Oxygen isotope geochemistry of phosphorite and dolomite and palaeo-ocean temperature estimation: A case study from the Neoproterozoic Doushantuo Formation, Guizhou Province, South China^{*}

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Abstract The Neoproterozoic Doushantuo Formation at Weng' an in Guizhou Province of South China consists of phosphorites and dolomites. Three types of samples are recongnized for the phosphate-bearing rocks. In Type I samples interstitial phosphates occur within the dolomite rocks, whereas in Type III samples, interstitial dolomites occur within the phosphorites; both of them may have diagenetic or rigin. The Type II samples are interbedded phosphorites and dolomites. Oxygen isotopic compositions of phosphate and coeval carbonate were analyzed. Phosphates of Type I and II samples show similar low $\partial^{18}O_{phos}$ (SMOW) values of 10. 9‰~ 12. 1‰ and 10. 7‰~ 12. 8‰ respectively, whereas Type III phosphates show higher $\partial^{18}O_{phos}$ (SMOW) values of 13. 2‰~ 15. 0‰. Dolomites from Type I and II samples show low er $\partial^{18}O_{arb}$ (PDB) values of $-6.2\%\sim-3.4\%$ and $-2.2\%\sim-0.7\%$, respectively, whereas in terstitial dolomites from Type III samples show low er $\partial^{18}O_{carb}$ (PDB) and $\partial^{13}C_{carb}$ (PDB) and $\partial^{13}C_{carb}$ (PDB) values of $-12.9\%\sim-8.6\%$ and $-4.4\%\sim-2.6\%$. Petrology and oxygen isotope data suggest that diagenetic alteration may have partially affected the studied rocks, but the dolomites from Type I and phosphates from Type III samples represent the most pristine isotopic compositions of primary carbonates and phosphates precipitated from seawater. Calculations of palaeocean temperatures from the most ¹⁸O enriched dolomite and phosphate indicate a temperature range of 32. 2 °C to 34. 0 °C for the seawater of the Doushantuo Formation period. Ce anomaly also suggests more oxic conditions and possibly shallower water depth in the upper strata of the Doushantuo Formation at Weng' an, Guizhou Province.

Keywords: oxygen isotopes phosphate dolomite Doushantuo Formation. Neoproterozoic South China.

Chemical and biogenic sediments such as carbonate and phosphate have long been used to reconstruct paleoenvironmental change. These rocks have the potential to preserve pristine isotopic compositions in equilibrium with ocean water during their deposition in the Phanerozoic^[1,2], or even in the Neoproterozoic^[3,4]. Many researchers have suggested that ocean water has undergone minor changes in terms of oxygen isotopic composition in the Phanerozoic, although a few also have proposed an opposite view with a secular change of seaw ater δ^{18} O through time^[1~6]. Diagenetic effects on isotopic compositions of marine sediments or some fossils have been often observed 7^{-9} . Hence, paleoenvironmental studies using stable isotopes of marine sediments should be cautious and should be based on detailed geological, petrological and geochemical studies. Recent study of Wenzel et al.^[8] showed that Silurian phosphatic conodont retained primary oxygen isotopes whereas the がの values of the coeval calcitic brachiopod shells were likely altered by diagenesis. In this study, we analyzed oxygen isotopic compositions of Neoproterozoic phosphorite from the Yangtze Platform in Guizhou. Together with detailed petrological investigation and studies of C-O isotopes of coeval dolomite and trace and rare earth elements of the samples, we attempt to obtain paleoenvironmental information especially palaeo-ocean temperatures for the Neoproterozoic Doushantuo interval in South China.

1 Geological setting of the studied section

The Yangtze Platform in South China offers one of the best preserved stratigraphical records in the world from the Neoproterozoic to early Cambrian era. Within the Neoproterozoic Doushantuo Formation in the Yangtze Platform occur phosphorite-bearing layer (s) of varying thickness in various regions that con-

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tain exquisitely preserved eggs and embryos^[10,11]. Phosphorite layers of economical significance have been mined in several areas in Guizhou Province^[12]. In this study, we examined a section of the Doushantuo Formation and collected samples of phosphorite and co-existing dolomite in the famous Weng' an phosphorite mine area. In this location, phosphatized biotas preserve abundant acritarchs and multicellular organisms in remarkable cellular detail and provide a particularly informative window on ancient life^[10, 11]. Fig. 1 shows the stratigraphic positions of the Doushantuo Formation at Weng' an, which consists mainly of phosphorite and interbedded dolomite. The Doushantuo Formation overlies the Marinoan (~590 ~610 Ma) tillite of the Nantuo Formation and is overlain by dolomite of the Dengying Formation. Wu et al.^[12] divided the Duoshantuo Formation at Weng' an into three cycles (Fig. 1). Cycle A in the lower strata consists of dolomite and interbedded fine phosphorite layers and dolomitic pelite and pelitic dolomite. Cycles B and C in the upper strata consist of massive phosphorite layers, breccia-like phosphorite layers and laminated phosphorites and dolomites.

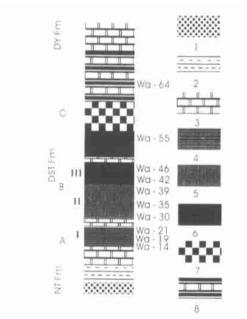


Fig. 1. Stratigraphic sections of Weng' an in Guizhou Province, South China. NT Fm, Nantuo Formation; DST Fm, Doushantuo Formation; DY Fm, Dengying Formation. 1, Tillite; 2, dobmitic pelite/dolomitic siltstone; 3, dolomite; 4, dolomitic pelite/pelitic dolomite with interstitial phosphates; 5, dolomite rocks with fine layer $(0, 1 \sim 3 \text{ mm})$ of phosphorite; 6, thick layers $(5 \sim 20 \text{ cm})$ of phosphorite; 7, breccia-like phosphorite and dolomite; 8, interbedded thin layers of phosphorite $(1 \sim 3 \text{ cm})$ and dolomite.

Petrology of the studied samples 2

Under a microscope, we distinguished three types of phosphate for the Doushantuo Formation. Type I phosphate from the lower strata occurs as brown interstitial material between euhedral dolomite crystals (Fig. 2(a)), and most likely formed in porewaters via diagenetic process. Type II phosphate

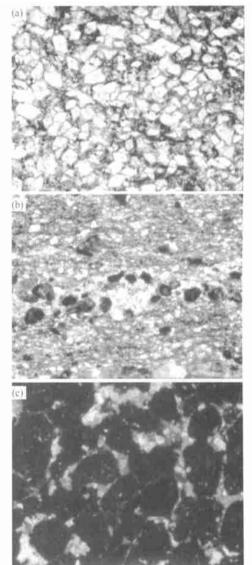


Fig. 2. Photomicrograph of the phosphorite and dolomite from the Doushantuo Formation at Weng' an, Guizhou Province. (a) Phosphate-bearing dolomite from lower strata of the Doushantuo Fm $(50\times, \text{ single polarized light})$. Dolomite crystals are in white color and diamond shape. Phosphate is in brown color and occurs as interstitial material. (b) Phosphate-bearing dolomite from lower strata of the Doushantuo Fm with well-developed lamination (50×, single polarized light). Large granular phosphates are in dark color and distributed as fine layers. Dolomites are in white color having varying sizes. Fine grains in brown cobr are also phosphate. (c) Granular phosphorite from upper strata of the Doushantuo Fm $(50 \times,$ crossed polarized light). Phosphates are in large sub-rounded granu-

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from the middle strata occurs as phosphate grains scattered as fine lamination in dolomite layers (Fig. 2 (b)). Type III phosphate occurs in the upper strata of massive and breccia phosphorite and interbedded thin layers of phosphorite and dolomite. Within the phosphorite layers and breccias, phosphate grains are between 85 vol. % and 98 vol. %. Pore space is filled with interstitial dolomite cement (Fig. 2(c)). Similar to the interstitial phosphate in the lower strata, the interstitial dolomite may have also formed from porewaters via diagenesis. A fine layer of collophanite is also found occasionally in thin sections in both the lower and upper parts of the Doushantuo Formation.

3 Analytical methods

We analyzed the oxygen isotopic compositions of phosphate and the oxygen and carbon isotopic compositions of coexisting dolomite from whole-rock pow-ders of the Doushantuo Formation. P_2O_5 and REE contents of whole-rock powders of these samples were also measured.

Analysis of oxygen isotopic composition of phosphate was carried out at the Key Laboratory of Isotope Geology in the Chinese Academy of Geological Sciences in Beijing after the method of Wan et al.^[13]. The whole-rock powders of phosphate-bearing samples were dissolved in mixed hydrochloric and nitric acids and converted to BiPO₄ after a series of chemical processes. Oxygen in BiPO₄ was extracted by the conventional method with BrF5 and oxygen isotopic compositions were measured using a MAT-251 mass spectrometer. The analytical precision of $\delta^{8}O_{phos}$ was better than 0.2 %

Analysis of oxy gen and carbon isotopic compositions of dolomites was carried out at the State Key Laboratory for Mineral Deposits Research of Nanjing University by the conventional method with 100%phosphoric acid and a MAT-252 mass spectrometer with an analytical precision of 0.2% for both δ^{13} C and δ^{8} O data. Contents of major elements were analyzed by XRF at Modern Analyses Center of Nanjing University. Concentrations of REE were extracted by mixed hydrochloric and nitric acids and then analyzed with a Finnigan Element II ICP-MS at the State Key Laboratory for Mineral Deposits Research of Nanjing University with an analytical precision of 5%.

4 Results

The oxygen isotopic compositions of the phosphorite from the Doushantuo Formation at Weng' an are expressed as $\eth^8 O_{\rm phos}$ (SMOW) and listed in Table 1. The oxygen isotopic compositions of coexisting dolomites are expressed both as $\delta^8 O_{carb}$ (SMOW) and $\delta^{18}O_{carb}$ (PDB), and the carbon isotopic compositions are expressed as $\delta^{3}C_{carb}$ (PDB) (Table 1). Overall, the $\delta^{8}O_{phos}$ (SMOW) values range from 10.7% to 15.0% and $\delta^{8}O_{carb}$ (PDB) range from -9.8% to -3.4% with one exception of -12.9 % The range of $\delta^8 O_{\text{phos}}$ (SMOW) from the Doushantuo Formation is plotted in the lower part of a temporal trend zone for $\delta^{8}O_{\text{phos}}$ defined by sedimentary phosphates from present back to 2000 Ma ago. Some of the studied phosphorite samples are plotted below the envelope of this temporal trend (Fig. 3).

Table 1. Oxygen and carbon isotopic compositions of phosphorite and coeval carbonate from Doushantuo Formation at Weng' and Guizhou Province, South China

Sample No.	$\frac{\eth^8 O_{phos}}{(SMOW)} \%$	$\frac{\delta^{13}C_{carb}}{(PDB)\%_{0}}$	∂ ⁸ O _{carb} (PDB) ‰	$\delta^{18}O_{carb}$ (SMOW)%	Temperature			D O
					Phosphate ^{a)}	Dolomit e ^{b)}	Ce/Ce *	$\begin{array}{c} P_2O_5\\ (wt. \ \%)\end{array}$
					1	2		
Type I								
WA-14	10.9	-2.2	-6.2	24.5	51.6	49.7	0.021	0.26
WA-19	11.0	-1.0	— 5. 0	25.7	51.2	41.9	-0.024	0.49
WA-21	12.1	-0.7	— 3 . 4	27.4	46.5	32.2	-0.032	0.32
Type II								
WA-30	12.3	-1.4	— 5 . 2	25.5	45.6	43.1	-0.084	4.0
WA-35	10.7	-1.6	— 5. 0	25.7	52.5	42.2	-0.064	10.6
WA-42	12.8	-2.2	— 5. 7	25.0	43.5	46.4	-0.088	10.7
Type III								
WA-39	13.2	-3.2	— 9. 8	20.7	41.7	75.6	-0.056	42
WA-46	15.0	-3.0	- 8.6	22.0	34.0	66.4	-0.066	21.7
WA-55	13.7	-4.4	-12.9	20.3	39.6	79.2	-0.214	36.7
WA-64	13.9	-2.6	- 8.7	22.0	38.7	66.3	-0.337	47

a) Palaeotemperature calculations using the phosphate-water oxygen istope equations of Longinelli and Nuti^[14]; b) palaeotemperature calculations using the dolamite water oxygen isotope equation of Fritz and Smith^[15], δ^{18} O value of seawater is supposed to be = 3%, see the text for details.

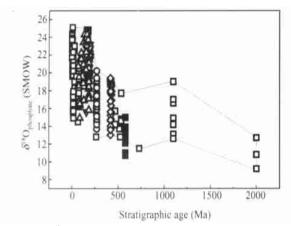


Fig. 3. δ^{18} O temporal trend for sedimentary phosphates in geological history from 2000 M a ago to present. Solid squares represent phosphorites from the Doushantuo Fm at Weng' an in Guizhou Province. Data of open symbols are from Shemesh et al. ^[16], Wenzel et al. ^[8], Hiatt and Budd^[17], Longinelli et al. ^[7, 18].

5 Discussion

5.1 Correlation of oxygen and carbon isotopes in dolomites

The dolomite rocks (Types I and II) from the lower strata of the Doushantuo Formation show generally higher $\delta^{8}O(SMOW)$ of 24.5 % ~ 27.4 % and δ^{3} C (PDB) of -2.2% ~ -0.7% than the dolomite cements (Type III) from the upper strata ($\delta^{8}0 =$ $20.3\% \sim 22.0\%$, $\delta^{3}C = -2.6\% \sim -4.4\%$). In a plot of $\delta^{13}C$ vs $\delta^{18}O$ of the dolomites, Type III dolomite cements display a steeper positive correlation line than the dolomite rocks of Types I and II (Fig. 4). Hudson^[19] suggested that the correlation of $\delta^{3}C$ and δ^{8} O is a useful indicator to the lithification and diagenetic processes of sedimentary carbonates. The remarked positive covariation between ^{ð3}C and ^{ð8}O for the type III dolomites may have resulted from mixing of porewaters with different compositions, i.e. meteoric water and seawater. Meteoric water is

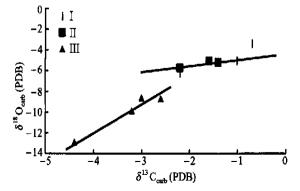


Fig. 4. Carbon and oxygen isotopic compositions for the three types of dolomites from the Doushantuo Formation. Weng'an,

depleted in ¹⁸O relative to seaw ater source, and it is usually also enriched in ¹²C due to involvement of ¹²Cenriched CO₂ from oxidation of organic matter in carbonate precipitation. Searl^[20] also utilized this relationship to identify mixing-zone dolomites in the lower Carboniferous limestones of South Wales.

5.2 Oxygen isotopic compositions of seawater

The 880 values of seawater in geological history are controversial. In general, two schools of thoughts have been proposed. One suggests a constant $\delta^8 O$ value for the seawater, and the other prefers a secular change of δ^{8} O value through time^[5-7, 18, 23-25]. For example, Silverman^[23] suggested an initial δ^{8} O close to the mantle value of +7% for the primordial ocean, and this value evolved to the present ocean value of 0% by progressive removal of ¹⁸O. Longinelli et al.^[7, 18] also suggested high 80 value for M esozoic ocean water (+3%). However, with increasing age in the Phanerozoic a general apparent trend of decreasing $\overset{\&}{\circ}{}^{8}$ O values (about 6[%]) is observed from carbonates, cherts and phosphates. On one hand, such trend was considered reflecting the evolution of the δ^{8} O value of ocean water^[24], or the lighter isotopic compositions in the past were considered being related to very high oceanic temperatures. On the other hand, such trend was interpreted as a result of increasing diagenesis with increasing age, as the $\delta^8 O$ value of ocean water was regarded being constant at about 0¹/₀₀ due to buffering by hydrothermal and weathering processes at mid-ocean ridges, based on studies of vertical profiles of ophiolites and model considerations^[5]. However, recently Lecuyer and Allemand^[25] considered that the specific ophiolite profiles could not represent the typical interaction between the seawater and oceanic crust. Their modeling results suggested that a long-lived hydrothermal system could lower the seawater δ^{18} O value by about 3% but could not cause a decrease as large as 6%. Wenzel et al.^[8] showed that while 880 phos values of Silurian consider to $\delta^{18}O_{\rm phos}$ values of modern biogenic apatites, supporting similar seawater oxygen isotopic compositions in the two eras, the $\delta^{8}O_{\text{phos}}$ values of coeval phosphatic inarticulate brachiopod are significantly lower, suggesting diagenetic effect on the latter fossil. Taken together, it appears that the variation of $\delta^8 O$ of ocean water through time is not over 3¹/₀₀ and that diagenesis does exist even in some mineralogically well preserved materials. Since no da-

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seawater, in this paper we will arbitrarily choose a $\eth^8 O$ value of -3% for the Neoproterozoic seawater to calculate the palaeotemperatures for the phosphorite deposition. Considering that a general decreasing trend of $\eth^8 O$ was observed through time and the maximal variation of $\eth^8 O$ was estimated to be 3% as discussed above, we believed that it is reasonable if the Neoproterozoic seawater was about 3% lower than present-day seawater ($\eth^{18}O = 0\%$).

5.3 Palaeotemperature calculations

Longinelli and Nuti^[14] proposed a phosphate-water oxygen isotope thermometer:

 $t(^{\circ}\mathbb{C}) = 111.4 - 4.3(^{\circ}\delta^{8}O_{\text{phos}} - ^{\circ}\delta^{18}O_{\text{w}}),$ where $\delta^{8}O_{\text{phos}}$ and $\delta^{8}O_{w}$ are the $\delta^{8}O$ values of phosphate and seawater, respectively. Using this equation, temperatures at which the phosphorites were deposited can be calculated, if oxygen isotope equilibrium was reached between phosphate and seawater during deposition and primary oxygen isotopes have not been altered afterwards. The above equation has been confirmed by Kolodny et al.^[21] and Lecuyer et al.^[22], and is the most widely accepted equation for palaeotemperature estimation^[17]. Hence, we also used this equation to calculate the seawater temperatures of the Doushantuo Formation (Table 1, Fig. 5). Assuming the δ^{8} O value of the Neoproterozoic seaw ater was -3% as discussed above, the calculated temperatures for the Type III phosphates are between 34.0 $^{\circ}$ C and 41.7 $^{\circ}$ C, whereas the Type I phosphates of possibly diagenetic origin show unreasonably higher temperatures of 46.5 \sim 51.6 °C. By comparison, the calculated temperatures from dolomite-water oxygen isotope equation of Fritz and Smith^[15] show that the Type III dolomites of diagenetic origin have unreasonably high temperatures of 66. $3 \sim 75.6$ °C. Type I dolomites display lower temperatures of 32.2 ~ 49.7 °C. The calculated temperatures from Type II dolomites and phosphates are similar, being 42.2 ~ 46.4 $^{\circ}C$ and 43.5 ~ 52.5 $^{\circ}C$, respectively (Table 1, Fig. 5). Due to diagenetic processes that are hard to distinguish among individual samples and that may lead to higher temperature estimates, it is more safe and reasonable to choose the dolomite rocks and phosphorites with the highest $\delta^8 O$ values to represent the most primary seawater temperatures. In this case, the palaeotemperature for the lower strata calculated from dolomite 880 value would be 32.2 °C, whereas the palaeotemperature for the upper strata calculated from phosphate δ^{8} value would be 34.0 °C (Table

1, Fig. 5). However, these estimated temperatures of $32.2 \sim 34.0 \,^{\circ}\text{C}$ should be considered as the maximal palaeotemperatures, and the real temperatures may be somehow lower than these estimates if the used δ^{8} O data were already slightly affected by diagenesis. Nevertheless, similar paleotemperatures (34 ~37 $^{\circ}$ C) have been deduced for the near shore phosphorites of the Upper Permian Phosphoria Formation from δ^{8} O values of the phosphorites^[17].

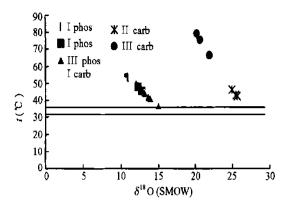


Fig. 5. Calculated palaeotemperatures from phosphate and dolomite $\delta^{18}O$ data.

5.4 Diagenetic effects

Under normal conditions secondary diagenetic alterations of phosphate should result in scattered isotope values and in a general evolution to lower $\delta^{8}O$ values. This is supported by the lower $\delta^{8}O$ values of the Type I and II phosphates of possibly diagenetic origin than the type III phosphates (Table 1). PO₄³⁻ ions can be derived from the degradation of organic matter in sediments which may catalyze phosphatization and early diagenesis^[26]. Early diagenetic phosphatization of fossils have been described elsewhere^[27].

Fig. 6 shows a broad correlation between $\delta^{18}O_{phos}$ values and P2O5 contents of the samples. Type I samples, in which the phosphates are of diagenetic origin, have the lowest $\delta^{18}O_{phos}$ and P2O5 contents. Type II samples are interbedded phosphorite and dolomite, although their P2O5 contents are much higher than the Type I samples, both of them show similar low $\delta^{18}O_{phos}$ values. Accordingly, we suggest that the type II samples may have also undergone to some extent diagenetic alteration. The diagenetic alteration may have similar effects on phosphates and dolomites in the Type II samples since both of them show a similar range of calculated temperatures that are higher than the temperatures calculated from

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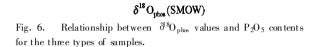
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 $P_2O_5(wt\%)$

the most pristine oxygen isotopic compositions of primary phosphate or dolomite (see discussion above).



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ΙI

Π 🔳

▲ III

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Both the interstitial phosphates of Type I samples and interstitial dolomites of Type III samples are of diagenetic origin. However, their δ^{8} O values are still related to the major constituents of the host rocks, as demonstrated by the positive correlation between $\delta^{18}O_{\text{phos}}$ and $\delta^{8}O_{\text{carb}}$ in Fig. 7. In the Type I samples, interstitial phosphates within the ¹⁸O-enriched dolomite rocks show higher $\delta^{8}O$ values. Likewise, in Type III samples, dolomite within the most ¹⁸O-enriched phosphorite ($\delta^{8}O = 15.0\%$) also has a higher $\delta^{8}O$ value (22.0%). In contrast, the Type II samples of interbedded phosphates and dolomites lack such a covariation (Fig. 7).

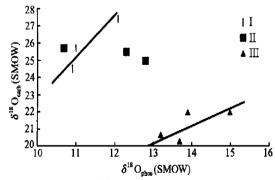


Fig. 7. Variation of $\,\eth^{8}O_{\,phos}$ and $\,\eth^{8}O_{ca,b}$ for the three types of samples.

5.5 Ce anomaly and palaeoceanographic conditions during the Doushantuo interval

Previous studies suggest that primary REE distribution-patterns are largely preserved during phosphorite diagenesis^[28]. Hence, their REE records can reflect the paleoredox conditions of the original depositional environment, and in particular, Ce anomaly has been used as a reliable paleoredox proxy. It has been suggested that negative Ce anomaly (Ce/Ce $\stackrel{*}{<}$ 0) indicates oxidizing conditions^[28]. Fig. 8 shows a progressively increased Ce anomaly from lower to upper phosphorite strata of the Doushantuo Formation, suggesting a change from suboxic to oxic condition at the time the Doushantuo phosphorites were deposited. Consequently, the more oxic depositional environment in the upper strata may have corresponded to a shallower water depth and probably warmer water temperatures since temperature decreases with water depth^[29]. However, the calculated temperatures of the low er phosphorite strata are generally higher than the upper strata, which again implies that the phosphorite in the lower strata may have undergone various degrees of diagenetic alteration that caused higher calculated temperatures for these phosphorite samples. As discussed above, if we take the dolomite and phosphorite with highest 8⁸0 values in the lower and upper strata (Table 1), respectively, then the calculated seawater temperatures are indeed slightly higher $(34.0 \degree C)$ in the upper strata than in the lower strata (32.2 °C). Different paleoceanographic areas and paleotemperatures across a marine paleoshelf have been suggested for the phosphorites of the Upper Permian Phosphoria Formation^[17].

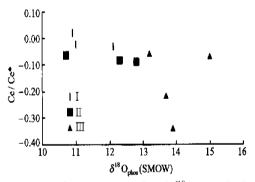


Fig. 8. Correlation of Ce anomaly and $\,\,\eth^8O_{\rm phos}$ for the three types of samples.

The change of palaeo redox conditions from lower to upper strata of the Doushantuo Formation is also supported from other evidence. For example, the pronounced rise of δ^{33} C in the cap carbonates of the bottom strata of the Doushantuo Formation after the Nantuo glaciation suggest that an increased rate of organic carbon burial occurred at that time^[4]. Under suboxic and anoxic conditions, bacterially stored phosphorous is readily remineralized in microbial degradation processes. The marine algae may have undergone decomposition in pore waters by microbial oxidation, and supply ample dissolved phosphorous to plishing House. All rights reserved. http://www.cnki.net the porewaters of the marine sediments. This process may create conditions favorable for the rapid nucleation of phosphate minerals and the eventual form ation of interstitial diagenetic phosphate of type I in the lower strata of the Doushantuo Formation^[30]. Whereas in oxic water conditions in the upper strata of the Doushantuo Formation, abundant marine algae rely on dissolved phosphate for the process of oxidative phosphorylation^[30]. Shen et al.^[30] suggested a pronounced bloom of microbial life during the Doushantou period favoring the large-scale formation of stromatolitic phosphorites.

6 Conclusions

(1) Three types of samples are recognized for the phosphate-bearing rocks from the Doushantuo Formation at Weng'an, Guizhou Province. The interstitial phosphates in Type I samples and the dolomite cements in Type III samples, respectively, are likely of diagenetic origin. In contrast, the dolomites in Type I samples and phosphates in Type III samples are likely the least altered samples.

(2) Oxygen isotope study suggests that the dolomites from Type I and phosphates from Type III samples show almost pristine isotopic compositions of carbonates and phosphates precipitated from seawater. Calculations of palaeocean temperatures from the most ¹⁸O-enriched dolomite and phosphate indicate a temperature of 32.2 °C for the lower strata and 34.0 °C for the upper strata of the Doushantuo Formation. These temperatures should be regarded as the maximal estimations for the palaeoseawater temperatures.

(3) Ce anomaly also suggests more oxic conditions and possibly shallower water depth in the upper strata of the Doushantuo Formation at Weng' an, which is also in consistence with the higher seawater temperatures deduced from oxygen isotopes.

(4) Diagenetic effects do occur for some of the studied samples, and it is related with phosphate contents, carbonate cement and can be readily recognized by petrographic observations and geochemical studies. Caution should be taken when reconstructing the paleo-environmental change in the Neoproterozoic by using stable isotopic compositions of carbonate and phosphorite. Nevertheless, our study provided a case suggesting that reasonable palaeotemperatures can be Acknowledgements Prof. Wu Xianghe from the Institute of Geology and Mineral Resources Research, Bureau of Geology and Mineral Resources of Guizhou Province, is thanked for his very helpful assistance in field work. Prof. Wan from the Chinese Academy of Geological Sciences is thanked for her help with the oxygen isotope analysis. We thank Prof. Harald Strauss and an anonymous reviewer for their constructive comments that helped us to better clarify our view and improve the paper significantly.

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