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High $\delta^{13}C$ Carbonates from the Songpan-Garzê Orogenic Belt: Implications for Correlation of Neoproterozoic Carbon Isotope Anomalies Across the Yangtze Platform, China

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Abstract

A detailed stable isotopic profile measured systematically across a thick Upper Neoproterozoic (Sinian) carbonate succession at Danba, western Yangtze Platform, China, records an overall positive $\delta^{13}C_{Carb}$ excursion. Even having experienced amphibolite facies metamorphism, most of carbonates in the interior of the marble layer preserve pre-metamorphic $\delta^{13}C$ and $\delta^{18}O$ values, which vary with stratigraphic level. The marbles can be divided into lower and upper units. The lower and upper units have distinctive isotopic composition ranges, $\delta^{13}C_{Carb}=\sim+5$ to $+7.3$‰ and $\delta^{18}O_{Carb}=\sim20$ to 25‰, and $\delta^{13}C_{Carb}=\sim+1.5$ to $+3$‰ and $\delta^{18}O_{Carb}=\sim28$ to 30‰, respectively. This pattern of variation, especially in $\delta^{13}C$, is similar to that reported for the unmetamorphosed upper Sinian Doushantuo and Dengying Formations in the eastern Yangtze Platform. This suggests that the positive Neoproterozoic $\delta^{13}C_{Carb}$ excursion can be correlated on a basinal scale within the Yangtze Platform. The data presented here establish that high $\delta^{13}C$ values of carbonates from the upper Sinian Doushantuo Formation are a regional feature across the Yangtze Platform.

Key words: Neoproterozoic, Sinian, Yangtze Platform, carbonate.

Introduction

Studies of the stable isotope geochemistry of sedimentary carbonates potentially provide important constraints on secular variations in the earth's exogenic carbon cycle (e.g., Veizer and Hoefs, 1976; Knoll et al., 1986; Hoffman et al., 1998b). Previous studies have shown that the carbon isotope composition of marine carbonates ($\delta^{13}C_{Carb}$) varies little during the Phanerozoic (average $\delta^{13}C_{Carb}\approx 0\pm 2$ ‰ PDB; e.g., Veizer et al., 1980; Strauss and Moore, 1992). In comparison, $\delta^{13}C_{Carb}$ values display marked secular variations during the Neoproterozoic (~850–540 Ma), with positive excursions to extremely high values (~+7 to +10‰; e.g., Knoll et al., 1995; Hoffman et al., 1998b). These high $\delta^{13}C$ values probably reflect changes in the relative mass balance of sedimentary carbon between oxidized and reduced reservoirs (Knoll et al., 1986), which may have several causes, including high burial rates of organic material (e.g., Iyer et al., 1995), high productivity and/or high sedimentation rates (Derry et al., 1992). These processes may also have caused an increase in atmospheric O_2 contents (e.g., Knoll et al., 1986; Kaufman and Knoll, 1995), which would have had a profound effect on global biological processes. In the Neoproterozoic, positive $\delta^{13}C$ excursions were bracketed by low-latitude glaciations, suggesting a link between carbon cycling and long-term global climate change (Kaufman, 1997). Hence, studying these excursions is potentially important for understanding the evolution of the Earth's biosphere, hydrosphere, and atmosphere.

If secular carbon isotope variations reflect global phenomena, they may serve as an important tool for stratigraphic correlation (Kaufman and Knoll, 1995; Knoll et al., 1995), and compilations of secular $\delta^{13}C_{Carb}$ trends from a number of basins worldwide have been made to suggest that as many as four positive carbon isotope excursions occurred during the Neoproterozoic (Kaufman, 1997; Hoffman et al., 1998a). Because positive carbon isotope excursions may also reflect more localised processes (Schidlowski et al., 1976), a necessary but commonly not assessed criterion is that secular carbon isotope trends are able to be correlated on a basin scale.

Secular carbon isotope trends involving high-$\delta^{13}C$, unmetamorphosed carbonates have been recognised for Neoproterozoic carbonates of the eastern part of the Yangtze Platform, China (Yangtze Gorge region; Lambert et al., 1987; Yang et al., 1999; Shen and Schidlowski,

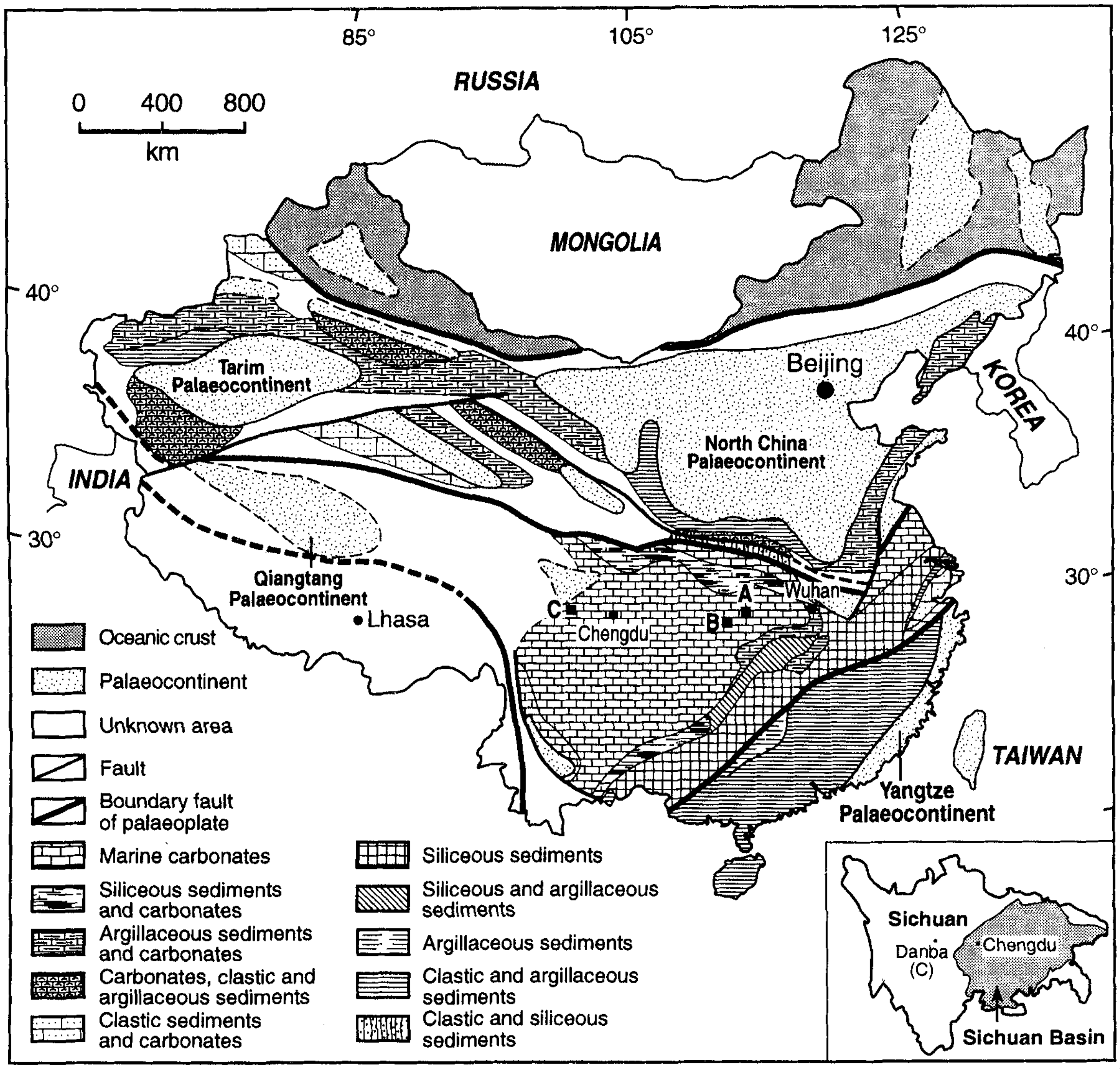

Fig. 1. Schematic map of Sinian palaeogeography and lithofacies, China (modified from Wang, 1985; Liu and Hü, 1994). A and B represent the type localities (squares) of the two upper Sinian sections from the Yangtze Gorge region of Lambert et al. (1987) and Yang et al. (1999), respectively. C represents the locality of the upper Sinian section from Danba. Inset on the lower right corner shows the physical features of Sichuan province and the Sichuan basin.

2000). In this study, however, we have selected a section through Neoproterozoic carbonates from the Danba area of the western Yangtze Platform, approximately 800 km across the basin from the type locality for the carbon isotope excursions (Fig. 1). In this area, although the Neoproterozoic rocks have been strongly deformed and metamorphosed, positive $\delta^{13}C$ values are largely preserved through metamorphism, allowing the regional distribution of ^{13}C-enriched carbonates to be established in the western Sichuan province (Fig. 1), and correlations to be made across the Yangtze Platform. These data establish that basin-wide, high $\delta^{13}C$ carbonates were precipitated during the Neoproterozoic on the Yangtze Platform, and reaffirm that these excursions are of global, rather than local, significance.

Geological Setting and Local Stratigraphy

Neoproterozoic (Sinian: 850 to ~570 Ma, Meyerhoff et al., 1991) rocks crop out widely in northern China, and the Yangtze region of southeastern and western China (Fig. 1). The Sinian System is typically characterised by a stable platform sequence of generally unmetamorphosed to slightly metamorphosed carbonate and terrigeneous strata, for which reason the Sinian represents a unique transitional period just before the first appearance of abundant, small Phanerozoic shelly fossils. The thickness of Sinian sequences generally ranges from 100–3000 m. The stratigraphy of the type section from the Yangtze Gorge, west of Wuhan (Fig. 1), has been described by Zhao et al. (1985) and Meyerhoff et al. (1991). At this

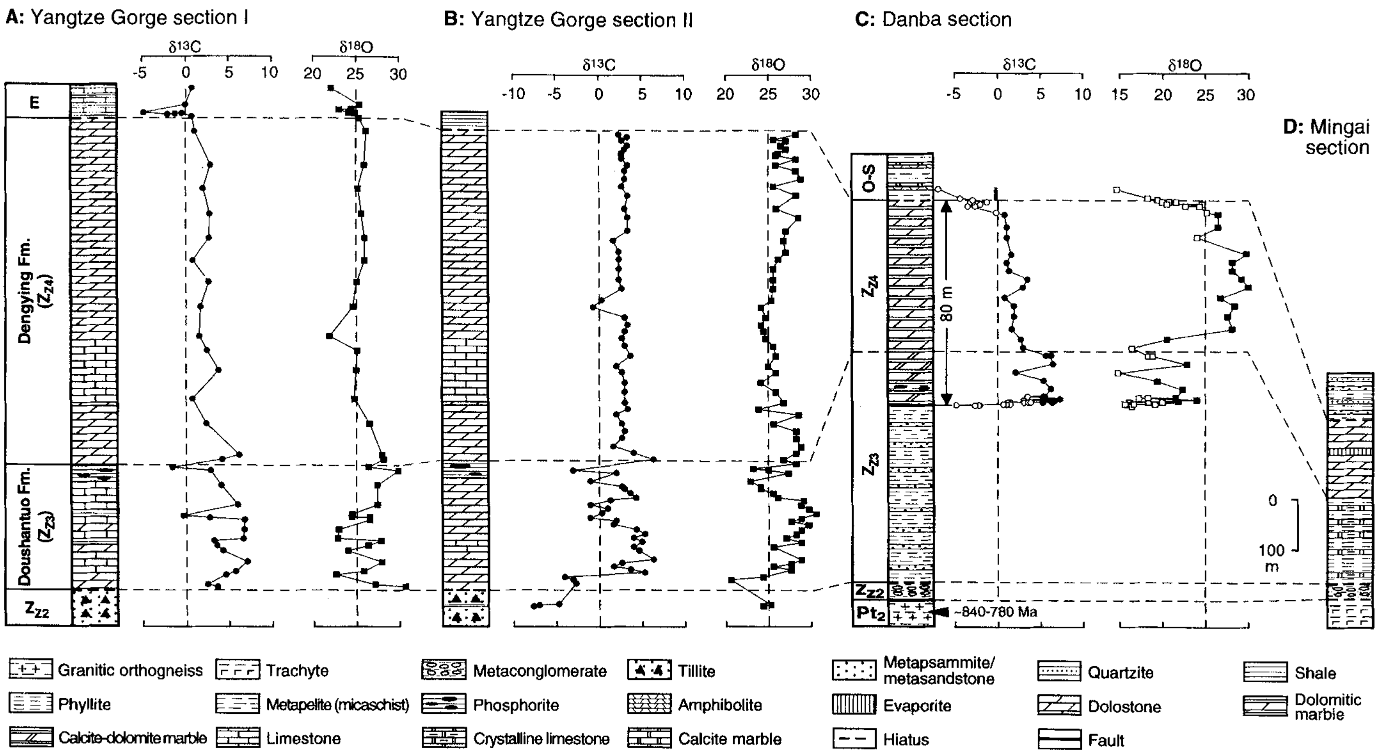

Fig. 2. Srtatigraphy and variations in $\delta^{13}C$ and $\delta^{18}O$ for carbonates from the three upper Sinian sections. (A) From the Yangtze Gorge of South China (Lambert et al., 1987); (B) from the Yangtze Gorge region of South China, ~50 km southwest of (A) (Yang et al., 1999); (C) from Danba of the western Yangtze Platform in this study and (D) from Mingai, ~60 km south of Danba (Zhao et al., 1978). The stratigraphic correlation is discussed in the text. E=Cambrian, O=Ordovician, Pt_2=pre-Sinian and S=Silurian. The Sinian system is divided into four units (Z_{Z1}, Z_{Z2}, Z_{Z3} and Z_{Z4}; see Meyerhoff et al., 1991). Note that except the top of the Nantuo Formation, the Z_{Z1} and Z_{Z2} are not shown. Filled symbols denote the unaltered or least altered samples, and open symbols the samples that have been affected by metamorphic decarbonation and/or infiltration of metamorphic fluids. Same scale for sections A, B and D.

locality, the Sinian is divided into an upper and lower series. The lower series (Z_{Z1+2}, Fig. 2) includes the Liantuo, Gucheng, Datangpo and Nantuo Formations in ascending order. The Liantuo Formation is composed of sandstones and unconformably overlies pre-Sinian metamorphic rocks. This formation is in turn unconformably overlain by the Gucheng Formation, which consists of glaciogenic sandstones, conglomerates and tillites. The overlying Datangpo Formation is composed mainly of calcareous shales, the thickness of which varies greatly in different regions. In contrast, the Nantuo Formation is a laterally persistent marker unit across the Yangtze region, and comprises glacial diamictite and fluvial sedimentary rocks. The carbonate-rich upper series is subdivided into two formations (Fig. 2). The Doushantuo Formation (Z_{Z3}) comprises limestones, dolomitic limestones and locally pyritic black shales and uppermost phosphorites. The uppermost Dengying Formation (Z_{Z4}) is dominated by dolostone and minor limestone. In some areas, the overlying Cambrian in the type section comprises fossiliferous shales interbedded with limestones.

Studies by Lambert et al. (1987) and Yang et al. (1999) have shown a secular variation in $\delta^{13}C_{Carb}$ in the type section of the Yangtze Platform (Fig. 2), where the Doushantuo and Dengying Formations have $\delta^{13}C_{Carb}$ values that range between +4 and +7‰ and +1.5 and +3‰, respectively. These carbonates are bounded by two large negative $\delta^{13}C_{Carb}$ excursions. The lower negative excursion ($\delta^{13}C_{Carb}$=–7 to –12‰) is observed in carbonates within diamictites of the Nantuo Formation and in the immediately overlying lowermost Doushantuo Formation. The upper negative excursion ($\delta^{13}C_{Carb}$=–7 to –12‰) occurs at the Neoproterozoic-Cambrian boundary and immediately overlies Neoproterozoic carbonates of the uppermost Dengying Formation with an average $\delta^{13}C_{Carb}$ of +1.5‰ (e.g., Lambert et al., 1987; Brasier et al., 1990; Yang et al., 1999; Shen and Schidlowski, 2000). Based on these data and correlations with other basins worldwide, Kaufman and Knoll (1995) and Yang et al. (1999) suggested that the Sinian type section in the Yangtze Gorge could be correlated with the terminal Proterozoic (~600–540 Ma), and that the lower Sinian negative $\delta^{13}C$ excursion corresponded to the Varangian glaciation.

Sinian sequences also occur in the Songpan-Garzê Orogenic Belt (SGOB) on the western margin of the

Yangtze Platform (Xu et al., 1992; Fig. 1), approximately 800 km from the type section in the Yangtze Gorge region. The SGOB is dominated by thick Triassic flysch sediments metamorphosed to low regional grades. Sinian sequences in the SGOB are restricted to local metamorphic terranes that are cored by pre-Sinian basement granitic rocks. The metamorphosed Sinian sequence is particularly well exposed in the Danba metamorphic terrane in central SGOB, western Sichuan province (Fig. 1). The general geology of the Danba terrane has been described by Hou et al. (1996). This terrane experienced greenschist to amphibolite facies Barrovian-type metamorphism during the late Triassic-Jurassic Indosinian orogeny (Hou et al., 1996), accompanied by regional shearing and recumbent folding. The Sinian rocks, which form fold closures around the Pre-Sinian basement orthogneisses, were metamorphosed from staurolite (P =6–7 kbar and T=580°–590°C) to sillimanite grade (P=5–6 kbar and T=620°–650°C, Huang et al., 2001). As the contact between the Sinian rocks and the basement orthogneiss was a major shear zone during the Indosinian (Xu et al., 1992), the Sinian succession has been variably subjected to tectonic thinning. The thickness of the Sinian strata varies greatly, from several metres to ~100 m across the Danba area. For this reason, we have collected carbonates from a thick section of the Sinian marble in the staurolite zone near the town of Gezong.

In the measured section (C in Fig. 2), the Sinian strata includes basal mylonitized metaconglomerates, metapelites interlayered with metapsammites in the lower part, and silicate-poor calcite-dolomite and dolomitic marbles in the upper part. The calcite-dolomite marbles contain 5–30% calcite and 60–90% dolomite. In the Danba area the Sinian-pre-Sinian boundary is defined as an unconformity based on the presence of the now deformed conglomerates (Hou et al., 1996). Minor finely-layered calcareous micaschists rich in apatite (5–10%) and pyrite (25%) are found within the calcite-dolomite marbles. Tremolite, chlorite and phlogopite occur locally in the marbles within ~0.5 m of the contact with adjacent metapelites, but are not abundant (2–8%). Within 5 m of the top of the marbles, 1–4 cm thick layers of quartzofeldspathic rocks are intercalated within the marbles, but only minor phlogopite and muscovite (<7%) were observed. The Sinian marble is unconformably overlain by the (Ordovician-) Silurian metapelites (Fig. 2).

At Mingai, ~60 km to the south of Danba, but still within the SGOB, the upper Sinian succession encompasses the same major lithological packages as seen in the Danba area in ascending order: metaconglomerates, phyllites and crystalline limestones and dolostones (section D in Fig. 2). Centimetre-thick gypsum layers were observed locally in the dolostones at this locality. The conglomerates at Mingai have previously been correlated with the basal glaciogenic unit of the Doushantuo Formation, which here unconformably overlies lower Sinian trachyte (Zhao et al., 1978). Regionally, the same conglomerate layer of variable thickness is widespread in the western Yangtze region (Sichuan province), indicating that it may represent a stable lithofacies during the mid-Sinian. The two sections (C and D) are lithologically similar, suggesting that they are stratigraphically equivalent. If this is the case, then the basinal conglomerates at Danba can be correlated with tillites of the basinal glaciogenic unit of the Doushantuo tillites in the eastern Yangtze platform, ~800 km away (Fig. 2), and calcite-dolomite marbles and dolomitic marbles of the carbonate package in Danba can be broadly correlated with the Doushantuo and Dengying Formations, respectively (Figs. 1 and 2). This tentative correlation is also supported by new stable isotope data discussed below. However, the absolute depositional age of Sinian metasediments in the Danba region is unconstrained. The emplacement ages of the granitic protoliths to the basement orthogneisses below the sheared unconformity have been dated at 840–780 Ma (U–Pb zircon; Roger and Calassou, 1997), providing a maximum depositional age of ~800 Ma for the Sinian conglomerates.

Analytical Methods

Mineral modal proportions within marbles and calcsilicate rocks were determined by point counting on (stained) thin-sections. Stable isotope analyses of ~10 mg of powdered carbonate whole-rock samples were carried out at Monash University following the method of McCrea (1950), by dissolving powdered samples in H_3PO_4 at 50°C for 12 hours to liberate CO_2. The liberated CO_2 was measured on a Finnigan Mat 252 mass spectrometer. $\delta^{13}C$ and $\delta^{18}O$ values are given relative to the PDB and SMOW standards, respectively. Internal calcite standards ISACC yielded $\delta^{13}C$=–6.3± 0.2‰ and $\delta^{18}O$=22.9± 0.2‰ (n=50). This standard was calibrated using IAEA-CO-1 and its long-term average $\delta^{13}C$ and $\delta^{18}O$ values are –6.37±0.06‰ and 12.68±0.13‰. Note that because at the high temperatures to which the Danba metacarbonates were metamorphosed (~590°C; Huang et al., 2001) isotopic fractionations between dolomite and calcite are small ($\Delta^{13}C_{Dol\text{-}Cal}$=0.4‰ and $\Delta^{18}O_{Dol\text{-}Cal}$=0.2‰; Sheppard and Schwarcz, 1970), the $\delta^{13}C$ and $\delta^{18}O$ values obtained are taken to represent the bulk carbonate isotope values for the calcite-dolomite marbles.

Isotopic Results

Carbon and oxygen isotope analyses of 53 non-graphitic samples across the carbonate package at locality C (Fig. 1) are given in table 1 and plotted in figures 2 and 3. Mineral abbreviations are after Kretz (1983). The main features of the isotope data are as follows:

(1) The data from the lower and upper units fall into two distinct fields, I and II respectively (Fig. 3), that correlate with the different mineral assemblage and bulk composition of the two marble types. The lower unit (calcite-dolomite marbles) has typical $\delta^{13}C_{Carb}$ values of +5 to +7.3‰ and maximum $\delta^{18}O_{Carb}$ values of 24 to 25‰. In contrast, the upper unit has $\delta^{13}C_{Carb}$ values of ~+1.5 to +3‰ and maximum $\delta^{18}O_{Carb}$ values of 28 to 30‰. The same isotopic variation was also observed in another two sections through the same marbles in the Danba area (Huang and Buick, unpublished data).

(2) Most of the massive, pure marbles in the middle of the marble layer are characterised by higher $\delta^{13}C_{Carb}$ and $\delta^{18}O_{Carb}$ values and there is no covariation of these two parameters.

(3) The $\delta^{13}C_{Carb}$ and $\delta^{18}O_{Carb}$ values decrease abruptly towards both margins of the marble layer over several metres, with the lowest values being observed at the contacts. The marginal $\delta^{13}C$ and $\delta^{18}O$ values are close to those of calcite in the immediately overlying Silurian calcic micaschist.

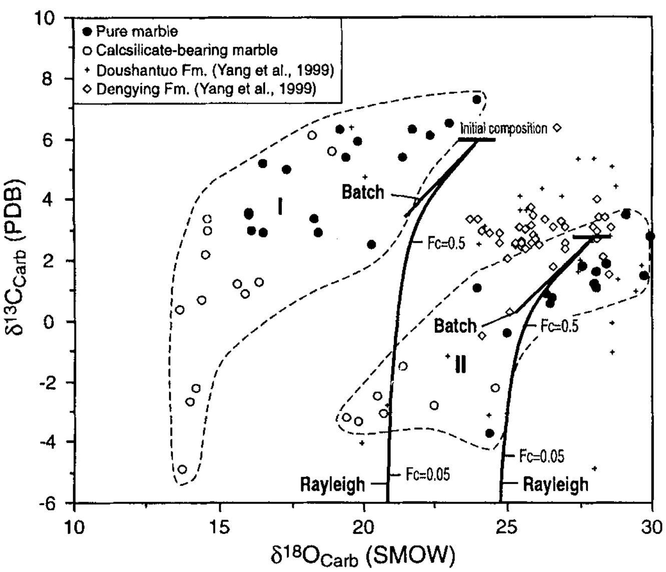

Fig. 3. $\delta^{13}C$ vs. $\delta^{18}O$ plot for carbonates from the Danba section. The data of Yang et al. (1999) are also incorporated into the plot scheme. The two sets of curves denote calculated trends resulting from Rayleigh and Batch devolatilisation from two starting compositions of $\delta^{13}C$=+6‰ and $\delta^{18}O$=24‰ and $\delta^{13}C$=+2.7‰ and $\delta^{18}O$=28‰, respectively. Fractionation factors applied are $\alpha^{13}C$ (=CO_2-rock)=1.00240 and $\alpha^{18}O$ (fluid-rock)=1.00653 at T=590°C. Fc represents the mole fraction of carbon remained in the rocks after devolatilisation. These have been calculated using the CO_2-calcite fractionations of Bottinga (1969) and isotope depletion equations of Valley (1986). Note that the data fall into two fields, corresponding to the lower unit (I–calcite-dolomite marble) and upper unit (II–dolomitic marble).

Table 1. Summary of isotopic results. Mineral abbreviations are after Kretz (1983).

Sample	$\delta^{13}C$ (PDB)	$\delta^{18}O$ (SMOW)	Distance (m)	Dol (%)	Cal (%)	Other mineral
Lower unit						
25–3	−2.7	14.0	6.12		82	Phl, Chl
25–4	−2.2	14.2	6.17		84	Tr, Phl, Chl, Qtz
25–5	−4.9	13.7	6.26		4	Micaschist
25–6a	0.7	14.4	6.32	44	38	Tr, Phl, Qtz
25–6b	0.4	13.6	6.33	60	24	Tr, Phl, Chl, Qtz
25–7a	1.3	16.4	6.37	60	20	Tr, Phl
25–7b	1.2	15.6	6.39	66	15	Tr, Phl, Chl
25–8	0.9	15.9	6.43	45	50	Phl
25–9	3.0	14.6	6.48	45	45	Phl
25–10	3.5	16.0	6.53	50	40	Phl
25–11	3.6	16.0	6.59	75	10	Phl
25–12	3.4	14.6	6.68	80	10	Phl
57–2	5.2	16.5	6.75	82	12	Phl
57–7	6.3	19.2	6.93	80	14	
57–13	6.3	21.7	7.19	82	15	
57–18	5.9	19.8	7.50	74	25	
57–19	2.9	18.4	7.61	60	40	Tr, Phl, Qtz
57–21	3.0	16.1	7.82	48	50	
57–23	7.3	24.0	7.94	86	11	
57–26	5.0	17.3	8.70	69	30	
57–27	3.4	18.3	8.90	70	28	
25–13	5.4	21.4	9.19	99	30	
25–14	6.1	22.3	12.25	55	40	
25–15	5.4	19.4	15.31	88	10	
25–16	2.2	14.5	18.37	65	20	Tr, Qtz
25–17	6.5	23.0	21.43	92	5	
25–18a	6.1	18.2	24.49		100	Calcite vein
25–18b	5.6	18.9	24.52	88	4	Tr, Qtz
25–19	2.9	16.5	27.56	74	25	
57–28	2.5	20.3	30.50	68	30	
Upper unit						
57–29	1.6	28.1	34.00	100		
57–30	1.8	27.6	38.50	100		
57–31	1.9	28.4	42.00	100		
25–20	0.8	26.6	45.73	100		
25–21	2.8	29.9	48.99	100		
25–22	3.5	29.1	52.05	100		
25–23	1.2	28.0	55.11	99		
25–24	1.1	28.1	58.17	100		
25–25	1.5	29.7	61.24	100		
25–26	1.1	24.0	67.36	100		
25–27	0.9	26.4	71.03	100		
25–28	0.6	26.5	75.32	97		
55–7	−0.4	25.0	76.50	96		
55–11	−3.7	24.4	78.50	95		
55–16	−2.8	22.5	79.00	60		Phl, Ms, Pl, Qtz
55–21	−2.2	24.6	79.50	90		Phl, Ms, Qtz
55–24	−2.5	20.5	79.80	30		Phl, Ms, Pl, Mc, Qtz
55–27	−3.1	20.7	80.10	50		Phl, Ms, Pl, Qtz
55–32	−1.5	21.4	80.35	35		Phl, Ms, Pl, Mc, Qtz
55–35	−3.3	19.8	80.45	30		Phl, Ms, Pl, Mc, Qtz
55–36	−3.2	19.4	81.00	60		Phl, Ms, Pl, Mc, Qtz
Silurian						
55–36Cal	−4.0	18.1	81.50	3		Calcic micaschist
55–39Cal	−7.6	14.6	87.00	3		Calcic micaschist

(4) Some heterogeneity in both $\delta^{13}C_{Carb}$ and $\delta^{18}O_{Carb}$ is observed in the lower marble unit.

Discussion and Conclusions

Diagenetic and metamorphic effects

Carbonates from the Danba section have high but variable $\delta^{13}C$ values that could have potentially developed during initial carbonate deposition, diagenesis or metamorphism. Determination of the timing of the development of these values is critical to evaluating their significance with regard to Neoproterozoic positive $\delta^{13}C$ excursions. In keeping with other studies (e.g., Wickham and Peters, 1993; Buick et al., 1998), we consider that these high $\delta^{13}C$ values predate metamorphism, and diagenesis, for reasons outlined below.

The possibility that these high $\delta^{13}C_{Carb}$ values have been developed during pre-metamorphic burial or meteoric diagenesis is unlikely, as these processes typically lower, or do not significantly reset, $\delta^{13}C$ values (Saltzman et al., 1998). Moreover, studies of Proterozoic carbonates suggest that diagenetic shifts in $\delta^{13}C_{Carb}$ values are markedly smaller (<1‰) than in Phanerozoic equivalents (Kaufmann et al., 1991; Strauss et al., 1992). Diagenetic methanogenic reactions produce both high-^{13}C CO_2 and low-^{13}C CH_4, and may therefore produce elevated $\delta^{13}C$ values. However, mixing of early formed high-^{13}C CO_2 with CO_2 derived from the subsequent oxidation of low-^{13}C CH_4 commonly leads to the precipitation of carbonates with a wide range of both large positive and negative $\delta^{13}C_{Carb}$ values. This results in significant carbon isotope heterogeneity (for example, on the order of 20‰ to 30‰ between samples) and in sub-vertical trends on $\delta^{13}C$ vs. $\delta^{18}O$ diagrams (Irwin et al., 1977), which are not seen in the present dataset. Therefore, diagenesis is unlikely to have resulted in the development of $\delta^{13}C$ values in the Sinian marbles.

It is similarly unlikely that the high $\delta^{13}C_{Carb}$ values were developed as a result of metamorphism. During metamorphism, isotopic resetting in carbonate-rich rocks can occur via devolatilisation reactions, infiltration of an externally derived fluid and isotopic exchange between marbles and country rocks, or a combination of these processes. Metamorphic devolatilisation reactions in carbonate-rich rocks typically release a mixed CO_2-H_2O fluid that is enriched in ^{13}C and ^{18}O with respect to the isotopic composition of the bulk rock (Valley, 1986). Therefore, progress of devolatilisation reactions tends to lower $\delta^{13}C_{Carb}$ and, to a lesser extent, $\delta^{18}O$ values (Valley, 1986). The isotopic shifts resulting from devolatilisation reactions can be calculated for the case that fluid produced is lost continuously (Rayleigh distillation) or as discrete batches (Valley, 1986). In the Danba section, some calcite-dolomite marbles contain ≤ 10% tremolite, which probably formed by the prograde decarbonation reaction:

$$5Dol + 8Qtz + H_2O = Tr + 3Cal + 7CO_2.$$

To produce this small amount of tremolite at peak temperatures of ~590°C appropriate to the staurolite zone at Danba (see above) should result in lowering of $\delta^{18}O_{Carb}$ and $\delta^{13}C_{Carb}$ values by only 0.3‰ and 0.25‰ for either Rayleigh or Batch devolatilisation (two curves in Fig. 3), using the equations given by Valley (1986) and $\Delta^{18}O_{CO_2\text{-}Cal}$ and $\Delta^{13}C_{CO_2\text{-}Cal}$ fractionations of Chacko et al. (1991). Strictly, the fractionation that should be used is that between calcite and the sum of the carbon species. That fractionation is smaller than $\Delta^{18}O_{CO_2\text{-}Cal}$ and so will lessen the effect of devolatilisation (Cartwright and Buick, 1995). Therefore, metamorphic decarbonation alone can not account for the large range of $\delta^{18}O$ and $\delta^{13}C$ values in the marble traverse, nor for the highly elevated $\delta^{13}C_{Carb}$ values of many of the marbles, as shown in figure 3. This suggests that the observed variation in stable isotope values across the marble layer reflects the effects of metamorphic fluid flow and/or isotopic exchange, or pre-metamorphic isotopic sedimentary variations, or both.

During metamorphism $\delta^{13}C_{Carb}$ values may be reset by infiltration of C-O-H fluids or through diffusive exchange between marble and other C-bearing rock types (e.g., metapelites that contain graphite). However, neither process will result in the elevated $\delta^{13}C_{Carb}$ values seen in the Danba marbles because all other carbon reservoirs, or CO_2-H_2O fluids equilibrated with them, have lower $\delta^{13}C$ than carbonates. The most common carbon reservoirs that could reset the carbonates are the sedimentary organic matter, magmatic fluids and surface water, with $\delta^{13}C$ values of –40 to –20‰, –10 to –5‰ and –10 to –8‰, respectively (Hoefs, 1997). Hence, introduction of an externally derived H_2O-CO_2 fluid, or fluid-mediated diffusive exchange between marbles and other rock types during metamorphism will lower $\delta^{13}C_{Carb}$ values. This suggests that ^{13}C-enriched Sinian marbles from Danba inherited these high $\delta^{13}C$ values from their sedimentary precursors.

The general preservation of high-^{13}C marbles at locality C does not mean that the marbles have been everywhere unaffected by metamorphic processes (e.g., Baker and Fallick, 1989; Wickham and Peters, 1993; Buick et al., 1998). Samples in the section C locally, especially on the margins, have significantly lower $\delta^{18}O$ values than those typical of normal marine carbonates (20–30‰; e.g., Hoefs, 1997), suggesting that some resetting of stable isotope values has been caused by metamorphic processes. The amount of lowering is much greater than can be accounted for by devolatilisation (0.3‰, Fig. 3), and hence small

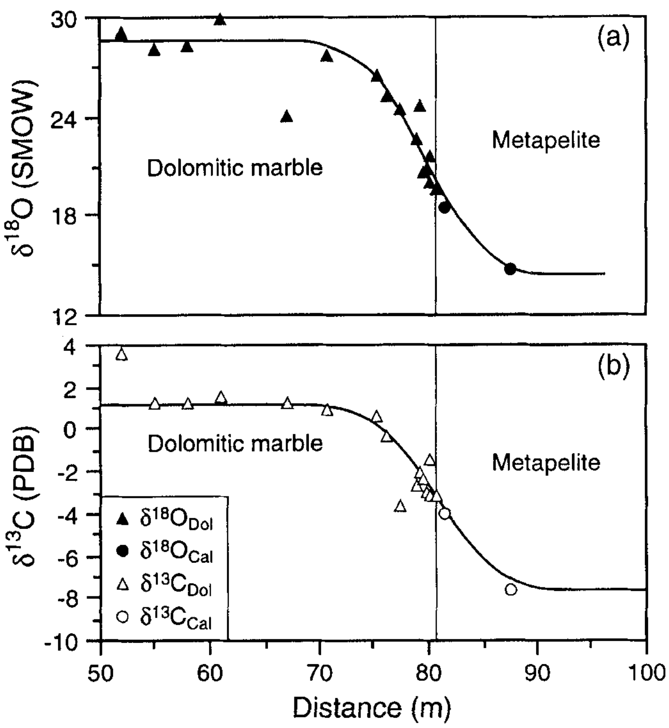

Fig. 4. The upper boundary profiles (a and b) of the Danba section (C), with least-squares best fits (continuous curves) to the one-dimensional advection-diffusion model for uniform flow from metapelites to marbles. The modelling indicates that isotopic exchange is dominated by fluid-mediated diffusion between the dolomitic marble and adjacent lower-^{18}O and -^{13}C country rocks (Huang and Buick, unpublished data).

scale lowering of $\delta^{18}O_{Carb}$ (and $\delta^{13}C_{Carb}$) within the stratigraphically lower part of the Danba section is interpreted as resulting from limited channelised metamorphic fluid flow within the marbles. In addition, Sinian marbles typically show limited lowering of both $\delta^{18}O_{Carb}$ and $\delta^{13}C_{Carb}$ on a metre scale adjacent to interlayered metapelites and quartzofeldspathic rocks (Fig. 4). These profiles are qualitatively similar to those predicted for fluid-hosted, diffusion-dominated isotopic exchange between marble and lower ^{18}O and ^{13}C country rocks, such as graphitic metapelites. Similar profiles have been described from a number of medium-grade metamorphic terranes, including those involving either Neoproterozoic high-^{13}C marbles (Wickham and Peters, 1993) or Mesozoic normal-^{13}C marbles (Bickle and Baker, 1990).

While the narrow boundary layers at the marble-metapelite contacts show coupled lowering of $\delta^{13}C_{Carb}$ and $\delta^{18}O_{Carb}$ that can be explained by metamorphic processes, carbonates within the interior of the marble layers generally show: (1) consistently higher $\delta^{13}C_{Carb}$ and $\delta^{18}O_{Carb}$ values and (2) no correlation between $\delta^{13}C_{Carb}$ and $\delta^{18}O_{Carb}$. As discussed above, metamorphic decarbonation reactions have had negligible effect on $\delta^{13}C_{Carb}$ and $\delta^{18}O_{Carb}$ values. Therefore, these carbonates preserve pre-metamorphic and pre-diagenetic sedimentary stable isotope values, which with obvious differences in bulk composition, can be used to divide the marble internally into two units. The $\delta^{13}C_{Carb}$ values fall within the narrow ranges ~+5 to +7.3‰ and ~+1.5 to +3‰ for the lower (calcite-dolomite marble) and upper (dolomitic marble) units, respectively.

It is emphasised that the possibility that the smooth lowering of $\delta^{13}C_{Carb}$ towards the upper contact of the Sinian marble to some extent reflects a primary isotopic signal developed during deposition, as reported by Brasier et al. (1990) and Shen and Schidlowski (2000), can not be excluded. However, the metamorphic effects (i.e., diffusion) on the carbonates at the upper boundary of the Sinian marble could not be separated from the primary $\delta^{13}C_{Carb}$ trend. If the lowering of $\delta^{13}C_{Carb}$ at the margin of the marble is a primary sedimentary signal, section C may contain the Neoproterozoic-Cambrian boundary. However, the sequence directly overlying the Sinian in the Danba area was defined as Ordovician or Silurian based on lithostratigraphy (but not on geochronology or biostratigraphy), suggesting that this scenario is unlikely.

Isotope variation and correlation

It is argued above that isotopic compositions of carbonates in the interior of the Sinian marble layer approximate depositional values that vary with original stratigraphic position in the Sinian succession. If this is accepted, then the $\delta^{13}C_{Carb}$ values, in particular, may reflect secular variations that may potentially be correlated with other widely spaced sequences representing the different parts of the Neoproterozoic basin (e.g., Kaufman and Knoll, 1995). The Danba Sinian carbonates, with exceptions occurring on the boundaries of the layer due to metamorphic effects, have positive $\delta^{13}C$ values (Fig. 2 and Table 1). Calcite-dolomite marbles from the lower unit record extremely high $\delta^{13}C$ values of +5 to +7.3‰, and the dolomitic marbles from the upper unit generally have $\delta^{13}C_{Carb}$ between ~+1.5 and +3‰ with a highest value of +3.5‰. The relatively high ^{13}C group has maximum $\delta^{18}O_{Carb}$ values of 20–25‰, and the lower $\delta^{13}C_{Carb}$ group has maximum $\delta^{18}O_{Carb}$ values of 28–30‰.

Lambert et al. (1987) first reported the secular variations in $\delta^{13}C$ for upper Sinian carbonates from the type Sinian section in the Yangtze Gorge region (Figs. 1 and 2). Lambert et al.'s (1987) results show that carbonates of the lower Doushantuo Formation have $\delta^{13}C$ values as high as +7‰, while dolomite from the immediately overlying Dengying Formation is characterised by relatively constant, lower $\delta^{13}C$ values of ~+2-3‰. Yang et al. (1999) also investigated the carbon isotope geochemistry of the upper Sinian elsewhere in the Yangtze Gorge region, and recorded a similar secular variation (Fig. 2). These two studies suggested that the carbon isotopic stratigraphy of the Sinian succession in the Yangtze Gorge region could be correlated on a ~50 km scale. It is evident from figure 3 that carbonates from the upper calcite-dolomite marble unit at Danba plot very close to those from the Denying Formation, whereas carbonates from the lower dolomitic marble unit show similar high $\delta^{13}C$ values as those from the Doushantuo Formation of Yang et al. (1999). Based on stratigraphic correlations in Danba and immediately to the south, the Danba Sinian marbles also appear to be correlated with the Doushantuo and Dengying Formations in the Yangtze Gorge type area for the Sinian succession. This tentative correlation is supported by the stable isotope data from Danba presented here (Figs. 2 and 3), although the negative $\delta^{13}C$ excursion from -5 to 0‰ observed in the type area has not been found at Danba (Fig. 2). Therefore, in spite of the tectonic thinning of the Danba Sinian marble package, and even though exact stratigraphic correlations can not be made, the Danba marbles preserve sedimentary $\delta^{13}C$ values that can be generally correlated with $\delta^{13}C$ profiles in the type sections, ~800 km away.

Several mechanisms have been invoked for the development of ^{13}C-rich carbonates in sedimentary environments, but they are contentious. On a basinal scale, ^{13}C-rich carbonates are known from current evaporitic environments (Stiller et al., 1985). This process can be precluded for the ^{13}C enrichment in the Danba area studied here for two reasons: (1) only a few cm-thick gypsum layers are observed in the middle part of the Denying dolomite in the western Yangtze Platform, and none is observed in the high-^{13}C Doushantuo Formation; and (2) evaporites are essentially absent in the Danba area and nearby least metamorphosed equivalents (Mingai).

Worldwide, major positive ^{13}C excursions during the late Neoproterozoic have been interpreted as a global pattern that was related to changes in the carbon isotopic composition of seawater (e.g., Kaufman and Knoll, 1995; Hoffman et al., 1998b). This change is caused by the fixation of low ^{13}C carbon into organic materials, resulting in an increase in O_2 concentration (Knoll et al., 1986). As organic carbon is essentially lacking in the Danba area, apart from minor graphite in metapelites, most of the organic materials must have accumulated elsewhere in the sedimentary environments of the Yangtze Platform (Fig. 1), or may have burned off through oxidation reactions during prograde metamorphism. In the Sichuan Basin (eastern Sichuan Province; Fig. 1), which is a large intracratonic basin within the Yangtze Platform, beds of gypsum and halite are very common in the upper Dengying Formation, and form seals for Sinian oil and natural gas reservoirs (e.g., Korsch et al., 1991; Meyerhoff et al., 1991). The gas consists of low ^{13}C methane (~94%; $\delta^{13}C$=-33.4‰), and minor ethane ($\delta^{13}C$=-30.5‰), propane ($\delta^{13}C$=-21.6‰) and butane ($\delta^{13}C$=-29.6‰; Korsch et al., 1991). The oil and natural gas reservoirs are considered to have resulted from accumulation of microbial matter contained within the Sinian carbonate rocks (Korsch et al., 1991; Meyerhoff et al., 1991); thus a large amount of organic materials is required to have sourced the significant oil and gas reservoirs. Korsch et al. (1991) suggested that strong ^{13}C enrichment in the Sinian succession in the Sichuan Basin was related to the gas. In the Sichuan Basin, the gas fields are spatially in close proximity to the oil fields, implying that the gas reservoirs may have formed at temperatures of ~160°–180°C or slightly higher (~3–4 km; Tissot and Welte, 1984). The carbon isotope fractionations between calcite and methane over this temperature range are ~36.5 to 40‰ (Bottinga, 1969); thus the $\delta^{13}C$ values of carbonates in equilibrium with methane in the gas are ~+4 to +7.6‰ (Sheppard and Schwarcz, 1970), which are similar to those obtained from the dolomitic marbles in the lower Sinian unit. It is therefore suggested that the large ^{13}C enrichment in Danba carbonates reflects a period of high fractional fixation of sedimentary carbon in the organic reservoir in the late Neoproterozoic ocean (Kaufman and Knoll, 1995; Yang et al., 1999).

Conclusions

Carbonates from the upper Sinian succession in the Danba area, western Sichuan province, display a large range of $\delta^{13}C$ and $\delta^{18}O$ values that fall into two fields on a $\delta^{13}C$ vs. $\delta^{18}O$ plot. These two fields correspond to different positions in the stratigraphy. While the role of diagenesis is not well constrained, diagenetic shifts in $\delta^{13}C$ and $\delta^{18}O$ are likely to have been small, and in each case would have tended to lower primary sedimentary values. Metamorphic decarbonation has shifted isotopic values in the marbles to a very small extent. The lowering of $\delta^{13}C_{Carb}$ and $\delta^{18}O_{Carb}$ values at the margins of the marble, and their covariation suggest that the carbonates of the marbles layer have been subjected to local (metre-scale) fluid-mediated isotopic diffusive exchange, whereas carbonates in the bulk of the marble layer were only locally affected by a channelised fluid flow during the regional metamorphism. Therefore, the majority of carbonates within the marble layer retain pre-metamorphic compositions that are inferred to have developed during sedimentary deposition. The available data broadly bracket two compositional plateaux for the lower and upper units, respectively.

Carbonate $\delta^{13}C$ values can be used as a tracer for regional scale stratigraphic correlation in the Yangtze Platform. The upper Sinian marble succession in Danba, although having suffered tectonic thinning accompanied by metamorphism, records a secular $\delta^{13}C$ variation that is overall similar to those obtained within the Doushantuo and Dengying Formations across the type sections of the Sinian systems in Yangtze Gorge region, ~800 km to the east. Moreover, the secular variation of $\delta^{13}C$ is comparable to that seen in the later Neoproterozoic successions worldwide. The data presented here strongly suggest that intra- and interbasinal correlations of post-glacial Neoproterozoic strata at the formation-scale are feasible, even in the presence of lithofacies variation and the effects of subsequent deformation and metamorphism. Therefore, based on those correlations the Sinian rocks from Danba are inferred to have deposited between ~600 and 540 Ma. High $\delta^{13}C$ values of +5 to +7.3‰ appear to characterise the upper Sinian Doushantuo Formation in the Yangtze platform on a regional scale. ^{13}C enrichment may have arisen from a high fractional burial rate of organic carbon in the late Neoproterozoic, as also evidenced by voluminous oil and gas deposits in the upper Sinian carbonates of the Sichuan Basin.

The preservation of pre-metamorphic $\delta^{13}C$ and $\delta^{18}O$ values at Danba and isotopic chemostratigraphic correlation on the basinal scale, demonstrate that metamorphic carbonates can also be used to study secular isotopic variations. Much of the Neoproterozoic worldwide has been metamorphosed. To be able to use the carbon isotope geochemistry of such rocks as indicators to global processes, or as correlation tools, is thus extremely valuable.

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