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# The carbon biogeochemical cycle across the Permian - Triassic boundary strata and its implications: isotope record from the Changhsingian Stage at Meishan, south China

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## ABSTRACT:

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The new dataset of the carbon and oxygen stable isotope values across the sedimentary sequence of the Changhsingian Stage at Meishan, south China documents the carbon biogeochemical cycle in detail. The cycle began with storage of organic carbon ($C_{org}$), mainly as biogenic carbon dioxide in clathrates, and carbon dioxide from anaeorobic methane oxidation (AMO) in the stratified sea water masses, which is reflected by a rapid increase in the $\delta^{13}C$ values. Storage of $C_{org}$ demanded a large biomass productivity, and thus consumption of a vast amount of carbon dioxide, which would have been associated with climatic oceanic water cooling. Oceanic water cooling and enhanced volcanism is actually reflected by a gradual increase in the $\delta^{18}O$ values. The long-term stasis between $C_{org}$ burial and reburial was then achieved, as reflected by the stable course of the $\delta^{13}C$ curve. At the same time, cool water circulation caused a continuous increase in the $\delta^{18}O$ values. At the end of the cycle, several factors including earthquakes and other tectonic movements marking the onset of major Siberian volcanism, together with a local temperature increase resulted in a change of ocean circulation, caused mixing of stratified sea water masses. This was followed by destruction of the existing clathrates, degassing of carbon dioxide, oxidation of organic matter, and a rapid decrease in the oceanic $\delta^{13}C$ values. Apart from the carbon dioxide that was released to the atmosphere, part of the methane must have been oxidised, creating additional carbon dioxide as well as water vapour. The carbon dioxide and water vapour must have initiated a greenhouse effect and caused thermal stratification of seawater which, in turn, initiated reconstruction of the redox in the Early Triassic.

The end of the cycle was associated with the end-Permian mass extinction. The global warming associated with methane release from clathrates led to collapse of terrestrial plants. At the same time, the mixing event brought methane and organic matter for oxidation, which caused massive consumption of oxygen and extinction of the terrestrial fauna. In the marine environment, the mixing event brought water masses rich in carbon dioxide, as well as excess hydrogen ions from anoxic zones, onto shelf areas, causing a collapse of marine biota.

The carbon biogeochemical cycle of the Changhsingian indicated by the initial rapid rise, long-term stasis, and final rapid drop in $\delta^{13}C$ values, seems to be a rule for a pattern of Phanerozoic $\delta^{13}C$ values in sedimentary carbonates. This suggests that a process of methane storage and release may have had a bearing on major geochemical perturbations throughout Earth history. However, methane storage, with or without the association of carbon dioxide and other forms of $C_{org}$, and its subsequent release, could have occurred in many different scenarios throughout the Phanerozoic. Therefore, the end of the carbon cycles may be associated with mass extinction only when release of methane is coupled with other phenomena, which is the case with the end-Permian event.

**Key words:** Meishan, Permian-Triassic boundary (PTB), Carbon isotope record, Biogeochemical cycle, Methane hydrates=Clathrates, Mass extinction.

## INTRODUCTION

The present authors have dealt already with Permo-Triassic sedimentary sections of China, either stressing the value of the isotope geochemistry record at the Permian-Triassic transition (GRUSZCZYŃSKI & *al.* 1990, HOFFMAN & *al.* 1998) or focusing on the precise biostratigraphical distinction between the Permian and Triassic (WANG 1994a, b, 1995, 1996). The impetus for the present study was an opportunity for analysing isotopically the whole sedimentary sequence of the Changhsingian Changhsing Formation, beginning with the latest Wuchiapingian Lungtan Formation and ending with the earliest Griesbachian Yinkeng Formation, from the D and Z sections of Meishan (YIN & *al.* 1996, WANG 1994a, b). Isotope research on that sedimentary sequence has been undertaken quite often (CHEN & *al.* 1984, BAUD & *al.* 1989, YAN & *al.* 1991, XU & YAN 1993, see also YIN & *al.* 1994). However, the research has been concentrated almost exclusively on the end-Permian event and the Permian-Triassic boundary (PTB) itself. Thus, according to AGER'S (1993) motto "Expect the Unexpected", a new dataset may always provide a new inspiration bearing on the origin of the end-Permian geochemical perturbation and on the origin of the Palaeozoic-Mesozoic mass extinction. Last not least, the present authors expected some new information to refresh the established model (GRUSZCZYŃSKI & *al.* 1989; MAŁKOWSKI & *al.* 1989) of the scenario for the Permo-Triassic crisis.

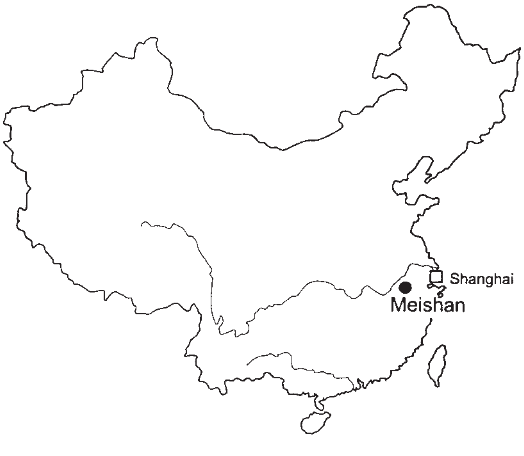


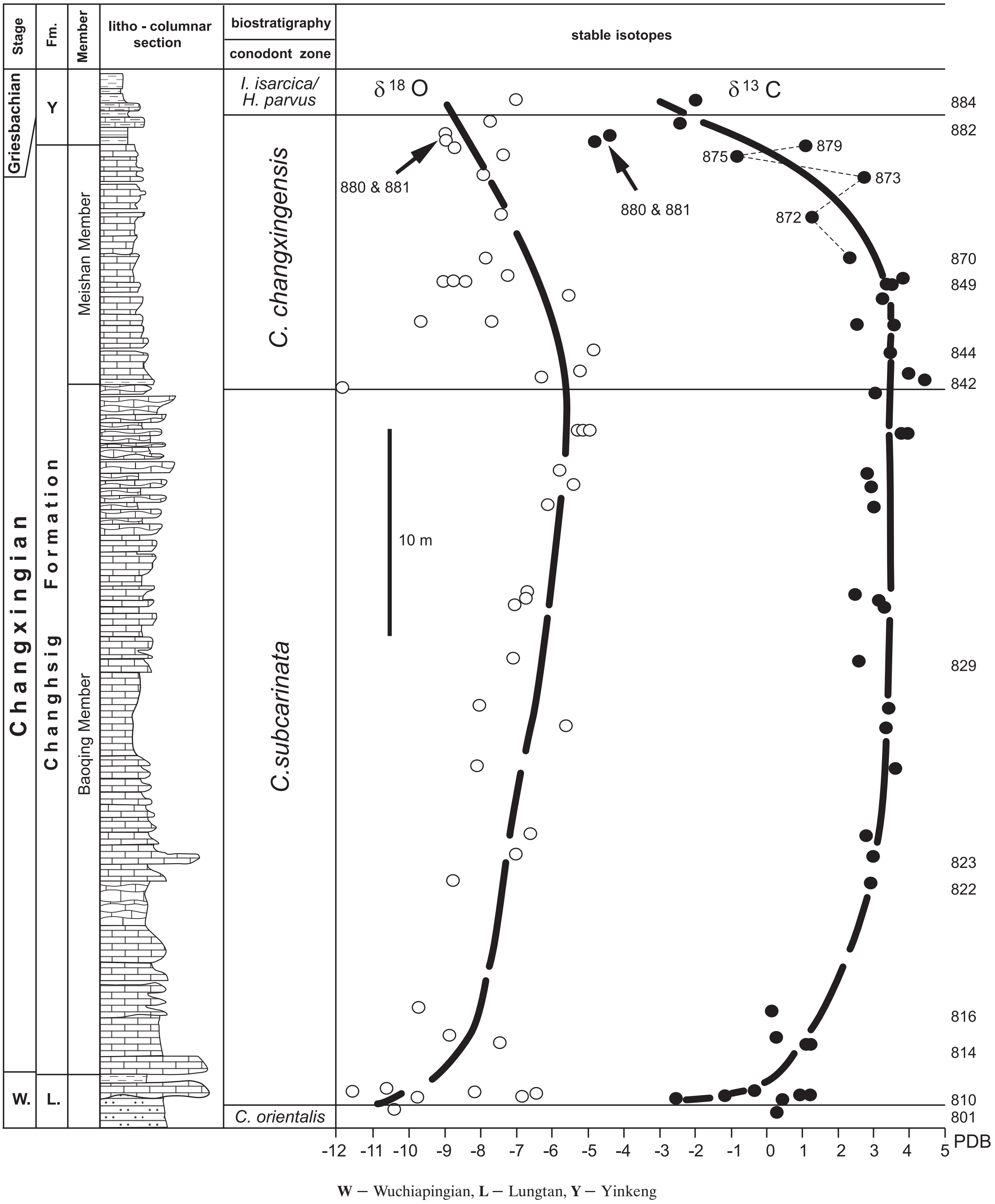
Fig. 1. Simple sketch of China territory showing the Meishan area

### Geological setting of the area

The Meishan area (Text-fig. 1) is located in the eastern part of the Yangtze Plate or the lower Yangtze Platform. In this area Silurian to lower Triassic marine sediments, as well as Jurassic and Quaternary continental rocks are exposed. The examined sections of Late Permian to Early Triassic sediments from Meishan are of great importance. Section Z was first proposed as a stratotype of the PTB (SHENG & *al.* 1984, WANG 1994b, 1995, WANG & *al.* 1996, KOZUR & *al.* 1996). Section D was finally approved as stratotype of the Changhsingian Stage (GAETANI 2000, ZHU & *al.* 2000). Although section D has been accepted recently as a stratotype of the PTB (YIN & *al.* 2001), NICOLL & METCALFE (2001) have suggested a minor hiatus in the middle of Bed 27 (YIN & *al.* 1996) at Meishan on the basis of a comparative study of the Shangsi section. They (NICOLL & METCALFE 2001) have found a 4.5 m of Permian sedimentary sequence in the Shangsi section which is represented by the minor hiatus in the Meishan section.

#### *Lithology and stratigraphy*

The Wuchiapingian Lungtan Formation is represented by sandstones, siltstones and mudstones, with a dark grey coarse-grained limestone at the top (Text-figs 2-2a). The limestone is rich in macrofossils such as the ammonoid *Pseudogastricoceras*, the bivalves *Palaeoneilo* and *Permopecten*, the brachiopod *Spinomarginifera*, and microfossils such as the conodont *Clarkina orientalis* and the foraminifer *Geinitzina* (Beds 1-3 - YIN & *al.* 1996, AEL 801-811 – WANG 1994a,b). The Changhsingian Changhsing Formation is subdivided into two members. The lower Baoqing Member is composed mainly of very fine- to fine-grained limestone including the characteristic ammonoid *Tapashanites* and microfossils – the foraminifer *Palaeofusulina* and the conodont *Clarkina subcarinata* (Beds 4-16 - YIN & *al.* 1996, AEL 812-839 – WANG 1994a,b). The upper



**W** – Wuchiapingian, **L** – Lungtan, **Y** – Yinkeng

Fig. 2. Pattern of the $\delta^{13}C$ and $\delta^{18}O$ values against the composite section of the Changhsingian Changhsing Formation. This section of the Changhsingian Changhsing Formation begins with the latest Wuchiapingian Lungtan Formation and ends with the earliest Griesbachian Yinkeng Formation. The samples AEL 801-849 are from D section of Meishan, whereas AEL 870-887 are from Zhongxin Dadui (Z) section of Meishan. All the AEL by WANG (1994a, b; 1996) are correlated with the beds recognised by YIN & *al.* (1994). For the crucial period covering Mass Extinction event these are as follows: WANG – AEL 847– 849 correspond with YIN – bed 20; WANG – AEL 870-871 YIN – bed 21; WANG – AEL 872 YIN – bed 22; WANG – AEL 873 YIN – bed 23; WANG – AEL 874-879 YIN – bed 24; WANG – AEL 880 YIN – bed 25; WANG – AEL 881 YIN – bed 26; WANG – AEL 882 YIN – bed 27; WANG– AEL 883 YIN – bed 28; WANG – AEL 884-885 YIN – bed 29

Meishan Member is represented by medium-grained bioclastic limestone with intercalations of fine-grained limestone and chert. The limestone contains the ammonoid *Pleuronodoceras*, the foraminifer *Palaeofusulina* and the conodont *Clarkina changxingensis* (Beds 17-24 – YIN & *al*. 1996, AEL 840-879 – WANG 1994a, b). The Griesbachian Yinkeng Formation begins with marl and marly limestone, passing gradually into very fine- to fine-grained limestone. Typical Mesozoic fossils include the bivalve *Claraia*, the ammonoid *Ophiceras* and the conodont *Isarcicella* (from Bed 27c upwards – YIN & *al*. 1996, from AEL 882(3) upwards – WANG 1994a, b). The lowermost part of the Yinkeng Formation is the PTB sedimentary sequence (YIN & *al*. 1996), including three Mixed Beds (SHENG & *al*. 1984) or Boundary Beds (WANG 1994b). Boundary Bed 1 is usually called the "Boundary Clay". It starts with the "White Clay", consisting of light coloured illite-montmorillonite claystone (Bed 25 – YIN & *al*. 1996; AEL 880 – WANG 1994a, b), and is covered by the "Black Clay" consisting of dark coloured montmorillonite-illite claystone (Bed 26 – YIN & *al*. 1996, AEL 881 – WANG 1994a, b). The "White Clay" contains remains of typical Permian macro- and microfaunas, whereas the "Black Clay" includes some Triassic ammonoids and bivalves (SHENG & *al*. 1984; WANG 1984). Boundary Bed 2 is represented by light grey silty limestone containing the diagnostic Triassic conodont *Hindeodus parvus* (ZHANG 1984; WANG 1994a, b; 1995). WANG (1994a, b) recognised the first appearance of *Hindeodus parvus* at the base of the upper half of Boundary Bed 2 (Bed 27c – YIN & *al*. 1996, AEL 882-3 – WANG 1994a, b), thereby locating the position of the PTB itself (WANG 1994a, b, 1995, 1996, 1999, YIN & *al*. 1994). Boundary Bed 3

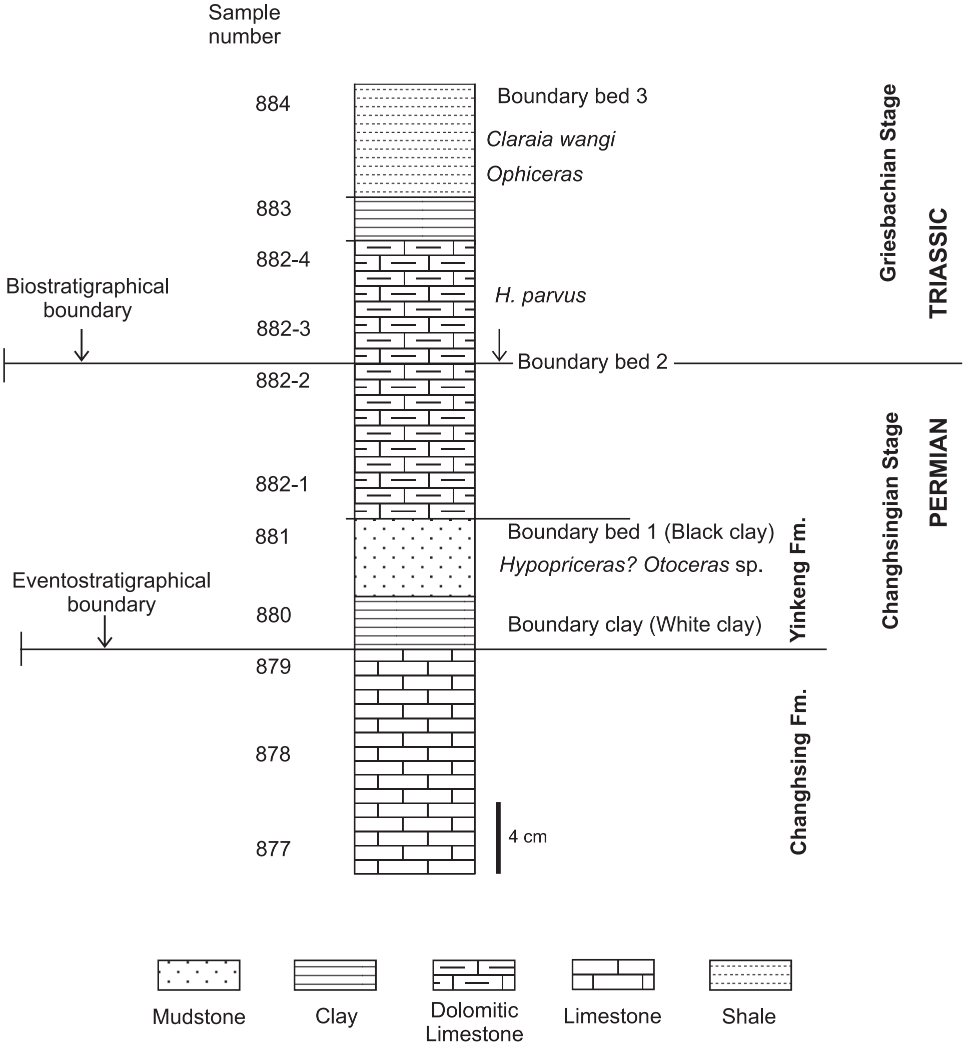


Fig. 2a. The Permo-Triassic biostratigraphical and event-stratigraphical boundaries in South China (after WANG 1994a, b)

(Beds 28-31 – YIN & *al*. 1996, AEL 883-887 - WANG 1994a,b) consists of clay and marl and contains typical remains of the earliest Triassic fauna, which is an *Isarcicella isarcica-Ophiceras-Claraia* assemblage with an admixture of Permian brachiopod relics.

### Materials and methods

All the samples were taken by Wang Cheng-yuan from the sedimentary sequence of the latest Wuchiapingian Lungtan Formation, Changhsingian Changhsing Formation and the Boundary Beds, namely from the D and Z sections. The samples were numbered according to the WANG (1994a, b) terminology and correlated with beds distinguished by YIN & *al*. (1994). Samples AEL 801-849 are from the D section of Meishan, whereas AEL 870-887 are from the Z (Zhongxin Dadui) section of Meishan. Samples AEL 801-849 come from Beds 1-20 (YIN & *al*. 1996), whereas samples AEL 870-887 come from Beds 21-31 (YIN & *al*. 1996). We have selected portions of fine-grained limestones and analysed them petrographically to find sectors of uniform micrite for isotope analysis. The assumed common burial history for the whole Changhsingian sedimentary sequence suggests that any diagenetic alteration was relatively insignificant and can be ignored. The $\delta^{13}$C values, at least, should not have differed from the original values (MARSHALL 1992). There is an exception to the above 'rule', namely samples taken from the "Boundary Clay" where calcium carbonate displays depleted $\delta^{13}$C and $\delta^{18}$O values (Text-fig. 2) resulting either from degradation of organic matter (COLEMAN 1985) or from meteoric or burial waters (HUDSON 1977).

We have selected 41 samples for analyses, some of which were analysed twice or three times to check reproducibility of the results. Samples were analysed for the $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O ratios using a Finigan MAT DELTA+ mass spectrometer, and the results have been expressed as ‰ versus the Vienna PDB standard.

## RESULTS AND DISCUSSION

### Description of the $\delta^{13}$C and $\delta^{18}$O values pattern through the investigated sections

In the case of the $\delta^{13}$C values, the starting point is almost –3‰ for sample AEL 810 (Bed 2 – YIN & *al*. 1996) immediately above the base of the *Clarkina subcarinata* conodont Zone (Text-fig. 2, ZHANG & *al*. 1996). The negative and positive excursions of carbon stable isotope range up of 4‰. The average value rises rather rapidly to 0.5‰ for samples AEL 814-816 (Beds 4b-5 – YIN & *al*. 1996) in the early *Clarkina subcarinata* Zone. $\delta^{13}$C values continue increasing, reaching values higher than 2.5‰ for samples AEL 822-823 (Beds 9-10 – YIN & *al*. 1996), and then stabilise, still in the lower part of the *Clarkina subcarinata* Zone. The trend of increasing $\delta^{13}$C values seems to be rather rapid, being biostratigraphically limited to the lower part of the *Clarkina subcarinata* Zone. The subsequent oscillating but stable course of the $\delta^{13}$C values reaches its maximum of 4.4‰ for sample AEL 842 (Bed 18 – YIN & *al*. 1996), at the base of the *Clarkina changxingensis* Zone. The stable course of $\delta^{13}$C values ends in between samples AEL 849 and 870 (Beds 20-21 – YIN & *al*. 1996), in the middle of this zone. A subsequent trend of decreasing, albeit widely fluctuating, $\delta^{13}$C values (Text-fig. 2) between samples AEL 870 and 879 (Beds 21-24 – YIN & *al*. 1996) is observed, until the values reach average minimum values of –2‰ for samples AEL 882 (Bed 27 – YIN & *al*. 1996) and 884 (Bed 29 – YIN & *al*. 1996), these being the latest Permian and the earliest Triassic samples respectively. The profound drop of about 6‰ in the $\delta^{13}$C values was rather rapid, embracing part of the Late Permian *Clarkina changxingensis* Zone, as well as the Early Triassic *Hindeodus parvus* Zone and the *Isarcicella isarcica* Zone (ZHANG & *al*. 1996). It appears that the rate of increase in $\delta^{13}$C values at the beginning of the Changhsingian was equal to the rate of decrease in those values at the end of the Changhsingian.

$\delta^{18}$O values show a very large range, of almost 6‰, between the more negative and more positive values, with a starting point of –10.5‰ for sample AEL 810 (Bed 2 – YIN & *al*. 1996), just above the base of the *Clarkina subcarinata* Zone (Text-fig. 2, ZHANG & *al*. 1996). Average $\delta^{18}$O values rise to –8.5‰ for samples AEL 814-816 (Beds 4b-5 – YIN & *al*. 1996). Thereafter, the gradual rise in $\delta^{18}$O values continues, reaching –5.5‰ not far below the base of the *Clarkina changxingensis* Zone. $\delta^{18}$O values then rise until an absolute maximum of –4.8‰ for sample AEL 844 (Bed 19 – YIN & *al*. 1996), not far above the base of the *Clarkina changxingensis* Zone. Above this level, a decreasing, albeit widely fluctuating, trend in $\delta^{18}$O values begins, up to sample AEL 872 (Bed 22 – YIN & *al*. 1996) with $\delta^{18}$O value of –8‰. Thereafter, a slight and gradual decrease in $\delta^{18}$O values is observed, until average values of –9‰ are reached at the PTB.

The absolute minima for both the $\delta^{13}$C (less than –5‰) and $\delta^{18}$O (less than –8.5‰) values for samples AEL 880 and 881 (Beds 25 and 26 – YIN & *al*. 1996, fig. 2) are most probably a result of diagenetic alteration, because the samples were taken from the Boundary Bed 1, i.e. the "White Clay" and "Black Clay" (Text-fig. 2a). Moreover, according to CAO & SHANG (1998), the existence of some bored hardgrounds and a faintly laminar black calcilutite crust within the boundary beds, suggest that the succession is both condensed and incomplete. As noted earlier, Metcalfe & *al.* (2001) have actually suggested that 4.5 m of the correlative Shangsi section are represented by an hiatus in the middle of AEL 882 (Bed 27 – Yin & *al.* 1996, just at the PTB position) in the Meishan section.

**Interpretation of the carbon and oxygen isotope record**

What we have described above is a geochemical cycle characterised by a change of the carbon and oxygen stable isotope values from low to high and then to low again, which is evident for the $\delta^{13}C$ curve, but not so clear for the $\delta^{18}O$ curve. This is different from comparable changes in the carbon and oxygen stable isotopic record in ancient carbonate systems that have been observed not only at the PTB (Gruszczyński & *al.* 1989, 1990) but in many other Phanerozoic examples (Hoffman & *al.* 1991). This might suggest that the factors controlling the biogeochemical carbon cycle were not entirely the same as those controlling the oxygen cycle, which was additionally controlled by other factors such as temperature or features of the hydrological cycle (Hoffman & *al.* 1991).

The rapid increase in $\delta^{13}C$ values from ~ – 0.5‰ to 3.5‰ at the beginning of the Changhsingian may have been related, according to the Spitzy & Degens (1985) formula:

$$N_B = N_A \frac{[1+\delta_{std.}\,(1+\delta_B/1{,}000]\;(\delta_A - \delta_M)}{[1+\delta_{std.}\,(1+\delta_A/1{,}000]\;(\delta_M - \delta_B)}$$

where $N_A$ is the initial reservoir mass of carbon, $N_B$ is the perturbing mass and $\delta$ denotes the isotopic compositions in standard notation, with subscripts indicating (A) initial, (B) perturbing, (M) resulting and the reference standard (std.) values, to the withdrawal from the system of a certain amount of carbon enriched in the light isotope. Assuming an oceanic dissolved inorganic carbon (DIC) reservoir as large as the present day one, 40000 GT=40000* $10^{15}$g (Holland 1978), such a change requires either 18824 GT=18824* $10^{15}$g of carbon of volcanic and/or hydrothermal origin ($\delta^{13}C$ ~ –5‰) or 13170 GT=13170* $10^{15}$g of carbon of terrestrial plant origin ($\delta^{13}C$ ~ –25‰) to be withdrawn from the system. This implies a decrease of almost 23 times the present day volcanic and hydrothermal activity, assuming a yearly flux of Mid Oceanic Ridges (MOR) $CO_2$ of 0.0082* $10^{15}$g (Pytkowicz 1983) and a maximum time span for the isotopic perturbation of 1* $10^5$y. Alternatively, it implies a decrease of more than 3 times the present day terrestrial DIC runoff to the ocean (mainly by riverine flux=RF), assuming a yearly flux of DIC, from land to the sea, of 0.4* $10^{15}$g (Sundquist 1985). To achieve this, either a decrease in land plant vegetation of the order of 30 times the recent terrestrial plant biomass (420 GT=420* $10^{15}$g, Sundquist 1985) is required, or alternatively storage of $C_{org}$ in the form of coal. However, diminished hydrothermalism and volcanism cannot be seriously considered since the Upper Permian Maimecha-Kotui volcanics prove the development of the Siberian Traps (Venkatesan & *al.* 1997). On the other hand, such a dramatic decline of terrestrial vegetation seems to be hardly recorded in the geological past, and sequestration of $C_{org}$ as coal would have prevented its easy mobilization. In conclusion, the decrease in RF and terrestrial vegetation, as well as the decrease in MOR and terrestrial volcanism, would not have been sufficient to account for the positive shift of the carbon isotope values.

In the former model (Gruszczyński & *al.* 1989, Małkowski & *al.* 1989), we assumed storage of $C_{org}$, in the form of particulate organic carbon (POC), dissolved organic carbon (DIC) and carbon dioxide derived from the degradation of organic matter by sulphate-reducing bacteria. However, in such a case the amounts of $CO_2$ required to have brought about such a geochemical perturbation must have been astronomical, and therefore we have to consider another source of carbon relatively enriched in the light isotope, such as clathrates. In modern marine sediments with a high content of organic matter, sulphate concentrations are likely to be largely depleted (Nissenbaum & *al.* 1972, see also Goldhaber & Kaplan 1974 for review). Under such anoxic conditions, degradation of organic matter via sulphate reduction is replaced by methanogenesis to produce methane and water (Irwin & *al.* 1977, Irwin 1980). This methane can be stored in the ice-like compounds called clathrates, in which it is trapped in crystalline cages formed by water molecules (Miller 1974, McDonald 1992). The amount of methane that can be stored in clathrates is impressive, up to 122 kg in a cubic metre of fully filled clathrate (McDonald 1992). Clathrates are stable only under certain conditions of temperature and pressure (Claypool & Kaplan 1974, McDonald 1992), for example at depths greater than 600 m (less than 26 bars), mathane clathrate is stable at temperatures lower than 8°C. Furthermore, the modern carbon reservoir in clathrates is 11500 GT=11500* $10^{15}$g (McDonald 1992), thus more than 1/3 of the present day oceanic carbon reservoir (Holland 1978).

This leads us to the inferred scenario of the Changhsingian event. In the anoxic zones of the ocean, storage of $C_{org}$ as clathrates, as $CO_2$ from the degradation of organic matter by sulphate- reducing bacteria and/or AMO, and as POC, shifted the carbon isotope curve towards more positive values. This shift requires, according to the Spitzy & Degens (1985) formula, approximately 14500 GT=14500* $10^{15}$g of marine planktonic carbon with an admixture of terrestrial plant carbon (assuming $\delta^{13}C$ ~ –20*‰*) to be stored, which means burial of almost 26 times the recent living biomass. In terms of methane, assuming a $\delta^{13}C$ value ~ –50*‰* (which is the value for the calcite in the concretions of the AMO source, COLEMAN, GRUSZCZYŃSKI, WAKSMUNDZKI & ISAACS *in prep*.), approximately 2600 GT=2600* $10^{15}$g of methane carbon, which is less than 1/7 of the recent methane reservoir, needed to be stored. Therefore, storage of the abovementioned mentioned forms of $C_{org}$ might be quite reasonable. On the other hand, storage of $C_{org}$ required above average primary productivity, and this would have been associated with $pCO_2$ depletion, and consequently with cooling of oceanic water. This would have shifted $\delta^{18}O$ also towards more positive values. A continuous and gradual increase in $\delta^{18}O$ values may also have been a reflection of enhanced volcanism, for volcanic and/or hydrothermal emanations are slightly enriched in the heavy isotope of oxygen (MUEHLENBACHS & CLAYTON 1976**,** MUEHLENBACHS 1986). There is independent evidence of igneous rocks for the Maimecha-Kotui volcanic event connected with the Siberian Traps (VENKATESAN & *al*. 1997, for review see WIGNALL 2001).

The subsequent stable course of the $\delta^{13}C$ curve reflects the long-term stasis between $C_{org}$ burial and reburial that was achieved up to the Late Changxingian (Text-fig. 2). On the other hand, the $\delta^{18}O$ values increase continuously, which might reflect cool water circulation, for volcanic basalt emanations associated with the Maimecha-Kotui phase of the Siberian Traps seems to be reducing at that time (VENKATESAN & *al.* 1997, for review see WIGNALL 2001).

The end of the geochemical cycle is finally manifested by a shift in both the $\delta^{13}C$ and $\delta^{18}O$ curves towards more negative values. The change in the seawater carbon isotope composition was from $\delta^{13}C$ values of ~ 4*‰* to –2*‰* at the end of the Changhsingian. According to the Spitzy & Degens (1985) calculations, this shift requires the addition of 78568 GT=78568* 1015g of carbon of volcanic and/or hydrothermal origin ($\delta^{13}C$ ~ –5*‰*), thus an increase of almost 96 times present day volcanic and/or hydrothermal activity. The onset of maximal Siberian volcanism is dated to the Permian-Triassic transition (RENNE & *al.* 1995, VENKATESAN & *al.* 1997, for review see WIGNALL 2001; Text-fig. 2 – AEL 880 – WANG 1994a, b, Bed 25 – YIN & *al.* 1996), therefore the volcanism would have supplied the amount of the light isotope of carbon only at the end of the existing ongoing isotope perturbation (Text-fig. 2). Moreover, the figure of 78568 GT from the SPITZY & DEGENS (1985) calculations is many orders of magnitude greater than the figures of 1000 GT (ERWIN 1993), 2000 – 13 000 GT (BERNER 2002) and 10 000 GT (WIGNALL 2001) calculated from the assumed $CO_2$ emanations from the Siberian Traps. As for the enhanced runoff, according to the SPITZY & DEGENS (1985) calculations, the shift in $\delta^{13}C$ would have require 49535 GT=49535* 1015g of carbon derived from terrestrial plants ($\delta^{13}C$ ~ *-25‰*) to be introduced to the seawater carbonate system. This would imply a devastation of slightly less than 100 times the Recent terrestrial biomass (560 GT=560* $10^{15}$g, SUNDQUIST 1985). Indeed, there is an example of increased RF into shallow shelf regions related to the end-Permian mass extinction (WARD & *al.* 2000) but there are no qualitative data. It seems that both volcanic emanation and RF might have played a role in the negative shift of the $\delta^{13}C$ curve, but not the major role. Consequently, a shift in both $\delta^{13}C$ and $\delta^{18}O$ curves towards more negative values could reflect mixing of stratified sea water masses and an increase in seawater temperatures. This might have been due to a trigger mechanism of combining several factors, including earthquakes and other tectonic movements marking the onset of major Siberian volcanism, and a local temperature increase changing the ocean circulation. The maximum of Siberian volcanism, as mentioned above, is dated to the Permian -Triassic transition (RENNE & *al.* 1995, VENKATESAN & *al.* 1997, for review see WIGNALL 2001), however the onset of such immense volcanism should have been associated with vigorous tectonic movements including earthquakes, and occasionally with continental slope slumping.

A local increase in temperature of the water masses is actually postulated at the end of the Permian (BEAUCHAMP & BAUD 2002, see also YIN & *al.* 1996, WIGNALL 2001). This might have caused mixing due to a change of oceanic circulation and possible downwelling of warm and salty water masses. Neglecting salinity changes (EPSTEIN & MAEYDA 1953) and assuming no polar ice cups (HARLAND & HEROD 1975, IMBRIE & IMBRIE 1986), a rise in sea water temperature of maximally 7°C, can be calculated from the almost 2*‰* decrease in average $\delta^{18}O$ values at the end of the Permian (Text-fig. 2). This is just slightly more than the rise in temperature calculated or assumed elsewhere (YIN & ZHANG 1996, WIGNALL 2001) Such a rise in temperature would also have been enough to lower the lysocline sufficiently to release at least 1200 GT of methane from the clathrates (DICKENS & *al.* 1997). According to the SPITZY & DEGENS (1985) calculations almost 4800 GT=4800* $10^{15}$g of methane carbon and carbon dioxide of AMO origin ($\delta^{13}C$ ~ –50*‰*) is needed for the observed change in the $\delta^{13}C$ values at the end of Permian. This amount of methane is slightly higher than the amount determined (ERWIN 1993) or calculated (BERNER 2002), however it is still about 1/3 of the recent reservoir of methane. Since ERWIN's (1993) assumption on release of methane being essential in explanation of the negative shift in the $\delta^{13}C$ values at the PTB, a lot of new evidence has been found, also in the earliest Triassic, of a vast amount of destruction of clathrates in both the marine and terrestrial environments (MORANTE 1996, KRULL & RETALLACK 2000, KRULL & *al.* 2000). In the case of our model, apart from methane and AMO carbon dioxide, vast amounts of $CO_2$, produced due to the degradation of organic matter by sulphate-reducing bacteria and by the oxidation of POC would also have affected the oceanic carbon stable isotope composition. The combined effect of all this, was certainly enough to have been reflected by the initial negative shift in the $\delta^{13}C$ curve. Finally, the predicted effect of seawater mixing bearing on the shift in the $\delta^{34}S$ curve (HOFFMAN & *al.* 1991) and $^{87}Sr/^{86}Sr$ curve (GRUSZCZYŃSKI & *al.* 1992) was recently observed in the sedimentary sections of Meishan (KAIHO & *al.* 2001), confirming our model.

Apart from the $CO_2$ released to the atmosphere, part of the methane must have been oxidised ethane must have been oxidised, creating additional $CO_2$ as well as water vapour. This $CO_2$ and water vapour must have initiated a greenhouse effect and caused thermal stratification of the seawater which, in turn, initiated reconstruction of the redox in the Early Triassic. A greenhouse effect is certainly observed in the Early Triassic (RETALLACK 1999), and the existence of stratified sea water masses has been modelled (HOTINSKI & *al.* 2001) or interpreted from Early Triassic sedimentary sequences around the world (WIGNALL & HALLAM 1993, WIGNALL & *al.* 1996, HALLAM & WIGNALL 1997).

## End of the carbon cycle and the end-Permian mass extinction: possibilities and myths

The end-Permian mass extinction in Meishan is postulated to have been rapid (JIN & *al.* 2000) and to have taken place 251 My ago (BOWRING & *al.* 1998). Apart from having been abrupt, the end-Permian mass extinction seems to have been synchronous across Gondwana (ESHET & *al.* 1995, LOOY & *al.* 1999, SMITH & WARD 2001) and around the Tethys and Severdrupian Basin (TWITCHETT & *al.* 2001). Assuming almost instantaneous mass extinction, equal instantaneous, massive processes that might have caused the extinction have been considered, including: (i) sudden upwelling or turnover of stratified sea water portions releasing toxic levels of $CO_2$ to the atmosphere (KNOLL & *al.* 1996); (ii) methane release leading to an instantaneous drop in the $\delta^{13}C$ values and a small rise in atmospheric $CO_2$ (due to $CH_4$ oxidation), not enough for mass mortality because of greenhouse warming (BERNER 2002), but perturbing the stratospheric ozone, thereby allowing catastrophic influence of UV-B radiation on the terrestrial flora (VISSCHER & *al.* 2001 in BERNER 2002), and lowering the $O_2$ amounts in the atmosphere (DICKENS 2001); (iii) carbon dioxide emanations from the Siberian Traps postulated to have been synchronous with the mass extinction (RENNE & *al.* 1995) and causing mass mortality by means of the greenhouse effect and acid rain; (iv) an extraterrestrial impact in the form of meteorites (BECKER & *al.* 2001) or an asteroid or a comet (KAIHO & *al.* 2001) hitting the Earth caused sudden mass mortality of the terrestrial biota and marine plankton leading to “strangelove” ocean conditions (BERNER 2002), and a further biotic crisis because of toxic levels of $CO_2$ and oxygen consumption, and acid rain (KAIHO & *al.* 2001); (v) reorganisation of the carbon cycle involving a drop in the global $C_{org}$ burial rate between the Permian and Triassic periods (BERNER 2002) due to a sudden drop in terrestrial productivity (VISSCHER & *al.* 2001) and a shift from a high biomass to a low biomass flora (ESHET & *al.* 1995, LOOY & *al.* 1999); this is, however, a specific case of hypothesis (iv). Considering all the hypotheses for explaining the synchronous mass extinction and negative shift in the $\delta^{13}C$ curve, BERNER (2002) concluded that extraterrestrial impact causing mass mortality, together with methane release and volcanic $CO_2$, might have been responsible for the end-Permian extinction (see also BOWRING & *al.* 1998).

Unfortunately, although we cannot exclude the existence of extraterrestrial impacts in the geological past, it is difficult to invoke extraterrestrial forces as an essential cause of the end-Permian mass extinction. Firstly, it is well known that the Earth has suffered a yearly shower of extraterrestrial material of 1 GT. Sedimentary sequences at the Permian-Triassic transition are always condensed and therefore the sediments should be enriched, in any case, in extraterrestrial material. Secondly, there is obvious enrichment in Ni, believed to be extraterrestrial (KAIHO & *al.* 2001), within the sediment layer corresponding to the time of extinction. Ni, as well as Co, are known to be associated with organic matter (ŁĄCKA, *pers. comm.*), and mass mortality must have provided an enrichment of organic matter in the sediment, and consequently of Ni. Thirdly, evaporation of reduced sulphur due to the bolide hitting the ocean (KAIHO & *al.* 2001), and its oxidation and precipitation as acid rain to cause mass mortality is simply unrealistic. According to the SPITZY & DEGENS (1985) formula, the mass of sulphur to be vapourized, oxidized and returned to the ocean to shift the $\delta^{34}S$ values by ~ 20‰ to ~ 5‰ requires more than 2.5 times the possible total of sulphur in the oceans. This amount is many times larger than that calculated from the WORDEN & *al.* (1997) models, and at least 5 times larger than that calculated by KAIHO & *al.* (2001). As for the volcanic emanations of $CO_2$ which might have been one among the many reasons for the end-Permian mass extinction, it seems that the major pulse of volcanism was slightly later than the major episode of mass mortality (WIGNALL 2001).

In our model it is clearly visible (Text-fig. 2) that mass extinction followed the onset of the negative shift in the $\delta^{13}C$ curve. Thus, reasons for that shift would be primary causes for the end-Permian mass extinction. The effect of global warming is inferred to have caused both the collapse of terrestrial production (VISSCHER & *al*. 2001), because of the devastating activity of a huge population of insects (HALLAM & WIGNALL 1997), and a shift in productivity from a high biomass to a low biomass flora (ESHET & *al*. 1995, LOOY & *al*. 1999). All this was probably associated with the release of methane from terrestrial clathrates (KRULL & RETALLACK 2000, KRULL & *al*. 2000). At the same time the mixing event brought methane and AMO carbon dioxide, vast amounts of $CO_2$, produced by the degradation of organic matter by sulphate-reducing bacteria and by oxidation of POC. All this must have led to the predicted (HOFFMAN & *al*. 1990, DICKENS 2001) massive consumption of oxygen, causing extinction of the terrestrial fauna (SMITH & WARD 2001), and a high partial pressure of carbon dioxide ($pCO_2$) and a low $O_2$ level in the atmosphere (SHELDON & RETALLACK 2002, see also BERNER 2002). In the marine environment, the water masses of high $pCO_2$ and excess hydrogen ions brought by the mixing event from the anoxic zones onto shelf areas must have caused a collapse of marine productivity (WANG & *al*. 1994). Such conditions we buffered by dissolution of shelf water carbonates (MAŁKOWSKI & *al*. 1991). In addition, a mixing event disturbing oceanic circulation caused expansion of the anoxic zones into certain shallow water regions of Panthalasa (ISOZAKI 1997) and Tethys (WIGNALL & TWITCHETT 1996) leading to hypocapnia and mass mortality.

### Changhsingian - the only carbon cycle in the Phanerozoic?

A general prediction for the existence of $C_{org}$ deposition and release cycles might be drawn from the natural tendency of redox stratified systems for temporary mixing (HOFFMAN & *al*. 1990). Most probably, the worldwide Palaeozoic ocean showed a tendency for stratification of the water masses (BERRY & WILDE 1978, HOFFMAN & *al*. 1991, KNOLL & *al*. 1996). The great Ordovician and Permo-Carboniferous glaciations do not appear to have affected this tendency towards stratification. The secular $\delta^{13}C$ and $\delta^{18}O$ clearly show a trend of rising values over time from the Cambrian until the Late Permian (HOLSER 1984, POPP & *al*. 1986, VEIZER & *al*. 1986), with distinctive cycles of initial rising and final falling of the isotope values (VEIZER & *al*. 1999), very much like the cycle recorded in the Changhsingian. The cycles were not so pervasive during the Mesozoic (VEIZER & *al*. 1999), because of the development of continental biota and many new exogenic feedback reactions. Because methane is considered to be the main factor influencing a cycle, the most plausible explanation of such cyclicity is initial binding of methane in clathrates and its subsequent release due to oceanographic, orogenic, climatic, or other internal changes of the ancient Earth exosystem. A geochemical cycle showing comparable features to those of the Changsinian cycle was recently documented for Early Jurassic times (HESSELBO & *al*. 2000, see also for review WEISERT 2000). This cycle was associated with the end-Toarcian mass extinction, and the sudden drop in $\delta^{13}C$ values was explained by methane release from the clathrates (HESSELBO & *al*. 2000). Mass extinctions were of different intensities throughout the Phanerozoic (SEPKOSKI 1989), and may have been related to the intensity of the geochemical perturbations associated with the termination of the carbon cycles. On the other hand, the end of many of the cycles associated with the release of methane cannot be generally associated with mass extinctions, for these must have been caused by a combination of many processes occurring within the Earth's exosystem.

## CONCLUSIONS AND IMPLICATIONS

Interpretation of the new carbon and oxygen isotope record across the sedimentary sequence of the Changhsingian Stage revealed a new scenario for the end-Permian geochemical cycle.

The biogeochemical carbon cycle of the Changhsingian indicated by the initial rapid rise, long-term stasis, and final rapid drop in the $\delta^{13}C$ values, seems to be a rule for the pattern of Phanerozoic $\delta^{13}C$ values in sedimentary carbonates. Such a cycle is not only observed at the Permian-Triassic transition but is also noted for the Early Jurassic.

This suggests that a process of methane storage and release may have had a bearing on major geochemical perturbations throughout Earth history. Of course, methane storage (with or without the association of carbon dioxide and other forms of $C_{org}$), and its subsequent release, could have occurred in several different scenarios throughout the Phanerozoic. Those final stages of the carbon biogeochemical cycles, reflected by falls in the $\delta^{13}C$ curve, were of different intensity during the Phanerozoic, as were the mass extinctions. This might have been caused by a single factor, or a combination of factors, including a decrease in the oxygen level in the atmosphere as a result of methane oxidation, and a temporary pH decrease due to large amount of $CO_2$ in the atmosphere-ocean system and an excess of hydrogen ions in the surface waters, and also by a limitation of nutrient supply. Such a system must have been pervasive for the Paleozoic and less significant in the Mesozoic. In conclusion, the end of geochemical carbon cycles may be associated with mass extinction, but only when release of the methane is coupled with other phenomena, reflected by the immense and rapid drop in the $\delta^{13}$C values, which is the case of the end-Permian event.

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