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Stable isotope geochemistry of marbles from the coesite UHP terrains of Dabieshan and Sulu, China

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Abstract

Marbles from Dabieshan and Sulu, China, suffered ultra high pressure (UHP) metamorphism in the coesite–eclogite facies at approximately 700°C and 30 kbars during Triassic continental collision and subduction. The marbles range in isotopic composition from +7 to +25 $\delta^{18}O_{VSMOW}$ and from 0 to +6 $\delta^{13}C_{VPDB}$. High $\delta^{13}C$ values are representative of unmodified protoliths and are similar to those of ^{13}C-enriched Sinian carbonate rocks from the Yangtze craton. High oxygen isotope ratios reflect pristine protoliths but the low values may have been caused by infiltration of low ^{18}O meteoric water during diagenesis and dolomitization, by fracture-controlled infiltration of water during subduction, by metamorphic mineral reactions, or by a combination of these processes. No evidence of regional isotopic transport during UHP metamorphism has been found. Sampling on scales of 1 to 100 m shows marbles to be inhomogeneous in both carbon and oxygen isotopes. Only samples separated by less than 10 cm have equilibrated oxygen and carbon isotope compositions. Limited isotopic equilibration between adjacent rocks is consistent with the preservation of unaltered UHP minerals and indicates that the metamorphic fluid–rock system was rock-dominated during and following peak metamorphism. A freely flowing, pervasive fluid phase was not present during UHP metamorphism. There is no evidence of isotopic exchange between marble and the upper mantle into which it was subducted. Correlation of geochemical similarities of UHP marbles with Sinian limestones implies that the subducted edge of the Yangtze craton extends at least as far north as the coesite–eclogite facies rocks of Dabieshan. Deposition of protolith carbonates may have taken place in a cold climate either preceding or following but not coincident with Neoproterozoic glaciation.

Keywords: Stable isotope geochemistry; Carbon isotope geochemistry; Oxygen isotope geochemistry; Ultrahigh-pressure metamorphism; Continental collision; China

1. Introduction

Stable isotope geochemistry has proven to be of value in recent studies of high pressure (HP) and ultra high pressure (UHP) metamorphism (Agrinier et al., 1985; Nadeau et al., 1993; Philippot, 1993; Sharp et al., 1993; Fruh-Green, 1994; Getty and Selverstone, 1994; Mattey et al., 1994; Yui et al., 1995; Van Wick et al., 1996; Zheng et al., 1996; Baker et al., 1997; Barnicoat and Cartwright, 1997; Yui et al., 1997; Philippot et al., 1998; Rumble, 1998; Rumble and Yui, 1998; Zheng et al., 1996;

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Zheng et al., 1998a,b; Fu et al., 1999). Measurement of carbon, hydrogen, and oxygen isotope ratios of coexisting minerals provides insights into protoliths, geothermometry, fluid sources, and fluid–rock interactions. These detailed investigations have had an impact beyond their immediate discipline because of their contribution towards understanding the geodynamic cycle of subduction, metamorphism, and exhumation. Research in the Sulu and Dabieshan UHP terrains of China, e.g., has shown that protoliths were subjected to alteration by meteoric water heated in a near-surface geothermal system prior to subduction (Yui et al., 1995, 1997; Zheng et al., 1996, 1998a; Baker et al., 1997; Rumble and Yui, 1998). The ancient geothermal system left an indelible record in the form of rocks strongly depleted in ^{18}O and D. Eclogites as well as their country rocks are depleted and, therefore, both must have experienced UHP metamorphism (Rumble, 1998). Mapping has shown the isotopically depleted zone to extend over hundreds of square kilometers in Sulu and Dabieshan (Baker et al., 1997; Zheng et al., 1998a) and suggests that the length scale of crustal slabs remaining structurally coherent throughout the duration of subduction and exhumation was of the order of 100 km (Rumble and Yui, 1998).

The present investigation uses new stable isotope and modal analyses to interpret the behavior of carbonate rocks during continental collision, subduction, UHP metamorphism, and exhumation. The significance of the carbonate rocks is that they are surface rocks, e.g. continental platform-passive margin sediments, that have been subducted into the upper mantle to depths of 80 km or more and subsequently exhumed. A regional survey of isotopic values is made to place constraints on the premetamorphic isotopic composition of carbonate sediments. A structurally coherent succession of marbles, eclogite, jadeite quartzite, gneiss and schist at Shuanghe, Anhui Province, Dabieshan (Cong et al., 1995) was chosen for detailed sampling in order to measure the length scale of isotopic equilibration (or lack thereof) between dissimilar rock types. We find that pristine protolith isotopic values have been preserved in some samples owing to the failure of contiguous carbonate beds to equilibrate despite the extreme P–T conditions of UHP metamorphism. A continuing theme of our results is the ambiguity in assigning the cause of observed isotopic metasomatism to metamorphic processes or to premetamorphic events such as diagenesis.

2. Methods

Samples for the regional survey of marble $\delta^{18}O$ and $\delta^{13}C$ values were culled from existing collections of Wang et al. The Shuanghe specimens were collected by Q. Wang for this study with special care to obtain detailed sample profiles across lithologic contacts at centimeter to meter scale. Hand specimens were cut into slabs, the flat faces polished, and a 1-mm-diameter diamond-tipped drill was used to obtain 3 to 5 mg of powder from selected mineral grains exposed on the flat, polished surfaces. Sampling with a small drill makes it possible to obtain in situ analyses located in relation to rock contacts or other petrographic features. The powders were reacted with 100% phosphoric acid at 60°C in individual reaction vessels maintained at temperature in an all-metal thermal reservoir. Reaction times range from 1 to 8 h, depending on the sequence of individual samples in the schedule of the automatic analyzer. Measured isotopic values of replicate analyses did not depend on acid reaction time. The CO_2 gas released by acid reaction was purified cryogenically and loaded automatically under computer control with a ‘MT-box’ into a Finnigan MAT 252 mass spectrometer. Reported $\delta^{18}O$ values of calcite have been corrected for acid fractionation with the equation of Swart et al. (1991) and of dolomite with the calibration of Rosenbaum and Sheppard (1986).

Staining of thin sections of marble with Alizarin Red-S facilitated modal analysis (1000 point counts per thin section) and revealed abundant dolomite. Quantitative analyses of calcite and dolomite abundances were measured from X-ray diffraction patterns of mineral powders using program GSAS (Larson and Von Dreele, 1986). Samples for X-ray diffraction were collected by drilling the same holes from which isotopically analyzed material was obtained. In samples consisting of calcite–dolomite mixtures, the isotopic composition of the coexisting minerals was calculated from the mass spectrometric analysis of bulk CO_2 by assuming that dolomite is enriched in both ^{13}C and ^{18}O by 0.5‰ relative to calcite under metamorphic conditions (Sheppard and Schwarcz, 1970; Taylor and Bucher-Nurminen, 1986). Calculations are based on the isotopic mass balance approximation of Craig (1953) where:

$$\delta^{13}\mathrm{C}_{\mathrm{CO}_2,\mathrm{bulk}} = X^*_{\mathrm{cc}}\delta^{13}\mathrm{C}_{\mathrm{cc}} + X^*_{\mathrm{dol}}\delta^{13}\mathrm{C}_{\mathrm{dol}},$$

X_{cc} and X_{dol} designate the atomic fraction of C in calcite and dolomite, respectively (computed from quantitative X-ray powder diffraction analysis), and subject to the constraint that $(\delta^{13}\mathrm{C}_{\mathrm{dol}} - \delta^{13}\mathrm{C}_{\mathrm{cc}}) =$ 0.5‰. In calculating δ^{18}O of coexisting calcite and dolomite, a similar equation was used, an equilibrium fractionation of 0.5‰ was assumed, and a correction was made for acid fractionation (Rosenbaum and Sheppard, 1986; Swart et al., 1991).

Results of analysis of standards gives -4.9 (± 0.05) $\delta^{13}\mathrm{C}_{\mathrm{VPDB}}$ and $+7.35$ (± 0.1) $\delta^{18}\mathrm{O}_{\mathrm{VSMOW}}$ for NBS-18, and 1.98 (± 0.1) $\delta^{13}\mathrm{C}_{\mathrm{VPDB}}$ and $+28.5$ (± 0.1) $\delta^{18}\mathrm{O}_{\mathrm{VSMOW}}$ for NBS-19. Recommended values for NBS-18 are -5.02 $\delta^{13}\mathrm{C}_{\mathrm{VPDB}}$ and $+7.15$ $\delta^{18}\mathrm{O}_{\mathrm{VSMOW}}$, and for NBS-19 1.95 $\delta^{13}\mathrm{C}_{\mathrm{VPDB}}$ and 28.6 $\delta^{18}\mathrm{O}_{\mathrm{VSMOW}}$ (Gonfiantini et al., 1995). Analyses of silicates for ^{18}O were made on O_2 gas analyte released by laser heating minerals with a CO_2 laser in BrF_5 reagent (Rumble and Hoering, 1994).

3. Regional geology and UHP metamorphism

In the regional survey of isotopic values discussed below, samples from three different geographic areas are compared. These are: northern Dabieshan (or N. Dabie), central Dabieshan (or Dabie), and Sulu (Fig. 1). Dabieshan and Sulu were once contiguous UHP-metamorphic terrains now separated by 600 km of left-lateral, strike-slip motion on the Tanlu fault in late Jurassic to Early Cretaceous times. The UHP terrains are segments of a Triassic orogenic belt trapped between the colliding Yangtze (S. China) and Sino-Korean (N. China) cratons. Following Triassic-UHP metamorphism, there was limited retrogression in the amphibolite facies followed by granite intrusion and contact metamorphism in the Cretaceous. The UHP terrains comprise predominantly quartz–feldspar gneisses with minor schist and amphibolite. Layers and blocks of marble, eclogite, and ultramafic rocks occur within the more abundant rock types. Central Dabie eclogite facies rocks are in contact to the north with N. Dabie rocks along the Wuhe–Shuihou fault and are flanked to the south by amphibolite and blue schist facies belts (Xu, 1993; Wang et al., 1995, 1996a,b; Hacker et al., 1996; Liou et al., 1996; Hacker et al., 1998).

Rocks of N. Dabie include tonalitic gneisses with amphibolite facies mineral assemblages, migmatites, and amphibolites and the foregoing with minor marble and ultramafic lenses. Relict granulite facies assemblages of garnet–orthopyroxene–clinopyroxene are found in blocks or lenses within tonalite gneiss. The area is extensively intruded by Cretaceous granitoids. Limited mineralogical evidence of UHP metamorphism has been found in N. Dabie at Raobazhai (Tsai et al., 1998). Recently published U/Pb age dates on zircons give a range of 126 to 134 Ma for Cretaceous granitoids and 134–137 Ma (lower intercepts of zircon discordia) for orthogneisses (Xue et al., 1997; Hacker et al., 1998). Triassic metamorphic ages have been measured at two localities (B.M. Jahn, personal communication; Li et al., 1993). Inherited U/Pb ages in zircon cores are 768 to 798 Ma (upper intercepts of discordia) (Hacker et al., 1998) and a granitic mylonite is concordant at 757 Ma (Xue et al., 1997). Metamorphic conditions of the relict granulite facies are estimated as 800°C and 9 to 11 kbars and of the succeeding amphibolite facies as 600°C and 5 to 7 kbars (Wang et al., 1995, 1996a,b; Zhang et al., 1995; Hacker et al., 1996).

Comparison of the three areas shows strong similarities in geologic history between Central Dabie and Sulu but that N. Dabie is different. A Triassic age for UHP metamorphism in Central Dabie and Sulu is well established by Sm/Nd mineral isochrons and by U/Pb dating of zircons in both coesite-bearing eclogites and their host gneisses. Both groups of rocks have zircons whose cores are 638 to 782 Ma (precision limited because discordia are controlled by younger metamorphic ages) and whose rims are 214 to 236 Ma (Ames et al., 1996; Rowley et al., 1997; Hacker et al., 1998). Mineral isochrons for the Sm/Nd and Rb/Sr systems give metamorphic ages of 210–230 Ma for central Dabie and Sulu (Li et al., 1993, 1994; Chavagnac and Jahn, 1996).

Available mineralogical evidence suggests that marbles experienced the same UHP metamorphism

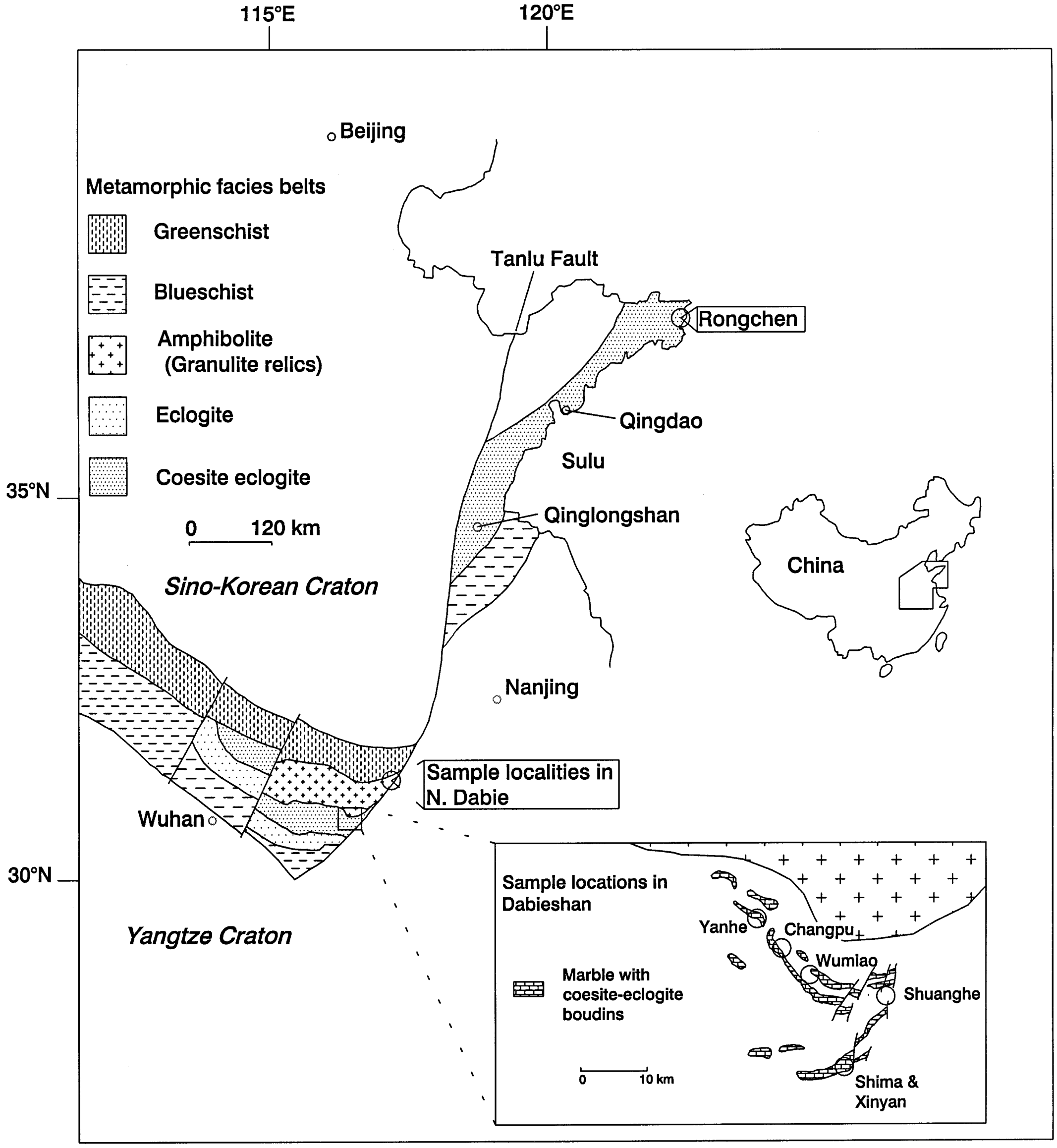

Fig. 1. Metamorphic facies belts of Dabieshan and Sulu. Inset boxes give sample locations in the Sulu UHP terrain at Rongchen, in the amphibolite facies N. Dabie terrain, and in the UHP terrain of central Dabieshan.

in Dabie and Sulu as did the included eclogites. The occurrence of UHP eclogite pods, boudins, and layers enclosed in marble is characteristic of the area. Coesite and its pseudomorphs are widely distributed as inclusions in garnet, zircon, omphacite, epidote and kyanite in eclogite throughout Dabieshan and Sulu. Quartz pseudomorphs after coesite are found in garnet porphyroblasts in impure marble (Zhang and Liou, 1996). Microdiamonds have been reported as inclusions in garnet from an eclogite boudin enclosed in marble at Wumiao, Dabieshan (Xu et al., 1992; Okay, 1993). Given estimates of metamorphic temperatures of 600°C and greater based on mineral geothermometers (Okay, 1993; Wang et al., 1995;

Carswell et al., 1997), the presence of coesite (Tabata et al., 1998) and diamond indicate pressure in excess of 26 kbars with corresponding depths of metamorphism of 100 km, or deeper. An eclogite-like assemblage of calcic garnet, diopside-jadeite (25%) clinopyroxene, phengite, and epidote has been reported from a calc–silicate layer in marble (Wang and Liou, 1991, 1993). The same authors describe textures of quartz pseudomorphs after coesite and calcite after aragonite. Coesite inclusions partially converted to quartz are included in dolomite from a calc–silicate band in marble at the Wumiao diamond locality (Schertl and Okay, 1994).

4. Geologic age

The geologic age of marble protoliths is not known definitively. Rowley et al. (1997) and Hacker et al. (1998), noting the prevalence of late Proterozoic U–Pb ages from zircon cores in para- and orthogneisses as well as eclogites, suggested correlating rocks of the Dabieshan UHP terrain with the Sinian system of the Yangtze platform. According to their correlation, protoliths of UHP marbles are stratigraphically correlative with Sinian carbonate sediments. As is to be discussed below, stable isotope data are consistent with their interpretation. Zheng et al. (1997), however, measured a ^{238}U–^{206}Pb isochron age of 435 ± 45 Ma on marbles associated with UHP eclogites from Dabieshan, a date that is interpreted to refer to diagenesis. Rowley et al. (1997) found a discordant U–Pb zircon population with an upper intercept of 447 Ma in eclogite from Maowu in Dabieshan. The eclogite is part of the Maowu eclogite–ultramafic complex, a layered intrusion emplaced into the crust before UHP metamorphism and subjected to crustal contamination (Liu et al., 1988; Okay, 1994; Fan et al., 1996; Jahn, 1998; Zhang et al., 1998). Although the majority of protolith ages measured to date are late Proterozoic, a mid-Proterozoic age of at least 1.7 Ga has been found in Sulu eclogites at Weihai on the Shandong peninsula (Jahn et al., 1996). Stable isotope data on equilibration of oxygen between eclogite pods and enclosing marble demonstrates that marbles and eclogites shared the same metamorphic history, in other words, their protolith ages are older than UHP metamorphism (Baker et al., 1997; this study, see below). Analyses of different isotope systems including Sm–Nd, Rb–Sr, (mineral plus whole rock isochrons for both systems) as well as U–Pb in zircons cited above agree that UHP metamorphism of eclogites and host gneisses took place in Triassic time between 214 and 245 Ma (Ames et al., 1996; Li, 1996; Li et al., 1993, 1994; Chavagnac and Jahn, 1996; Rowley et al., 1997; Hacker et al., 1998). The carbon isotope geochemistry of the marbles provides a basis for ‘‘chemostratigraphic’’ correlation in order to determine the age of marble protoliths. The unusually high values of δ^{13}C found in marbles from Dabieshan (Baker et al., 1997; Yui et al., 1997; Zheng et al., 1998b; this study) correlate with data reported from unmetamorphosed limestones from the Yangtze Craton (Lambert et al., 1987; Wang et al., 1996a) and from Neoproterozoic basins (age range from 600 to 850 Ma) worldwide (Kaufman and Knoll, 1995). Wickham and Peters (1993) report localities in the northern Great Basin of the western United States where high δ^{13}C values in Neoproterozoic marbles have survived amphibolite facies metamorphism. We adopt the working hypothesis that protoliths of Dabieshan marbles are Neoproterozoic in age, consistent with the majority of radiometric protolith ages determined to date. The existence of an Ordovician thermochemical event that disturbed the U–Pb systematics of the marbles (Zheng et al., 1997), possibly related to the emplacement of layered intrusions (Rowley et al., 1997), remains an intriguing possibility and calls for additional study.

5. Regional survey of isotopic values

There are many processes in play during diagenesis, compaction, and metamorphism that threaten the pristine isotopic values of unaltered protoliths. Sedimentary geochemists use various criteria to screen diagenetically altered samples from unaltered ones. These screens include strong ^{18}O depletion, anomalously high Mn/Sr ratios, petrographic evidence of recrystallisation, and dolomite formation (Derry et al., 1992). Unfortunately, if these were applied to UHP marbles, there would be no samples left to consider! In fact, it is just those changes in mineralogical, chemical and isotopic composition that metamorphic petrologists wish to study. It is crucially important to establish pristine protolith compositions, however, because a benchmark is needed against which to measure changes that have occurred as a consequence of metamorphism. The strategy adopted herein is to obtain a sample set as widely distributed geographically as possible with the hope that the resulting measured range of variation may be used to set limits on premetamorphic isotopic compositions. An inherent weakness of the plan is that lack of stratigraphic control makes it impossible to distinguish changes in sedimentary facies from secular shifts with geologic age. A compensating advantage of the scheme is that by widely casting the sampling net variations caused by different intensities of metamorphism and deformation and different pressure (P) and temperature (T) conditions may be detected.

The regional data set plotted in Fig. 2 shows similarities with unmetamorphosed sediments but depletion effects are evident also. Taking the highest δ^{18}O and δ^{13}C as most likely to represent protolith values (O'Neil, 1987), it may be seen that there is overlap with values of Sinian carbonates. The upper limit on δ^{18}O, 23‰, is within the range of values for unmetamorphosed marine limestones of the Donshantou and Dengying Formations in the Yangtze Gorges section (Lambert et al., 1987; Wang et al., 1996a). The high δ^{13}C values of +4‰ to +5.5‰ in some Dabieshan samples are consistent with ^{13}C enrichments found in Sinian strata (Lambert et al., 1987; Wang et al., 1996a). It is concluded that protolith values of δ^{18}O and δ^{13}C have been preserved in some UHP marbles. Note that there may be two distinct groups of protolith values. Samples from Rongchen in Sulu and from N. Dabie (Fig. 1, Fig. 2) have relatively high δ^{18}O values, +18‰ to +25‰. Their δ^{13}C values are −1‰ to +1‰ (one is +3‰), lower than those of central Dabie marbles but within the range of typical marine carbonates.

The regional distribution of samples may be used to assess the possible effects of variations in metamorphic or deformation intensity. The samples from North Dabie are from a terrain for which there is limited evidence of UHP metamorphism but unmistakable evidence of amphibolite and granulite facies metamorphism as well as Cretaceous granitic intrusions. The analyses span the range in δ^{18}O seen in

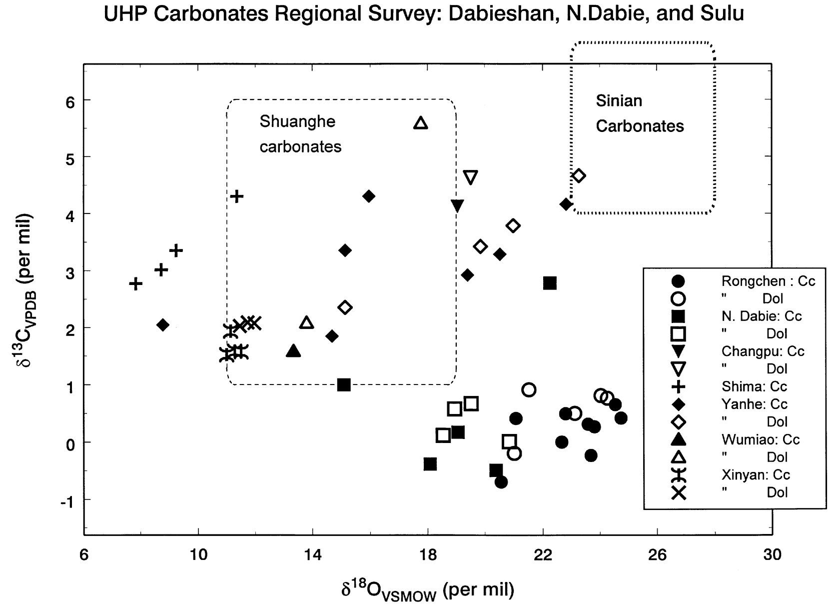

Fig. 2. $\delta^{18}O_{VSMOW}$ vs. $\delta^{13}C_{VPDB}$ of UHP carbonates. Localities are plotted in Fig. 1. Outline boxes give range of values at Shuanghe (see Figs. 3 and 4) and range of unmetamorphosed Sinian carbonates from the Yangtze platform (Lambert et al., 1987; Wang et al., 1996a,b). Taolichong is plotted with the data of nearby Yanhe.

UHP marbles (from +15‰ to +22‰) but the δ^{13}C values (−1‰ to +3‰) are at the low end of the range of Dabieshan UHP rocks. Marbles from Rongchen in the Sulu UHP terrain resemble N. Dabie samples in that they are low in ^{13}C (−1‰ to +1‰) but somewhat higher in δ^{18}O (+19‰ to +25‰). Note that some analyses of unmetamorphosed Sinian carbonates are as low as −5‰ δ^{13}C and +22‰ δ^{18}O (Lambert et al., 1987; Wang et al., 1996a). Thus, it is concluded that δ^{13}C values of −1‰ to +3‰ in N. Dabie and Sulu are consistent with preservation of protolith compositions. As noted above, two distinct marble protolith groups may exist: (1) Central Dabieshan and (2) N. Dabie and Sulu. Two marble samples from the Wumiao diamond locality (Xu et al., 1992; Okay, 1993) show a range of values (δ^{18}O +14‰ to +18‰; δ^{13}C +1.8‰ to +5.5‰) that lies within that of marbles with coesite-bearing eclogite pods. It is concluded that differences between the N. Dabie data and analyses from the Dabie and Sulu UHP terrains cannot be unambigiously attributed to differences in metamorphism.

Many of the samples in the data set are depleted in ^{18}O in relation to unaltered protoliths. The cause of the depletions cannot be assigned a priori to UHP metamorphism nor can they be definitively attributed to premetamorphic processes. Yao and Demicco (1997), e.g., have documented dolomitization by formation waters diluted by low-^{18}O meteoric water that resulted in carbonates depleted by some 10‰ in δ^{18}O but relatively unchanged in δ^{13}C, reminiscent of dolomitic Dabieshan marbles. Ambiguous examples are known from low-grade metamorphic rocks: oxygen isotope shifts of as much as 3‰ to 7‰ in weakly metamorphosed, chlorite-zone limestones and dolostones, may have been caused by metamorphic devolatilization *or* premetamorphic infiltration of meteoric water during diagenesis (Rumble et al., 1991). Samples from Dabieshan with high δ^{13}C (+3‰ to +6‰) but low δ^{18}O (+10‰ to +18‰) plot above typical decarbonation trajectories on a graph of δ^{18}O vs. δ^{13}C (Valley, 1986, Fig. 6). Decarbonation reactions typically show covariation of decreasing δ^{13}C and complimentary decreasing δ^{18}O (Rumble, 1982; Valley, 1986). The implied alteration pathway of the unusual Dabieshan samples, in contrast, is decrease in δ^{18}O but with no change in δ^{13}C. We propose as a preliminary working hypothesis that high δ^{13}C, low δ^{18}O carbonates formed prior to metamorphism by reacting with pore waters depleted in ^{18}O by dilution with meteoric water. It may be argued that infiltration of carbonate rocks by CO_2-free water would be capable of altering δ^{18}O but leave δ^{13}C unchanged. The presence of a calcite vein not in oxygen isotope equilibrium with its wall rocks (Fig. 5B) supports the hypothesis of fracture-controlled, channelized infiltration but we do not have enough samples of veins to make an evaluation. The failure of contiguous carbonate beds to equilibrate isotopically denies the presence of a pervasive, freely infiltrating fluid phase during metamorphism. We do not rule out isotope shifts caused specifically by metamorphism and these will be discussed in Section 6 on Shuanghe carbonate rocks.

6. Shuanghe locality

Shuanghe in Dabieshan was chosen for detailed stable isotope mapping because it is a structurally coherent slab of many different rock types that experienced UHP metamorphism (Cong et al., 1995). The locality is relatively well exposed and, therefore, provides an opportunity for closely spaced sampling traverses across lithologic contacts in order to evaluate mechanisms of isotopic equilibration between dissimilar rock types during metamorphism. The slab is a north-dipping monoclinal succession of interlayered epidote–two mica schist, garnet–biotite gneiss, eclogite, jadeite quartzite, and marble (Fig. 4). Marble layers host eclogite boudins whose garnet porphyroblasts contain coesite inclusions. Peak metamorphic conditions are estimated as 700 ± 50°C and 27 to 32 kbars (Cong et al., 1995; Carswell et al., 1997). Retrogression during exhumation produced symplectitic coronas of albite replacing jadeite, augite and sodic plagioclase after omphacite, and amphibole and sodic plagioclase after garnet. Sampled marbles are virtually pure carbonate. Of the 44 samples for which modal analyses were performed, 33 contain 90%, or more, of carbonate and only 8 have less than 80%. Silicates, when present, consist of small amounts of quartz, plagioclase, phengite, phlogopite, tremolite, and diopside with symplectites of plagioclase–amphibole–biotite or plagioclase–quartz–amphibole.

Oxygen and carbon isotope data from Shuanghe overlap the same range of δ^{18}O and δ^{13}C seen in the regional data set. Regional values are +8‰ to +25‰ in δ^{18}O and −1‰ to +6‰ δ^{13}C. Shuanghe samples range from +10‰ to +20‰ in δ^{18}O and +1‰ to +6‰ δ^{13}C (Fig. 3). The regional and the Shuanghe data sets are similar in the absence of strongly covariant trends in δ^{18}O and δ^{13}C (Fig. 3). This absence may reflect a sampling bias in that analyses were made on relatively pure marbles rather than rocks with calc–silicate minerals. Isotopic analyses of samples with abundant calc–silicate minerals are expected to show covariant δ^{18}O and δ^{13}C because of the stoichiometric constraints of metamorphic devolatilization reactions (Rumble, 1982; Valley, 1986). Shuanghe δ^{13}C data are all plausible unmodified protolith values. The δ^{18}O analyses, however, overlap pristine protoliths only at the upper limit of their range (cf. Lambert et al., 1987; Wang et al., 1996a). These observations support a working hypothesis that carbon isotope results represent protolith values whereas oxygen isotope ratios have been altered.

A map view of Shuanghe data shows weak stratigraphic control on isotopic values, at a scale of 100 m (Fig. 4). The easternmost dolomitic marble band (labeled ‘A’ in Fig. 4A) is +18‰ δ^{18}O and +1.7‰ δ^{13}C except for one sample, which is +9.9‰ and +4.0‰, respectively. The westernmost calcitic marble layer (‘G’, Fig. 4A) is mostly +13‰ to +14‰ δ^{18}O and 4.2‰ to 5.3‰ δ^{13}C except for a few samples with δ^{18}O as high as +20‰ and δ^{13}C as low as +1.7‰. Thus the two largest carbonate beds are distinctly different in their calcite/dolomite ratio but overlap in both δ^{18}O and δ^{13}C. Marble outcrops between the eastern and western bands overlap these values. A pattern of local oxygen isotopic variability is also shown by silicate minerals in eclogite and wall rock gneisses. Data on omphacite from the two large eclogite bands flanking marble ‘A’ (Fig. 4A) show variations in δ^{18}O from +5.3‰ to +7.0‰ across strike (Zheng et al., 1998a; cf. Fu et al., 1999). Omphacites from eclogite lenses 0.5 km south of Fig. 4 range from −0.9‰ to +2.0‰ (Zheng et al., 1998a).

Isotopic mapping at a scale of 1 m resembles that at 100 m. There is no strong consistency in values either parallel or perpendicular to the strike (Fig. 5; localities D and E in Fig. 4A). The map distribution shows that samples separated by as little as 2 m failed to equilibrate in terms of either δ^{18}O or δ^{13}C, or both (Fig. 5). Evidence of channelized, fracture-

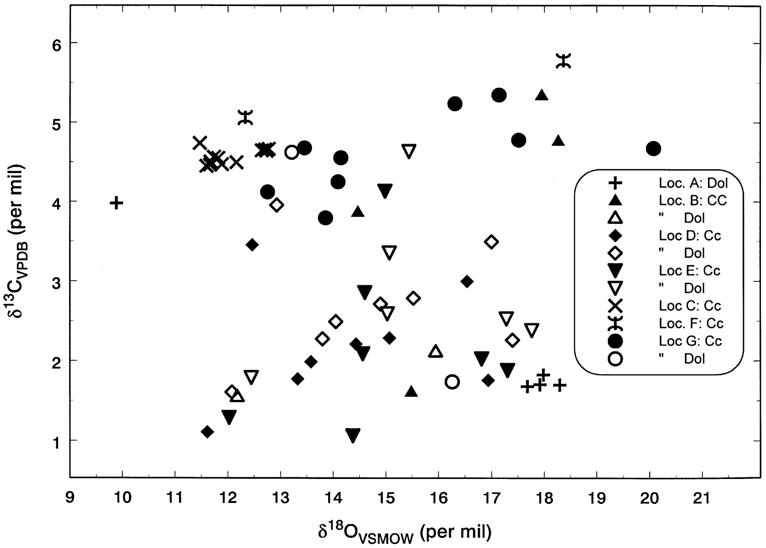

Fig. 3. $\delta^{18}O_{VSMOW}$ vs. $\delta^{13}C_{VPDB}$ of UHP carbonates from Shuanghe. Location of Shuanghe is given in Fig. 1. Localities A...G are plotted in Fig. 4.

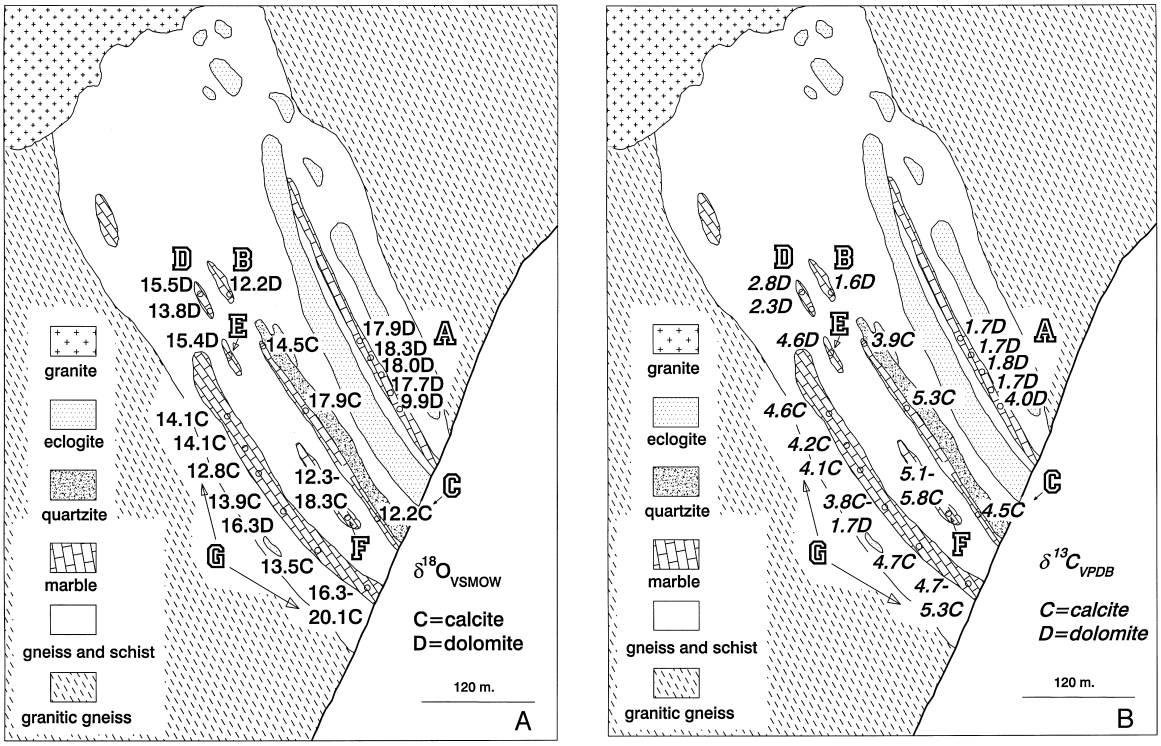

Fig. 4. (A) Map of $\delta^{18}O$ at Shuanghe. Data given for the dominant mineral at each site, but in most samples, both calcite and dolomite coexist. Dash indicates a range of values. Location of outcrops discussed in text given by large hollow letters A . . . G. Geologic map simplified after Cong et al. (1995). (B) Map of $\delta^{13}C$ at Shuanghe. Data given for the dominant mineral at each site but in most samples both calcite and dolomite coexist. Dash indicates a range of values. Location of outcrops discussed in text given by large hollow letters A . . . G. Geologic map simplified after Cong et al. (1995).

controlled fluid infiltration may be seen in the calcite–phengite vein of Fig. 5B; vein calcite is not in oxygen isotope equilibrium with wall rock dolomite ($\delta^{18}O_{dol}$–$\delta^{18}O_{cc}$ = −2.0‰) but approaches carbon isotope equilibrium, i.e., $\delta^{13}C_{dol}$–$\delta^{13}C_{cc}$ = 0.7‰.

Examples of possible isotopic equilibration only begin to appear in samples spaced less than 10 cm. Calcitic marble in the hand specimens of Fig. 6 (locality ‘C’ in Fig. 4A) is homogeneous isotopically over distances of 4 to 6 cm. Furthermore, there are indications of at least partial approach to equilibrium between silicate minerals in eclogite boudins and marbles enclosing them. Measured garnet $\delta^{18}O$ of +7.9‰ and +8.1‰ (Fig. 6; Table 1) from small boudins greatly exceed garnet values of −5 to +1 per mil from eclogite hosted by biotite gneisses from nearby Dabie localities (Baker et al., 1997). These workers found that garnet from small, 10-cm eclogite boudins in marble is +9.5 to +11 per mil but that garnet from a 3-m-thick boudin is +2.3 $\delta^{18}O$ (cf. Zheng et al., 1998a). Calcite–garnet $^{18}O/^{16}O$ fractionations in specimens shown in Fig. 6 give temperature estimates of 500°C to 600°C (Table 1) (calibration of Rosenbaum and Mattey, 1995). These temperatures are 100°C lower than peak metamorphic temperatures calculated from silicate geothermometers (Cong et al., 1995; Carswell et al., 1997) but overlap the oxygen isotope geothermometry of Zheng et al. (1998a). The foregoing observations are consistent with isotopic equilibration between dissimilar rock types limited to distances of 10 cm but with little or no effective isotopic transport over distances greater than 1 m. Baker et al. (1997) came to a similar conclusion regarding the length scale of isotopic transport and suggest that the mechanism of equilibration between small eclogite bodies and host

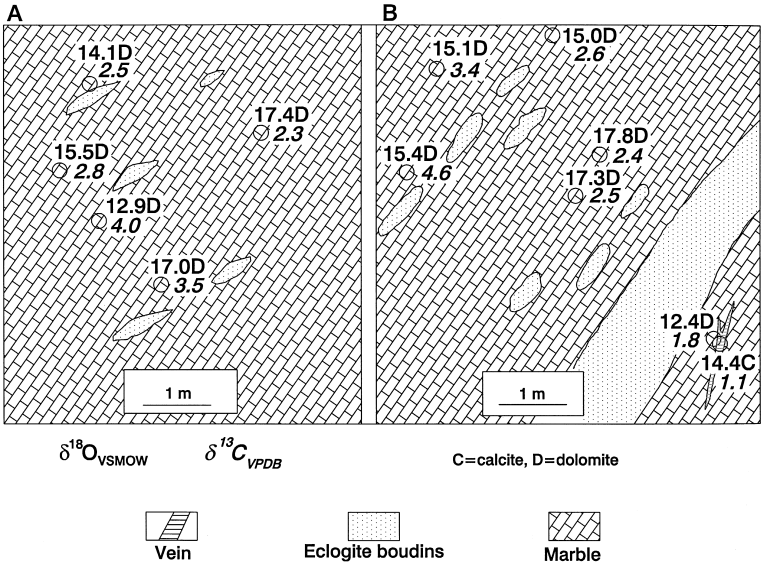

Fig. 5. Map of δ^{18}O and δ^{13}C for localities D (Fig. 5A) and E (Fig. 5B) at Shuanghe shown in Fig. 4. Data given for the dominant mineral, but both calcite and dolomite are present in most samples.

marbles was via ^{18}O-enriched CO_2–H_2O fluids released by devolatilization reactions. The data presented herein do not fully support the proposed mechanism, however, because the covariation in δ^{18}O and δ^{13}C expected from devolatilization reactions has not been found. The discrepancy may be due to sampling bias as our samples include predominantly pure calcitic and dolomitic marbles in which devolatilization would not control isotopic compositions owing to a lack of silicate reactant minerals.

Modal analyses of carbonate–silicate proportions make it possible to evaluate whether isotope shifts are independent of or controlled by the stoichiometry of metamorphic devolatilization reactions. In the easternmost dolomitic marble band (‘A’, Fig. 4A), e.g., all the analyzed rocks contain more than 90% carbonate. Sample 96105 (Table 2; Fig. 4) depleted in ^{18}O by 8‰ and enriched in ^{13}C by 2.3‰ relative to other samples along strike is 100% dolomite. Samples with 70% to 80% carbonate have the same range in δ^{18}O and δ^{13}C as rocks with 90% to 100% of calcite and dolomite. Models of isotopic changes caused by metamorphic reactions show that for small amounts of reaction progress only small shifts in δ^{18}O and δ^{13}C are to be expected (Rumble, 1982; Rumble et al., 1982; Valley, 1986). The rocks of Shuanghe, with a predominance of carbonate and a lack of reaction products, should have undergone little or no change in isotopic composition as a consequence of metamorphic devolatilization reactions. The observed large changes in isotopic composition are independent of mineralogical changes. We conclude that the observed range in δ^{18}O and δ^{13}C of marbles was not caused by reactions between carbonate reactants and silicate products.

Our results demonstrate that unmodified protolith values of δ^{18}O and δ^{13}C are commonly preserved in UHP marbles. The persistence of unaltered values argues strongly against the existence of freely infiltrating, pervasive fluids during subduction, metamorphism, and exhumation (Baker et al., 1997; Zheng et al., 1998a,b). The potential influence of fracture-controlled infiltration, however, cannot be evaluated at the present time because we do not have enough analyzed vein samples. Changes in isotopic composition do not correlate with mineralogical indicators of prograde metamorphism. Retrograde metamorphism is ubiquitous throughout the Dabie and Sulu UHP terrains but has had no major effect on isotopic values, apart from reversing garnet–omphacite oxygen isotope fractionations (Yui et al., 1997). It has been proposed that retrograde fluids were derived locally from gneissic wall rocks and, as such, would

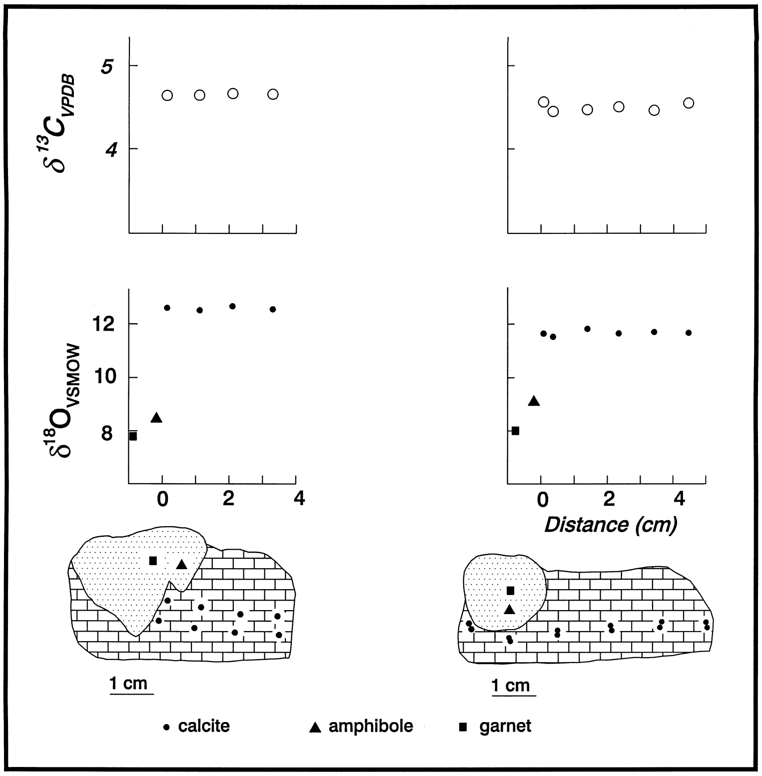

Fig. 6. Profiles of $\delta^{18}O$ and $\delta^{13}C$ in two-hand specimens from Shuanghe at locality C in Fig. 4. Silicate analytical data are given in Table 2. Calcite data are averages of paired drill holes.

be expected to have the observed mineralogical effects (amphibolite alteration rinds enclosing eclogite boudins, microscopic symplectitic reaction coronas) but would have little capacity to alter isotopic compositions (Baker et al., 1997). The foregoing discussion eliminates for UHP marbles many of the customarily cited metamorphic controls on stable isotope composition. Yet isotopic values of many samples appear to be altered from those of pristine protoliths. Such alteration must have taken place prior to UHP metamorphism. We suggest that the observed large variations in $\delta^{18}O$ originated during diagenesis and dolomite formation and were caused by the mixing of low-^{18}O meteoric water with pore waters. The irregular distribution of altered and pristine ^{18}O values is a consequence of premetamorphic fractures focusing water flow. A weakness of our hypothesis is that the sample set is dominated by relatively pure marbles. A study of carbonate rocks containing more calc–silicate mineral assemblages might show stronger metamorphic effects on stable isotope compositions.

Table 1
Oxygen isotope compositions of coexisting silicates and calcite with temperature estimates

Sample	Gt[a]	Amp	Cc	Gt-Amp[b]	Cc-Gt[b]	Cc-Amp[b]	Cc-Gt[c]
96509	8.14	8.89	12.74	415°C	468°C	482°C	507°C
96510	8.00	8.50	11.67	607	585	583	600

[a] Mineral abbreviations are gt = garnet, amp = amphibole, cc = calcite.

[b] Calibration of Zheng (1993a; b).

[c] Calibration of Rosenbaum and Mattey (1995).

7. Protolith environment

Accepting that at least some UHP marbles have tenaciously preserved pristine $\delta^{18}O$ and $\delta^{13}C$ despite

Table 2
Calcite/dolomite proportions, oxygen and carbon isotope compositions, and location of labeled Shuanghe outcrops (see Fig. 4)

Sample	%Cc[a]	Calcite[b]		Dolomite[c]		Location in Fig. 4[d]
		^{18}O	^{13}C	^{18}O	^{13}C	
Sulu						
Qinglongshan						
95-QL-3B	100.0	−2.95	−0.31			
Rongchen						
SL91-8	na[e]	24.74	0.42			
SL91-8A	na	23.68	−0.23			
SL91-8B	16.4	22.66	0.00	23.11	0.50	
SL91-8I	49.5	23.58	0.31	24.03	0.81	
SL91-9E	na	24.54	0.65			
SL92-9A	22.0	23.81	0.27	24.26	0.77	
SL92-9D	1.0	21.07	0.41	21.52	0.91	
SL92-9J	1.0	20.56	−0.70	21.02	−0.20	
SL95-9B	na	22.79	0.49			
Dabieshan						
N. Dabie						
94-7A	100.0	15.09	1.00			
94-7B	100.0	22.26	2.78			
94-8A	0.0			18.95	0.58	
94-DB-08E	1.0	19.06	0.17	19.52	0.67	
95-16B	1.0	20.39	−0.49	20.84	0.01	
95-16C	1.0	18.09	−0.38	18.55	0.12	
Changpu						
CP-7	4.0	19.05	4.13	19.51	4.63	
Shima						
MHM-17	na	7.84	2.77			
MHM-19	na	8.73	3.01			
94-DB-57A	100.0	11.35	4.30			
94-DB-57C	100.0	9.24	3.35			
Shuanghe						
SH-05	na	11.49	4.02			
SH06	na	11.40	4.34			
SH07	na	12.50	4.26			
SH08	na	11.42	4.00			
92-72B	0.0			18.35	1.61	
92H17	na	17.04	0.54			
92HW20	na	12.41	4.79			
94-DB-184-B	100.0	12.03	4.37			
95-015	100.0	12.78	4.35			
96101	0.0			17.92	1.71	A
96102	0.0			18.30	1.70	A
96103	0.0			17.98	1.83	A
96104	0.0			17.68	1.68	A
96105	0.0			9.89	3.98	A
96201	100.0	18.27	4.77			B
96202	100.0	17.95	5.34			B
96204	100.0	14.47	3.87			B
96205	1.0	15.48	1.62	15.95	2.12	B
96206	0.0			12.18	1.56	B
96301	3.6	13.58	1.99	14.05	2.49	D
Dabieshan						
Shuanghe						
96302	3.0	15.07	2.29	15.53	2.79	D
96303	32.0	16.94	1.76	17.40	2.26	D
96304	32.6	12.47	3.46	12.93	3.96	D
96305	17.1	16.54	3.00	17.00	3.50	D
96307	15.7	11.61	1.11	12.08	1.61	D
96308	16.5	13.33	1.78	13.80	2.28	D
96309	31.1	14.44	2.21	14.90	2.71	D
96401	53.8	14.60	2.86	15.07	3.36	E
96402	13.9	14.98	4.13	15.44	4.63	E
96403	21.9	14.56	2.09	15.03	2.59	E
96404	25.8	16.82	2.03	17.28	2.53	E
96405	25.0	17.30	1.88	17.76	2.38	E
96406	14.7	12.03	1.29	12.45	1.79	E
96406c	na	14.37	1.06			E
96502	100.0	11.47	4.73			C
96504	100.0	12.16	4.49			C
96509A	100.0	12.74	4.64			C
96509B	100.0	12.64	4.64			C
96509C	100.0	12.78	4.66			C
96509D	100.0	12.71	4.65			C
96510A	100.0	11.59	4.45			C
96510B	100.0	11.89	4.47			C
96510C	100.0	11.67	4.50			C
96510D	100.0	11.67	4.46			C
96510F	100.0	11.74	4.56			C
96510G	100.0	11.81	4.55			C
96601	100.0	12.33	5.06			F
96602	100.0	18.36	5.77			F
96701	100.0	14.15	4.55			G
96702	100.0	14.09	4.25			G
96705	90.0	12.76	4.12	13.22	4.62	G
96706	100.0	13.86	3.79			G
96707	0.0			16.26	1.74	G
96708	100.0	13.46	4.68			G
96710	100.0	16.31	5.23			G
96711	100.0	17.51	4.78			G
96712	100.0	20.08	4.67			G
96713	100.0	17.14	5.34			G
Taolichong						
93-46B	na	8.78	2.05			
94-DB-45F	30.0	14.68	1.85	15.14	2.35	
Tongbai						
92-8D	12.2	6.61	−1.14	7.08	−0.64	
92-D2	6.3	22.86	−0.49	23.32	0.02	
Xinyan						
XH05	na	11.13	1.94			
XH09	na	9.31	−4.24			
94-18B	1.0	11.27	1.59	11.73	2.09	
94-18C	1.0	11.50	1.58	11.97	2.08	
94-18D	1.0	10.99	1.53	11.46	2.03	

Table 2 (continued)

Sample	%Cc[a]	Calcite[b]		Dolomite[c]		Location in Fig. 4[d]
		^{18}O	^{13}C	^{18}O	^{13}C	
Dabieshan						
Yanhe						
94-52A	59.4	20.53	3.28	20.99	3.78	
94-52B	15.8	22.81	4.16	23.26	4.66	
94-52E	20.2	19.40	2.92	19.85	3.42	
94-DB-53B	100.0	15.95	4.30			
94-53C	100.0	15.13	3.35			
Wumiao						
W-44	0.0			17.76	5.58	
MW-45	13.3	17.93	3.05	18.39	3.55	
92-W-50	39.6	13.34	1.58	13.80	2.08	

[a] Calcite weight fraction relative to dolomite.

[b] Calcite isotopic composition. Coexisting pairs calculated, see text.

[c] Dolomite isotopic composition. Coexisting pairs calculated, see text.

[d] Letter gives outcrop location in Fig. 4.

[e] na = Mineral proportions not analyzed; sample assumed to be 100% calcite.

UHP metamorphism, we now explore the consequences and implications for estimating conditions of protolith deposition. Comparison of the characteristic features of the Shuanghe locality described above with dolomitized limestones (Yao and Demicco, 1997) reveals a number of similarities: (1) There are along-strike and across-strike variations in the proportions of calcite and dolomite; (2) The stable isotopic values of altered limestones and replacement dolostones follow a trajectory of decreasing δ^{18}O but with little change in δ^{13}C; (3) Contiguous outcrops contain carbonates that failed to achieve oxygen isotopic equilibrium. The comparison does not prove that Shuanghe carbonate rocks acquired their stable isotope signature and mineralogy during dolomitization but it does demonstrate the potential for diagenesis to play an important role in controlling isotopic compositions.

It is a tenet of conventional wisdom that the coesite–eclogite facies rocks of Dabieshan are correlative with unmetamorphosed sediments and igneous rocks of late Proterozoic age exposed on the Yangtze platform (Rowley et al., 1997; Hacker et al., 1998). Stated dynamically, the younger, thinner Proterozoic Yangtze craton is believed to have been subducted beneath the older, thicker overlying Archaen Sino–Korean craton during Triassic continental collision. Our results are consistent with this tectonic hypothesis and indicate that the northern edge of the subducted Yangtze craton extends at least as far north as Central Dabieshan and may lie in N. Dabie, in agreement with the correlations of Rowley et al. (1997) and Hacker et al. (1998). It has already been shown above that U–Pb zircon age dates of UHP eclogites and gneisses (upper discordia intercepts) and high δ^{13}C compositions of UHP marbles are mutually consistent with correlating UHP marbles and Sinian limestones because rocks of such ages and with high δ^{13}C are known on the Yangtze platform. Many Sinian carbonates are dolomitized just as they are at Shuanghe. Also present on the platform are glacial tillites of the Nantou Formation below the ^{13}C-enriched limestones of the Doushantou Formation (Lambert et al., 1987; Wang et al., 1996a). The Sinian limestones and tillites are examples of a worldwide association of interstratified glacial deposits and ^{13}C-enriched carbonates of Neoproterozoic age (Kaufman et al., 1997; Hoffman et al., 1998). We now wish to call attention to the unusually low-δ^{18}O, low-δD eclogites, gneisses, schists, quartzites, and meta-granites of Sulu and Dabie. It is generally agreed that isotopic depletion was imposed on the rocks by an active geothermal system charged with meteoric water and operating at Earth's surface before continental collision and subduction (Yui et al., 1995; Zheng et al., 1996, 1998a; Baker et al., 1997; Rumble, 1998; Rumble and Yui, 1998). Depletions of this magnitude are known from geothermal areas located in cold climates (Blattner et al., 1997). It may be seen that isotopic evidence of a cold climate in UHP rocks is correlative with the presence of glacial deposits on the Yangtze craton (cf. Rowley et al., 1997). Some stipulations must be made, however. Unmetamorphosed carbonates immediately overlying and underlying Neoproterozoic glacial deposits usually have negative δ^{13}C values, attributed to a collapse of biological activity in surface oceans caused by global glaciation (termed 'snowball Earth') (Wang et al., 1996a; Kaufman et al., 1997; Hoffman et al., 1998). The cold climate recorded by low δ^{18}O and low δD may not have coincided with the deposition of high δ^{13}C carbonates. The stratigraphic correlations attempted herein are not strictly synchronic. We simply note that both

Dabie UHP rocks and Sinian sediments share similar features over the same interval of time in the late Proterozoic.

8. Conclusions

The relatively pure marbles of this study have shown little tendency to change their oxygen and carbon isotopic composition during UHP metamorphism except on a localized scale in response to noncarbonate rocks with which they are in contact. In this, they behave much as pure marbles of lower pressure metamorphic regimes. In the absence of silicate reactants to permit devolatilization reactions, there are few metamorphic processes capable of changing stable isotope values of marbles. Additional study is needed of vein–wall rock relationships to evaluate the role of fracture-controlled infiltration during metamorphism.

The unresponsiveness of the marbles is a disadvantage when considered in the context of studies of metamorphic processes. Retention of pristine protolith compositions is, however, an advantage in attempts to reconstruct depositional conditions. High δ^{13}C values make it possible to correlate UHP marbles stratigraphically with ^{13}C-enriched Neoproterozoic limestones, and, thus, to confirm that the marbles are similar in geologic age to the eclogites and gneisses with which they are interlayered.

The failure of UHP marbles to equilibrate isotopically on a local scale under the extreme P–T conditions of UHP metamorphism may seem surprising. Indeed, one may legitimately be shocked to realize that Dabieshan UHP marbles, originally deposited near Earth's surface, were subducted into the upper mantle and failed to communicate metasomatically with the largest reservoir on the planet. But such refractory behavior is also known in Sulu eclogites with record $\varepsilon_{\mathrm{Nd}}$ values of $+170$ to $+260$ (Jahn et al., 1996) and in Dabie and Sulu rocks with negative δ^{18}O and δD, as discussed above.

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