. After many calculations and demonstrations of isotopic data, we can differentiate marine and continental limestone by combining $\delta^{13}\text{C}$ with $\delta^{18}\text{O}$ values (Zhang, 1985) using the following empirical formula:

$$Z = 2.048 \times (\delta^{13}\text{C} + 50) + 0.498 \times (\delta^{18}\text{O} + 50) (\text{PDB})$$

$Z > 120$ indicates marine limestone, $Z < 120$ continental limestone, and $Z = 120$ undetermined limestone.

Liu et al. (2018) analyzed the correlation between Z values and $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ values, discovered that Z values reflect changes of paleo-salinity, Z values can effectively reflect paleo-salinity in ocean water when there is a distinct positive correlation between Z values and $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ values.

Data Reliability Analysis of Carbon and Oxygen Isotopes

Compared with carbon isotope, oxygen isotope is more likely to be affected by tectonic movements, hydrothermal activities and freshwater leaching. Accordingly, before using carbon and oxygen isotope composition to analyze paleo-ocean environment, it must be determined whether samples have undergone isotope exchange, or still retain the original characteristics of their carbon and oxygen isotopes. If not, samples are not significance for the paleo-geological environment. There are main four methods for analyzing the reliability of such data:

(1) Mn/Sr. Sr prefers to host in the marine carbonate rocks. Kaufman and Knoll (1995) once indicated that carbonate rocks formed by fluid replacement often underwent substitution of Mn and outflow of Sr, influenced by fluids in the diagenetic and post-diagenetic periods. Only when the Mn/Sr < 10 , it might know that carbonate rocks have not suffered post-alteration, and potentially reflect the ocean's original isotope composition (Derry et al., 1992).

(2) $\delta^{18}\text{O}$ value. Oxygen isotope in carbonate rocks is very sensitive to diagenetic alteration and is also used for discriminating carbonate rock alterative level and testing data reliability (Derry et al., 1994; Kaufman and Knoll, 1995): when $\delta^{18}\text{O} > -5\text{‰}$, carbonate rocks have not suffered alteration, whereas $\delta^{18}\text{O}$ range -5‰ to -10‰ indicates light alteration and $\delta^{18}\text{O} < -10\text{‰}$ indicates alteration is so strong that the data will not convey paleoenvironmental information and data should be abandoned.

(3) Correlativity of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. A scatter graph about $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in carbonate rocks in Neoproterozoic, drawn by Kaufman and Knoll (1995), shows that $\delta^{13}\text{C}$ values scarcely changed, along with a decrease in $\delta^{18}\text{O}$ values, perhaps because fluids caused oxygen isotope fractionation and formed a new geochemical balance. As a result, carbonate rocks have not undergone alteration when there is no visible positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values.

(4) Age effect. The empirical formulas for calculating paleotemperature and paleo-salinity are more effective for carbonate rocks after the Mesozoic. Before the Mesozoic, active diagenesis, tectonic and

hydrothermal movements might have changed the original carbon and oxygen isotopes composition. The older has undergone strong diagenesis, original information will have been largely lost. Because oxygen isotope is sensitive to temperature, its level of changeability is higher than carbon isotope, in what Shao (1994) called the "age effect".

To eradicate the "age effect", Shao (1994) proposed to use the relationship between $\delta^{18}\text{O}$ values and geological age. In this approach, the difference between the average $\delta^{18}\text{O}$ value of paleo-marine limestone and Quaternary marine limestone ($\delta^{18}\text{O}_w \approx -1.2\text{‰}$), that is, $\delta^{18}\text{O} - (-1.2\text{‰})$ is used to correct the samples' $\delta^{18}\text{O}$ values before making calculations based on the corrected data.

Results

The Dengying dolomites are mainly distributed in the Yangtze platform but are also scattered in the Qinling, Huaxia and Tarim plates. The Xichuan area is located in the intersect zone of the Yangtze platform and Qinling orogen, and the Dengying Formation is exposed completely, with great thickness (about 200–400 m), is a perfect location to study the sedimentary environment and geochemical characteristics of Dengying Formation. To reconstruct the paleo-environment of the Xichuan area and tectonic evolution of the Qinling orogen, and research biological vicissitudes, climate, paleo-sea-level change, paleotemperature, paleo-salinity, it is necessary to know the carbon and oxygen isotope composition of the Dengying dolomites.

Geological Conditions

The Xichuan area belongs to the south Qinling stratigraphic division, in the north Yangtze platform, with east Qinling orogen, and is mainly controlled by the Zijinguan-Shigang regional synclinorium, Xiaodouling-Tianguan fracture, and Jianhuanzhai-Huangfengya fracture, with a NWW-SEE strike. The area exposed upper Sinian to Paleozoic stratigraphy entirely— a series of deep to shallow marine continental clastic rocks and carbonate rocks (Yan et al., 1992). From lower to upper, it includes the Dagou (Pt₁d) quartzites and gneiss in the early Proterozoic; Wudang (Pt₂₋₃w) middle-shallow metamorphic rocks in the middle-late Proterozoic; Yaolinghe (Pt₃y) conglomerates and extrusive rocks, and Sanchuan (Pt₃s) quartz sandstones, marbles in the late Proterozoic. The Doushantuo (Z₂d) metamorphic feldspar-quartz sandstones and sericite schists, and Dengying (Z₂dn) dolomites in the late Sinian. The Shuigoukou (Є₁s) mudstones, silicolites, and middle-upper Cambrian (Є₂₋₃) dolomites, limestones in the Cambrian. The Bailongmiao (O₁b) fine-grained dolomites, sparry clastic limestones, and microcrystalline limestones in the early Ordovician; Baishangou (D₂b) conglomerates, quartz sandstones, and clastic shale in the middle Ordovician. The Lianggouzu (C₁l) sparry bio-clastic and clastic limestones in the early Carboniferous. But there is absence of early Sinian, middle-late Ordovician, Silurian, early and late Devonian and middle-late Carboniferous deposits (Fig. 2).

The Dengying carbonate rocks are dolomites, with the east area is thicker than the west. The first and third members are white to creamy white and the second is gray-black (Zheng et al., 2017, 2018). It is integrated with the underlying Doushantuo Formation and is fault or parallel unconformity with the above Shuigoukou Formation.

Composition of Carbon and Oxygen Isotopes and Reliability Analysis

In this study, we choose 14 samples from the Xichuan area of southwestern Hanan Province, their compositions of oxygen and carbon isotopes are listed in Table 1. The $\delta^{13}\text{C}$ values range -1.58‰ to 3.76‰ , with an average value of 1.55‰ ; and their $\delta^{18}\text{O}$ values range -14.91‰ to -1.88‰ , with an average value of -6.85‰ . To ensure whether the data are effective, their reliability should be analyzed.

From Table 1, Mn/Sr values range 0.25 to 4.82, data are valid. About 14 samples, except HW-4 ($\delta^{18}\text{O} = -14.91\text{‰}$), HW-5 ($\delta^{18}\text{O} = -12.67\text{‰}$), and HW-8 ($\delta^{18}\text{O} = -12.51\text{‰}$); the other 11 samples' $\delta^{18}\text{O}$ values exceed -10‰ . They might have experienced few diageneses, so that the isotope compositions still preserve original information, and thus are valid. Also, correlative analysis between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Fig. 3) indicates that the data are valid because they do not exhibit a positive correlation, the multiple correlation coefficient is 0.0425.

Removal the invalid data (No. HW-4, HW-5, HW-8), they had experienced strong tectonic movements and hydrothermal alteration, not reflect the paleoenvironment. Total 11 samples' $\delta^{13}\text{C}$ values range 0.81‰ to 3.76‰ , with an average value of 2.22‰ , and $\delta^{18}\text{O}$ values range -8.34‰ to -1.88‰ , with an average value of -5.08‰ . Because Dengying carbonate rocks underwent a long period of strong diagenesis, their compositions show high levels of deviation, requiring correction of the "age effect" to eradicate any potential effect. According to the method used by Shao (1994), the difference between the average $\delta^{18}\text{O}$ value of 11 samples and Quaternary marine limestone is taken as the corrective value, it is -3.88‰ ($-5.08\text{‰} - (-1.20\text{‰}) = -3.88\text{‰}$); calibration results are shown in Table 1.

Paleoenvironment Analysis

The empirical formula for calculating paleotemperature (T) is $T (^{\circ}\text{C}) = 16.9 - 4.38 (\delta^{18}\text{O}_{\text{CaCO}_3} + 0.22) + 0.10 (\delta^{18}\text{O}_{\text{CaCO}_3} + 0.22)^2$, and that for calculating of paleo-salinity (S) is $\delta^{18}\text{O} (\text{SMOW}) = -21.2 + 0.61\text{S} (\text{‰})$. The calculation results are shown in Table 2, using corrected data to plot curve graphs of paleotemperature, paleo-salinity, and paleo sea-levels are shown in Fig. 4.

From Fig. 4, in the Xichuan area, southwestern Henan Province, the $\delta^{13}\text{C}$ values of the Dengying carbonate rocks have undergone two stages of change that are similar in first rising, then slowly falling. It indicates that the area might have experienced two transgression-regression cycles. The $\delta^{18}\text{O}$ values are

changeable early, showing more negative excursion, then tend toward stability and positive excursion later on.

During the Dengying age, corresponding to $\delta^{13}\text{C}$ values' changeability, the Xichuan area featured a warm climate, abundant biomass, active biological activities, and a high organic carbon burial rate. Then, prompted by negative $\delta^{13}\text{C}$ excursion, temperatures began to fall, biological activities also began to diminish, and the organic carbon burial rate fell in the middle Dengying. In the middle-late Dengying, temperatures began to rise, organism developed, and organic carbon burial rate increased until the late Dengying, when biological variety was effected by falling temperatures and organic carbon burial rate.

From the calculated results, paleotemperature is 7.40 °C to 35.05 °C, with an average value of 21.09 °C. Temperatures were high during the early Dengying, until the middle-late Dengying, when they fell to 7.40°C. By Liu's (2017) calculations, the average temperature is 25°C; using the empirical formula $\text{Sr} (10^{-6}) = 2,578 - 80.8T$ (Zhang, 1997) produces a result similar to this calculation.

The Z values of 127.80 to 135.02, with an average value of 131.25 (which exceed 120), demonstrates that the Dengying Formation once was a sedimentary period of marine carbonate rocks, and from the early to late time, Z values show gradual accretion. Paleo-salinity is 8.38‰ to 19.30‰, with an average of 13.89‰, and overall change was stable.

Based on the preceding calculations of paleotemperature and paleo-salinity, the Dengying carbonate rocks deposited in hot, dry tropical monsoon climate zone, as also shown by Yan et al. (1992) and Li et al. (2008). The paleomagnetism results show that the Xichuan area was at 10°-15° north latitude during the late Sinian.

Discussion

The present structural framework of the Qinling orogenic belt is the result of the interaction of the North China, South Qinling, and South China blocks, it was having experienced multiple orogenic movements and magmatic intrusion (Meng and Zhang, 2000). The Jinning movement resulted in the closure of the ocean basin, with folding of the strata have formalized the series of Qingling folds during early Neoproterozoic. During the early Sinian, the south Qinling lacked the lower Sinian deposit, as a result of the lifting of strata, then, Caledonian movement created a continental crust of the south's settled, deposited the Doushantuo and Dengying Formation during the late Sinian (Bureau of geological and mineral of Henan province, 1989). During the Neoproterozoic, the southern area experienced settlement, accompanied with strong granite magmatic movements, the invasion times were 979 – 911 Ma, 849 – 815 Ma, 759 – 711 Ma separately, caused by collision, extension and rifting. Many researchers have suggested that this came as a response to the collision and cracking of the Rodinia supercontinent (Chen Zhihong et al., 2006; Li et al., 2008; Wang Xiaoxia et al., 2012; Hu Nie et al., 2019).

Z values are more than 120, whose 11 samples' $\delta^{18}\text{O}$ values are exceed -10‰ , indicating that the Dengying formation was deposited marine carbonate rocks in the Xichuan area. Moreover, the $\delta^{18}\text{O}$ values of 3 samples (HW-4, HW-5, and HW-8) are less than -10‰ , clearly showing that few samples affected by strong diagenesis, their isotope composition have changed. When the Rodinia supercontinent cracked during the late Neoproterozoic, strong extension altered tectonic conditions, so that deep hydrothermal intrusion triggered fractionation of oxygen isotope, rendering oxygen isotope composition was unstable during early Dengying, with a few parts suffering intense orogenic movements. During the late Dengying, extension was weakened, level of fractionation decreased, and oxygen isotope composition gradually stabilized and trended toward positive excursion.

Conclusions

(1) Carbon and oxygen isotope composition is usually used to quantitatively or qualitatively characterize ancient ocean sea-level changes, paleotemperature, paleo-salinity, and the like. Certain data are need to analyze reliability: Mn/Sr is less than 10, $\delta^{18}\text{O}$ exceeds -10‰ , $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ have not positively correlation, and correct "age effect" of $\delta^{18}\text{O}$ values.

(2) The changeable characteristics of $\delta^{13}\text{C}$ indicate that it experienced potentially two transgression-regression cycles, with sea-level changing frequently. $\delta^{18}\text{O}$ values are also unstable, showing negative excursion early but a gradual trend toward positive excursion in the later stage.

(3) Paleotemperature is 7.40 to 35.05°C , with an average value of 21.09°C , but decreased gradually from the early to late Dengying. Paleo-salinity is 8.38‰ to 19.30‰ , with an average value of 13.89‰ , and was low in the early, increased to the late. Z values are 127.80 to 135.02 (all exceed 120), with an average of 131.25 , and tend to increase from the early to the late Dengying,.

(4) Some $\delta^{18}\text{O}$ values of few samples are less than -10‰ , perhaps because the changeable characteristics of carbon and oxygen isotopes are correlative with strong hydrothermal movement when the Rodinia supercontinent cracked.

Declarations

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Authors' contributions

Lan Zhang and Hong Xie conceived the research, Lan Zhang drafted the manuscript, Hong Xie and Qingguang Li guide the revision of the manuscript. All authors contributed to data interpretation, discussion. All authors read and approved the final manuscript.

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Availability of data and materials

All data collected were reported as shown in the text and are fully available without restriction from authors upon request.

Consent for publication

All authors have consented to publication.

Competing interests

The authors declare that they have no competing interests.

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Tables

Due to technical limitations, Tables 1 & 2 are only available for download from the Supplementary Files section.

Figures

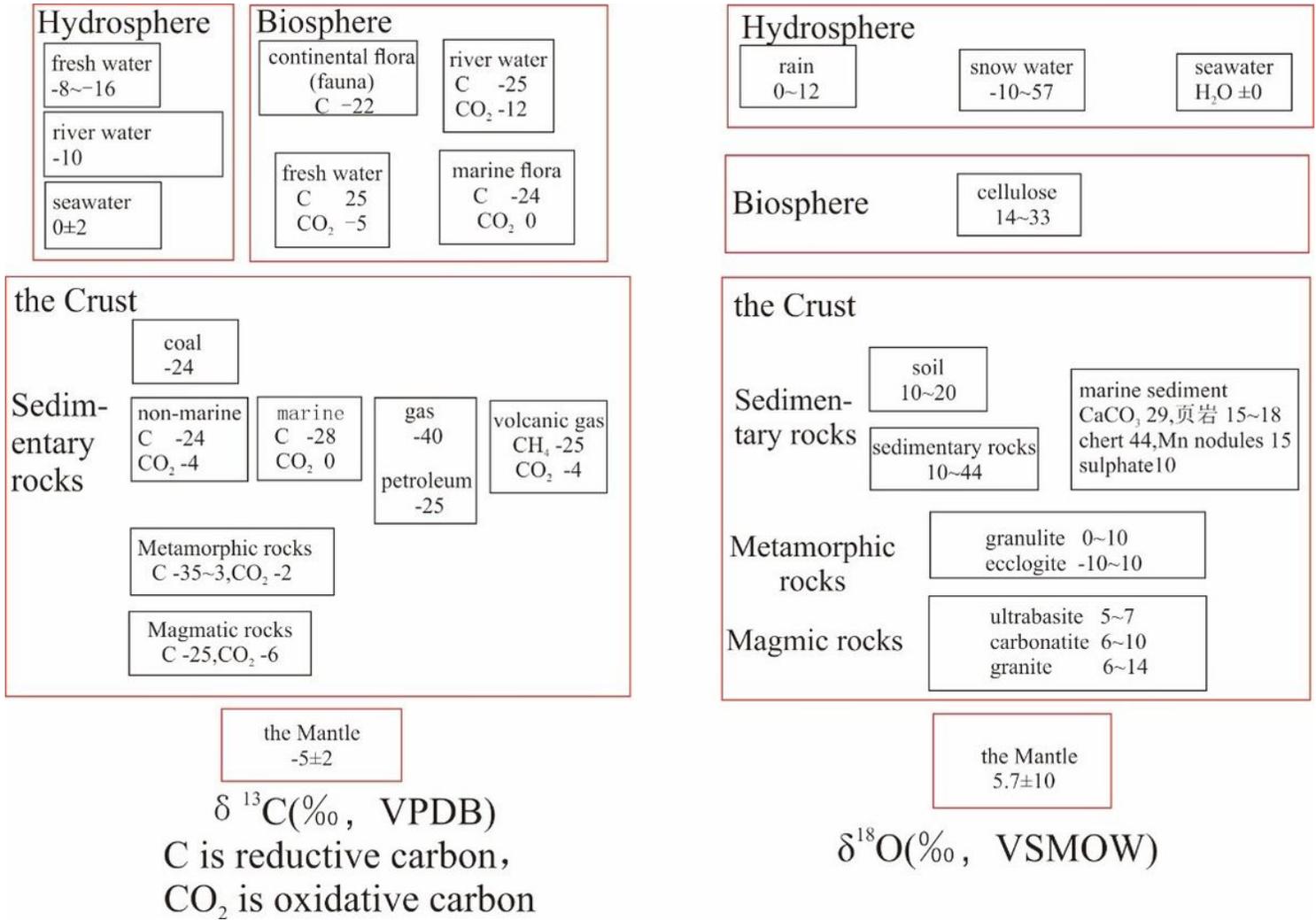


Figure 1

The distribution characteristics of carbon, oxygen isotopes (From Zheng, 2000).

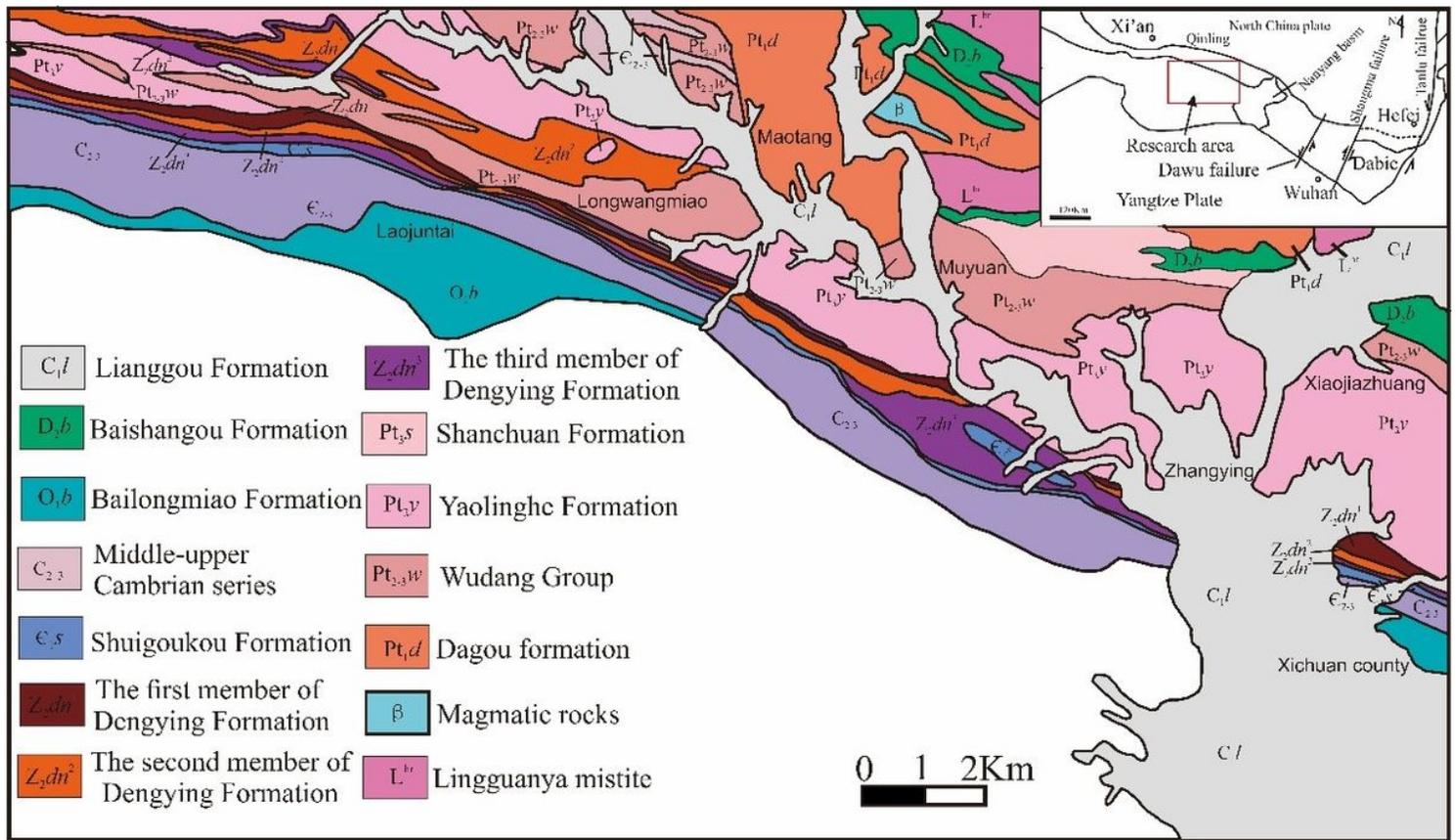


Figure 3

Xichuan area's geological map (From Liu, 2017). Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

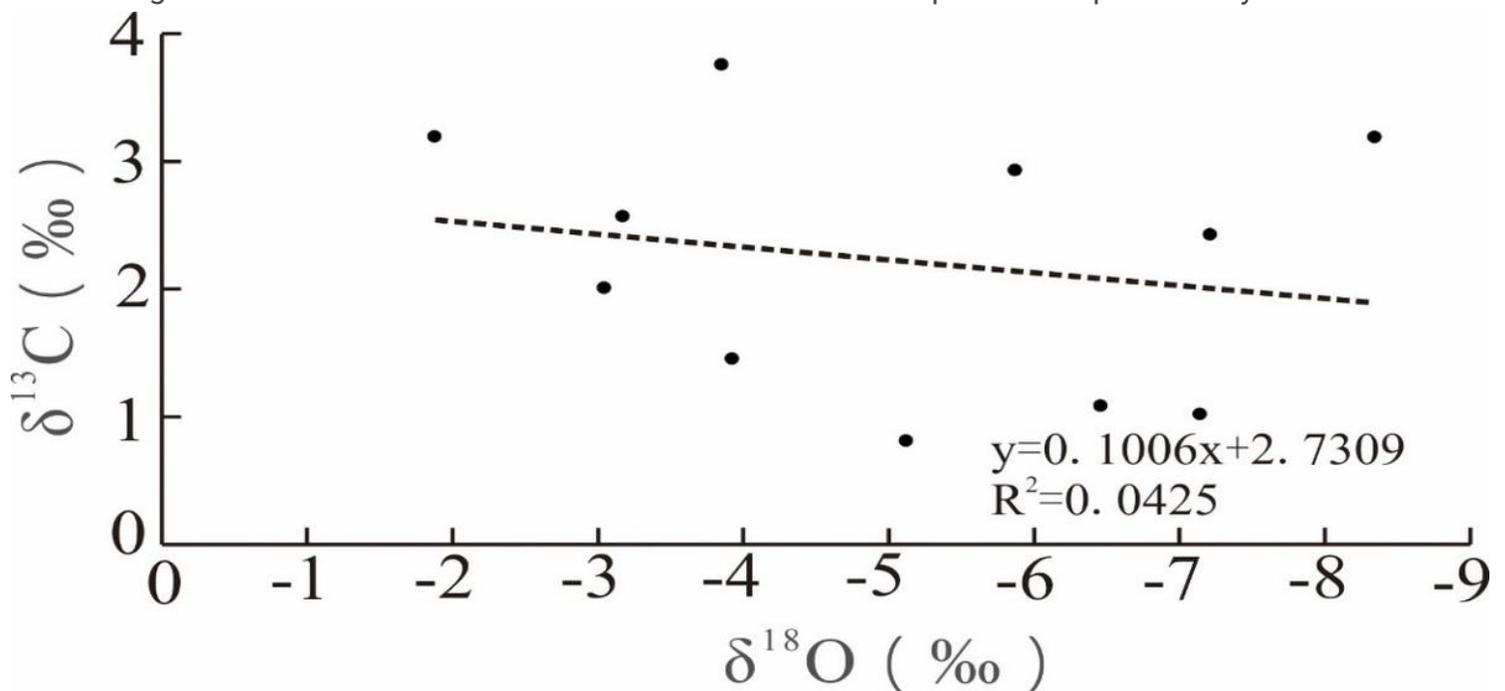


Figure 6

Scatter plot of Dengying carbonate rocks in the Xichuan area.

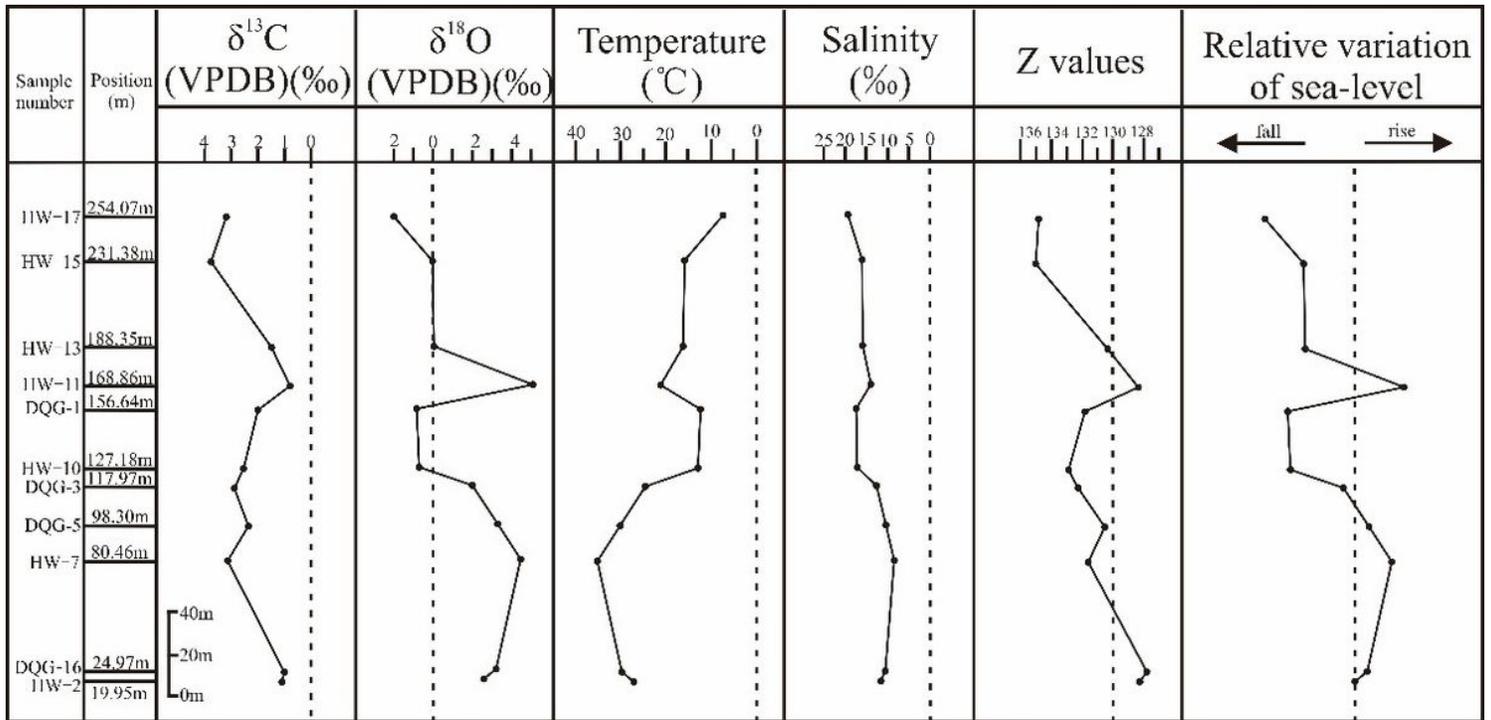


Figure 7

Curve graph of carbon, oxygen isotopes from the Xichuan area.

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