

Isotopic evolution of the terminal Neoproterozoic and early Cambrian carbon cycle on the northern Yangtze Platform, South China^{*}

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Abstract Profound geotectonic, climatic and biological changes occur during the terminal Neoproterozoic and its transition into the early Cambrian. These are reflected in temporal variations of the chemical and isotopic composition of seawater. We are studying a sequence of sedimentary rocks at the Shatan section, northern Yangtze Platform, Sichuan Province of China. This succession comprises, in ascending stratigraphic order, predominantly calcareous sediments of the Sinian upper Dengying Formation and black shales of the lower Cambrian Guojiaba Formation (time equivalent of Niutitang Fm.). Paleoenvironmental setting represents shallow-water shelf deposits. The objective of our study is to provide temporal records for the isotopic compositions of organic and carbonate carbon throughout this time interval. Organic carbon isotope values display a range between -35.8‰ and -30.1‰ with clear stratigraphic variations. Carbonate carbon isotope data vary between -3.5‰ and $+0.5\text{‰}$. These secular variations are interpreted to reflect perturbations of the global carbon cycle, specifically changes in the fractional burial of organic carbon. However, local conditions have further affected the isotopic signals.

Keywords: terminal Neoproterozoic, Early Cambrian, carbonate and organic carbon isotopic composition, Yangtze Platform, Shatan section.

The seawater carbon isotopic composition represents an important tool for developing a global correlation scheme, particularly for those sections lacking age-diagnostic biostratigraphic markers and/or precise radiometric age determinations^[1-9]. Paired carbonate and organic carbon isotope determinations provide a possibility of interpreting not only changes in the global carbon cycle through time, but changes in atmospheric $p\text{CO}_2$ as well^[10].

China's Yangtze Platform is characterized by a well developed succession of terminal Neoproterozoic to early Cambrian sedimentary rocks including the Neoproterozoic Nantuo Tillite, calcareous sediments of the Neoproterozoic Doushantuo and Dengying formations and black shales of the lower Cambrian Niutitang/Guojiba Formation. Thus, the Yangtze Platform offers the opportunity to study the interaction between atmosphere, hydrosphere, biosphere and lithosphere during this critical interval in Earth history. Despite a number of previously published carbon isotope studies^[9], a detailed reconstruction for this succession via C-isotope chemostratigraphy is still incomplete. This is particularly true for the application of organic carbon isotope data.

Our systematic investigation documents secular variations in $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$, which are interpreted as perturbations of the global carbon cycle, and specifically changes in the burial of organic carbon.

1 Geological setting, section and samples

A conformable succession of lithologically diverse marine sediments was deposited on the Yangtze Platform, South China, during the Precambrian-Cambrian transitional period. Well preserved rocks document a series of different geological features including sea level fluctuation, ocean anoxia, phosphorite deposition and the Cambrian bio-radiation. The Precambrian-Cambrian boundary has been dated elsewhere at 544 Ma^[11].

A well developed succession of late Neoproterozoic to Early Cambrian sedimentary rocks is exposed in the Nanjiang area of northern Sichuan Province, northwestern Yangtze Platform. High-resolution carbon isotope chemostratigraphic data are reported here from the Shatan section, Shatan Village, Nanjiang County, northern Sichuan Province, China. The biostratigraphy of the Shatan section has been well

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studied^[12-14]. This PC-C boundary section comprises the upper part of the Dengying Fm. (Mofangyan member) and the lower part of Guojiaba Fm., representing shallow water deposition. Lithologies include light grey carbonates, black shale, and siliceous rocks, with abundant small-shelly fossils preserved in the upper part of the Dengying Fm.

Totally 46 unweathered samples of carbonate, black shale and siliceous rocks were collected at the Shatan section.

2 Analytical methods

Samples were chipped and pulverized for geochemical analyses. Carbonate and organic carbon abundances were determined gravimetrically during the removal of carbonate with diluted HCl. Subsequently, the following analytical methods for isotope analysis were applied.

2.1 Carbonate carbon and oxygen isotopic compositions

CO₂ for isotope analysis was liberated via phosphorylation with 100% H₃PO₄^[15-17]. Different reaction schemes were applied: 25 °C for 24 h (limestone); 50 °C for 24 h or 75 °C for 16 h (dolomite), and 75 °C for 24 h (other rocks). All carbon and oxygen isotope data were measured on a Finnigan MAT 252 mass spectrometer in Guiyang Institute of Geochemistry, Chinese Academy of Sciences, China. The analytical procedure was controlled by measuring the Guiyang laboratory standard GBW 04406 for its $\delta^{13}\text{C}_{\text{carb}}$ ($\delta^{13}\text{C}_{\text{carb-standard}}$: -10.85‰; standard deviation: 0.05‰) and $\delta^{18}\text{O}_{\text{carb}}$ ($\delta^{18}\text{O}_{\text{carb-standard}}$: -12.40‰; standard deviation: 0.15‰) values. Results are reported as $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ relative to the Vienna Pee Dee Belemnite Standard (VPDB). Standard deviation was usually better than $\pm 0.1\%$.

In order to constrain carbonate diagenesis, elemental abundances were measured for Mn, Fe, Ca, Mg and Sr^[18-22]. Samples were digested in 3 mol/L HCl and elemental concentrations measured with in atomic absorption spectroscope. Results were corrected for the amount of insoluble residue.

2.2 Organic carbon isotopic composition

Organic carbon isotopic compositions were measured from the kerogen fraction for 36 samples. Kerogen extraction was performed according to a procedure modified

after Lewan^[23] and Fu and Qin^[24]: sample powder was dissolved in a mixture of 18% HCl and 40% HF in order to remove carbonates and silicates.

Kerogen carbon isotopic compositions ($\delta^{13}\text{C}_{\text{org}}$) were measured in the Geologisch-Paläontologisches Institut, Westfälische Wilhelms-Universität Münster, Münster, Germany, using an EA-ConFlo-MS. The data are reported in the standard delta notation relative to the VPDB standard.

Kerogen preservation was assessed by its H/C atomic ratio, following the determination of C, H, N elemental abundances.

In addition, organic carbon abundance (TOC) and isotopic composition ($\delta^{13}\text{C}_{\text{org}}$) were measured for 31 samples via sealed quartz tube combustion and subsequent mass spectrometric analysis^[25] at the Geologisch-Paläontologisches Institut, Westfälische Wilhelms-Universität Münster, Münster, Germany. Organic carbon isotope results from the two different analytical procedures agree within 0.3‰.

3 Results

Organic carbon isotope values range between -35.8‰ and -30.1‰ with clear stratigraphic variations (Fig. 1). Associated H/C values for kerogens lie between 0.3 and 1.1. Carbonate carbon isotope data vary between -3.5‰ and +0.5‰ (Fig. 1). $\Delta\delta$ values ($\Delta\delta = \delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$) range from 30.3‰ to 34.6‰.

4 Carbonate diagenesis

Carbonate diagenesis can obliterate primary depositional signatures which reflect seawater chemistry. In general, an increase in the elemental abundances of Fe and Mn and a decrease in Sr concentrations can be observed during diagenesis^[18,26]. An increase in the Mg/Ca ratio indicates progressing dolomitization. Furthermore, diagenesis would cause decreases in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. That reflects the incorporation of CO₂ derived from the oxidation of organic matter during carbonate precipitation and the consequence of meteoric water alteration. In order to quantify the degree of carbonate diagenesis, certain thresholds have been proposed. Only samples with Mn/Sr < 10, $\delta^{18}\text{O} > -10\%$ and $\Delta\delta$ values around $30 \pm 2\%$ (with values up to $33 \pm 2\%$ for organic-rich sediments) are thought to have likely retained their primary carbon isotope signals^[3,20].

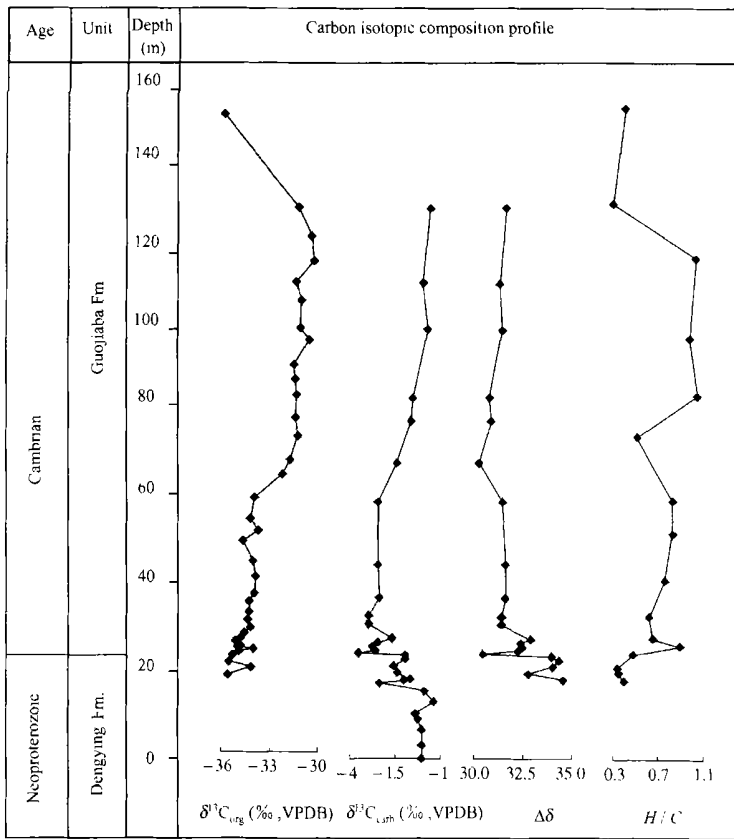


Fig. 1. Stratigraphic variations in $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$, $\Delta\delta$ and H/C for the Shatan section, Nanjiang, Sichuan Province, China.

Mn/Sr ratios determined for carbonates from the Dengying Formation display values between 0.3 and 9.3, with most ratios < 2 . Carbonate oxygen isotope data vary between -12.7‰ and -4.4‰ , with most values < -10 . Hence, carbon isotope values are thought to reflect near primary values.

5 Discussion

The Precambrian-Cambrian transition is one of the critical time intervals in Earth history. Major changes in continental configuration, global climate and biological evolution characterize this time interval, resulting in distinct variations of oceanic and atmospheric chemical compositions^[5, 27, 28]. Furthermore, it is generally believed that geotectonic evolution and climate played important roles in the diversification of life on Earth at the dawn of the Phanerozoic^[1-9, 27].

Stratigraphic variations in $\delta^{13}C_{carb}$ display a decrease from values around 0‰ to a minimum value of -3.5‰ across the Precambrian-Cambrian transition, followed by a gradual increase in $\delta^{13}C$ to values around $+0.5\text{‰}$ in the Lower Cambrian black shales of the Guojiaba Formation. In addition, $\Delta\delta_{org-carb}$ val-

ues fluctuate during Neoproterozoic and lowest Cambrian (Fig. 1), followed by more constant values in the Lower Cambrian. $\delta^{13}C_{org}$ values measured for the black shales of the Guojiaba Formation document a temporal trend which parallels the carbonate carbon isotopic variation.

The evolution towards more negative carbon isotope values across the Precambrian-Cambrian transition followed by a gradual increase in ^{13}C appears to be a prominent feature which has previously been reported from other equivalent successions worldwide^[3, 29]. It reflects temporal variations in global carbon turnover, i. e. a decrease in photosynthetic carbon fixation followed by an increasing demand for carbon dioxide during primary production and subsequent fractional organic carbon burial.

The transition into the Cambrian is marked by the deposition of black shales (Gujiaaba/Niutitang Fm.), suggesting the onset of anoxic conditions. The wide geographic deposition of organic and pyrite-rich black shales across the Yangtze Platform suggest the existence of a large stratified ocean during Early Cambrian time, or at least the existence of numerous isolated anoxic basins in the region. Fluctuations in

$\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ in the lower part of the Guojiaba Fm. suggest rapidly changing environmental conditions. Thus, we cannot rule out the effect of local perturbations. Finally, an evolution to heavier $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ values indicates an increase in organic carbon burial, possibly related to increasing productivity (such as Cambrian bio-radiation).

Secular variations in the carbon isotopic compositions of carbonate and organic carbon are interpreted to reflect perturbations of the global carbon cycle. These are coupled to changing environmental conditions as well as the biological evolution during the terminal Neoproterozoic and its transition into the early Cambrian^[3-9, 30, 31].

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