Low $\delta^{18}O$ eclogites from the Kokchetav massif, northern Kazakhstan

H. MASAGO,[1,*] D. RUMBLE,[2] W. G. ERNST,[3] C. D. PARKINSON[4] AND S. MARUYAMA[1]
[1]Department of Earth and Planetary Science, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo, 152–8551, Japan
[2]Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd., NW, Washington, DC, 20015–1305, USA
[3]Department of Geological and Environmental Sciences, Stanford University, Stanford, CA, 94305–2115, USA
[4]Department of Geological Sciences, University of South Carolina, Columbia, SC, 29208, USA

ABSTRACT Oxygen isotopic compositions of silicates in eclogites and whiteschists from the Kokchetav massif were analyzed by whole-grain CO_2-laser fluorination methods. Systematic analyses yield extremely low $\delta^{18}O$ for eclogites, as low as −3.9‰ for garnet; these values are comparable with those reported for the Dabie-Sulu UHP eclogites. Oxygen isotopic compositions are heterogeneous in samples of eclogite, even on an outcrop scale. Schists have rather uniform oxygen isotope values compared to eclogites, and low $\delta^{18}O$ is not observed. Isotope thermometry indicates that both eclogites and schists achieved high-temperature isotopic equilibration at 500–800 °C. This implies that retrograde metamorphic recrystallization barely modified the peak-metamorphic oxygen isotopic signatures. A possible geological environment to account for the low-$\delta^{18}O$ basaltic protolith is a continental rift, most likely subjected to the conditions of a cold climate. After the basalt interacted with low $\delta^{18}O$ meteoric water, it was tectonically inserted into the surrounding sedimentary units prior to, or during subduction and UHP metamorphism.

Key words: eclogite; Kokchetav massif; low $\delta^{18}O$; whiteschist.

INTRODUCTION

Since the first report of metamorphic diamond over a decade ago (Sobolev & Shatsky, 1990), the Kokchetav massif has attracted the interest of geoscientists worldwide. Kokchetav metamorphic rocks represent the deepest recovered relics of subduction so far identified on Earth. In contrast to previously described and relatively well-known ultrahigh-pressure metamorphic (UHPM) terranes, the remarkable abundance of microdiamond and other mineralogical indicators of burial to depths as much as 200 km (e.g. Maruyama & Parkinson, 2000) are unique features of the complex.

The significance of the Kokchetav massif and the much greater depths of burial indicated by microdiamond and other phases, is that UHPM rocks are not just mineralogical curiosities, and the sole preserve of metamorphic petrologists. Study of UHPM rocks, especially those of the Kokchetav massif, challenges the conventional understanding of a wide range of geodynamic and petrochemical processes, and impinges on much more general fields of experimental mantle mineralogy, genesis of arc magmas, fluid transport, and geochemical recycling between crust and deep upper mantle, and tectonic processes responsible for growth and destruction of continents. The 30–200 km vertical sequence represented by Kokchetav HP–UHPM rocks provides an excellent natural laboratory for direct study of these processes.

Considerable attention was focused initially on the mineralogy and petrology of the highest grade, diamond-bearing rocks of the massif. Recent, integrated structural and petrochemical studies of the entire complex have produced a substantial database essential for the quantitative investigation of devolatilization processes in the upper mantle. One fertile, but so far neglected avenue of research, concerns the role of fluids in ultradeep subduction, and the information that can be gleaned from relics exhumed from depths corresponding to the diamond stability field. Specifically, the investigation of Kokchetav rocks, along with previous stable isotope studies of UHPM rocks in the Western Alps and the Dabie–Sulu terrane of east–central China, may clarify the source and nature of fluids involved in UHP and retrograde metamorphism.

The recognition of UHPM rocks derived from depths appropriate for magmatic arc generation provides a unique opportunity to investigate the nature and source of deep fluids, and the extent of rock–fluid interaction. The most negative $\delta^{18}O$ values ever recorded for high-T silicates have been reported from coesite-bearing eclogites and quartzites from China (Yui *et al.*, 1995; Zheng *et al.*, 1996; Baker *et al.*, 1997; Rumble, 1998). Isotopic equilibrium between minerals

* *Now at*: Department of Earth and Planetary Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113–0033, Japan (masago@solid.eps.s.u-tokyo.ac.jp).

and host rocks suggests that these Dabie-Sulu rocks acquired negative $\delta^{18}O$ compositions during meteoric water–rock interactions prior to subduction and UHPM. They were then isolated from fluid interaction during descent to, and return from, mantle depths. This hypothesis, which evokes a unique set of conditions, can be tested with isotopic characterization of UHPM minerals from microdiamond-bearing rocks from the Kokchetav massif. Important conclusions derived from the stable isotope work in east-central China are: (1) an external oxygen-bearing fluid did not attend UHPM or the subsequent exhumation; and (2), a large tract of UHPM rocks (about 40 × 50 km in lateral dimensions) retained isotopic integrity during its return to the surface.

The aims of the present reconnaissance study are: (1) to determine oxygen isotopic compositions of Kokchetav silicate minerals in both retrograded and non-retrograded UHPM (diamond- and coesite-grade) rocks; and (2) to provide constraints on fluid–rock interactions related to the Kokchetav metamorphism.

Abbreviations of minerals and components in this article are those used in Kretz (1983) except for the following: Phn = phengite; Coe = coesite.

GEOLOGICAL BACKGROUND AND SAMPLE DESCRIPTION

The Kokchetav massif is situated in the Central Asian Fold Belt, a major Late-Proterozoic–Early Cambrian tectonic zone. The massif strikes roughly NW–SE; it extends for over 150 km in length, and is *c.* 20 km wide. The massif is composed of several fault-bound lithotectonic units termed Unit I, II, III and IV on the basis of lithology (Kaneko *et al.*, 2000; Maruyama & Parkinson, 2000; Fig. 1). All four units underwent HP–UHPM, and metamorphic grade increases towards the structurally intermediate Unit II, from epidote-amphibolite facies (Unit IV) through amphibolite (Unit I and III), quartz-eclogite (Unit III) and coesite-eclogite facies to diamond-eclogite facies (Unit II). All these HP–UHPM units are underlain by rocks of the low-pressure Daulet metamorphic suite. This LP/HT unit is characterized by sillimanite–cordierite series metapelites, probably due to contact metamorphism by the overlying HP–UHPM rocks (Terabayashi *et al.*, 2002).

Twenty-seven samples, including representative, relatively unretrograded eclogite, amphibolitized eclogite, whiteschist/metapelite and quartz vein material, were selected for oxygen isotope analyses from Unit II of the Kulet, Barchi-Kol and Kumdy-Kol areas. Mineral compositions were analyzed employing a JEOL8800 electron microprobe analyzer in the Department of Earth and Planetary Science of Tokyo Institute of Technology.

Samples from the Kulet Area

The Kulet region contains the largest and most complete exposures of Unit II. Eclogites and associated metasedimentary schists are exposed mainly around Lake Zheltau. As in many other parts of Unit II, the geology of this region is characterized by block-in-matrix relationships involving abundant lensoidal eclogite bodies enclosed in the enveloping metapelite. The elongation direction of the eclogite lenses is roughly NE–SW in the eastern half of the region, and NW–SE in the western half; they are roughly concordant with the strike of the foliation of the enveloping schists. The length of the eclogite bodies varies from a few metres to approximately 1 km. Relatively small blocks of eclogite are concentrated in the central part on the south side of the lake. The highest metamorphic grades occur in this central part, where coesite inclusions in whiteschist garnet are common (Parkinson, 2000). Coesite-bearing rocks are limited to a narrow fault-bounded zone in which adjacent eclogites also yield coesite-grade *P–T* conditions up to 31 kbar, 760 °C (Ota *et al.*,

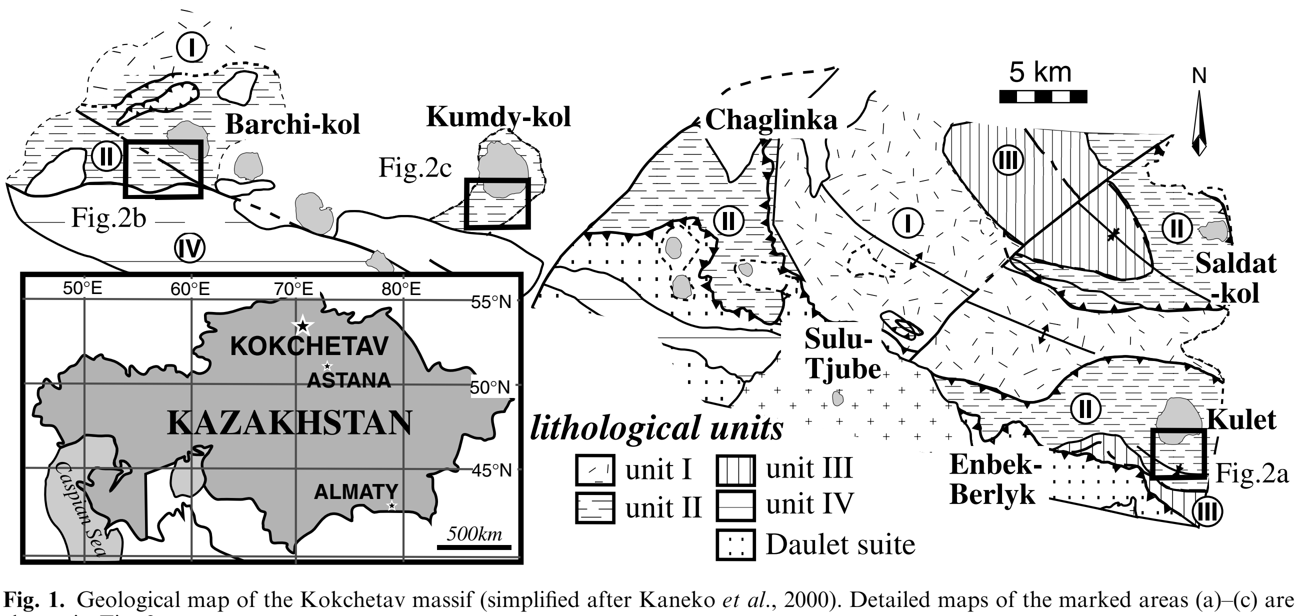

Fig. 1. Geological map of the Kokchetav massif (simplified after Kaneko *et al.*, 2000). Detailed maps of the marked areas (a)–(c) are shown in Fig. 2.

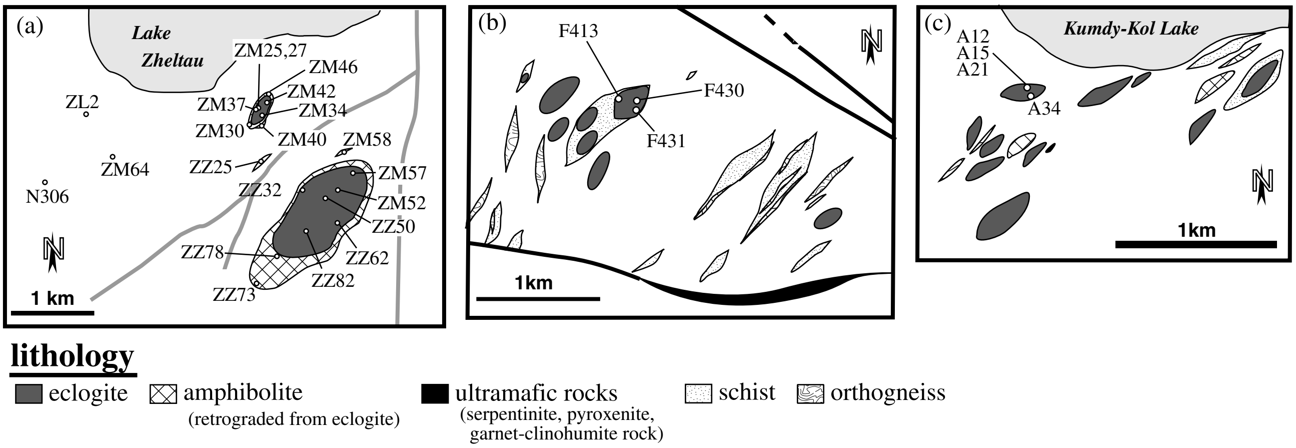

Fig. 2. Geological map and sample locations in studied areas. (a) Kulet, (b) Barchi-Kol and (c) Kumdy-Kol.

2000). Eclogite samples for this study were taken from the largest eclogite body, which has dimensions of about 1 km × 350 m, and an adjacent smaller body, located on the south-east side of the lake (Fig. 2a). These rocks are within the quartz-EC (EC = eclogite) facies zone of Ota *et al*. (2000). However, thermobarometric results using the Grt–Cpx–Phn geobarometer of Waters & Martin (1993), coupled with the Grt–Cpx cation exchange thermometer of Krogh (1988), are close to the quartz–coesite transformation curve, at 27–29 kbar, 650–730 °C.

Ten eclogite samples of quartz-eclogite from two adjacent bodies, and six mica schist samples were analyzed (Fig. 2a). The eclogite body is more-or-less amphibolitized by retrograde hydration along rims and fracture/veins. Some small bodies are completely amphibolitized. However, the degree of amphibolitization is not necessarily related to the size of the eclogite body. Fresh eclogite (ZZ32, ZZ50, ZZ62, ZZ82, ZM52 & ZM57) and amphibolitized eclogite (ZZ73 & ZZ78) were sampled from the larger eclogite body (EC body 1). Eclogites are medium- to fine-grained, and contain the mineral assemblage: Grt + Omp + Qtz + Rt ± Zo ± Phn. Garnet is typically almandine-rich ($Alm_{43-59}Prp_{14-29}Grs_{21-30}Sps_{01-02}$). Clinopyroxene is omphacite, with compositions of $Jd_{33-36}Di_{46-53}Hd_{12-18}$, the acmite component being generally negligible. Phengite has Si contents in the range 3.4–3.5 p.f.u. Peak equilibrium eclogitic mineral assemblages are relatively well preserved. However most samples display Hbl + Pl symplectites around omphacite grain boundaries. Samples ZZ78 and ZZ73 are well foliated garnet- and epidote-amphibolite, respectively. They are amphibolitized eclogites in which the eclogitic minerals and textures have been almost completely obliterated. Minute relict omphacite blebs are preserved in ZZ78. The garnets composition in ZZ78 shows a slight decrease in Fe/Mg ratio towards the rim, and the compositional range overlaps that of garnet in fresh eclogites; they may therefore retain relics of the peak metamorphic stage. Amphibole is also compositionally zoned: ZZ78 amphibole has barroisite cores and hornblende rims; ZZ73 amphibole is more irregular, and composition varies from hornblende to actinolite.

The smaller eclogite body (EC body 2) is composed of two petrographically and compositionally distinct types of eclogite. The body appears to be a composite of two smaller components, separated by a thin metapelite intercalation. The first type (ZM25 & ZM27), occupying the south-western half of the body, is composed of very coarse-grained Hbl + Zo with interlocking textures, and has a gabbroic (or at least, coarse-grained igneous precursor) appearance. Fine-grained eclogitic phases (Grt + Omp + Rt + Qtz) are present in the interstices between hornblende and zoisite. Both garnet and omphacite are rich in Mg, with compositions of $Alm_{43-50}Prp_{25-32}Grs_{21-27}Sps_{01}$ for garnet, and $Jd_{32-35}Di_{54-55}Hd_{11}$ for omphacite (the acmite component is negligible). Phengite is also present, but texturally appears to be a retrograde product. The second eclogite type (ZM34 & ZM42), which occupies the north-eastern half of the body, is medium-grained and contains Grt + Omp + Rt + Qtz as well as large porphyroblasts of retrograde amphibole. Garnet and omphacite are more Fe-rich than in ZM25 and ZM27; they are in the ranges $Alm_{54-62}Prp_{13-17}Grs_{20-32}Sps_{01}$, and $Jd_{31-35}Di_{44-48}Hd_{21-22}$, respectively.

Sample ZM46 is a medium-grained amphibolitized eclogite composed of Amp + Grt + Qtz + Pl. ZM30 is also an amphibolitized eclogite, with very coarse-grained Amp + Grt + Pl. Apatite and titanite are common accessories. Amphibole is compositionally zoned, with barroisitic cores and hornblende rims. Garnet compositions are similar to those of the fresh eclogites.

Sample N306 is a whiteschist that contains Grt + Ky + Phn + Tlc + Rt + Qtz/Coe. Coesite inclusions are abundant in the mantles of large garnet porphyroblasts, and peak *P–T* condition were estimated as 34–37 kbar, 720–760 °C (Parkinson, 2000). Garnet cores also include prograde microassemblages of quartz, zoisite, margarite, chlorite and graphite. ZZ25 is a fine-grained psammitic schist composed of Qtz + Phn + Grt. The modal abundances of mica and garnet are rather low. Four pelitic schists (ZM40, ZM58, ZL2 & ZM69) contain the assemblage Qtz + Phn ± Grt ± Ky ± Bt. Sample ZM40 is a metapelite derived from the intercalated layer between the northern and southern eclogite components of EC body 2. ZM58 was sampled from the matrix near EC body 1. Sample ZM69 was taken from a shallow trench, and contains coarse-grained garnet and kyanite blades up to 1 cm long. ZL2 is an unusual kyanite-rich schist with a very distinctive bluish colour, and contains high-Cr_2O_3 kyanite (up to 1.9 wt%). Garnet and biotite in this rock also have abnormally high Cr_2O_3 contents. Vein quartz (ZM37) from a 1-m wide quartz vein cutting EC body 2, is almost monomineralic, and has a coarse-grained, interlocking texture.

Samples from the Barchi-Kol Area

Three eclogite samples were taken from a single body defined by a distinctive hummocky topography, reflecting a number of widely dispersed eclogite outcrops (Fig. 2b). Samples F430 and F431 were collected from the same exposure. F413 was collected from an outcrop 100 m from the other two. The rocks are all medium-grained, and contain Grt + Omp + Rt + Qtz ± Phn ± Ap. Polycrystalline quartz pseudomorphs after coesite are present in omphacite grains. Eclogitic minerals have sharp grain boundaries; retrograde alteration is generally minor. Thin films of retrograde hornblende and/or Hbl + Pl symplectites occur at the rims of some omphacite grains. Retrograde biotite fringes some phengite grains. Peak *P–T* conditions were estimated to be 35–40 kbar, 770–825 °C (Masago, 2000).

Samples from the Kumdy-Kol Area

Kumdy-Kol is the highest grade, highly diamondiferous part of the Kokchetav massif (Fig. 2c). To the south of Kumdy-Kol, diamond-grade eclogites crop out as numerous small lensoidal blocks within metapelitic schist, together with minor amounts of garnet-clinopyroxenite, garnet-titanoclinohumite rock, garnet-biotite-gneiss and diopside-dolomite marble. *P–T* estimates for rocks of the Kumdy-Kol area include 60 kbar, 950–1050 °C for eclogite (Okamoto *et al.*, 2000), and up to 70 kbar at 980 °C for diopside-dolomite marble (Ogasawara *et al.*, 2000).

Three eclogite samples and one metapelitic schist sample were selected for analysis. Eclogites were derived from two adjacent bodies. The schist was taken from an outcrop close to eclogite A21 (Fig. 2c). Eclogite samples A15, A21 and A34 are medium- to coarse-grained rocks and dominantly bimineralic (Grt + Omp), with minor amounts of quartz and rutile. The metapelitic rock (A12) is a diamondiferous garnet–phengite schist composed of Grt + Phn + Qtz + Ky + Pl. Rutile, ilmenite, zircon and apatite are accessory minerals. Microdiamond was identified as inclusions in zircon, garnet and kyanite (Katayama *et al.*, 2001).

ANALYTICAL METHODS

Oxygen isotope analyses were made by laser-ablation fluorination at the Geophysical Laboratory, Carnegie Institution of Washington. Samples were prepared as mineral separates by a combination of sieving, panning, magnetic separation, heavy-liquid separation, acid dissolution and hand picking. Approximately 2 mg of mineral separates were heated to incandescence and melted by CO_2-laser with 10.5 μm wavelength (Sharp, 1990) in the presence of BrF_5 to extract oxygen. Oxygen isotopes were analyzed using a Finningan MAT 252 mass spectrometer. Comparison materials UWG-2 garnet and NBS-28 quartz were utilized as standards for interlaboratory normalization. The precision of analyses is better than 0.2‰.

RESULTS

Results of analyses for Kulet samples are listed in Table 1. Samples from the smaller eclogite body (body 1 in Fig. 3) have rather uniform δ^{18}O compositions from + 3.5 to + 4.7‰ for garnet, + 4.6‰ for omphacite (one sample), + 7.4 to + 8.8‰ for quartz and + 1.6‰ for rutile (one sample). In contrast, samples from the larger eclogite body (body 2 in Fig. 3) have a rather wide variation of δ^{18}O values, ranging from −3.9 to + 1.1‰ for garnet, from −3.5 to −0.5‰ for omphacite, from + 0.1 to + 5.1‰ for quartz and −5.4‰ for rutile. The whiteschists and other metapelitic schists have rather uniform δ^{18}O values throughout the area: from + 6.1 to + 7.5‰ for garnet, from + 9.9 to + 10.7‰ for quartz, and + 6.7 to + 6.8‰ for phengite (Fig. 3). ZM37 vein quartz has a δ^{18}O of + 8.7‰.

Figure 4 illustrates the spatial variation of δ^{18}O values in the Kulet region. δ^{18}O values from eclogite body 2 display a rather heterogeneous distribution. The lowest δ^{18}O eclogite sample (−3.9‰ for garnet) is located in the central part, at the top of the eclogite hill; the highest δ^{18}O eclogite sample (+ 1.1‰ for garnet) is located on the outermost margin of the body. However, the distribution of intermediate δ^{18}O eclogite samples appears to be random.

The results of analyses of Barch-Kol samples are listed in Table 2. Two eclogite samples (F430 & F431) exhibit nearly identical δ^{18}O values: from −0.4 to −0.1‰ for garnet, from + 0.5 to + 1.2‰ for omphacite, from + 2.5 to + 3.2‰ for quartz, and from −2.6 to −2.4‰ for rutile. The other sample (F413–100 m distant, but from the same eclogite body) has very different δ^{18}O values of + 5.1‰ for garnet, + 5.0‰ for omphacite, + 9.0‰ for quartz and + 2.2‰ for rutile.

Eclogite samples from the Kumdy-Kol region (Table 3; Fig. 3) display considerable variation, ranging from + 7.0 to + 12.5‰ for quartz, and from + 4.3 to + 7.9‰ for garnet. They can be subdivided into two groups. Samples A15 and A21 have rather similar δ^{18}O values, and A34 possesses values about 4‰ lower. The diamondiferous schist, A12, has δ^{18}O values about 3‰ heavier than the Kulet schists, + 13.5‰ for quartz, + 10.5‰ for garnet, + 10.3‰ for phengite and + 11.6‰ for kyanite. The δ^{18}O values of garnet and phengite display a reverse fractionation and are clearly out of isotopic equilibrium.

Table 1. Oxygen isotope compositions (δ^{18}O, ‰) in Kulet samples.

Sample no.	Lithology	Qtz	Grt	Omp	Amp	Rt	Zo/Ep	Pl	Phn	Ky	Bt
Eclogite body 1											
ZM52	ec	0.1	−3.9	−4.3	−4.1	−6.9	−2.5				
ZM57	ec	1.2	−2.4	−2.5	−2.4						
ZZ32	ec	5.1	1.1	0.5	1.2	−2.2	2.0				
ZZ50	ec	1.2	−3.5	−3.4							
ZZ62	ec	1.8	−3.4	−3.9	−3.2		−2.6				
ZZ82	ec	3.9	−1.1	−0.5	−0.5						
ZZ78	am (retro-ec)	3.0	−2.4		−1.4	−5.4					
ZZ73	am (retro-ec)				−0.2		1.5				
Eclogite body 2											
ZM25	ec	8.9	4.7		5.1	1.6	6.2				
ZM27	ec	8.4	4.2		4.5		4.9				
ZM34	ec	7.4	4.4	4.6		1.6					
ZM42	ec	7.4	3.9	3.7	4.3						
ZM46	am (retro-ec)		3.5		4.1						
ZM30	am (retro-ec)		5.2		5.6			9.7			
Schist											
ZZ25	psam sch	10.7	6.8								
ZM40	pel sch	10.9	6.7						7.5		
ZM58	pel sch	9.9							6.6		
ZM64	pel sch		6.8						7.5	7.6	
ZL2	pel sch		7.5						7.4	8.1	6.0
N306	whiteschist	10.1	6.1						7.2	6.9	
Quartz vein											
ZM37		8.7									

ec: eclogite; am (retro-ec): amphibolite (retrograded from eclogite); psam sch: psammitic schist; pel sch: pelitic schist.

ISOTOPE THERMOMETRY

Figure 5 shows oxygen isotopic fractionations between garnet and coexisting minerals. Garnet is compositionally and isotopically resistant to late-stage alteration. It is therefore one of the most reliable phases preserving isotopic compositions attending the peak of the metamorphism. Isopleths in Fig. 5 show isotopic equilibration at computed temperatures. The calibrations of Sharp (1995), Matthews (1994) and Javoy (1977) were used.

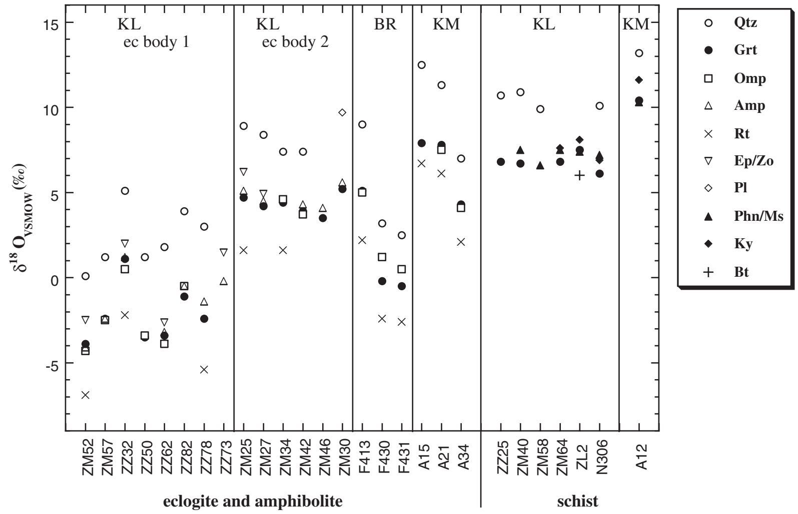

Fig. 3. δ^{18}O values of eclogites, amphibolites and schists. KL: Kulet, BR: Barchi-Kol and KM: Kumdy-Kol.

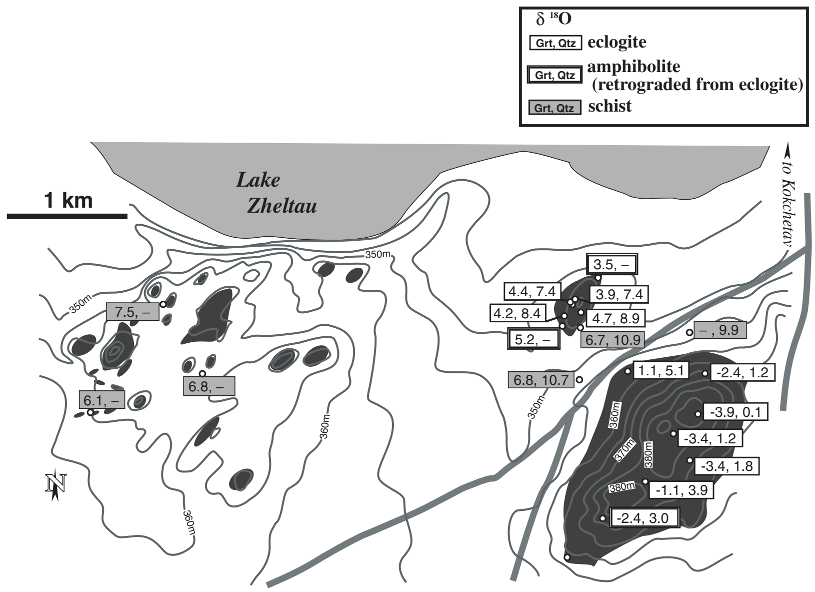

Fig. 4. Distribution of δ^{18}O values in Kulet district. Shaded objects represent eclogite bodies.

Table 2. Oxygen isotope compositions (δ^{18}O, ‰) in Barchi-Kol samples.

Sample no.	Lithology	Qtz	Grt	Omp	Rt
F413	ec	9.0	5.1	5.0	2.2
F430	ec	3.2	−0.1	1.2	−2.4
F431	ec	2.5	−0.4	0.5	−2.6

Table 3. Oxygen isotope compositions (δ^{18}O, ‰) in Kumdy-Kol samples.

Sample no.	Lithology	Qtz	Grt	Omp	Rt	Phn	Ky
A15	ec	12.5	7.9		6.7		
A21	ec	11.3	7.8	7.5	6.1		
A34	ec	7.0	4.3	4.1	2.1		
A12	pel sch	13.5	10.5			10.3	11.6

For eclogites, omphacite–garnet pairs generally yield petrologically unrealistically high temperatures > 1000 °C. In some samples, omphacite has a lower δ^{18}O value than that of garnet, and is clearly out of equilibrium. Most of temperatures deduced from the quartz–garnet and garnet–rutile pairs are within the range 600–700 °C. Garnet–amphibole pairs generally yield petrologically unrealistically low temperatures < 200 °C, suggesting isotopic disequilibrium. Temperatures estimated from garnet–zoisite pairs scatter over a wide range from 550 to 900 °C. The isotopic fractionation between garnet and zoisite is small, thus analytical uncertainties may be responsible for the apparent variation in temperatures.

The thermometric results of the whiteschist show very good correspondence. Garnet–kyanite and garnet–phengite pairs yield equilibrium temperatures of

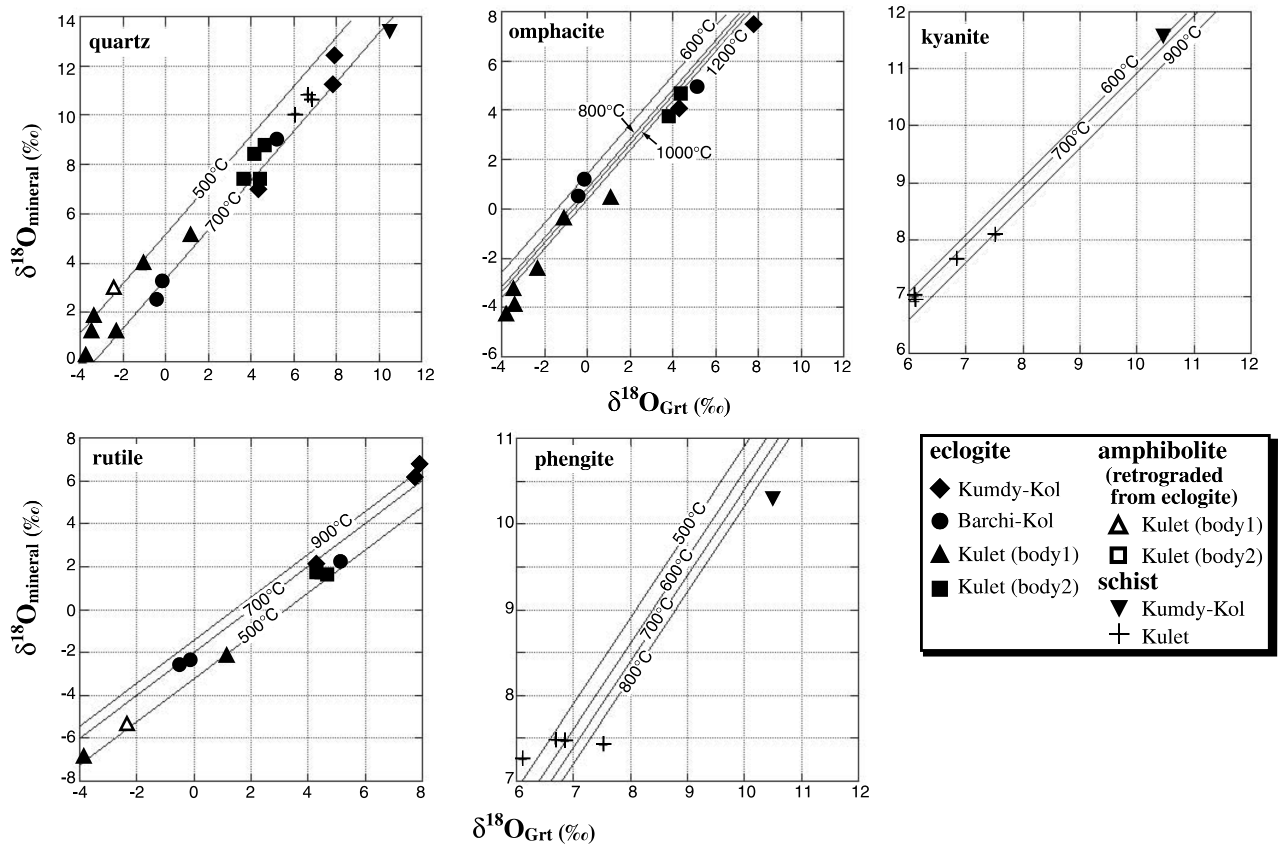

Fig. 5. Oxygen isotope fractionations between analyzed minerals and coexisting garnet from eclogites, amphibolites, and schists.

750–800 °C. Quartz–garnet pairs yield temperatures of about 600 °C. For the other schists, garnet–kyanite and quartz–garnet pairs yield about 800 °C and 600 °C, respectively. Garnet–phengite pairs scatter and yielded unrealistically high temperatures.

DISCUSSION

Origin of low $\delta^{18}O$ in Kokchetav eclogites

Eclogites of the Kokchetav massif yield very low $\delta^{18}O$ values, with the most negative being −3.9‰ for garnet in eclogite ZM52, from eclogite body 1 in the Kulet area. This is an unusually low value for eclogites. Oxygen isotopic compositions of various metamorphic rocks are summarized in Fig. 6. Typical eclogites have values from + 2 to + 5‰ for garnet. Note that low $\delta^{18}O$ eclogites have been reported from the Dabie–Sulu UHPM terrane (Yui *et al.*, 1995, 1997; Zheng *et al.*, 1996, 1998, 1999; Baker *et al.*, 1997; Rumble & Yui, 1998). This study reports a second UHPM terrane with abnormally low $\delta^{18}O$ eclogite.

Low $\delta^{18}O$ eclogites were found in both the Kulet and Barchi-Kol areas. These two areas are separated by about 60 km, and are of different metamorphic grades; the former is Qtz–EC facies and the latter is Coe–EC facies. Low $\delta^{18}O$ signatures were not detected in diamond-grade Kumdy-Kol eclogites, but that may simply reflect the limited number of samples analyzed.

Kokchetav eclogite bodies appear to be isotopically heterogeneous. Eclogite body 2 in Kulet shows a wide variation, ranging from −3.9 to + 1.1‰ for garnet. Even the much smaller Barchi-Kol eclogite body has an isotopic variation from −0.4 to + 5.1‰ for garnet. Similar local but widespread heterogeneities have been reported from other HP and UHPM terranes, including Sulu and Dabie areas (Rumble & Yui, 1998; Philippot & Rumble, 2000), as well as mafic blueschists and eclogites of the Western Alps (Barnicoat & Cartwright, 1997).

It is generally regarded that dehydration during subduction does not significantly change a slab's oxygen isotopic composition. Fractionation of oxygen isotopes during dehydration under the temperatures of interest is < 1‰ (Valley, 1986). Numerical simulation of oxygen isotope fractionation by dehydration from amphibolite resulted in a change of < 0.2‰ (Barnicoat & Cartwright, 1997). The only possible way to effectively and substantially lower the $\delta^{18}O$ of a rock is interaction with markedly negative $\delta^{18}O$ fluid. The

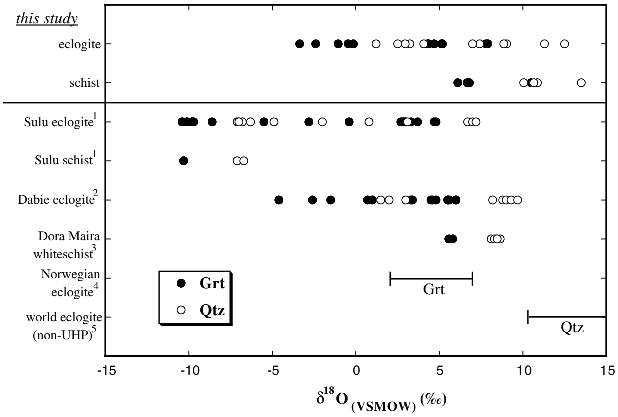

Fig. 6. Comparison of the Kokchetav oxygen isotope mineral analyses with published data. 1: Zheng *et al.* (1996, 1998); Yui *et al.* (1997); Rumble & Yui (1998), 2: Baker *et al.* (1997), 3: Sharp *et al.* (1993), 4: Agrinier *et al.* (1985) and 5: Sharp *et al.* (1993).

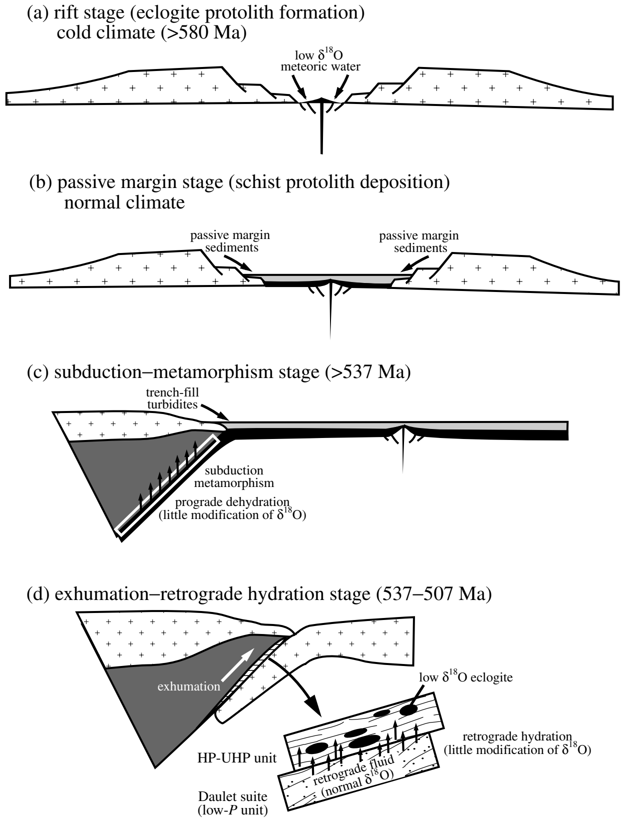

Fig. 7. Tectonic model of evolution of the Kokchetav UHPM belt and origin of low δ^{18}O values in eclogites.

only known source with negative δ^{18}O is meteoric water, especially in a cold climate (high latitude and/or high altitude). Thus, the low δ^{18}O Kokchetav protoliths must have interacted with meteoric water at some time after initial magmatic crystallization. The opportunity for eclogitic rocks to interact with meteoric water is limited to either during a presubduction episode (protolith) or after exhumation of the UHPM belt to the surface. Thermometric results show high temperature ($>$ 500 °C) oxygen isotope equilibrations for eclogitic minerals. This appears to preclude near-surface alteration subsequent to UHP metamorphism and exhumation.

Major, trace and rare earth element abundances of Kokchetav metabasites are generally comparable with MORB (Yamamoto *et al.*, 2002). One possible geological setting whereby newly erupted basalts could interact with meteoric water is a transition from a continental rift to an oceanic environment, analogous to present-day Afar and Dead Sea (e.g. Windley, 1995), but in contrast, under cold climate conditions in as much as all known negative δ^{18}O metabasalts are related to cold climates (Blattner *et al.*, 1997). The Earth experienced extreme global climatic conditions at all latitudes during the Neoproterozoic (i.e. immediately prior to the Kokchetav UHPM orogenic event). Hoffman *et al.* (1998) proposed that global icehouse conditions alternated with greenhouse conditions as many as four times between 750 and 580 Ma, based on widespread glacial deposits and the correlation of associated carbonate sediments by isotopic stratigraphy. It is interesting to speculate that the parental basalts of the Kokchetav eclogites, presumably erupted some time during the Neoproterozoic (although we have no independent confirmation of protolith ages), may preserve the isotopic signature of extremely cold climatic conditions related to a 'Snowball Earth'.

Speculative tectonic model

Basaltic protoliths of the Kokchetav eclogite were erupted in a continental rift, and underwent extensive but heterogeneous infiltration by very cold meteoric water during 'Snowball Earth' climatic conditions, sometime between 750 and 580 Ma. As a result, heterogeneous, low δ^{18}O compositions were recorded in eclogite protoliths (Fig. 7a). The abundance of orthogneiss, impure marble and whiteschist, with which the eclogites are presently intercalated, probably originated in a passive continental margin sedimentary basin, and interacted with normal δ^{18}O seawater during intermissions of and/or after the 'Snowball Earth' period (Fig. 7b).

The parental basalt and passive margin sediments were tectonically juxtaposed prior to – or during – subduction to depths approaching 200 km, and recrystallized under coesite- to diamond-grade eclogite facies conditions until 537 ± 9 Ma (Katayama *et al.*, 2001). Isotopic fractionation due to progressive dehydration was negligible. Oxygen isotopes were re-equilibrated among coexisting minerals, essentially in a closed system; the rocks were isolated from fluid interaction during their descent to mantle depths (Fig. 7c).

During exhumation, all of the Kokchetav HP–UHPM units underwent hydration at mid-crustal depths by the fluid derived mainly from the underlying low-pressure Daulet Suite (Terabayashi *et al.*, 2002) at 507 ± 8 Ma (Katayama *et al.*, 2001). The degree of hydration varies from forming thin films or symplectites of secondary hydrous minerals on the grain boundaries to whole-rock-scale recrystallization (Fig. 7d). This process may have caused minor modifications in isotopic equilibration. Grain boundary diffusion-induced isotopic exchange might also have played a role in producing limited isotopic disequilibrium.

In conclusion, Kokchetav eclogites have low negative $\delta^{18}O$ values, and are directly comparable to similar negative $\delta^{18}O$ values for coesite-bearing eclogites and quartzites, schists, and gneisses from east-central China. In both UHPM terranes, these compositions were acquired during meteoric water–rock interactions prior to UHP metamorphism.

ACKNOWLEDGEMENTS

This research was conducted under the auspices of the Stanford University–Tokyo Institute of Technology Geophysical Laboratory Collaborative Research Project led by J. G. Liou and S. Maruyama. The work could not have been completed without the support of our colleagues in the field and in the lab including M. Ishikawa, Y. Kaneko, I. Katayama, J. G. Liou, Y. Ogasawara, and R.Y. Zhang. Rumble is indebted to A. Baizhumova and D. Kravtsov for hospitality in Kazakhstan. Critical review by T.-F. Yui and Z. D. Sharp improved the quality of the manuscript. This study was financially supported in part by a Research Fellowship of the Japan Society for the Promotion of Science for Young Scientist (Masago), and by the US National Science Foundation, EAR 97–25346 (Rumble) and EAR 97–25347 (Liou).

REFERENCES

Agrinier, P., Javoy, M., Smith, D. C. & Pineau, F., 1985. Carbon and oxygen isotopes in eclogites, amphibolites, veins and marbles from Western Gneiss Region, Norway. *Chemical Geology*, **52,** 145–162.

Baker, J., Matthews, A., Mattey, D., Rowley, D. B. & Xue, F., 1997. Fluid–rock interaction during ultra-high pressure metamorphism, Dabie Shan, China. *Geochimica et Cosmochimica Acta*, **61,** 1685–1696.

Barnicoat, A. C. & Cartwright, I., 1997. Focused fluid flow during subduction: Oxygen isotope data from high-pressure ophiolites of the western Alps. *Earth and Planetary Science Letters*, **132,** 53–61.

Blattner, P., Grindley, G. W. & Adams, C. J., 1997. Low $\delta^{18}O$ terranes tracking Mesozoic polar climates in the South Pacific. *Geochimica et Cosmochimica Acta*, **61,** 569–576.

Hoffman, P. F., Kaufman, A. J., Halverson, G. P. & Schrag, D. P., 1998. A Neoproterozoic snowball Earth. *Science*, **281,** 1342–1346.

Javoy, M., 1977. Stable isotopes and geothermometry. *Journal of the Geological Society of London*, **133,** 609–636.

Kaneko, Y., Maruyama, S., Terabayashi, M. *et al.*, 2000. Geology of the Kokchetav UHP–HP metamorphic belt, northern Kazakhstan. *Island Arc*, **9,** 264–283.

Katayama, I., Maruyama, S., Parkinson, C. D., Terada, K. & Sano, Y., 2001. Ion micro-probe U–Pb zircon geochronology of peak and retrograde stages of ultrahigh-pressure metamorphic rocks from the Kokchetav massif, northern Kazakhstan. *Earth and Planetary Science Letters*, **188,** 185–198.

Kretz, R., 1983. Symbols for rock-forming minerals. *American Mineralogist*, **68,** 277–279.

Krogh, E. J., 1988. The garnet–clinopyroxene Fe-Mg geothermometer – a reinterpretation of existing experimental data. *Contributions to Mineralogy and Petrology*, **99,** 44–48.

Maruyama, S. & Parkinson, C. D., 2000. Overview of the geology, petrology and tectonic framework of the high-pressure–ultrahigh-pressure metamorphic belt of the Kokchetav Massif, Kazakhstan. *Island Arc*, **9,** 439–455.

Masago, H., 2000. Metamorphic petrology of the Barchi-Kol metabasites, western Kokchetav UHP–HP massif, northern Kazakhstan. *Island Arc*, **9,** 358–378.

Matthews, A., 1994. Oxygen isotope geothermometers for metamorphic rocks. *Journal of Metamorphic Geology*, **12,** 211–219.

Ogasawara, Y., Ohta, M., Fukasawa, K., Katayama, I. & Maruyama, S., 2000. Diamond-bearing and diamond-free metacarbonate rocks from Kumdy-Kol in the Kokchetav Massif, northern Kazakhstan. *Island Arc*, **9,** 400–416.

Okamoto, K., Liou, J. G. & Ogasawara, Y., 2000. Petrology of the diamond-grade eclogite in the Kokchetav Massif, northern Kazakhstan. *Island Arc*, **9,** 379–399.

Ota, T., Terabayashi, M., Parkinson, C. D. & Masago, H., 2000. Thermobaric structure of the Kokchetav ultrahigh-pressure massif deduced from a north–south transect in the Kulet and Saldat-kol regions, northern Kazakhstan. *Island Arc*, **9,** 328–357.

Parkinson, C. D., 2000. Coesite inclusions and prograde compositional zonation of garnets in whiteschist of the Kokchetav UHP–HP massif, Kazakhstan: a record of progressive UHP metamorphism. *Lithos*, **52,** 215–233.

Philippot, P. & Rumble, D., 2000. Fluid–rock interactions during high-pressure and ultrahigh-pressure metamorphism. *International Geological Review*, **42,** 312–327.

Rumble, D., 1998. Stable isotope geochemistry of ultrahigh-pressure rocks. In: *When Continents Collide: Geodynamics and Geochemistry of Ultrahigh-Pressure Rocks* (eds Hacker, B. R. & Liou, J. G.), pp. 241–259. Kluwer Academic Publishers, Dordrecht.

Rumble, D. & Yui, T. F., 1998. The Qinglongshan oxygen and hydrogen isotope anomaly near Donghai in Jiangsu province, China. *Geochimica et Cosmochimica Acta*, **62,** 3307–3321.

Sharp, Z. D., 1990. A laser-based microanalytical method for the in-situ determination of oxygen isotope ratios of silicates and oxides. *Geochimica et Cosmochimica Acta*, **54,** 1353–1357.

Sharp, Z. D., 1995. Oxygen isotope geochemistry of the Al_2SiO_5 polymorphs. *American Journal of Science*, **295,** 1058–1076.

Sharp, Z. D., Essene, E. J. & Hunziker, J. C., 1993. Stable isotope geochemistry and phase equilibria of coesite-bearing whiteschists, Dora Maira Massif, western Alps. *Contributions to Mineralogy and Petrology*, **114,** 1–12.

Sobolev, N. V. & Shatsky, V. S., 1990. Diamond inclusion in garnets from metamorphic rocks: a new environment for diamond formation. *Nature*, **343,** 742–746.

Terabayashi, M., Ota, T., Yamamoto, H. & Kaneko, Y., 2002. Contact metamorphism of the Daulet Suite by solid intrusion of the Kokchetav HP–UHPM slab. In: *Anatomy of a Diamond-Bearing Ultrahigh-Pressure Metamorphic Terrane: the Kokchetav Massif of Northern Kazakhstan* (eds Parkinson, C. D., Katayama, I. & Liou, J. G.). Chapter VI–3, p. 413. Universal Academy Press, Tokyo.

Valley, J. W., 1986. Stable isotope geochemistry of metamorphic rocks. In: *Stable Isotopes in High Temperature Geological Processes* (eds Valley, J. W., Taylor, H. P. & O'Neil, J. R.), pp. 445–489. Mineralogical Society of America. Washington DC.

Waters, D. J. & Martin, H. N., 1993. Geobarometry in phengite-bearing eclogites. *Terra Abstract*, **5,** 410–411.
Windley, B. F., 1995. The Evolving Continents, 3rd edn. Chap. 5. *Rifts to Oceans*, 61–62. John Wiley & Sons, Chichester.
Yamamoto, J., Maruyama, S., Parkinson, C. D. & Katayama, I., 2002. Geochemical characteristics of metabasites from the Kokchetav massif: Subduction zone metasomatism along an intermediate geotherm. In: *Anatomy of a Diamond-Bearing Ultrahigh-Pressure Metamorphic Terrane: the Kokchetav Massif of Northern Kazakhstan* (eds Parkinson, C. D., Katayama, I. & Liou, J. G.). Chapter V–1., pp. 363–372. Universal Academy Press, Tokyo.
Yui, T. F., Rumble, D., Chen, C. H. & Lo, C. H., 1997. Stable isotope characteristics of eclogites from the ultra-high-pressure metamorphic terrain, east-central China. *Chemical Geology*, **137,** 135–147.
Yui, T. F., Rumble, D. & Lo, C. H., 1995. Unusually low δ^{18}O ultrahigh-pressure metamorphic rocks from the Sulu terrain, eastern China. *Geochimica et Cosmochimica Acta*, **59,** 2859–2864.
Zheng, Y.-F., Fu, B., Gong, B. & Li, S., 1996. Extreme ^{18}O depletion in eclogite from the Su-Lu terrane in East China. *European Journal of Mineralogy*, **8,** 317–323.
Zheng, Y.-F., Fu, B., Li, Y., Xiao, Y. & Li, S., 1998. Oxygen and hydrogen isotope geochemistry of ultrahigh-pressure eclogites from the Dabie Mountains and Sulu terrane. *Earth and Planetary Science Letters*, **155,** 113–129.
Zheng, Y. F., Fu, B., Xiao, Y., Li, Y. & Gong, B., 1999. Hydrogen and oxygen isotope evidence for fluid–rock interactions in the stages of pre- and post-UHP metamorphism in the Dabie Mountains. *Lithos*, **46,** 677–693.

Received 30 January 2002; revision accepted 6 September 2002.