

Yilin Xiao · Zeming Zhang · Jochen Hoefs
Alfons van den Kerkhof

Ultrahigh-pressure metamorphic rocks from the Chinese Continental Scientific Drilling Project: II Oxygen isotope and fluid inclusion distributions through vertical sections

Received: 31 May 2005 / Accepted: 21 December 2005 / Published online: 30 March 2006
© Springer-Verlag 2006

Abstract In order to reconstruct the formation and exhumation mechanisms of UHP metamorphic terrains, the Chinese Continental Scientific Drilling Program (CCSD) has been carried out in Donghai of the Dabie-Sulu ultrahigh-pressure (UHP) metamorphic belt, East China. Eclogite, gneiss, amphibolite (retrograded from eclogite), ultramafic rocks, and minor schist and quartzite have been drilled. Aiming to reveal the fluid behaviour in a vertical sequence of an UHP slab, we investigated fluid inclusion and oxygen isotope characteristics of selected drillcores from the main hole and the pilot-holes PP2 and ZK 703 of the CCSD. More than 540 laser-ablation oxygen isotope analyses on garnet, omphacite, quartz, kyanite, amphibole, phengite, rutile, epidote, amphibole, plagioclase, and biotite from various rocks in the depth range of 0–3,000 m (mainly eclogite and gneiss) show that the investigated rocks can be divided into two groups: ^{18}O -depleted rocks (as low as $\delta^{18}\text{O} = -7.4\text{‰}$ for garnet) indicate interaction with cold climate meteoric waters, whereas ^{18}O -normal rocks (with bulk $\delta^{18}\text{O} > +5.6\text{‰}$) have preserved the O-isotopic compositions of their protoliths. Meteoric water/rock interaction has reached depths of at least 2,700 m. Oxygen isotope equilibrium has generally been achieved. Isotopic compositions of mineral phases are homogeneous on a mm to cm scale regardless of lithology, but heterogeneous on the scale of a few metres. Oxygen isotope distributions in the verti-

cal sections favour an “in situ” origin of the UHP metamorphic rocks. The very negative $\delta^{18}\text{O}$ eclogites usually have higher hydroxyl-mineral contents than the normal $\delta^{18}\text{O}$ rocks, indicating higher water content during UHP metamorphism. Fluid inclusion data suggest that rocks with depleted ^{18}O compositions have had different fluid histories compared to those with normal $\delta^{18}\text{O}$ values. Rocks with depleted ^{18}O mainly have primary medium-to-high salinity inclusions in omphacite, kyanite and quartz, and abundant secondary low-salinity or pure water inclusions in quartz, indicating a high-salinity-brine-dominated fluid system during peak UHP metamorphism; no carbonic inclusions have been identified in these rocks. By contrast, primary very high-density CO_2 inclusions are commonly found in the rocks with normal $\delta^{18}\text{O}$ values. These observations suggest that fluid and oxygen isotope composition of minerals are related and reflect variable degrees of alterations of the Dabie-Sulu UHP metamorphic rocks.

Communicated by T. L. Grove

Y. Xiao (✉) · J. Hoefs · A. van den Kerkhof
Geowissenschaftliches Zentrum der Universität Göttingen,
Goldschmittstrasse 1, 37077 Göttingen, Germany
E-mail: yxiao@gwdg.de
Tel.: +49-551-395253
Fax: +49-551-393982

Z. Zhang
Institute of Geology, Chinese Academy of Geological Sciences,
Baiwanzhuang Road 26, 100037 Beijing, China

Introduction

Ultrahigh-pressure (UHP) metamorphic terrains play a critical role in the global geochemical cycle, because they are locations at which crustal materials were both recycled into the mantle and returned to the Earth's surface (for review, see Chopin 2003). These processes can be facilitated by the presence and movement of fluids at a variety of scales and levels. It has been long recognized that large amounts of fluid are released through compaction, dewatering, and dehydration that are associated with subducted oceanic crust (e.g., Peacock 1990). Although continental subduction may be relatively dry, substantial quantities of H_2O can still be transported to depths greater than 100 km by many hydrous phases such as epidote, phengite, zoisite, serpentine, and lawsonite (e.g., Thompson 1992), and

by nominally anhydrous minerals such as garnet and clinopyroxene under UHP conditions (e.g., Su et al. 2002, 2004). Therewith, UHP metamorphic terrains probably play an integral role in mantle metasomatism and partial melting.

As the largest UHP terrain so far found worldwide, the Dabie-Sulu metamorphic belt in East China has attracted extensive interest from the geoscience community. In the need for understanding the fluid regimes—which may greatly assist in the development of genetic models for UHP metamorphic rocks—in the past decade, a considerable number of studies have been devoted to determine the chemical and isotopic compositions of fluids during UHP metamorphism of the terrain. For example, oxygen isotope investigations of abundant surface samples from the Dabie-Sulu metamorphic belt have shown that UHP metamorphic rocks in an area over 15,000 km² have the lowest “world record” of $\delta^{18}\text{O}$ values (bulk $\delta^{18}\text{O} = -10\%$; e.g., Yui et al. 1995; Rumble and Yui 1998; Zheng et al. 1998; and references therein). The oxygen isotope anomaly was interpreted to have resulted from water/rock interaction with very ¹⁸O-depleted meteoric waters formed under extremely cold climatic conditions related to “Snowball Earth” during the Neoproterozoic, based on combined oxygen isotope and U–Pb dating studies on zircons from various UHP metamorphic rocks (Rumble et al. 2002; Zheng et al. 2004). Previous fluid inclusion investigations on metamorphic rocks from Dabie Shan have demonstrated that at least five compositionally different fluids have been present, and that the different fluids could be related to different metamorphic stages (Xiao et al. 1998, 2000, 2001, 2002; Fu et al. 2001, 2003).

These investigations on surface samples not only have provided important constraints on the structural picture of fluid behaviour during UHP metamorphism, but also pose the question how fluid/rock interactions take place along a vertical section of an UHP terrain. Studies of layered rocks at the outcrop scale have demonstrated the important control of lithology on flow geometry (e.g., Nabelek et al. 1984). Oxygen isotope investigations on vertical profiles of oceanic crust showed that the oxygen isotope composition varies with depths throughout the complete section (e.g., Gregory and Taylor 1981; Miller et al. 2001). This could also be true in a continental UHP vertical section but so far has not been observed. To clarify the question, we investigated the oxygen isotope and fluid inclusion distribution in drillcores of UHP rocks from the Chinese Continental Scientific Drilling Program (CCSD).

The CCSD in Donghai of the Dabie-Sulu UHP metamorphic belt in East China is aiming to reconstruct the formation and exhumation mechanisms of UHP metamorphic terrains; one of the major goals is to investigate the variation of fluid composition with depth, the flow patterns, and cycling mechanisms, as well as changes of the fluid regime in time (Xu et al. 1998).

Using a combined study of petrological observations, fluid inclusions, and oxygen isotope investigations on selected drillcores from the CCSD, the present work aims to reconstruct the fluid behaviour during UHP and subsequent retrograde metamorphism. Specifically we expect to: (1) verify the minimum depths of the meteoric water/rock interactions in the Dabie-Sulu area, (2) reveal the oxygen isotope characteristics in a 3,000 m vertical profile of an UHP slab, (3) obtain information about possible changes of fluid composition with depth, and (4) determine the fluid evolution during UHP metamorphism of the rocks.

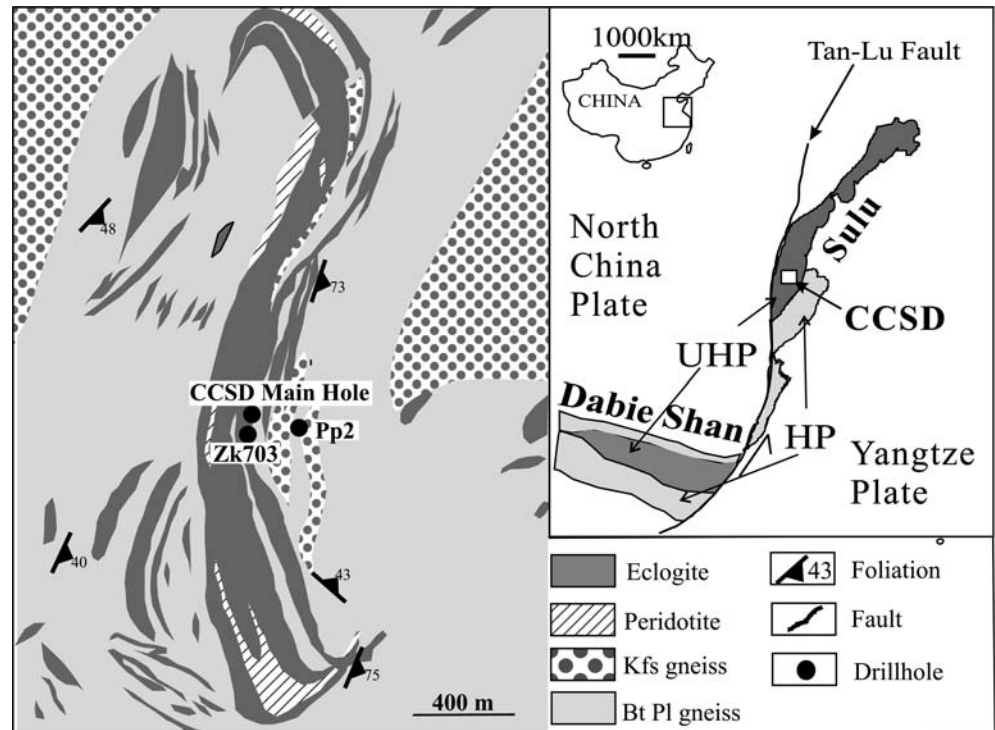
Geological background

The Dabie-Sulu UHP metamorphic terrain extends in a WNW–ESE direction for longer than 2,000 km, situated within the collision zone between the North China (Sino-Korean) Plate and the Yangtze Plate. In the east, the collision zone was displaced approximately 500 km by the NE-trending Tan-Lu fault to the northeast from the Dabie Shan to form the Sulu terrain (inset of Fig. 1), which is located in the northern Jiangsu (Su) and the eastern Shangdong (Lu) provinces of China.

The Sulu terrain can be divided into fault-bounded UHP and HP metamorphic belts. The UHP belt consists mainly of amphibolite–granulite facies granitic gneiss, amphibolite, metamorphosed garnet peridotite and pyroxenite, and minor marble; abundant eclogite bodies occur as lenses, discontinuous layers, nodules, or boudins in the gneiss, ultramafic bodies, and marbles, ranging in size from centimetres to several hundreds of metres. Some eclogites occur as discontinuous layers of several tens of metres to kilometres. Peak metamorphic conditions are defined by coesite-bearing eclogites with temperatures of 650–850°C and pressures of 25–40 kbar (for review, see Liou et al. 1998). A retrograde granulite facies overprint after coesite–eclogite facies metamorphism has been recognized by Wang et al. (1993) and Yao et al. (2000). Preliminary chronological studies indicate that the protoliths of the UHP eclogites and surrounding gneisses are Proterozoic in age (Jahn et al. 1996), and that the UHP rocks formed around 220–240 Ma during an early Mesozoic collision (Li et al. 1994; Rumble et al. 2002; Liu et al. 2004).

The Donghai area, which has been selected as the drill-site of the CCSD, is located in the southern part of the Sulu UHP terrain (Fig. 1). Eclogite and associated kyanite quartzite, garnet–jadeite quartzite, and ultramafic rocks are distributed as intercalated layers of gneissic country rock. All rock types have been subjected to the same UHP event (Liu et al. 2002). At Donghai, one famous eclogite outcrop is Qinglongshan, in which the world-record lowest $\delta^{18}\text{O}$ values for eclogites have been reported (as low as -15% for rutile; Yui et al. 1995; Zheng et al. 1996; Rumble and Yui 1998).

Fig. 1 Simplified geological map of the Dabie-Sulu orogenic belt showing the major geological background of the Donghai area and the location of the CCSD drill site



Sample descriptions and petrological observations

The CCSD consists of three pilot holes (PP1, 430 m; PP2, 1,028 m; and PP3, 720 m), and a main drill hole which reached its final depth of 5,180 m in March 2005. Besides the pilot holes of the CCSD, many shallow holes have been drilled for mineral exploration in the Sulu area; among these holes, ZK703 and PP2 are the drill holes closest to the main hole. Surface distance between ZK 703 and the main hole is about 80 m, whereas those between ZK703 and PP2, and between PP2 and the main hole are about 300 and 200 m, respectively (Fig. 1).

ZK 703 reached a depth of 558 m, with core recovery of > 85%. The drill cores consist mainly of eclogite with a composite thickness of about 350 m, which are interlayered with gneiss, phengite-quartz schist, jadeite quartzite, and kyanite quartzite (Zhang et al. 2000). The contact between different rock types is generally sharp and un-tectonized. The recovered rock types include eclogite, amphibolite (retrograde eclogite), garnet peridotite, orthogneiss, paragneiss, and minor schist, quartzite and jadeite, with eclogite + gneiss > 95%. By contrast, the main rock types in PP2 are granitic gneiss and paragneiss, with only minor intercalated layers of eclogite, schist, and amphibolite. The core recovery is up to 90%.

Eclogite and gneiss are also the principal lithologies of the main hole. The core recovery is > 80%. Eclogites have a total thickness of about 1,200 m, and mainly occur at depth intervals of 0–1,100 m and 1,600–2,050 m; gneisses mainly occur from 1,100 to 1,600 m and from 2,050 to 3,000 m; other rock types comprise ultramafic rock (600–700 m) and rarely schist and quartzite.

After general inspection of the drill cores, we selected 48 samples from the main hole, 10 samples from ZK703 and 8 samples from PP2, mainly focussed on eclogite and gneiss. The depths range from 97 to 3,000 m. Lithologies, mineral assemblages, and depths of samples are listed in Table 1. Samples sites are shown in Fig. 2.

Mineral assemblages of eclogites from the CCSD can vary from sample to sample. Fresh eclogite is mainly composed of garnet + omphacite + rutile ± phengite ± kyanite ± quartz ± zoisite. Rutile occurs in all investigated eclogites with volume percents of 1–5%. Kyanite is a major phase in some samples, coexisting with primary garnet and omphacite. Phengite is common in most samples, occurring either as an interstitial mineral in matrix or as inclusions in garnet.

Paragneiss consists mainly of quartz + plagioclase + biotite + epidote ± K-feldspar ± phengite ± rutile ± amphibole, whereas orthogneiss contains mainly K-feldspar + plagioclase + quartz with minor garnet and biotite. The contact between different gneisses is usually sharp or, sometimes, shows cm-thick gradations. Although the major mineral assemblages of gneiss indicate only amphibolite-facies metamorphism, mineral inclusions (e.g., coesite) in zircons from these rocks indicate that they have been subjected to UHP metamorphism together with eclogite (Liu et al. 2002).

Analytical techniques

More than 540 oxygen isotope analyses have been carried out on various mineral phases, including garnet, omphacite, quartz, phengite, rutile, epidote, amphibole,

Table 1 Oxygen isotopic compositions of major mineral phases in UHP metamorphic rocks from the CCSD, Sulu, China

Sample ^a	Lithology	Depth (m)	Oxygen isotopic compositions									
			Grt	Cpx	Amp	Phen	Ky	Ep	Qtz	Fel	Bt	Ol
Main hole												
MH01	Eclogite	101	2.9(6) ^c	3.5 (3)		3.7(2)				6.2 (2)		3.6
MH02	Eclogite	103	2.9 (4)	3.4 (2)						6.1 (2)		3.5
MH03	Eclogite	312	1.7(8)	2.1(4)		2.8(5)	3.1*			4.9 (5)	4.9*	2.6
MH04	Eclogite	352	1.5 (2)	2.0 (2)	2.2 (2)							2.0
MH05a	Retro. eclogite	366	1.3 (10)							4.3 (1)		
MH05b	Gneiss	366	1.2 (5)							4.3 (5)		
MH05c	Gneiss	366	1.8 (8)							4.8 (1)		
MH06	Eclogite	450	3.3 (2)	3.4 (3)	3.5(1)	4.2 (2)						3.5
MH07	Retro. eclogite	493	0.1 (2)		0.7 (2)					2.5 (2)		0.8
MH08	Eclogite	511	1.5 (4)	2.0 (2)						4.1 (3)		2.0
MH09	Retro. eclogite	520	1.4 (2)							4.8 (2)		2.1
MH10	Eclogite	572	0.3 (3)	0.0 (3)						2.6(1)		0.2
MH11	Eclogite	576	0.7 (2)	1.2 (2)								0.9
MH12	Ultramafic rock	680	5.3 (3)	5.4 (3)								5.3 (2) 5.3
MH13	Paragneiss	928	-1.9 (1)					-2.0 (3)	1.7 (2)		-4.3 (2)	-0.6
MH14	Eclogite	962	-5.5 (5)	-5.6* -5.4 (2)	-5.1*	-4.4 (2)						-5.2
MH15	Eclogite	1,003	-6.3 (4)	-5.2 (1)		-4.7 (3)		-5.8 (2)	-3.4 (1)			-5.5
MH16	Eclogite	1,066	-4.5 (4)	-4.2 (4)			-3.5 (4)	-3.9 (3)				-4.0
MH17	Orthogneiss	1,260								1.5 (6)	0.3 (3)	-1.0 (1)
MH18	Orthogneiss	1,385								5.4 (3)	4.6 (4)	2.6 (2)
MH19	Orthogneiss	1,518								1.3 (3)	0.7 (2)	-1.7 (1)
MH20	Eclogite	1,690	5.9 (2)	6.1 (2)		6.4 (1)						6.0
MH21	Orthogneiss	1,731								6.9 (2)	6.4 (4)	6.6
MH22	Eclogite	1,778	6.2 (4)	5.9 (4)						8.5 (1)		6.2
MH23	Orthogneiss	1,850								8.2 (3)	7.6 (5)	5.1 (1)
MH24	Eclogite	1,855	5.4 (7)	5.7 (4)						8.2 (1)		5.7
MH25	Eclogite	1,940	5.3 (2)	5.7 (2)		6.3 (2)						5.6
MH26	Eclogite	1,950	5.4 (4)	5.8 (3)		6.1 (1)	5.9 (4)					5.7
MH27	Eclogite	1,964	5.9 (2)	6.5 (2)		7.1 (2)	6.4 (1)					6.5
MH28	Eclogite	1,993	5.6 (7) 5.5*	6.0 (5) 5.9*						8.5 (2)	8.3*	5.9
MH29	Orthogneiss	2,065								8.5	7.3	7.8
MH30	Paragneiss	2,197	4.2							6.8	5.4	6.0
MH31	Retro. eclogite	2,272	5.2		4.9					7.7		5.2
MH32	Paragneiss	2,363					0.6			4.3	1.4	1.9
MH33	Orthogneiss	2,426	-3.6							-0.3	-1.2	-0.9
MH34	Paragneiss	2,552	-6.6							-2.3		-2.8
MH35	Paragneiss	2,566	-7.4							-2.4		-3.2
MH36	Paragneiss	2,651								0.1	-0.4	0.0
MH37	Retro. eclogite	2,688	-1.0							2.6		-0.5
MH38	Paragneiss	2,699	-4.0									-1.0
MH39	Retro. eclogite	2,706	-0.4 (4) -0.6*		0.5 (3)		1.4 (2)			-0.3	-1.4	3.3*
MH40	Eclogite	2,711	-1.6							2.4		-1.0
MH41	Orthogneiss	2,752								3.7	3.3	3.5
MH42	Eclogite	2,767	4.9	6.1						8.9		5.6
MH43	Retro. eclogite	2,774	4.1							8.2		5.0
MH44	Paragneiss	2,868	2.3							6.3	4.4	5.1
MH45	Paragneiss	2,966								6.6	4.5	5.3
MH46	Orthogneiss	2,980								5.6	4.1	4.8
ZK 703												
703-2	Eclogite	97	2.3 (12)	3.1 (7)	3.2 (2)					5.4 (3)		3.2
703-8	Retro. eclogite	121	3.9 (7)				4.8 (2)			6.4 (5)		4.5
703-19	Eclogite	183	3.2 (6)	3.4 (5)						5.5 (4)		4.0
703-5s(e)	Eclogite	204	-0.2 (5)		0.2 (2)					2.1 (5)		0.5
703-5s(g)	Gneiss	204								2.0 (6)	1.3 (5)	-1.3
703-26	Eclogite	220	2.5 (5)	2.9 (3)						5.5 (1)		2.8

Table 1 (Contd.)

Sample ^a	Lithology	Depth (m)	Oxygen isotopic compositions										
			Grt	Cpx	Amp	Phen	Ky	Ep	Qtz	Fel	Bt	Ol	Bulk ^b
703-27	Eclogite	224	2.7 (3)	3.0 (1)						5.6 (2)			3.0
703-28	Eclogite	235	3.0 (5)	3.4 (2)						6.0 (3)			3.5
703-54	Eclogite	446	1.2 (3)	1.6 (4)		1.1 (3)				4.2 (2)			1.9
PP2													
PP2-1	Paragneiss	178						-1.4 (2)	1.2 (8)	0.5 (8)	-1.9 (2)		0.1
PP2-2	Retro. eclogite	182	-3.4 (5)		-2.8 (1)			-2.5 (2)					-3.0
PP2-3	Retro. eclogite	267	-5.7 (9)			-4.7 (1)							-5.3
PP2-4	Retro. eclogite	286	-4.2 (2)			-3.5 (2)	-3.1 (2)		-1.4 (1)				-3.8
PP2-5	Paragneiss	556						1.2 (2)	3.4 (4)	2.3 (4)	0.4 (5)		2.2
PP2-6	Retro. eclogite	677	-3.5 (9)		-3.6 (4)				-0.2 (2)				-3.6
PP2-7	Eclogite	989	3.1 (6)	3.8 (5)					6.1 (3)				3.5
PP2-8	Paragneiss	992						-0.3 (4)	1.4 (4)	0.8 (3)	-0.9 (2)		0.9

^aSamples from depths above 2,000 m were analysed by UV laser probe, whereas those below 2,000 m were analysed by CO₂ laser probe (except MH 39, which was measured by both methods)

^bBulk $\delta^{18}\text{O}$ values were estimated based on mineral phase oxygen isotopic compositions and modal abundance

^c $\delta^{18}\text{O}$ values of minerals represent the average of the analyses; numbers in bracket indicate the numbers of analyses

*Values represent the results of CO₂ laser analysis

plagioclase, and biotite. Individual mineral phases in samples from depths above 2,000 m were analysed “in situ” using UV-laser fluorination, whereas those from depths between 2,000 and 3,000 m were measured with a CO₂ laser system at the same laboratory in Göttingen. The CO₂ laser method is not suitable for “in situ” analysis, but saves time as several samples can be loaded together in the sample chamber. The reason for the measurement of samples above 2,000 m by UV laser is simply that the CO₂ laser system was not available until July 2004.

In order to check for any systematic error between the two methods, a few samples were analysed by both UV and CO₂ laser measurements (Table 1). The results are reported in the conventional δ notation relative to standard mean ocean water (SMOW). Whole-rock oxygen isotope compositions were calculated based on modal abundances (visual estimation) and the average of measured mineral isotope ratios. Major and trace elements for the same samples were also measured and are available upon request from the first author (see also Zhang et al. 2006, this issue).

Samples for “in situ” analysis were prepared as polished thick sections (~15 mm×15 mm×2 mm). The sections were cleaned with distilled water using an ultrasonic bath and then dried overnight at ~300°C under vacuum; analytical procedures have been described in detail in Wiechert et al. (2002). To ensure representative mineral compositions, electron microprobe analysis was performed after in situ UV laser measurement using a JXA-8900 JEOL Superprobe equipped with WD/ED combined microanalyser (see Xiao et al. 2002).

The CO₂ laser measurements were typically carried out on 1–1.5 mg mineral separates obtained by hand-picking under a binocular microscope. Mineral separates were loaded in a nickel holder with eighteen 2-mm-deep holes. After evacuation and heating to ~80°C overnight, the sample chamber was loaded with 15–25 mbar F₂,

and the mineral fragments were heated with the CO₂ laser. It is important to operate the laser in a suitable energy level to ensure that samples do not jump out of the hole. The lasing time is variable from 1 min for quartz to 10–15 min for garnet, olivine, and omphacite. Oxygen is purified in a way similar to the UV laser method as described by Wiechert et al. (2002), collected in a molecular sieve and transferred to the Finnigan Delta plus for the measurement of ¹⁸O/¹⁶O ratios. $\delta^{18}\text{O}$ values measured by both UV and CO₂ lasers for the same sample indicate that the accuracy of the two methods is the same within errors ($\pm 0.2\%$) (Table 1).

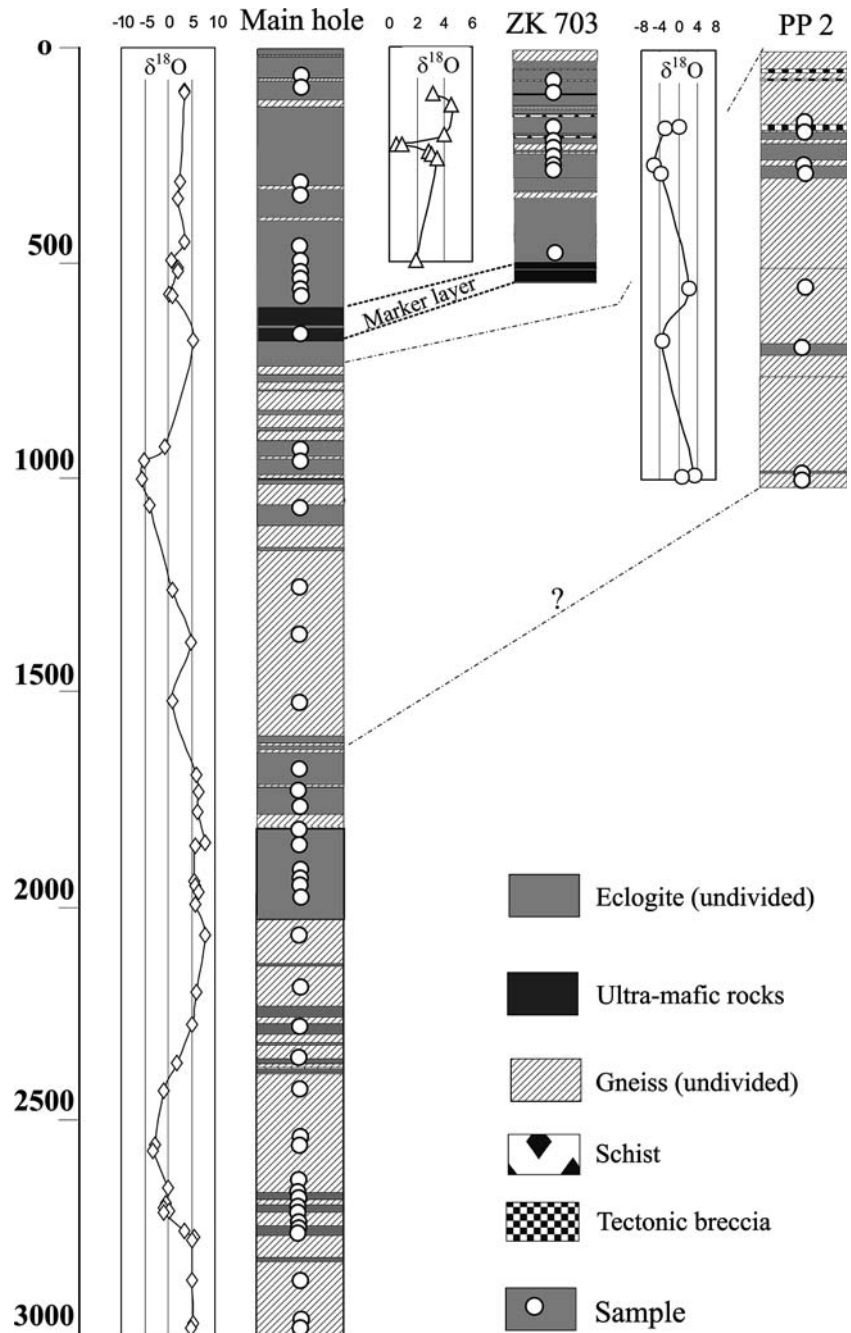
Microthermometric data for fluid inclusions were obtained using a Linkam heating–freezing stage, provided with a video system for ease of observation. Measurements were performed on doubly polished unmounted sections of ~200 μm thickness cooled with liquid nitrogen. Temperature readings were calibrated by measuring a set of synthetic fluid inclusions. Accuracies are generally about 1°C, but for CO₂ melting are 0.2°C.

Oxygen isotopes

Oxygen isotope compositions are presented in Table 1, mostly as averages of triplicate or more determinations. Large variations in O-isotope ratios for samples from different depths were observed, with ranges from -7.4 to +6.2‰ for garnet, -5.5 to +6.5‰ for omphacite, -4.2 to 7.2‰ for phengite, -1.4 to 7.3‰ for plagioclase, and -2.4 to +8.9‰ for quartz. The main features of the $\delta^{18}\text{O}$ data are presented graphically in Figs. 2, 3, 4, 5, 6, and 7. The most important results of the oxygen isotope data are as follows:

- (1) All investigated samples can be divided into two groups according to their whole-rock $\delta^{18}\text{O}$ values: ¹⁸O-depleted rocks (as low as $\delta^{18}\text{O} = -7.4\%$ for

Fig. 2 Lithological and oxygen isotope profiles of the investigated drill cores of the CCSD



garnet) and normal metamorphic rocks with $\delta^{18}\text{O} > +5.6\text{‰}$ (Hoefs 2004). For the ^{18}O -depleted rocks, cold climate meteoric waters are the only major terrestrial reservoirs with $\delta^{18}\text{O}$ values low enough to generate the observed oxygen depletions, as demonstrated by previous oxygen isotope studies in the Dabie-Sulu UHP metamorphic belt (e.g., Yui et al. 1995; Zheng et al. 1996). Heterogeneities of oxygen isotope distributions in both vertical (variation with depths) and horizontal directions (comparison between rocks from PP2, ZK703, and the main hole) suggest channelized water/rock interactions in three dimensions. On the other hand, rocks with $\delta^{18}\text{O}$ values $>5.6\text{‰}$ do not indicate any meteoric

water/rock interaction. Although significant interaction with the mantle during subduction to mantle depths may modify the oxygen isotope composition to the measured range, Sr–Nd–Pb isotopic studies suggest that there is no systematic isotopic difference between the rocks with depleted ^{18}O and those with $\delta^{18}\text{O} > 5.6\text{‰}$, so that this process is unlikely (Y. L. Xiao et al., in preparation). Therefore, we consider that these rocks have preserved the O-isotopic compositions of their protoliths.

(2) Oxygen isotope depletions are observed down to 1,600 m and again from 2,300 to 2,700 m (Figs. 2, 3), regardless of lithology, indicating that water/rock interaction extended to a depth of about 2,700 m.

Fig. 3 Oxygen isotopic compositions versus depths (for clarity not all measured values are presented in this figure)

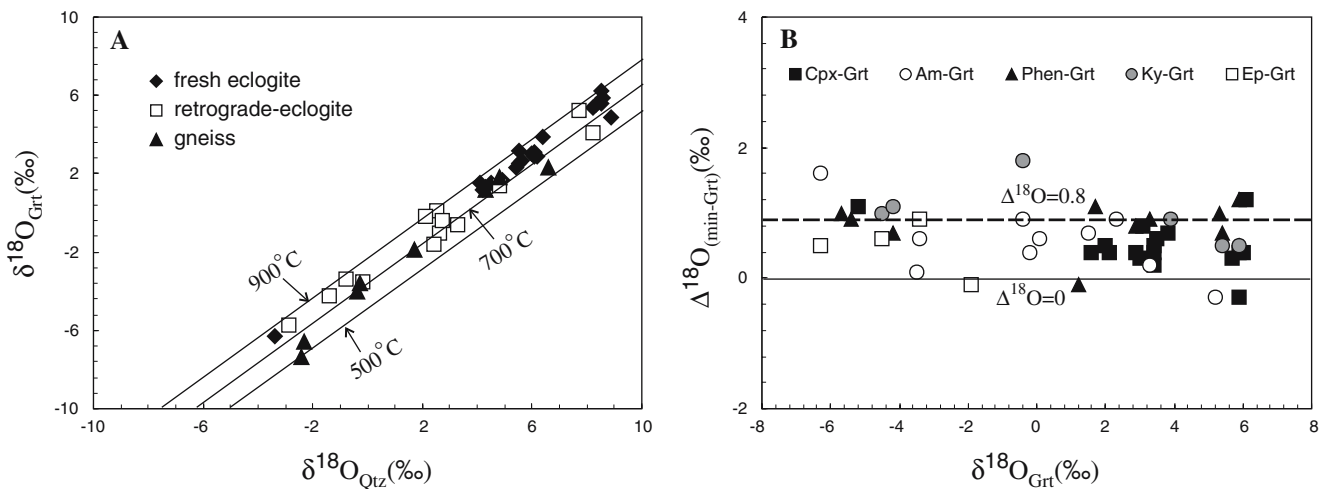
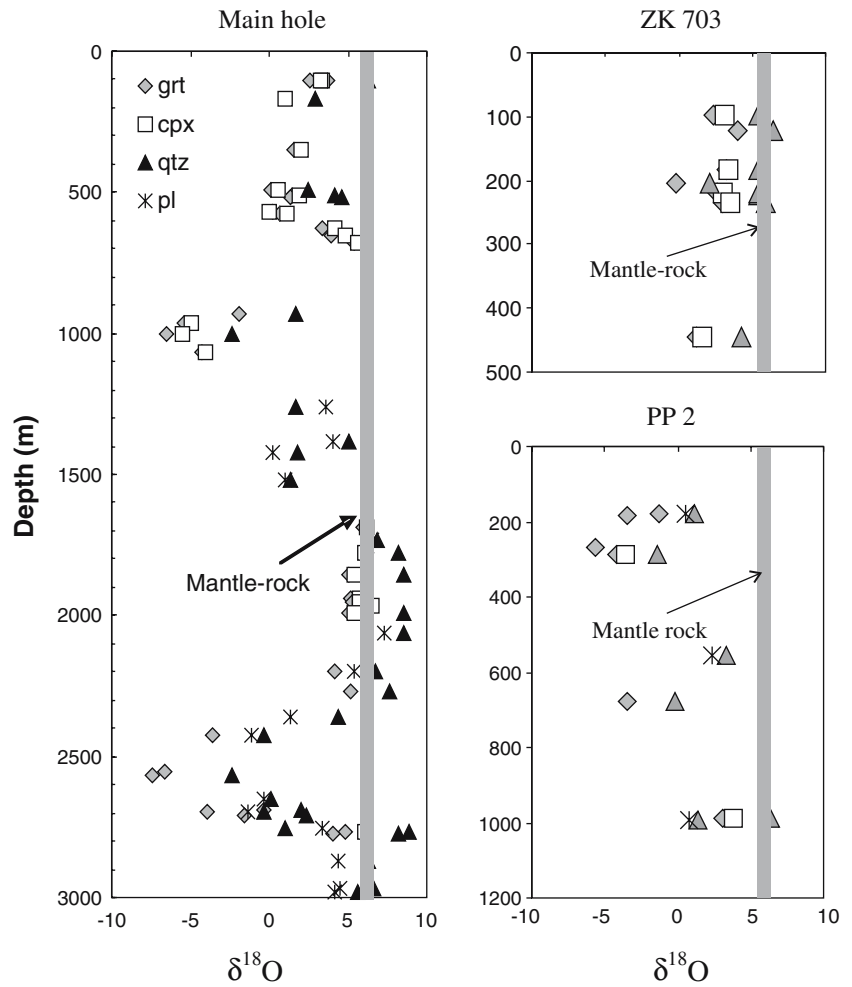


Fig. 4 a Plot of oxygen isotopic compositions of quartz versus coexisting garnet in various rocks from the CCSD. Slope = 1 equilibrium fractionation lines at different temperatures are drawn by applying the method of Zheng (1993). **b** Oxygen isotope fractionations between clinopyroxene/amphibole/phengite/kyanite/

epidote and garnet versus $\delta^{18}\text{O}$ of garnet. Two reference lines marking the limit of equilibrium isotopic fractionation between phengite/kyanite and garnet ($\Delta^{18}\text{O}=0.8\text{‰}$) and between clinopyroxene/amphibole/epidote and garnet ($\Delta^{18}\text{O}=0\text{‰}$) are also shown (after Yui et al. 1997)

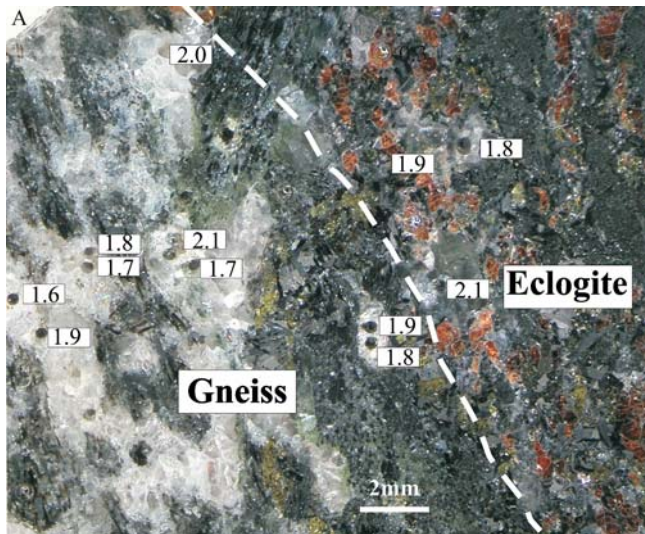


Fig. 5 “In situ” oxygen isotope mapping for gneiss and eclogite in close contact. Quartz in eclogite and gneiss show more or less the same $\delta^{18}\text{O}$ values, suggesting that the rocks have already obtained their depleted isotope values before subduction (photomicrograph from sample 703-5s, 204 m)

- (3) The lowest $\delta^{18}\text{O}$ values occur at depths of 900–1,100 m and 2,500–2,600 m (Fig. 2), corresponding to boundaries between eclogites and thick ortho-(granitic)-gneiss layers. Zircon from the orthogneiss layers suggests intrusion ages of 663–750 Ma (Liu et al. 2004), which are consistent with the time of meteoric water/rock interactions (Rumble et al. 2002; Zheng et al. 2004). Therefore, the ^{18}O data support the conclusion that the heating engines driving hydrothermal circulation of meteoric waters were granitic plutons intruded during the Neoproterozoic global glaciation (Rumble et al. 2002; Zheng et al. 2004).
- (4) Oxygen isotope fractionations of individual mineral phases indicate oxygen isotope equilibrium during UHP metamorphism except in two samples (Fig. 4). In a strongly retrograded eclogite (PP2-2), the average $\delta^{18}\text{O}$ value of garnets (13 spots, -3.46‰) is slightly enriched compared to secondary amphiboles (4 spots, -3.74‰), which clearly indicates isotopic

disequilibrium, resulting probably from retrograde metamorphism. In a “fresh” eclogite (MH-09), garnets (5 spots, -5.44‰) have almost identical $\delta^{18}\text{O}$ values with omphacites (2 spots, -5.51‰), which may indicate either very high equilibrium temperatures, or alternatively, oxygen isotope disequilibrium.

- (5) Minerals from eclogite and gneiss near their mutual contact show very similar O-isotope compositions (Figs. 5, 6). On the other hand, samples from a 15-m-thick eclogite indicate gradual variations of $\delta^{18}\text{O}$ values for individual mineral phases (Fig. 7). These features demonstrate that the amount of infiltrating fluid across the rock contacts was not sufficient to obliterate isotopic differences in the protoliths.

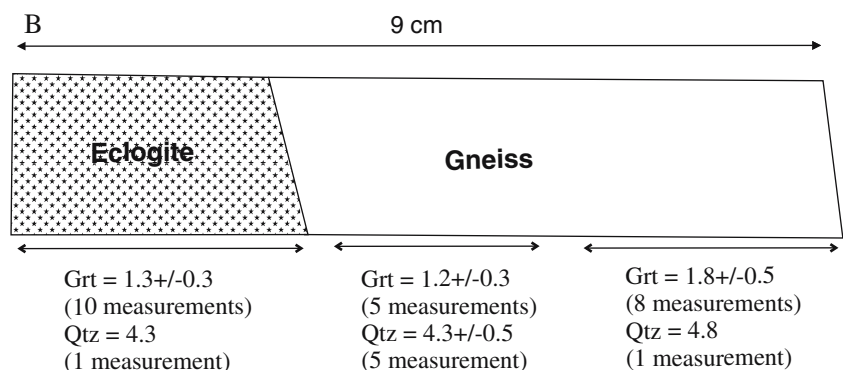
Oxygen isotope geothermometry

Achievement of O-isotopic equilibrium at the mm-to-cm scale in the investigated samples allows temperature estimates. Among the various mineral phases in eclogite, quartz–garnet oxygen isotopic fractionations give the best estimate of peak metamorphic temperatures (Rumble and Yui 1998). Application of the quartz–garnet thermometer of Zheng (1993) yields temperatures of 700–900°C and 760–860°C for eclogites and gneisses from depths above 2,300 m, whereas 590–870°C and 500–660°C from depths of 2,300–3,000 m, respectively (Fig. 8; see also Fig. 4a).

The difference in oxygen isotopic temperatures between rocks from depths above 2,300 m and those below 2,300 m may indicate that rocks from different depths have undergone different P – T conditions during subduction. However, temperatures estimated from Mg–Fe cation exchange thermometers for the eclogites from 2,300 to 3,000 m range from 785 to 850°C, which are consistent with the temperatures estimated for the rocks above 2,300 m but are obviously higher than those from quartz–garnet oxygen isotope thermometer (Fig. 8).

A systematic error between the CO_2 and the UV laser probes is unlikely because the two systems have been checked numerous times with different standards and

Fig. 6 Garnet and quartz from eclogitic and gneissic parts have very similar $\delta^{18}\text{O}$ values at the lithologic boundary (sample MH5a–c, 366 m); however, within a few centimetres $\delta^{18}\text{O}$ values of garnet and quartz in gneiss increase by $\sim 0.5\text{‰}$, indicating a gradual change in O-isotopic compositions



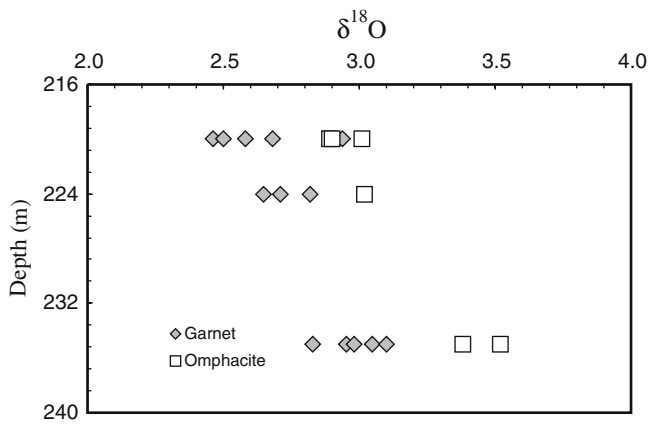


Fig. 7 Eclogites between 220 and 235 m show a gradual increase of $\delta^{18}\text{O}$ values for individual mineral phases (garnet and omphacite) with increasing depths, indicating heterogeneous oxygen isotopic distributions within the same rock-body. An increase of $\delta^{18}\text{O}$ values with depth within the same layer probably indicates the direction of the fluid flow, as the isotopic front infiltrating through a rock usually becomes less steep with increasing distance from the contact

four samples were analysed by both UV and CO_2 laser methods. $\delta^{18}\text{O}$ data from CO_2 laser method indicate that mineral separates collected from three relatively fresh samples have very similar $\delta^{18}\text{O}$ values as obtained with the UV laser probe (see Table 1). However, minerals collected from a retrograded eclogite (MH 39) show slightly variable $\delta^{18}\text{O}$ values for a given mineral and larger $\Delta^{18}\text{O}$ values between quartz and garnet (Table 1). By comparison of conventional and UV-laser oxygen-isotope data, Wiechert et al. (2002) have demonstrated that oxygen isotope data from conventional fluorination method represents a mean of both altered and unaltered minerals. Here, we suggest that temperatures estimated from oxygen isotope data by UV laser probe probably represent peak metamorphic conditions, whereas those by CO_2 laser probe may reflect a mean of both peak and retrograde metamorphic temperatures.

Most gneisses recovered by the CCSD experienced significant retrograde metamorphism. Compared to those from the upper part, eclogites from depths below 2,300 m show much stronger retrogression and have mostly become garnet amphibolites. Therefore, it is likely that the low temperatures estimated from CO_2 -laser oxygen-isotope results do not represent the peak conditions of these rocks. Instead, they may record an average of peak- and retrograde-stage temperatures. Therefore, ^{18}O data obtained from “in situ” analysis may be more suitable for peak temperature estimates.

Fluid inclusions

Fluid inclusions mostly occur in quartz and, only rarely in garnet, omphacite, kyanite, and epidote. Most inclusions occur in healed fractures, indicating their secondary origin. Isolated or randomly scattered inclusions are

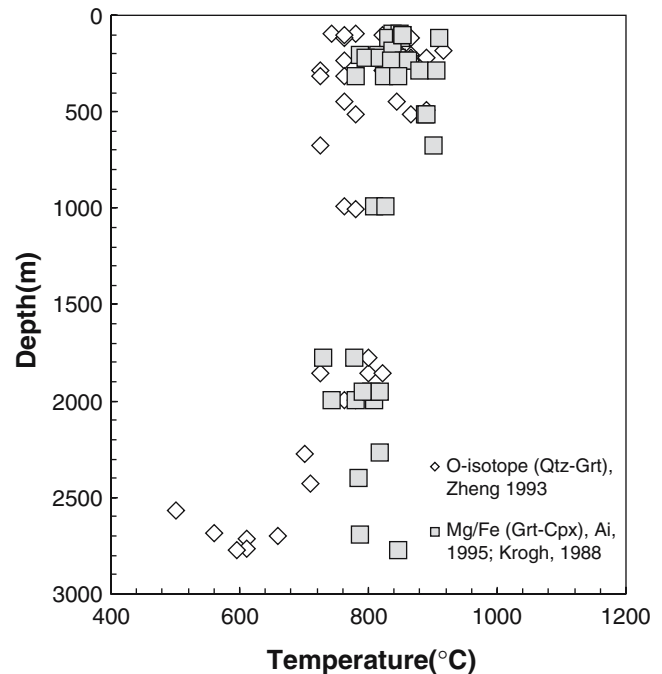


Fig. 8 Comparison of temperatures estimated from Mg–Fe cation exchange thermometers (Krogh 1988; Aranovich and Pattison 1995) and those from oxygen isotope quartz–garnet pair (after Zheng et al. 1993). Temperatures estimated from Mg–Fe cation exchange thermometers are consistent with those estimated from quartz–garnet isotopic thermometer for rocks above 2,300 m, but show a large difference for rocks below 2,300 m (see text for explanation)

assumed to be of primary origin. These features are similar to fluid inclusions in Dabie Shan (Xiao et al. 2002; Fu et al. 2003). Quartz in eclogites from depths above 1,600 m (with depleted oxygen isotopic compositions) has much higher fluid inclusion abundance than those in eclogites from depth below 1,600 m.

According to microthermometric results (compositions) and microscope observations (textural criteria), five types of fluid inclusions were identified:

- (1) Texturally earliest fluid inclusions are aqueous inclusions occurring either in quartz blebs in garnet or in the allanite core of zoned epidote porphyroblasts (Type 1). The inclusions in quartz blebs (Fig. 9a) usually have two phases composed of liquid (L) and vapour (V). They show eutectic temperatures $> -21^\circ\text{C}$, and final ice melting temperatures between -6 and -12°C , indicating an NaCl-bearing low-to-intermediate salinity aqueous system. No additional gas component has been detected. In a few grains of zoned epidote minerals used for the Sr–Nd–Pb isotope study by Romer and Xiao (2005), fluid inclusions in the allanite cores have high abundance and are small in size, whereas those in the epidote rims have less abundance and larger size (Fig. 9b). Fluid inclusions in the two occurrences have distinct compositions: inclusions in the allanite cores have ice-melting

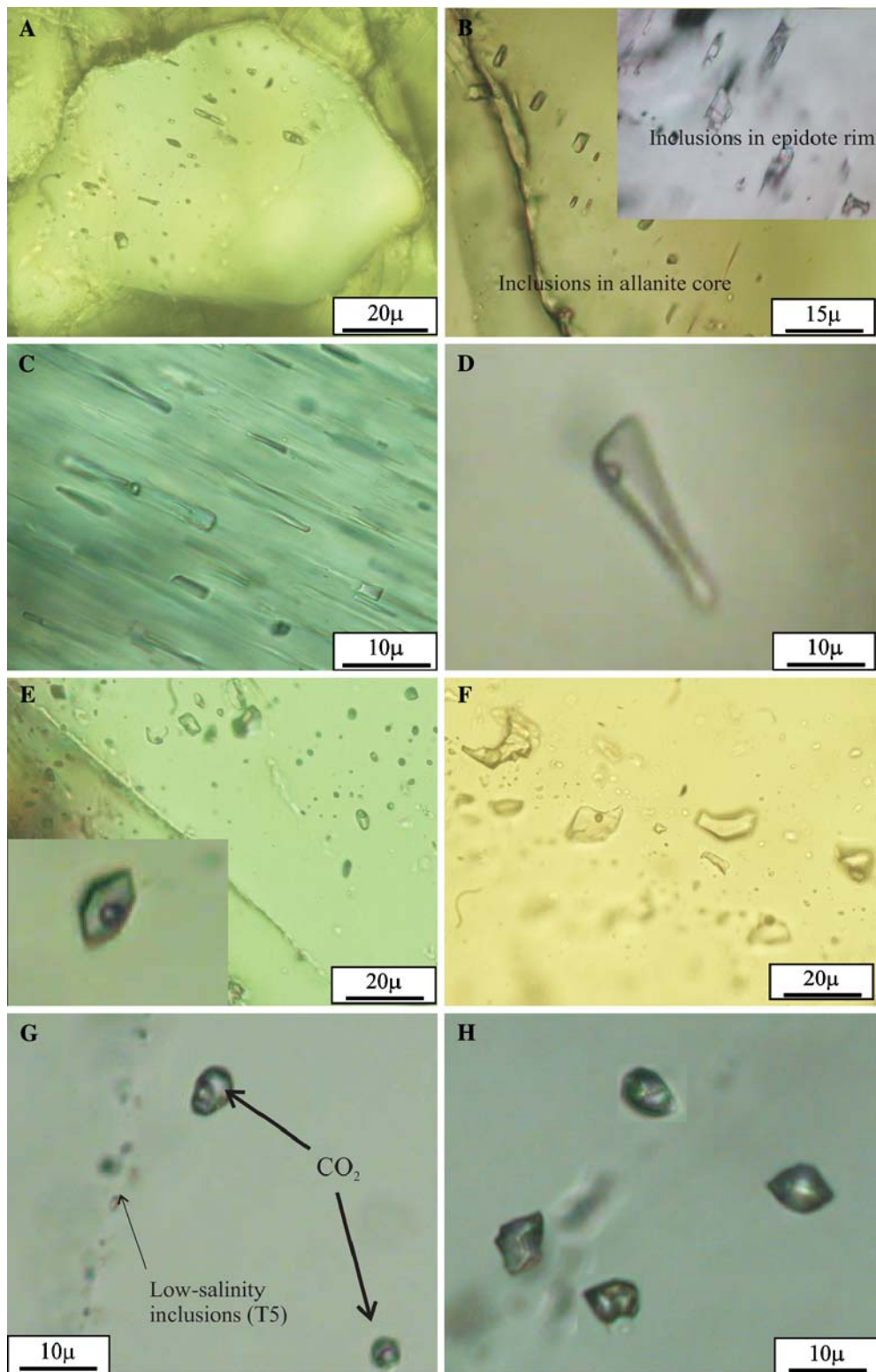


Fig. 9 Photomicrographs of various fluid inclusions in the rocks from the CCSD. **a** Texturally earliest fluid inclusions occurring in quartz blebs in garnet (Type 1); **b** fluid inclusions in a single zoned allanite–epidote crystal (ca. 2.2 mm×4.0 mm); note that fluid inclusions in the allanite core (Type 1) are highly abundant and small in size, whereas those in the epidote rim (Type 3) are less abundant and larger in size; **c** high-salinity brines (Type 2) in an omphacite crystal, tubular morphologies parallel to the growth

axes of the host mineral indicate their primary origin; **d** isolated primary high-salinity aqueous inclusions in kyanite; **e** intermediate-salinity aqueous inclusions (Type 3) occurring as scattered groups in quartz; **f** secondary low-salinity aqueous inclusions in matrix quartz (Type 5); and **g–h** primary very high-density CO_2 inclusions in matrix quartz (Type 4); they usually occur in the core of the host grain, suggesting an early formation

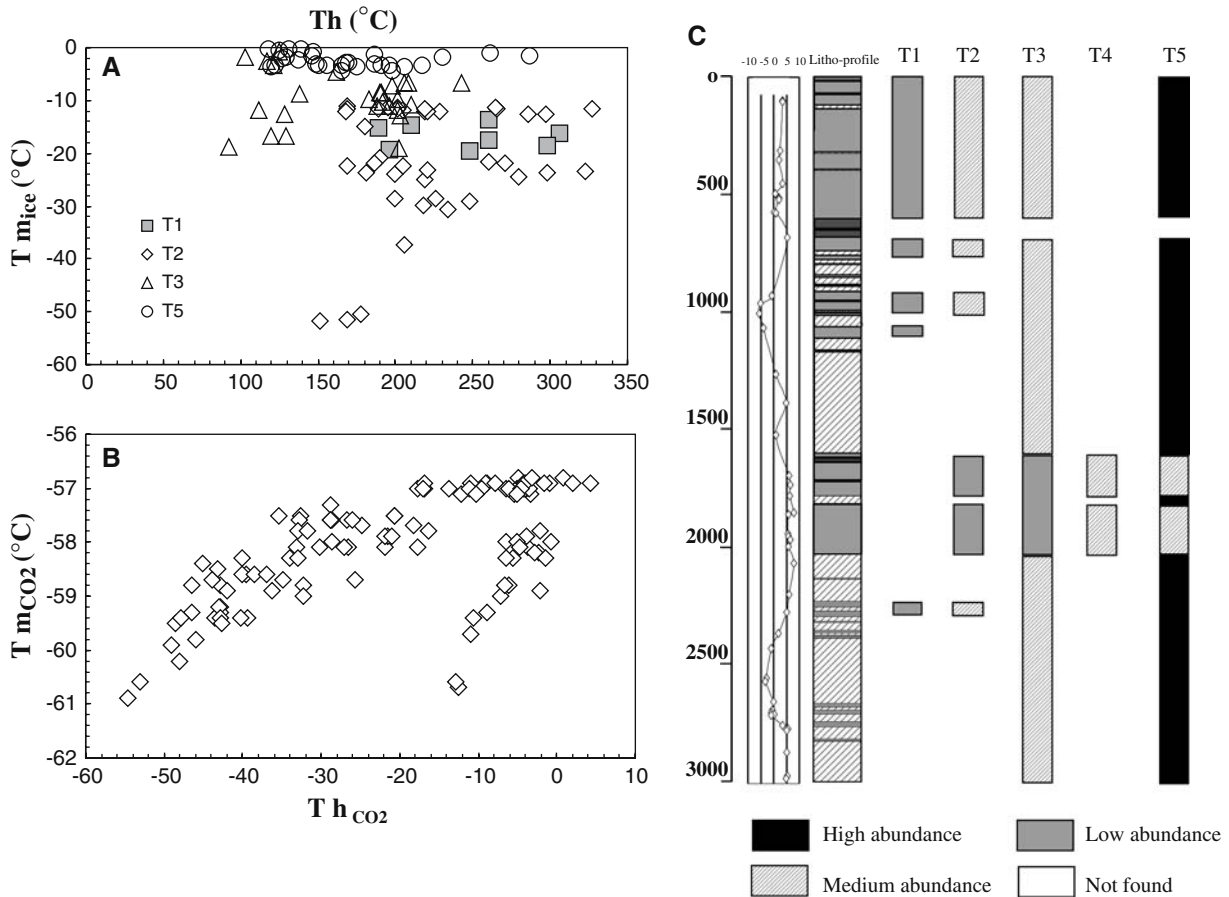


Fig. 10 a Microthermometric results of aqueous inclusions in the investigated samples; T 1 (Type 1), fluid inclusions in quartz blebs within garnet; T 2 (Type 2) primary high-salinity (Ca^{2+} and/or Mg^{2+} bearing) inclusions in omphacite and kyanite; T 3 (Type 3) primary intermediate salinity inclusions in matrix quartz; T 4

(Type 4) very high-density CO_2 inclusions in quartz; T 5 (Type 5) secondary inclusions in quartz. **b** Microthermometric results of CO_2 inclusions in quartz. **c** Distributions of fluid inclusions in the main hole of the CCSD (0–3,000 m); the legend indicates the abundance of fluid inclusions

temperatures of -19.3 to -12.6°C , while those in the epidote rims have higher temperatures of -13.1 to -6.8°C , corresponding to lower salinity. Petrographic observations suggest that the allanite cores probably formed during prograde metamorphism (Romer and Xiao 2005), and thus their trapped fluid reflects prograde metamorphic conditions.

- (2) Ca-rich or NaCl-dominated high-salinity inclusions in garnet, omphacite, and kyanite show tubular morphologies parallel to the growth axes of the host minerals (Type 2, Fig. 9c), and/or occur in scattered groups or are isolated (Fig. 9d), indicating a primary origin. Most inclusions in garnet do not show any phase changes during cooling and subsequent heating. However, halite crystals, amphibole, and mica in the inclusions occur as reaction products between the host garnet and the fluid (Zhang et al. 2005), suggesting that they are leaked high-salinity inclusions. Few fluid inclusions in omphacite and kyanite are oversaturated with salt. They have either three phases (S_{haliteLV}) or two phases (S_{haliteL}). Their extremely low eutectic temperatures between -75

and -60°C indicate Ca^{2+} (and/or Mg^{2+})-dominated salt solutions. The inclusions show low final ice-melting temperatures of -52 to -11°C . These inclusions have similar textural features as high-salinity brines from Bixiling. They represent relic UHP metamorphic fluids (Xiao et al. 2000).

- (3) Primary low-to-intermediate salinity inclusions occur randomly in quartz from both eclogite and gneiss (Type 3, Fig. 9e). Two observations suggest that this type of inclusions was trapped during the retrograde symplectite-forming stage: firstly, the fluid inclusions usually occur along the rim of quartz grains and only rarely in the cores; secondly, quartz grains in contact with retrograde symplectites usually contain more and larger fluid inclusions than those in contact with fresh omphacite or garnet, indicating a close relationship between fluid inclusion abundances and retrogression. Therefore, we assume that this type of fluid inclusions was trapped during the retrograde amphibolite-facies metamorphic stage. These inclusions are usually monophasic or rarely two phased. Most inclusions have eutectic

temperatures $> -21^{\circ}\text{C}$, and final ice-melting temperatures ranging from -19 to 0°C , indicating NaCl-bearing solutions.

- (4) Primary high-density CO_2 inclusions occur in quartz from eclogites with $\delta^{18}\text{O}$ values $> 5.8\%$. They occur in scattered groups or are isolated (Type 4, Fig. 9g, h) and usually have negative crystal shapes, indicating their primary origin. Unlike the low-intermediate salinity inclusions in quartz, these carbonic inclusions usually occur in the core of the host grain, suggesting an early formation. As shown in Fig. 10, microthermometric results suggest that most inclusions are mainly CO_2 with minor other gas component(s). According to laser Raman analysis of carbonic inclusions in eclogite from another pre-pilot hole of the CCSD (PP1), the additional gas phase is N_2 (Zhang et al. 2005). Some of these inclusions have homogenization temperatures as low as -50°C , corresponding to a density of $> 1.0 \text{ g/cm}^3$. Such high-density carbonic inclusions have only been reported in mantle peridotites (Frezzotti et al. 1992; Andersen and Neumann 2001) and in eclogite-facies metasediments of the Munchberg Gneiss Complex (Klemd et al. 1992). It is noted that, carbonic inclusions have not been observed in samples from depths above 1,600 m (those with depleted oxygen isotopic compositions). This demonstrates different fluid systems between the rocks with ^{18}O -depleted compositions and those with normal $\delta^{18}\text{O}$ values.
- (5) Secondary almost pure water inclusions are most abundant and bound to healed fractures (Type 5, Fig. 9f). Based on these textural criteria, they represent the latest evidence of fluid activity. The fluid inclusions are monophasic (L) or two-phased (LV, with fill degrees of 80–95 vol%). Most two-phase inclusions have homogenization temperatures of 90–200°C.

Discussion

Vertical oxygen isotope distributions and its tectonic implications

Distribution patterns and gradual transitions between ^{18}O -depleted and ^{18}O -normal rocks (Figs. 2, 3) from the CCSD provide important constraints for the origin of the Dabie-Sulu UHP metamorphic belt. There is debate between those who argue that the eclogites are exotic tectonic blocks whose metamorphism is unrelated to that of the gneisses (exotic origin) and those who advocate in situ UHP metamorphism (in situ origin) (for review, see e.g., Rumble et al. 2003). On the one hand, the fact that eclogites carry UHP index mineral assemblages, whereas their wall rocks (orthogneisses) have usually amphibolite-facies assemblages, plus the geochemical evidence that eclogites whose protoliths are ocean-floor basalts interlayered with continental

metasediments (Zhai and Cong 1996) suggest tectonic juxtaposition rather than in situ UHP metamorphism in the area. On the other hand, evidence from field mapping, mineralogical studies, and geochronological data supports the hypothesis of “in situ” origin for the UHP rocks (e.g., Xue et al. 1997; Li et al. 2000; Liu et al. 2004). Present oxygen isotope data demonstrate the following characteristics: (1) oxygen isotope distribution pattern of the 3,000 m profile shows systematic variations; transitions from rocks with depleted $\delta^{18}\text{O}$ values to those with normal oxygen isotopic compositions are gradual; (2) eclogites and gneisses that are in close contact have very similar oxygen isotope ratios (Figs. 4, 5). It has been convincingly demonstrated that the meteoric water/rock interaction occurred before the UHP event (e.g., Zheng et al. 1996, 2004; Rumble and Yui 1998; Rumble et al. 2002). These features thus indicate that the investigated UHP rocks have similar relative positions compared to the meteoric water/rock interaction before subduction, even though they have been subjected to very deep subduction and subsequent exhumation; i.e., the UHP rocks are not dismembered tectonic mélanges, but represent a subducted and exhumed coherent slab during UHP metamorphism. Therefore, the vertical oxygen isotope distribution patterns of the CCSD rocks provide additional support to the hypothesis of “in situ” UHP metamorphism.

An “in situ” origin of the drilled sequence allows us to estimate depths of meteoric water penetration. Oxygen isotope depletions have been observed down to 2,700 m, regardless of lithology. Therefore, we suggest that the ancient meteoric water/rock interaction has reached depths of at least 2,700 m, which must be considered as a minimum value because the investigated rocks represent the deep roots of an orogenic belt that has been partly eroded during exhumation. Previous studies on surface samples have demonstrated that the meteoric water/rock interaction in the Dabie-Sulu metamorphic belt extends over an area of more than 15,000 km^2 (e.g., Zheng et al. 2004). Considering 2,700 m as a reference depth, we can estimate that more than 40,000 km^3 have interacted with meteoric water. This implies a huge amount of very ^{18}O -depleted meteoric water that had to be present during the period. The “snow-ball Earth” scenario is the most likely explanation for the presence of such a vast amount of meteoric water.

The scale of oxygen isotope heterogeneity

For providing constraints on fluid mobility during UHP metamorphism, it is important to know whether oxygen isotope equilibrium is achieved on a mm-to-cm scale or m and larger scales. As has been demonstrated, oxygen isotopes of individual mineral phases suggest isotopic equilibrium on a mm scale. Rarely recognized oxygen isotope disequilibrium in retrogressive eclogites suggests limited retrograde fluid/rock interactions during exhumation.

(1) *Centimetre scale* Minerals from eclogite and gneiss that are in close contact (sample Zk703–5s and MH5a,b) show very similar oxygen isotopic compositions that are lower than in normal metamorphic rocks (Figs. 5, 6). Without infiltration of meteoric water across lithologic contacts, eclogitic and gneissic rocks would have very different $\delta^{18}\text{O}$ values. The similarity in $\delta^{18}\text{O}$ values suggests that eclogites and gneisses have been in close contact during meteoric water/rock interaction before subduction.

(2) *Metre scale* On a m scale, we observed variable oxygen isotopic compositions. Three samples from the same eclogitic body in ZK703 (from 220, 224, and 235 m) show a gradual increase of $\delta^{18}\text{O}$ values of individual mineral phases (e.g., garnet) with increasing depth (Fig. 7). It is likely that the isotopic front infiltrating through the rock became less steep with increasing distance from the contact (e.g., Chamberlain and Conrad 1993). An increase of $\delta^{18}\text{O}$ values with depth within the same layer thus probably indicates the direction of fluid flow.

Garnet in gneiss from 178.5 m shows $\delta^{18}\text{O} -1.3\text{‰}$ (mean of two measurements), but eclogite garnet from 181.5 m is -3.4‰ (mean of five measurements); gneiss from 1,850 m (PH-23) and eclogite from 1,855 m (PH24) show bulk $\delta^{18}\text{O}$ values of 7.0 and 5.8‰, respectively (see Table 1). These differences in isotopic compositions for different rock types, regardless of whether the rocks have interacted with meteoric water or not, preclude pervasive infiltration across lithologic boundaries within a distance of 3–5 m. The above observations are consistent with the study by Baker et al. (1997) who estimated the length scale of oxygen isotope exchange between marble hosts and coesite–eclogite pods in Dabie Shan to be greater than 10 cm but less than 3 m.

(3) *Outcrop scale* Detailed surface mapping, the vertical lithological profile of drill hole ZK703, and the upper 680 m of the main hole (Fig. 2) suggest that the same eclogitic body has been drilled in the two holes (see also Xu et al. 2004). Comparison of the two holes may therefore indicate whether oxygen isotope compositions within the scale of an individual rock body are homogeneous or not [distance between ZK703 and the main hole is about 80 m; a layer of garnet peridotite appearing in both holes has been taken as the marker layer for comparison (see Figs. 1, 2)]. As shown in Fig. 3, there is a range of bulk $\delta^{18}\text{O}$ values from -1 to 4‰ in either horizontal or vertical directions, indicating a heterogeneous oxygen isotope distribution at the >100 m scale of single rock bodies.

Fluid evolution of the UHP metamorphic rocks from CCSD

The combination of oxygen isotope compositions of minerals with fluid inclusion data is very instructive.

High-salinity aqueous fluid inclusions are prevalent in ^{18}O -depleted CCSD rocks, whereas rocks with $\delta^{18}\text{O}$ values $>5.6\text{‰}$ are dominated by high-density CO_2 inclusions. Therefore, the high-salinity fluid inclusions are probably related to the process which established the low $\delta^{18}\text{O}$ signature and, are not primarily related to the lithology. The metamorphic rocks with $\delta^{18}\text{O} > 5.6$ may reflect the characteristics of their protoliths.

In eclogites with ^{18}O -depleted compositions, the earliest fluid inclusions are those trapped in quartz blebs in garnet and in the allanite-core of a zoned epidote. Since petrographic observations indicate that these minerals formed during prograde metamorphism (Romer and Xiao 2005), they should have preserved prograde fluids. This indicates that the fluid during prograde metamorphism was of NaCl-bearing medium salinity. Primary Ca-rich or NaCl-dominated high-salinity fluid inclusions in garnet, omphacite, kyanite, and quartz (Fig. 9d–f) are assumed to represent the fluid composition during or close to the peak of metamorphism. Matrix minerals recrystallize and reequilibrate during the transformation from coesite- to quartz-eclogite facies. However, due to the very low water activity during UHP metamorphism (Chopin 2003; Rumble et al. 2003) and the protection of the enclosed minerals, reequilibration affects fluid density rather than composition. This assumption is consistent with previous studies on surface samples for the UHP rocks from Dabie Shan (Xiao et al. 2000, 2002; Fu et al. 2001, 2003). Remnants of early retrograde fluid (formation of retrograde symplectite or amphibole after omphacite) are preserved as primary low-to-intermediate salinity inclusions in quartz (Fig. 9g, h). The latest generation of retrograde fluid is reflected by the fracture-related secondary low-salinity (almost pure water) inclusions in quartz (Fig. 9f).

Rocks that interacted with meteoric water might be relatively water-rich before the UHP metamorphic event. This assumption is supported by the observation that samples with very low $\delta^{18}\text{O}$ values are usually enriched in UHP-phase hydroxyl-bearing minerals, such as epidote, allanite, and phengite. For instance, the Qinglongshan eclogitic outcrop which has the lowest $\delta^{18}\text{O}$ values (Yui et al. 1995; Zheng et al. 1996; Rumble and Yui 1998) contains the highest abundance of epidote and phengite in the Dabie-Sulu area. Thus, rocks that interacted with meteoric water would have higher initial water activity than those that did not. Although prograde dehydration would remove most water from the rocks, a relatively high water activity may still be preserved compared to rocks that did not interact with meteoric water, as they have been subjected to the same process. The relatively high water activity implies low CO_2 contents, as concluded by previous fluid inclusion studies (e.g., Klemd et al. 1995; Touret and Huizenga 1999).

Eclogites with normal oxygen isotopic compositions indicate a different fluid history. Oxygen isotope data imply that these rocks have not interacted with meteoric

water. Evidence for a prograde metamorphic fluid has not been found in these rocks. However, the primary high-density CO₂ inclusions (Fig. 9g, h), which have not been found in samples with low $\delta^{18}\text{O}$ values, indicate that CO₂ was an important fluid component during or shortly after the UHP metamorphic stage. The high density of these inclusions, plus the fact that the fluid system was closed even at amphibolite facies retrograde metamorphism (e.g., Xiao et al. 2002; Fu et al. 2003), suggests that the CO₂ most likely derived from an internally buffered fluid. Although Ca-rich brines have been found in omphacite and/or kyanite in these samples, their abundance is much lower. Furthermore, secondary low-salinity inclusions in quartz are less abundant than in the low $\delta^{18}\text{O}$ eclogites.

In contrast to the compositional differences, the fluid systems of the two rock groups share a similar evolution. In general, fluids in both groups evolved from high water activity (represented by low-to-medium salinity fluid inclusions) to low water activity (demonstrated by high-salinity brines and/or high density CO₂ inclusions) from prograde to peak metamorphism. After the peak of metamorphism the fluid composition changed from high-salinity to almost pure water. All rocks have had very low water activity during peak metamorphism. These features are similar to the fluid evolution in the Dabie area (e.g., Fu et al. 2001; Xiao et al. 2002).

The above observation is consistent with data from other UHP terrains worldwide. Detailed fluid inclusion studies of coesite-bearing rocks from the Dora Maira Massif (Philippot et al. 1995) document a change from low-salinity aqueous fluids containing minor CO₂ on the burial path to complex saline brines with an impressive inventory of dissolved elements near the metamorphic peak. Investigations on microdiamond-bearing granulites from the Western Gneiss Region, Norway (Larsen et al. 1998) imply that the peak of metamorphism was associated with N₂-CO₂ volatiles, indicating very low water activity; at the transition towards lower-grade metamorphism H₂O increased from 5 to 60 vol%.

A possible reason why fluid phases of UHP metamorphic rocks decrease in water activity with increasing progressive metamorphism but increase in water activity during retrograde metamorphism might be related to dehydration and hydration reactions, respectively. Approximately 3–4 wt% of water from mafic rocks is liberated during transition from blueschist (4–5 wt%) to eclogite (1 wt%) during subduction (Spandler et al. 2003). However, in contrast to the large amount of liberated water, elements, even fluid-mobile elements (B, LILE) are not removed during dehydration but may be efficiently subducted to sub-arc depths (Spandler et al. 2004). Such a decoupling of fluid and element release in the subducted slab would cause an increase of Ca, Mg, and Na concentrations and thus the salinity in the fluid phase. Aranovich and Newton (1997) have demonstrated that the presence of NaCl decreases significantly the water activity. The presence of either high-salinity aqueous inclusions or CO₂-dominated inclusions

is consistent with the very low water activity during UHP metamorphism. On the other hand, during the subsequent exhumation process with decreasing pressure, H₂O released from UHP hydrous minerals (phengite, zoisite, epidote, lawsonite, etc.) and from nominally anhydrous minerals (garnet, omphacite, etc.) will significantly increase the water activity. Furthermore, during late retrograde metamorphic stages (e.g., after amphibolite facies), due to a tectonic extension environment in the Dabie-Sulu area (Xiao and Li 1993), a surface fluid may be easily introduced into the rock fluid system, as indicated by the high abundance of texturally featured pure-water inclusions.

Summary

- (1) Rocks in the CCSD can be divided into two groups according to their bulk oxygen isotope compositions: ¹⁸O-depleted rocks (as low as $\delta^{18}\text{O} = -6\text{‰}$) and ¹⁸O-normal rocks (with $\delta^{18}\text{O} > +5.6\text{‰}$). The former is interpreted to have interacted with cold-climate ancient meteoric water before subduction, whereas the latter may have preserved oxygen isotopic compositions of their protoliths. Oxygen isotope distributions imply that extensively developed meteoric water/rock interactions reached depths of at least 2,700 m.
- (2) Oxygen isotope distributions favour an “in situ” origin of the UHP metamorphic rocks. Similar peak metamorphic temperatures from different depths, estimated from both oxygen isotopic and Mg–Fe cation exchange thermometers, imply structural coherence throughout subduction and exhumation of the Dabie-Sulu UHP terrain.
- (3) Minerals achieved high temperature oxygen isotopic equilibrium at grain-size scale. On mm-to-cm scales at lithological boundaries, regardless of rock types, infiltration of meteoric water has homogenized isotopic compositions. O-isotopic heterogeneities between rock types, and even within the same eclogitic layer, are observed at the scale of a few metres.
- (4) Fluid and oxygen isotope compositions are related and reflect variable degrees of alteration of the Dabie-Sulu UHP rocks before subduction. Rocks that interacted with meteoric water have different fluid compositions from those preserving O-isotopic compositions of basaltic protolith (see Zhang et al. (2006), this issue). The fluid system of the former evolved from NaCl-bearing low-intermediate salinity aqueous during prograde metamorphism to divalent-cation-rich (e.g., Ca²⁺, Mg²⁺) brines towards lower salinity solutions at early retrogression, and became almost pure water probably due to the admixture of a fluid during later retrograde metamorphism. No obvious CO₂ component has been found. However, a high-density CO₂ fluid is important in rocks with $\delta^{18}\text{O}$ values $> 5.6\text{‰}$.

Acknowledgements This study was supported by the National Science Foundation of Germany (DFG, HO 375/22), and partly by the National Science Foundation of China (For Z Z, 2003CB716501). We thank R. Przybilla for assistance during oxygen isotope analysis. Reviews by Dr. U. Wiechert and an anonymous reviewer, and editorial comments by Prof. Grove have improved the manuscript.

References

- Andersen T, Neumann ER (2001) Fluid inclusions in mantle xenoliths. *Lithos* 55:299–318
- Aranovich LY, Newton RC (1997) H₂O activity in concentrated KCl and KCl-NaCl solutions at high temperatures and pressures measured by the brucite-periclase equilibrium. *Contrib Mineral Petrol* 127:261–271
- Aranovich LY, Pattison DRM (1995) Reassessment of the garnet-clinopyroxene Fe–Mg exchange thermometer: I. Evaluation of the Pattison and Newton (1989) experiments. *Contrib Mineral Petrol* 119:16–29
- Baker J, Matthews A, Matthey D, Rowley D, Xue F (1997) Fluid-rock interactions during ultra-high pressure metamorphism, Dabie Shan, China. *Geochim Cosmochim Acta* 61:1685–1696
- Chamberlain CP, Conrad ME (1993) Oxygen-isotope zoning in garnet: a record of volatile transport. *Geochim Cosmochim Acta* 57:2613–2629
- Chopin C (2003) Ultrahigh-pressure metamorphism: tracing continental crust into the mantle. *Earth Planet Sci Lett* 212:1–14
- Frezzotti ML, Burke EAJ, De Vivo B, Stefanini B, Villa IM (1992) Mantle fluids in pyroxenite nodules from Salt Laker Crater (Oahu, Hawaii). *Eur J Mineral* 4:1137–1153
- Fu B, Touret JLR, Zheng YF (2001) Fluid inclusions in coesite-bearing eclogites and jadeite quartzites at Schuanghe, Dabie Shan, China. *J Metamorph Geol* 19:531–548
- Fu B, Touret JLR, Zheng YF (2003) Remnants of premetamorphic fluid and oxygen isotopic signatures in eclogites and garnet clinopyroxenite from the Dabie-Sulu terranes, eastern China. *J Metamorph Geol* 21:561–578
- Gregory RT, Taylor HP (1981) An oxygen isotope profile in a section of Cretaceous oceanic-crust, Samail Ophiolite, Oman—evidence for d18O buffering of the oceans by deep (less than 5 Km) seawater-hydrothermal circulation at Mid-Ocean Ridges. *J Geophys Res* 86:2737–2755
- Hoefs J (2004) Stable isotope geochemistry, 5th edn. Springer, Berlin Heidelberg New York
- Jahn BM, Cornichert J, Cong BL, Yui TF (1996) Ultrahigh- ϵ_{Nd} eclogites from an ultrahigh-pressure metamorphic terrane of China. *Chem Geol* 127:61–79
- Klemm R, Van den Kerkhof AM, Horn EE (1992) High-density CO₂-N₂ inclusions in eclogite-facies metasediments of the Münchberg Gneiss Complex, SE Germany. *Contrib Mineral Petrol* 111:409–419
- Klemm R, Broecker M, Schramm J (1995) Characterisation of amphibolite-facies fluids of Variscan eclogites from the Orlica-Snieznik dome (Sudetes, SW Poland). *Chem Geol* 119:101–113
- Krogh EJ (1988) The garnet-clinopyroxene Fe–Mg geothermometer: a reinterpretation of existing experimental data. *Contrib Mineral Petrol* 99:44–48
- Larsen RB, Eide EA, Burke EAJ (1998) Evolution of metamorphic volatiles during exhumation of microdiamond-bearing granulites in the Western Gneiss Region, Norway. *Contrib Mineral Petrol* 133:106–121
- Li SG, Wang S, Chen Y, Liu D, Qiu J, Zhou H, Zhang Z (1994) Excess argon in phengite from eclogite: evidence from dating of eclogite minerals by Sm–Nd, Rb–Sr and ⁴⁰Ar/³⁹Ar methods. *Chem Geol* 112:343–350
- Li SG, Jagoutz E, Chen Y Z, Li QL (2000) Sm–Nd and Rb–Sr isotopic chronology and cooling history of ultrahigh-pressure metamorphic rocks and their country rocks at Shuanghe in the Dabie Mountains, Central China. *Geochim Cosmochim Acta* 64:1077–1093
- Liou JG, Zhang RY, Ernst WG, Rumble D, Maruyama S (1998) High-pressure minerals from deeply subducted metamorphic rocks. *Rev Mineral* 37:33–96
- Liu FL, Xu ZQ, Liou JG, Katayama I, Masago H, Maruyama S, Yang JS (2002) Ultrahigh-pressure mineral inclusions in zircons from gneissic core samples of the Chinese Continental Scientific Drilling site in eastern China. *Eur J Mineral* 14:499–512
- Liu FL, Xu ZQ, Liou JG, Song B (2004) SHRIMP U–Pb ages of UHP and retrograde metamorphism of gneisses, south-western Sulu terrane. *J Metam Geol* 22:315–326
- Miller JA, Cartwright I, Buick IS, Barnicoat AC (2001) An O-isotope profile through the HP-LT Corsican ophiolite, France and its implications for fluid flow during subduction. *Chem Geol* 178:43–69
- Nabelek PI, Labotka TC, O’Neil JR, Papike JJ (1984) Contrasting fluid/rock interaction between the Notch Peak granitic intrusion and argillites and limestones in western Utah: evidence from stable isotopes and phase assemblages. *Contrib Mineral Petrol* 86:25–34
- Peacock SM (1990) Fluid process in subduction zones. *Science* 248:329–337
- Philippot PP, Chevallier P, Chopin C (1995) Fluid composition and evolution in coesite-bearing rocks (Dora-Maira massif, Western Alps): implications for element recycling during subduction. *Contrib Mineral Petrol* 121:29–44
- Romer R, Xiao YL (2005) Initial Pb–Sr(–Nd) isotopic heterogeneity in a single allanite-epidote crystal: implications of reaction history for the dating of minerals with low parent-to-daughter ratios. *Contrib Mineral Petrol* 148:662–674
- Rumble D, Yui TF (1998) The Qinglongshan oxygen and hydrogen isotope anomaly near Donghai in Jiangsu Province, China. *Geochimica et Cosmochimica Acta* 62:3307–3321
- Rumble D, Giorgis D, Orelund D, Zhang ZM, Xu HF, Yui TF, Yang JS, Xu ZQ, Liou JG (2002) Low $\delta^{18}\text{O}$ zircons, U–Pb dating, and the age of the Qinglongshan oxygen and hydrogen isotope anomaly near Donghai in Jiangsu province, China. *Geochim Cosmochim Acta* 66:2299–2306
- Rumble D, Liou JG, Jahn BM (2003) Continental crust subduction and ultrahigh pressure metamorphism. *Treatise Geochem* 3:293–319
- Spandler C, Hermann J, Arculus R, Mavrogenes J (2003) Redistribution of trace elements during prograde metamorphism from lawsonite blueschist to eclogite facies; implications for deep subduction-zone processes. *Contrib Mineral Petrol* 146:205–222
- Spandler C, Hermann J, Arculus R, Mavrogenes J (2004) Geochemical heterogeneity and element mobility in deeply subducted oceanic crust; insights from high-pressure mafic rocks from New Caledonia. *Chem Geol* 206:21–42
- Su W, You ZD, Cong DL, Ye K, Zhong ZQ (2002) Cluster of water molecules in garnet from ultrahigh-pressure eclogite. *Geology* 30:611–614
- Su W, Ji ZP, Ye K, You ZD, Liu JB, Yu J, Cong BL (2004) Distribution of hydrous components in jadeite of the Dabie Mountains. *Earth Planet Sci Lett* 222:85–100
- Thompson AB (1992) Water in the Earth’s upper mantle. *Nature* 358:295–302
- Touret JLR, Huizenga JM (1999) Precambrian intraplate magmatism: high temperature, low pressure crustal granulites. *J African Earth Sci* 28:367–382
- Wang QC, Ishiwatari A, Zhao Z, Hirajima T, Enami M, Zhai M, Li J, Cong BL (1993) Coesite-bearing granulite retrograded from eclogite in Weihai, eastern China. *Eur J Mineral* 5:141–152
- Wiechert U, Fiebig J, Przybilla R, Xiao YL, Hoefs J (2002) Excimer laser ablation isotope-ratio-monitoring mass spectrometry for in-situ $\delta^{18}\text{O}$ analysis. *Chem Geol* 182:179–194
- Xiao YL, Li SG (1993) P–T–t path and its tectonic implication for eclogite from the Shima, Dabie Mountains (in Chinese with English abstract). *Geotectonica et Metallogenia* 17:239–250

- Xiao YL, Hoefs J, van den Kerkhof A, Zheng YF (1998) Fluid inclusions in ultrahigh-pressure eclogites from Dabie Shan, eastern China. *Mineral Mag* 62A:1667–1668
- Xiao YL, Hoefs J, van den Kerkhof A, Fiebig J, Zheng YF (2000) Fluid history of UHP metamorphism in the Dabie Shan, China: a fluid inclusion and oxygen isotope study on the coesite-bearing eclogite from Bixiling. *Contrib Mineral Petrol* 139:1–16
- Xiao YL, Hoefs J, van den Kerkhof A, Li SG (2001) Geochemical constraints of the eclogite and granulite facies metamorphism as recognized in the Raobazhai complex from North Dabie Shan, China. *J Metam Geol* 19:3–19
- Xiao YL, Hoefs J, van den Kerkhof A, Simon K, Fiebig J, Zheng YF (2002) Fluid evolution during HP and UHP metamorphism in Dabie Shan, China: constraints from mineral chemistry, fluid inclusions and stable isotopes. *J Petrol* 43:1505–1527
- Xu ZQ, Yang WC, Zhang ZM, Yang TN (1998) Scientific significance and site-selection researches of the first Chinese continental scientific deep drillhole. *Continent Dyn* 3:1–13
- Xu ZQ, Zhang ZM, Liu FL, Yang JS, Tang ZM, Cheng SZ, Cai YC, Li TF, Cheng FY (2004) The structure profile of 0–1200 in the main borehole, Chinese Continental Scientific Drilling and its preliminary deformation analysis. *Acta Petrologica Sinica* 20:53–72
- Xue F, Rowley DB, Tucker RD, Peng XZ (1997) U–Pb zircon ages of granitoid rocks in the North Dabie Complex, eastern Dabie Shan, China. *J Geol* 105:744–753
- Yao YP, Ye K, Liu JB, Cong BL, Wang QC (2000) A transitional eclogite- to high pressure granulite-facies overprint on coesite-eclogite at Taohang in the Sulu ultrahigh-pressure terrane, Eastern China. *Lithos* 52:109–120
- Yui TF, Rumble D, Lo CH (1995) Unusually low $\delta^{18}\text{O}$ ultra-high-pressure metamorphic rocks from the Sulu Terrain, eastern China. *Geochim Cosmochim Acta* 59:2859–2864
- Yui TF, Rumble D, Chen CH, Lo CH (1997) Stable isotope characteristics of eclogites from the ultra-high-pressure metamorphic terrain, east-central China. *Chem Geol* 137:135–147
- Zhai MG, Cong BL (1996) Major and trace element geochemistry of eclogites and related rocks. In: Cong BL (ed) *Ultrahigh pressure metamorphic rocks in the Dabie-Sulu region of China*. Science Press, Kluwer Academic, Dordrecht, pp 69–89
- Zhang ZM, Xu ZQ, Xu HF (2000) Petrology of ultrahigh-pressure eclogite from the ZK703 drillhole in the Donghai, eastern China. *Lithos* 52:35–50
- Zhang ZM, Shen K, Xiao YL, van den Kerkhof A, Hoefs J, Liou JG (2005) Fluid composition and evolution attending UHP metamorphism: study of fluid inclusions from drill cores, southern Sulu belt, eastern China. *Int Geol Rev* 47:297–309
- Zhang ZM, Xiao YL, Xu ZQ, Hoefs J, Yang JS, Liu FL, Liou JG (2006) UHP metamorphic rocks from the Chinese Continental Scientific Drilling Project—I. Petrology and geochemistry of the main hole (0–2050 m). *Contrib Mineral Petrol* (this issue)
- Zheng YF (1993) Calculation of oxygen isotope fractionation in anhydrous silicate minerals. *Geochim Cosmochim Acta* 57:1079–1091
- Zheng YF, Fu B, Gong B (1996) Extreme ^{18}O depletion in eclogite from the Su-Lu terrain in East China. *Eur J Mineral* 8:317–323
- Zheng YF, Fu B, Li YL, Xiao YL, Li SG (1998) Oxygen and hydrogen isotope geochemistry of ultrahigh-pressure eclogites from the Dabie Mountains and the Sulu terrane. *Earth Planet Sci Lett* 155:113–129
- Zheng YF, Wu YB, Chen FK, Gong B, Li L, Zhao ZF (2004) Zircon U–Pb and oxygen isotope evidence for a large-scale ^{18}O depletion event in igneous rocks during the Neoproterozoic. *Geochim Cosmochim Acta* 68:4145–4165