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Carbon and Oxygen Isotopic Characteristics of Longmendong Formation in Muxu River Section of Qishan, Shanxi Province and Its Significance

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Abstract: *The lower and upper Longmen cave formation of Late Ordovician in the Muxu river section of Qishan in the southwest margin of Ordos are Sandaogou formation of Middle Ordovician and beiguoshan formation of Upper Ordovician respectively, with continuous and complete strata. The average values of carbon and oxygen isotopes of carbonate rocks are 0.57‰ and -10.73‰ respectively, with poor correlation, which basically preserves the characteristics of original isotopic composition. The paleosalinity Z is between 120 and 130, which reflects that the late Ordovician was a marine sedimentary environment, which is consistent with the geological research results. According to the base value characteristics and drift changes of carbon isotope curve of Longmenshan formation, it can be divided into XH1-XH4 cycle segments. Generally speaking, the early carbon isotope values are mainly positive drift, with large scale and long time; The late stage is dominated by negative drift, with small scale and short time. This reflects that the sea level fluctuated greatly in the early Late Ordovician, with strong activity, and the sea level fluctuated slightly in the late Ordovician, showing a downward trend as a whole. Carbon and oxygen isotope variation curve of longmendong formation and global Ordovician $\delta^{13}C$ variation curves shows that longmendong formation is deposited in the late Ordovician, which is equivalent to Sandbian and Katian periods. There is a positive drift event of GICE carbon isotope, which is regionally comparable.*

Keywords: *Carbon and oxygen isotopes; Late Ordovician; Muxu river section; Carb-onate rocks; Southwest margin of Ordos*

1. Introduction

Stable carbon and oxygen isotopes of carbonate rocks are widely used to restore the paleosalinity, paleotemperature, sea-level change trend of water bodies and global stratigraphic correlation [1,2]. The change of carbon and oxygen isotope values is generally controlled by global factors such as paleoclimate, paleotemperature and paleoecilogy. Therefore, it has a global consistent and synchronous change trend with basin subsidence, sedimentary facies belt, paleoenvironmental change and sea-level rise and fall. Oxygen isotopes in rocks are more susceptible to later geological processes. For the division and correlation of Paleozoic strata, carbon isotopes or strontium isotopes are mostly selected as indicators and basis [3]. It is generally believed that the carbon isotopic composition and its variation law of marine carbonate strata are related to the global initial productivity and total carbon burial, while the strontium isotopic composition often reflects the crust mantle material flow balance related to global tectonic activity, sea-level change or weathering, and it is consistent in global seawater [4-7]. Through the study and analysis of carbon and oxygen isotopes in the Muxu river section of the late Ordovician in the southwest margin of Ordos block, this paper defines the geological age of longmendong formation and discusses the relative changes of sea level in the Ordovician, which provides a basis for further understanding the paleogeographic environment of this region and the comparison of global strata.

2. Regional geological overview

The Muxu river section is located in the western section of Weibei uplift on the southwest edge of Ordos block (Fig. 1), which is well exposed along Meilin highway. Under this section is the Middle

Ordovician Sandaogou formation, which is mainly composed of light gray microcrystalline fine-grained limestone and dolomitic limestone. It is a carbonate platform sedimentary environment. At the bottom of longmendong formation is a set of dense accumulated calcareous breccia with a thickness of about 10m. The gravel diameter is mostly 5cm ~ 20cm, oval [8]. This set of strata constitutes the bottom boundary of longmendong formation. The top of longmendong formation is covered by breccia of beiguoshan formation of Upper Ordovician. Longmendong formation is well exposed, continuous and complete.

Carbon and oxygen isotope samples were collected in the measured profile. The weathering degree of the collected rock samples is weak, and the development parts such as recrystallization and calcite vein are basically avoided, so as to reduce the impact of later diagenetic alteration on carbon and oxygen isotopes in the rocks and reflect the original sedimentary environment at that time as much as possible. The lithology of the sample is mainly mudstone, siltstone, siltstone, limestone, dolomite, etc., with a total of 205 blocks.

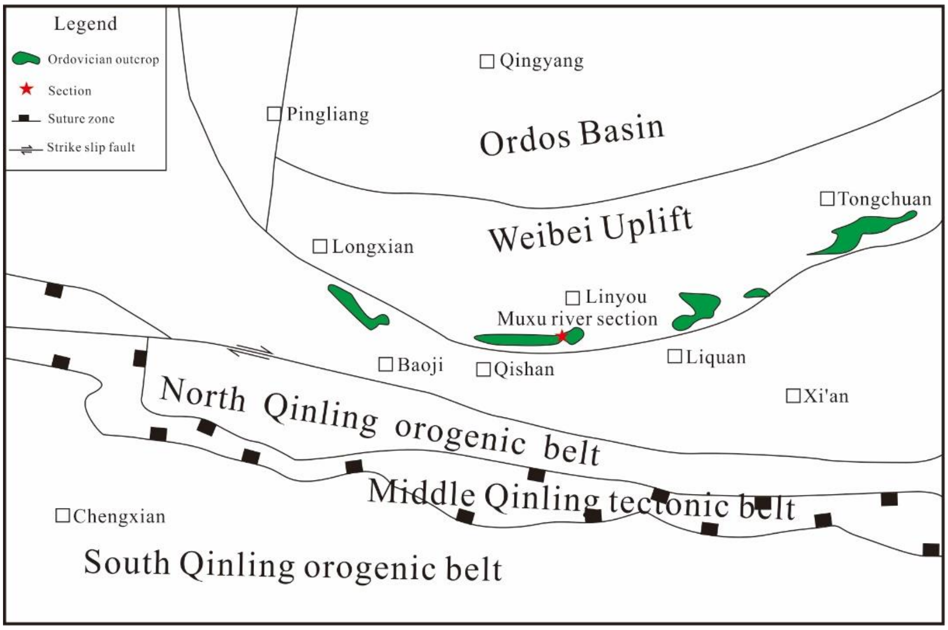

Figure 1: Regional geological structure

3. Sample test and effectiveness evaluation

3.1. Sample processing and analysis

The processing and testing of carbon and oxygen isotope samples were completed in the analysis and experiment center of exploration and Development Research Institute of PetroChina Southwest Oil and Gas field Company. In the laboratory environment of 22 ℃ ~ 23 ℃, 100% phosphoric acid is used to react with powder samples to collect CO_2 gas. The analysis of carbon and oxygen isotopes was completed by MAT-252 gas isotope mass spectrometer (using PDB standard). The analysis accuracy adopts the Chinese national standard sample GBW04405, and the standard deviation of $\delta^{18}O$ and $\delta^{13}C$ is ± 0.05 ‰ and ± 0.06 ‰ respectively.

3.2. Effectiveness evaluation

In order to detect that carbon and oxygen isotopes are affected by late burial diagenesis, water diagenesis and other factors, it is very important to evaluate the effectiveness of samples. The carbon isotopes of 205 samples ranged from - 6.19‰ to 5.16‰, with an average of 0.57‰. The average value of oxygen isotope is -3.09‰ ~ -16.84‰, with an average of -10.74 ‰. The cross examination of carbon and oxygen isotopes shows that the correlation between them is poor and belongs to discrete type (Fig. 2), and the oxygen isotope data mostly fluctuates around - 10‰ [9-12], indicating that the carbon and oxygen isotope data basically preserve the characteristics of original isotope composition and have high reliability. Only five samples with carbon isotope < -5‰ and five samples with carbon isotope > 5‰ may be affected by more serious late alteration.

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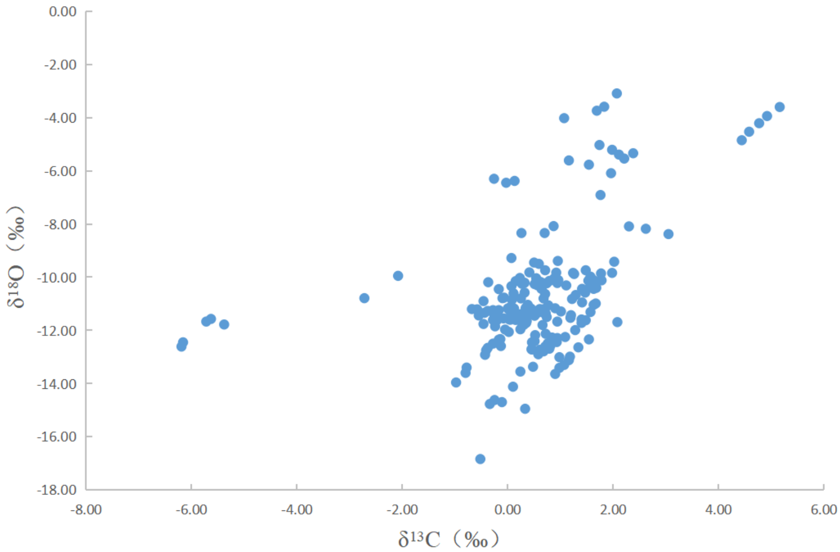

Figure 2: Correlation of carbon and oxygen isotopes in Muxu river section

4. Isotopic composition characteristics

Fig. 3 shows the change trend of carbon and oxygen isotope curve of Upper Ordovician longmendong formation. Combined with the change of lithology combination, the change of carbon isotope composition of the whole section can be roughly divided into four cycles.

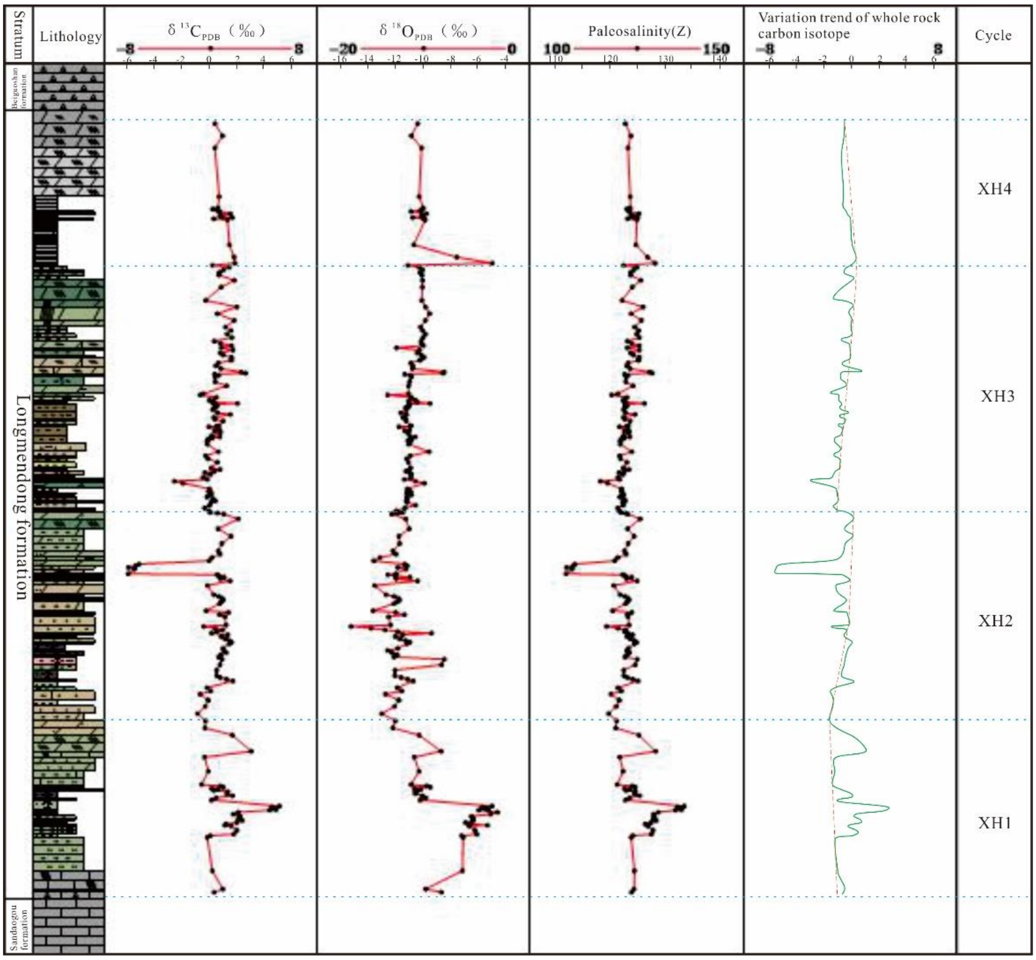

Figure 3: Variation curve of carbon and oxygen isotopes of carbonate rocks of longmendong formation

Cycle I (XH1) is composed of samples 38-1 to 54-2 at the bottom of longmendong formation, with a thickness of about 183m. A set of rock assemblages dominated by limestone, dolomite and shale are developed. $\delta^{13}C$ values are mostly positive, with an average of 1.48‰. On the whole, from the beginning of the cycle to the end of the cycle, $\delta^{13}C$ increases gradually, and increases to the positive value of 5.16‰ in the middle of the cycle $\delta^{13}C$ value is mostly between 4 ‰ - 5‰, and then begins to drop gradually to near 0. It can be regarded as a positive drift cycle.

Cycle II (XH2) consists of samples 54-3 to 72-3. The total thickness of this cycle stratum is about 222m, which is characterized by the extensive development of clastic rock series, The $\delta^{13}C$ value first decreased and then increased, with an average of 0.11‰. At the beginning of this cycle, $\delta^{13}C$ value is mostly positive, hovering around 1‰ and relatively stable, reaching the end of the cycle $\delta^{13}C$ value began to be negative, and longmendong formation appeared the negative value of $\delta^{13}C$ value is -6.19‰, and several consecutive values nearby fluctuate between -5‰ and -6.5‰, which can be identified as a negative drift event, and then the $\delta^{13}C$ value began to rise steadily and became stable at the end of the cycle.

Cycle III (XH3) consists of sample 73-1 to sample 108-3. The thickness is about 260 meters. The rock type is the combination change from sandstone mudstone to dolomite, The $\delta^{13}C$ value is small and the fluctuation increases, and the average value is 0.43‰. Of this cycle $\delta^{13}C$ is relatively stable, mostly hovering between -1‰ and 1‰. There is an isotopic mutation between this cycle and XH2 cycle, with a negative offset of about 1‰. In the middle and upper part of the cycle, $\delta^{13}C$ values are basically positive and tend to increase gradually. At the end of the cycle, The value of $\delta^{13}C$ decreases to about 0. Generally speaking, this cycle belongs to a positive drift.

Cycle IV (XH4) consists of sample 109-1 to sample 116-3, with a thickness of about 166 meters. The lithology of the lower section is gray and dark gray shale, and the upper section is gray limestone and dolomitic limestone, $\delta^{13}C$ value decreased first and then increased, with an average of 0.88‰. The cycle starts at the beginning $\delta^{13}C$ approached 2‰ and gradually dropped to -1 ‰, then began to increase and stabilized at 0.5‰ at the end. The overall isotope value is relatively stable and there is no obvious carbon isotope event. Combined with cycle 3, this cycle belongs to the continuation of cycle 3, and the carbon isotope shows positive drift from the beginning of cycle 3 to the end of cycle 4.

The variation of oxygen isotope values in Muxu river profile is complex, $\delta^{18}O$ values are distributed between -16‰ and -2‰, with an average of -10‰. From the bottom to the middle of longmendong formation, oxygen isotope oscillations are more frequent, and the amplitude is significantly greater than that of carbon isotope in the same layer. From the middle to the upper part of the longmendong formation, there is almost no large oscillation in the oxygen isotope curve, The $\delta^{18}O$ value has been stable at about -10‰. Except once the curve of this section is relatively stable except that the large negative value of $\delta^{18}O$ value is -3.59‰. Because the whole curve is highly volatile and unstable, it is not enough to subdivide it into several cycles.

5. Discussion

5.1. Carbon isotope and paleosalinity

The relative change of ancient seawater salinity can be judged by Z value [13-16]. When Z>120, the sedimentary water body is paleomarine environment; When Z＜ 120, the sedimentary water body is paleofreshwater environment; When Z=120, it is an undetermined limestone sedimentary environment. Generally speaking, most of the Z values in longmendong group are between 120 and 130, which is similar to the $\delta^{13}C$ value has obvious correlation (Fig.4), which is reflected in the paleomarine sedimentary environment, which is consistent with the change of regional environment [17].

In the lower and middle sections of longmendong formation, the Z value shows abnormal changes (Fig.3). In the lower part of longmendong formation, the interval with Z >120 appears, corresponding to $\delta^{13}C$ value and the mean values of $\delta^{18}O$ were 4.32‰ and -4.23‰ respectively, which were high. Abnormally high $\delta^{18}O$ indicates that it may have been affected by the later water rock alteration, resulting in the change of carbon and oxygen isotopes. In the middle part of longmendong formation, the Z value is small, and the corresponding carbon isotope is very low, with an average of -5.82‰, while the oxygen isotope is in the normal range, with an average of -12.01‰. The corresponding lithology is laminated light grayish green silty dolomite, light yellowish green argillaceous siltstone and dolomitic siltstone. It is a closed lagoon environment, which may be affected by fresh water injection and microbial action, resulting in very low carbon isotope.

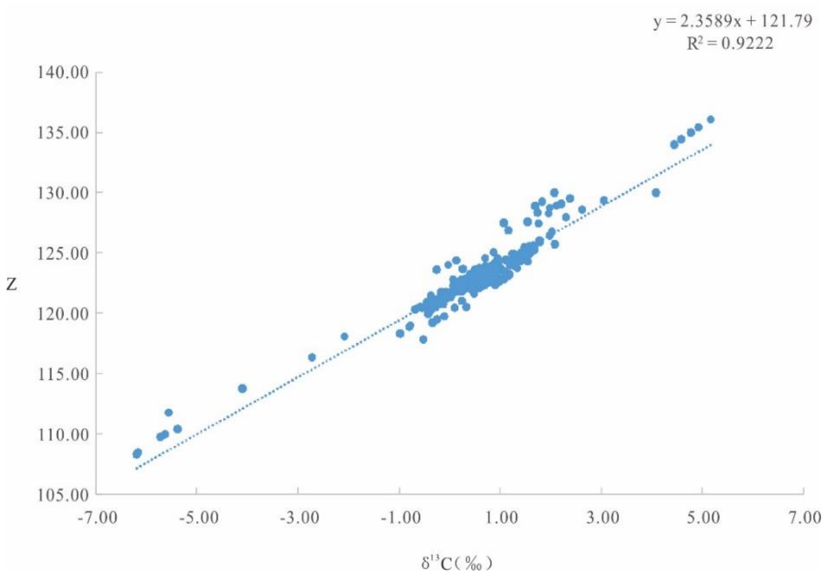

Figure 4: Relationship between carbon isotope and paleosalinity of longmendong formation

5.2. Carbon isotope and sea level change

In the late Ordovician, terrestrial organisms were poor. Under the condition of little fluctuation of atmospheric CO_2 partial pressure, the relative changes of ^{12}C and ^{13}C in sediments were controlled by the rise and fall of sea level. When the earth's surface temperature rises, the sea water increases, the sea level rises, the land area decreases, the sediment entering the ocean due to weathering and denudation decreases, the marine life flourishes, and the buried amount of organic carbon increases. Therefore, the ^{13}C in the sea water is relatively enriched, which is in equilibrium with the carbon isotope of the sea water $\delta^{13}C$ will be significantly positive. On the contrary, when the earth's surface temperature decreases, the land glaciers increase, the sea level decreases, and the marine organisms shrink, which reduces the buried amount of organic carbon. The seawater is relatively rich in ^{12}C and poor in ^{13}C, and the carbonate rocks are relatively rich in $\delta^{13}C$ will have negative bias [18-20]. Therefore, the positive and negative drift changes of carbon isotopes can be used to reflect the fluctuation of sea level.

It can be seen from the carbon and oxygen isotope curve in Fig. 3 that the overall cycle is negative, indicating that the sea level should be in a downward state during this period. However, there are two periods of positive carbon isotope drift in Cycle I, corresponding to the rising trend of sea level. Generally speaking, the sea level of Cycle I rises in the initial stage, decreases in the middle stage, rises again in the end and then begins to decline. The sea level of Cycle II continues the state of Cycle I, which is in the decline state in the early stage and gradually rises in the middle stage. After a short-term rapid decline of sea level in the middle and late stage, it returns to the rise state until the end of Cycle II. Compared with Cycle I, the overall sea level of Cycle II is declining. During the transition from Cycle II to Cycle III, the sea level suddenly changed from rising to falling in a short time. It is speculated that abnormal events may occur at this time, and then the sea level began to rise slowly without too drastic changes, but on the whole, the sea level is still falling at this stage. Cycle IV belongs to the continuous development of Cycle III. After a slight rise in the early stage, it began to decline again.

In general, the sea level in Qishan area in the late Ordovician rose first and then continued to decline until the arrival of the hernantian ice age. However, in terms of stage change, it is relatively oscillatory, the sea advance and regression are carried out alternately, and sometimes there are abnormal events leading to the sudden change of sea level.

Because the oxygen isotope is greatly affected by diagenetic alteration, it is difficult to reflect the change of sea level, but the oxygen isotope with light alteration can reflect the condensation and melting of continental glaciers to a certain extent. When the earth is in the ice age, the sea level drops, the salinity rises, and ^{16}O is sealed by a huge ice sheet, then ^{18}O will be enriched in the sea water; In the interglacial period, on the contrary, glaciers melt and release a large amount of ^{16}O. As the sea level rises, ^{18}O in seawater will be reduced [21-23]. This is consistent with the sea level fluctuation reflected by the carbon isotope curve.

5.3. Comparison between carbon isotope curve of Muxu river profile and international carbon isotope curve

Predecessors have studied the global Ordovician carbon isotope stratigraphy for half a century. Large quantities of carbon isotope events with global isochronous significance have been identified in the Ordovician of major plates such as the Baltic plate, Lauren plate and Siberian plate abroad and the Yangtze plate and Tarim plate in South China [24-30].

Chen Xu et al. (2008) summarized a global Ordovician $\delta^{13}C$ variation curve, including Yichang, China, hernandian curve of Nevada, USA, Cadian curve of central continent of North America and Estonian curve earlier than Cadian [31]. The positive partial mdice event of carbon isotope in the middle Darwinian stage [32-34], the gice event during the transition from the sambician stage to the Cadian stage [35-38] and so on are well recorded on this curve. The peak value of this curve well reflects the difference of their corresponding chronostratigraphic units and peak values.

The top and bottom strata of longmendong formation in Muxu river section are developed, indicating that longmendong formation is a set of continuous and complete sedimentary records. Based on the rock assemblage and sedimentary structure, it is considered that the overlying beiguoshan formation is a set of glacier ice water deposition [39,40], which should be consistent with the internationally recognized hernandian continental glacial event. The Sandaogou formation underlying the longmendong formation is classified into the Middle Ordovician according to paleontological fossils, which is equivalent to Majiagou Formation in North China stratigraphic area, guniutan formation and shizipu formation in Yangtze stratigraphic area. Therefore, longmendong formation should be the deposition of Sangbian and Katian periods, which can be compared with Pingliang Formation and Yaoxian formation on the western margin of Ordos [41, 42].

The comparison between the carbon isotope curve of longmendong formation of Muxu river section and the international comprehensive carbon isotope curve shows that (Fig.5), XH1 and XH2 can be compared with the international comprehensive curve of Sangbian period, and XH3 and XH4 can be compared with the Katian period of the international comprehensive curve.

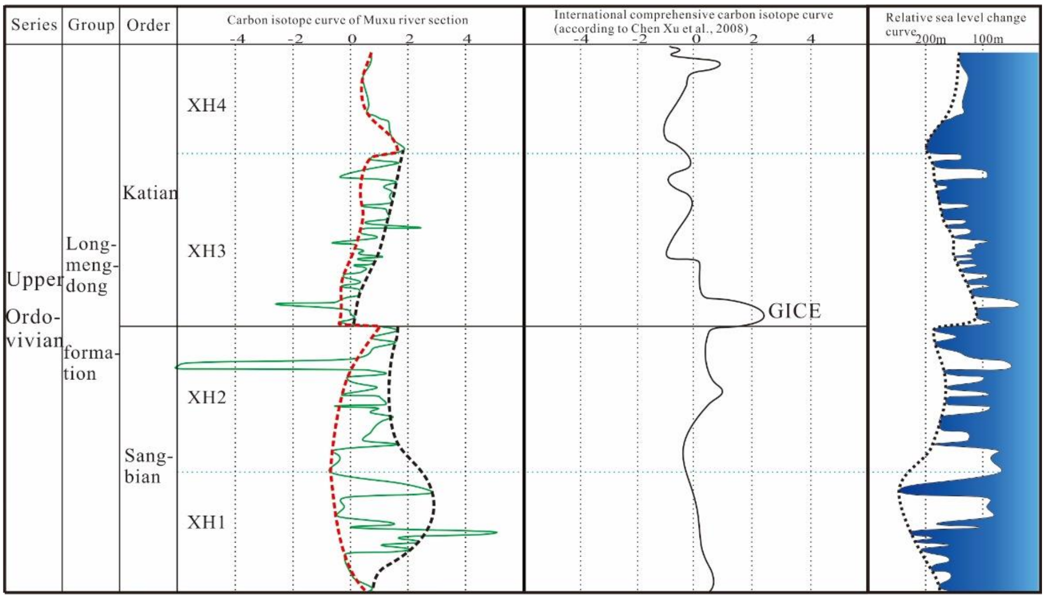

Figure 5: Comparison between carbon isotope curve of longmendong formation in Qishan area and global carbon isotope curve

Through the data analysis above and in combination with Fig.5, it can be seen that the change of Cycle I is basically consistent with the international curve at the same time, and the carbon isotope has a negative drift trend as a whole. The difference is that there are still some small positive drift in Cycle I, which is not recorded on the international curve, indicating that the carbon isotope and sea-level change have regional characteristics. The change trend of carbon isotope in the second stage of cycle still corresponds to the international curve as a whole, but the regional characteristics still exist. For example, there is a relatively large negative drift in this section at the end of Cycle II, and there is no record on the international curve; The positive drift event of gice carbon isotope at the junction of Sangbian and Katian stage is related to the section in this study, that is, near the junction of Cycle II and Cycle III, the carbon isotope shows a trend of positive bias first and then negative bias, The peak value of $\delta^{13}C$ is 2.08‰. Although there is a deviation in the time of occurrence, it can basically correspond to the GICE event. It is speculated that it may be because the carbon isotope drift event occurred in a fixed time period, but the specific time of occurrence is not necessarily the same, and there may be a time difference; Entering Cycle III and Cycle IV, the evolution trend of carbon isotope deviates from the international curve. On the whole, the change trend of carbon isotopes in Cycle I and Cycle II and the rise and fall of sea level can be compared with the global contemporaneous period. GICE events can also be identified in this profile, but Cycle III and Cycle IV are quite different from the international curve, showing regional characteristics.

6. Conclusion

(1) The lower and upper parts of the upper Ordovician longmendong formation on the Muxu river section of Qishan in the southwest edge of Ordos block are in integrated contact with Sandaogou formation and beiguoshan formation respectively, with good exposure and continuous integrity, which is equivalent to the deposition of Sangbian period and Katian period, and can be compared with Pingliang Formation in the west edge of Ordos and Yaoxian formation in the south edge.

(2) The carbon isotopes of 205 samples ranged from -6.19‰ to 5.16‰, with an average of 0.57‰. The average value of oxygen isotope is -3.09‰ ~ -16.84‰, with an average of -10.74‰. The carbon and oxygen isotopes are discrete and basically preserve the original geochemical composition characteristics. The salinity Z value is between 120 and 130, indicating that the late Ordovician was a marine sedimentary environment, which is consistent with the geological research results.

(3) The vertical variation of carbon isotope curve of longmendong formation in Muxu river section can be divided into four cycle segments according to the characteristics of base value and fluctuation. The base value of XH1 carbon isotope curve changes from large to small, and there are many positive drifts, reflecting that the sea level has experienced many short-term huge drops on the background of medium-term rise; The base value of XH2 isotope curve changes from rapid increase to slow increase, which reflects that the sea level first decreases and then increases, and the carbon isotope at the junction of XH2 and XH3 is positively biased to 2.08‰, which may be the embodiment of a tectonic event. The base value of XH3 isotope curve increases slowly, and the carbon isotope mostly shows a small negative offset. XH4 isotope curve shows a complete cycle of first decreasing and then increasing, and the fluctuation range of sea level is small. Generally speaking, the early carbon isotope values are mainly positive drift, with large scale and long time; The late stage is dominated by negative drift, with small scale and short time. This reflects that the sea level fluctuated greatly in the early Late Ordovician, with strong activity, and the sea level fluctuated slightly in the late Ordovician, showing a downward trend as a whole.

(4) The comparison of carbon and oxygen isotope variation curve of longmendong formation and the global Ordovician$\delta^{13}C$ variation curves shows that longmendong formation is deposited in the late Ordovician, which is equivalent to Sangbian and Katian periods. There is a positive drift event of gice carbon isotope, which is regionally comparable.

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