Carbon and strontium isotope variations and responses to sea-level fluctuations in the Ordovician of the Tarim Basin

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Abstract In the Ordovician, a carbonate platform system grading from the platformal interior eastwards to basin was developed in the Tazhong area of the Tarim Basin, and the study column is located in the place where the paleoslope occurred. The isotope compositions of the carbonates there are thus considered as having reflected those of simultaneous sea waters in view of its good connection with the open seas. The carbon and strontium isotope compositions of the Ordovician carbonates in the Tazhong area are analyzed, and their relationships to the sea-level fluctuations are discussed as well. Studies have revealed that the carbon isotope composition is related positively with the sea-level fluctuations, whereas an opposing situation occurs to the strontium isotope variation. Similar responses of carbon and strontium isotope compositions to the sea-level fluctuations are reported elsewhere in the world, suggesting that the Ordovician sea-level fluctuations of the Tarim Basin were of eustatic implication.

Keyword: Tarim Basin, Ordovician, carbon and strontium isotope, sea-level fluctuation.

The carbon isotope in the nature is stored mainly in two carbon reservoirs, organic carbon and carbonate carbon. The ${}^{13}C$ value of marine carbonates mainly depends on the relative amount of the two carbon reservoirs, of which the oxygenated carbon is dominated by carbonate sediments rich in ¹³C, while the reduced one is dominated by organic carbons rich in ¹²C. Many authors^{$[1-4]$} have extensively studied the secular variation of carbon isotope composition of carbonate rocks since the Phanerozoic in order to document the global carbon cycles, carbon fluxes, climatic changes and sea-level fluctuations.

Generally, most of Sr being input into the ocean is derived from the continental weathering, 87 Sr/ 86 Sr ratio is hence a combined reflection of the continental surface, all rocks and surficial areas subject to the chemical weathering in ocean basins^[5]. In this case, the time-dependent variation of 87 Sr $/86$ Sr is interpreted as having been resulted from the differential supplies of Sr amounts between different sources^[6]. As the sea-level rises, weathering slows down and surface runoffs decrease, leading to a less supply of Sr from the sialtic weathered zone on the crust, and subsequently resulting in the decrease of ${}^{87}Sr/{}^{86}Sr$ ratio in the ocean. By the contrast, the sea-level fall results in the increase of ${}^{87}Sr/{}^{86}Sr$ ratio in the ocean. The variation of strontium isotope compositions is, therefore, an indicator of sea-level fluctuations to some extent.

The carbon and strontium isotope compositions and variations of primary carbonates in the geologic record are important approaches to study global events such as weathering, orogeny, climate and sea-level changes, and to the global correlation^[7-14]. However, less attention has been paid to the strontium isotope variations for the Lower Paleozoic, especially for the Ordovician^[15, 16]. Scattered relevant studies, mainly involving in the Upper Proterozoic to the Lower Paleozoic [17, 18], Devonian-Carboniferous^[19—23] and Permian^[24], have been reported elsewhere in China, but no study on the aspect of the Ordovician strontium isotope has been conducted. This study aims to document the carbon and strontium isotope compositions of the Ordovician marine carbonates and their responses to sea-level fluctuations.

1 Geological setting and sampling

The sample locality is situated at the Tazhong area of the Tarim Basin, where a transitional zone between the carbonate platform and the basin from west to east was developed in the Ordovician. The well Tazhong 12 is chosen as the representative of this study since a platform marginal environment, which was sensitive to sea-level fluctuations and circulated well with the open sea, is identified in the borehole cores. The unaltered micritic limestones, which most likely represent the primary carbon and strontium isotope compositions of the sea water, were sampled. 86 samples were collected from four borehole cores, of which 42 are from well Tazhong 12, 13 from well Tazhong 29, 20 from well Tazhong 30 and 11 from well Badong 2. 656m of the Ordovician strata was penetrated (4644—5300 m below surface) in Tazhong 12. The Lower Ordovician is located from 5120 to 5300 m depth, containing conodonts *Scolopodus asperus*, *S. bicostatus, S. opimus* and *Drepanodus suberectus*; the Upper Ordovician is located from 4644 to 5120 m depth, containing conodonts *Pseudobelodrna indinata, Plecpodrna bidentata, Aphelognathus* sp*.* and *Oulodus* sp*.,* and corals *Quepora* sp*., Heliolitis* sp*.* and *Eofletckeriella* sp*.* The sampling interval is 15.62 m in average, which can meet the requirement of documenting the long-term variations of carbon and strontium isotopic composition.

2 Methods and results

The carbon isotope analyses were carried out at the C-O Isotope Laboratory of Institute of Geology and Geophysics, Chinese Academy of Sciences. Carbon (and oxygen) isotope compositions were detected in a MAT-251 mass spectrometre, and the isotopic ratios were reported in ‰ relative to the PDB standard. Duplicate precision of analysis was better than 0.08‰. The strontium isotope analyses were performed at the Rb-Sr Isotope Ultraclean Laboratory of Institute of Geology and Geophysics, Chinese Academy of Sciences. Unaltered micrites were chosen and ground into powders, then were dissolved with 2.5 mol/L HCI; the residues were re-dissolved with HF + HCIO₄ in a Teflon container at a low temperature. Rb and Sr were separated with AG50W \times 8 (H⁺) cation exchange column. Isotopic ratios were measured on a VG354 solid mass spectrometre. Duplicate precision of analysis was better than 0.03‰.

The analysis results indicate that $\delta^{3}C$ value is generally in the range of -4.52% -2.71% in wells of Tazhong 12, 29, 30 and Badong 2, mostly close to 1‰, within the range for the normal marine carbonates. 42 samples were collected in well Tazhong 12, with a maximum value of $\delta^{3}C$ up to 2.10‰, and a minimum of -1.45 ‰. The δ^{13} C of the Lower Ordovician is relatively low, in the range of -1.45% – 0.17 % with an average of -1.08 %. Relatively high values of $\delta^{3}C$ occur in the Mid-Upper Ordovician, in the range of -0.15% - 2.10 ‰ with an average of 0.92 ‰ (fig. 1, table 1).

The ${}^{87}Sr/{}^{86}Sr$ ratios vary between 0.707 and 0.710 in the wells of Tazhong 12, 29, 30 and Badong 2, generally in the range for the normal marine carbonates. In well Tazhong 12, the ${}^{87}Sr/{}^{86}Sr$ ratios are in the range of 0.7073 – 0.7094, with an average of 0.7083; and those in well Tazhong 29 are in the range of $0.7080 - 0.7084$, with an average of 0.7083. In well Tazhong 30, the ratios are in the range of 0.7080—0.7088, with an average of 0.7083, and those in well Badong 2 are in the range of $0.7081 - 0.7083$, with an average of 0.7082. The average isotopic ratio of the four wells is 0.7082 (table 1, fig. 1).

Fig. 1. The relationships between sea-level fluctuations and $\delta^3 C$, ${}^{87}Sr/{}^{86}Sr$ values in the Ordovician of well Tazhong 12. 1, Mixed shelf facies; 2, shelf storm sedimentary facies; 3, open platform facies; 4, restricted platform facies.

3 Carbon and strontium isotope compositions and their relationships to sea-level fluctuations

3.1 Carbon isotopes

The carbon isotopes of the Early Ordovician in the Tazhong area are relatively light. In the

well Tazhong 12 (5176—6296 m below surface), for example, the $\delta^{3}C$ is mostly negative, ranging from -1.45% to 0.17 ‰, with an average of -1.08 ‰. A rapid increase of $\delta^{13}C$ value from –1.12‰ up to 2.02 ‰ occurred in the transitional period from the Early Ordovician to the Mid-Late Ordovician (5176 – 4976 m deep) (fig. 1). $\delta^{3}C$ is mostly positive, ranging from 0.15‰ to 2.10 ‰, with an average of 0.92 ‰, apparently heavier than that of the Lower Ordovician carbonates, with a less peak amplitude.

 δ^{3} C gradually increases from the Early Ordovician to the Late Ordovician, and a rapid increase in carbon isotope weight with high amplitudes occurred in the transitional period. By comparing δ^{3} C variations with the sea-level fluctuations(fig. 1), a positive relationship between them is revealed, such that relatively high $\delta^{3}C$ values correspond to relatively highstanding sea-levels, and *vice versa*. During the transgressive periods, the sea-level rise leads to the increasing of the shelf area, deepening of water, rising of wave bases and upward shifting of photosynthesis-influenced depth. These would result in the photosynthesis attenuation in the lower waters, increase of oxygen-consumption amounts of the primary waters and consumption of oxygen dissolved in water, which further lead to the expansion of oxygen-depleted or anoxic environments. Moreover, the lesser meridional gradients during the transgressions will result in more equable climatic conditions, and this would lead to the decrease of oxygen dissolution in water and re-oxygenation rate of bottom water, and eventually to the oxygen-depleted conditions or expansion of anoxic water. Furthermore, a sea-level highstand will result in the formation of warm saline at bottom, density stratification of seawater and increasing biomass productivity and nutrient supply in the surface water column. All these will facilitate the burial and preservation of organic carbon. In the total dissolved carbon reservoirs of modern oceans, $\delta^{13}C$ value will keep zero, as the output ratio of the organic carbon to the carbonate carbon is 1: 4. A positive excursion of $\delta^{3}C$ will occur, as the burial rate of the organic carbon is faster than that of the carbonate carbon^[25]. With the increase of the buried organic carbon in carbonates, accompanied with the decrease of erosional organic carbon influxes to oceans due to the reduction of landmasses, $CO₂$ dissolved in seawaters is rich in 13 C. In this case, the carbonates fractionally equilibrated with seawater possess relatively heavy isotopic carbons, leading to the increase of $\delta^{3}C$ of carbonate carbons and decrease of δ^{3} C of organic carbons. On the contrary, δ^{3} C values of the carbonate carbon atoms will decrease, while those of organic carbon atoms will decrease during sea-level lowstands.

3.2 Strontium isotopes

The strontium can remain in seawater for 19 $Ma^{[5]}$, while the full mixing of seawater only takes 1 $\text{ka}^{[6]}$. Thus the strontium isotopes of seawater in open sea are constant in any given time, as proven by the results of ${}^{87}Sr/{}^{86}Sr$ ratios of modern ocean seawater. However, the ${}^{87}Sr/{}^{86}Sr$ in seawater varied with times since the Phanerozoic. The primary ${}^{87}Sr/{}^{86}Sr$ ratios of carbonates are generally in the range of $0.706 - 0.710$. They are commonly contributed by three kinds of sources: (1) mantle-derived strontium supplied by ocean mid-ridge hydrothermal or sea-floor volcanic activities, whose primary ${}^{87}Sr/{}^{86}Sr$ values are relatively low, commonly ca. 0.704; (2) terrigenous strontium supplied by old crustal sialic rocks through chemical weathering, possessing a high primary ${}^{87}Sr/{}^{86}Sr$, generally ca. 0.720; (3) strontium provided by marine carbonates through chemical weathering, with a primary ${}^{87}Sr/{}^{86}Sr$ of ca. 0.708. The marine strontium isotope compositions are mainly contributed by the latter two sources, if no large-scale sea-floor volcanic activity takes place. Moreover, intensity of the weathering is directly related to the sea-level fluctuations, so the weathering rate will decrease as the sea-level rises, resulting in less strontium influxes from weathered sialic rocks and subsequently the decrease of marine strontium isotopic ratios. On the contrary, the marine strontium isotopic ratios will increase as the sea-level falls.

Arthur et al.^[26] has documented the relationship between ${}^{87}Sr/{}^{86}Sr$ variations and sea-level fluctuations of the Mesozoic and Cenozoic, and argued that the increase of ${}^{87}Sr/{}^{86}Sr$ coincided with rise of sea-level, and *vice versa*. A similar pattern from the Silurian to the Cretaceous was also documented by Vail et al.^[27]. The ${}^{87}Sr/{}^{86}Sr$ ratios of marine sediments therefore reflect the sea-level fluctuations.

A similar relationship between strontium isotopic patterns and sea-level fluctuations in the Cambrian has also been documented by Montanez et al.^[15]. During sea-level falls, the continental area above the sea level increased, which led to the increase of ⁸⁷Sr influxes to seas from continental crusts, and subsequently the rise of ${}^{87}Sr/{}^{86}Sr$ in marine carbonates. An opposing pattern occurred during sea-level highstands.

Therefore, it is very useful to take the ${}^{87}Sr/{}^{86}Sr$ to document the sea-level change history in view of the negative relationship between the strontium isotopic patterns and sea-level fluctuations, provided that continuous sampling is conducted for the borehole cores.

The average of ${}^{87}Sr/{}^{86}Sr$ of carbonates is 0.7083 in the Tazhong area, and herein is provisionally supposed to represent the Ordovician mean sea level in this area. In this case, the sea level is supposed to having been lower than the mean sea level, as the ${}^{87}Sr/{}^{86}Sr$ value is larger than 0.7083. Taking Tazhong 12 as an example, the sea-level change trend is well illustrated as seen in fig. 1 and table 1. The ${}^{87}Sr/{}^{86}Sr$ ratios vary undulantly, mostly less than 0.7080 (with an average of 0.7077 by four samples) at the depths of $5300 - 5245$ m (lower part of the Lower Ordovician), suggesting a relative sea-level highstand (up to the progressive maximum highstand), which were likely modulated by frequent rises and falls. The ${}^{87}Sr/{}^{86}Sr$ values are relatively stable at the depth of 5245—5170 m (upper part of the Lower Ordovician), and mostly are larger than 0.7082 (with an average of 0.7088), suggesting a stable sea-level lowstand (reaching the progressive lowest level). The isotopic pattern varies greatly at the depth of 5075—4803 m (lower part of Mid-Upper Ordovician) from 0.7083 to 0.7094, with an average of 0.7085 (by 6 samples), suggesting a notable sea-level rise, but greatly undulatory in the late Early Ordovician. These isotopic values tend to stable again at the well depth of 4744—4640 m (upper part of the Mid-Upper Ordovician),

mostly ranging from 0.708 to 0.7082 and averaging 0.7081 (by 16 samples), suggesting a progressive sea-level rise and slightly higher sea level than the everage one during this time.

The vertical variations of ${}^{87}Sr/{}^{86}Sr$ in Tazhong 12, revealed that a sea-level fall from relatively highstanding to lowstanding occurred in the Early Ordovician, then a progressive sea-level rise took place from the Middle through the Late Ordovician, and remained in a sea-level highstand. This pattern coincides with that achieved by the sequence stratigraphic approach^[28], and is well correlated with that in South China and other places in the world^[29].

4 Conclusions

Based on the study on the carbon and strontium isotopes in the Ordovician marine carbonates in the Tarim Basin, especially in the well of Tazhong 12, the relationship between the isotope evolution and eustatic sea-level fluctuations is discussed and following conclusions are drawn:

(1) The carbon and strontium isotopes of unaltered Ordovician marine carbonates represent those of primary seawaters, their evolution trends are consistent with the global evolution curve, i.e., a gradual increase of $\delta^{3}C$ and a decrease of ${}^{87}Sr/{}^{86}Sr$ occurred from the Early through Mid-Late Ordovician. This suggests that the carbon and strontium isotopic patterns are of global significance and useful tools for studying global events and stratigraphic correlations.

(2) A positive and a negative relationships between carbon and strontium isotopes respectively with sea-level fluctuations are revealed. A negative relationship between carbon and strontium isotopes is thus present as well.

(3) The sea level in the Early Ordovician was relatively low, which rose rapidly and undulantly between the Early and Mid-Late Ordovician, and reached a stable highstand of sea level in the Mid-Late Ordovician.

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