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Li abundances in eclogite minerals: a clue to a crustal or mantle origin?

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Abstract The mineral phases of 33 eclogite and garnet clinopyroxenite samples from various tectonic settings were analysed for Li by secondary ion mass spectrometry (SIMS). In all samples, Li is preferentially incorporated into clinopyroxene (0.4 to 80 μ g/g), whereas co-existing garnet contains only minor amounts of Li (0.01 to 3.7 μ g/g). When present, glaucophane shows Li abundances which are similar to those of clinopyroxene, but phengite contains significantly less Li than clinopyroxene. Additional phases, such as amphibole, quartz, clinozoisite and kyanite, have low Li concentrations $(<1 \mu g/g)$. No correlation is apparent between the Li contents and major-element compositions of clinopyroxene or garnet. On the basis of both measured Li concentrations in clinopyroxene and estimated Li abundances in the whole rocks, the investigated samples can be subdivided into high-Li and low-Li groups. These groups coincide with the mode of origin of the rocks. Metabasaltic (metagabbroic) eclogites from high-pressure terranes belong to the high-Li group whereas, except for one eclogite, all kimberlite- and basanite-hosted xenoliths have low Li contents. Samples from eclogites and garnet clinopyroxenites associated with orogenic peridotites fall into both groups. It is suggested that the high-Li eclogites originated from basaltic oceanic crust whereby the notable Li enrichment of some samples was probably caused by low-temperature hydrothermal alteration prior to subduction. Furthermore, the low-Li

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eclogites and garnet clinopyroxenites may represent high-pressure cumulates from mafic melts percolating through the mantle.

Introduction

Eclogites occur in different geologic settings and may form at highly variable pressure-temperature (P-T) conditions (e.g. Carswell 1990). In collisional belts, for example, low-T (<550 °C) eclogites form characteristic constituents of high-P metamorphic ophiolitic rock associations or continental margin sequences (e.g. Schliestedt 1990; Okrusch and Bröcker 1990; Rubatto et al. 1998; Widmer et al. 2000), and medium-T (550-900 °C) eclogites often occur as lenses in low-P metamorphic gneisses and migmatites (e.g. Trommsdorff 1990; Cuthbert and Carswell 1990; O'Brien and Carswell 1993; Kalt et al. 1994). Many of these eclogite bodies have been shown to represent high-P metamorphic equivalents of basaltic oceanic crust or continental basalts. However, the origins of some high-T (>900 °C) eclogites (or garnet clinopyroxenites) which occur as layers or lenses within, or as tectonic slivers in close spatial association to orogenic peridotites remain enigmatic. Moreover, various models have been proposed for the origin of eclogitic and garnet clinopyroxenitic xenoliths entrained in kimberlites and alkali basalts: (1) eclogites are relicts of the Earth's primary differentiation process (e.g. Anderson 1981a, 1981b; McCulloch 1989), (2) eclogite xenoliths represent fragments of subducted oceanic crust (e.g. Helmstaedt and Doig 1975; Ringwood 1975; Helmstaedt and Schulze 1979; Jagoutz et al. 1984; MacGregor and Manton 1986; Helmstaedt and Schulze 1989; Jacob et al. 1994; Jacob and Foley 1999), (3) eclogites are residues of high-P melting of subducted oceanic crust (e.g. Hatton and Gurney 1987; Ireland et al. 1994; Barth et al. 2001), and (4) eclogites form as cumulates during high-P fractionation of partial melts in the mantle (e.g. O'Hara and Yoder 1967; Caporuscio and Smyth 1990).

The major-element chemistry of garnet was first employed by Coleman et al. (1965) in an attempt to classify the different types of eclogite observed in the field. Their group A eclogites contained Mg-rich garnet and were considered to have formed as high-pressure cumulates. Group B and C eclogites had garnets which were richer in Fe and Ca and were interpreted to be related to metamorphosed basaltic oceanic crust. More recently, trace element and isotope data have been employed to clarify the origin of the group B and C eclogites (e.g. Sobolev and Sobolev 1980; Shervais et al. 1988; Taylor and Neal 1989; Caporuscio and Smyth 1990; Jerde et al. 1993; Ireland et al. 1994; Jacob et al. 1994; Snyder et al. 1997; Barth et al. 2001). In some cases, different origins have been proposed for eclogite xenoliths from a single suite, reflecting the different mantle domains which were sampled by the host magma (e.g. Taylor and Neal 1989; Snyder et al. 1997). In addition, eclogites could also have experienced later chemical modification through repeated, partial melt extraction or metasomatic overprint. These subsequent effects add further complications for interpreting the origin and evolution of eclogites.

Recent studies have demonstrated that the Li contents of whole rocks and individual mineral phases can provide important additional constraints on geochemical processes such as partial melting, crystal fractionation, metasomatism and low-temperature alteration (e.g. Chan et al. 1992, 1993, 1999; Seitz and Woodland 2000; Decitre et al. 2002; Paquin and Altherr 2002). For example, the partitioning of Li between clinopyroxene, orthopyroxene and olivine in equilibrated mantle peridotites and pyroxenites is apparently independent of pressure and temperature (Seitz and Woodland 2000). Thus, Li can be used as a chemical tracer without having to account for differences caused by variable equilibration pressures and temperatures between samples. In addition, the behaviour of Li in submarine basalts has been well characterised (Ryan and Langmuir 1987; Chan et al. 1992, 1993, 1999). Based upon these recent results, we have undertaken a study on the Li contents of minerals in eclogites from a number of localities world-wide, anticipating that their Li signatures would reflect their mode of origin and/or the effects of subsequent chemical changes which occurred under mantle conditions. Some samples were chosen because their geological relations unequivocally indicate that they originated as basaltic oceanic crust which was subsequently metamorphosed at high pressures (e.g. samples from Syros, Greece, and from the Münchberg Complex, Germany). Comparison of these eclogites with data from submarine basalts also provides insights into Li mobility during subduction. The origins of the remaining samples, especially those recovered as xenoliths from kimberlite pipes and alkali basaltic vents, are less certain. Here, we show that the Li contents of clinopyroxene can provide further constraints on the genesis of these mantle-derived eclogites.

Analytical techniques

Mineral analyses were performed at Heidelberg using a Cameca SX51 electron microprobe in wavelength dispersive mode. Operating parameters were 10–15 s counting time with an acceleration voltage of 15 kV and a beam current of 20 nA. For spot analyses the electron beam was focused to less than 1 µm in size. Corrections to the raw data were made using the Cameca PAP correction program. Minerals and synthetic glasses were used as standards. Analyses of Li were accomplished using a modified Cameca 3f-IMS ion microprobe at Heidelberg. Analyses were made using a ¹⁶O⁻ primary beam at an acceleration voltage of 12.5 kV. A focused beam with an intensity of 10 nA gave a beam diameter of $20-25 \,\mu\text{m}$. Samples were coated with a ~ 50 -nm-thick layer of gold. Positive secondary ions were accelerated through a nominal 4.5 kV. The energy window was set to 40 eV. We employed the energy filtering technique with an offset of -75 V at a mass resolution of $\sim 1,000$ to suppress interfering molecules and to minimise the matrix effects (Ottolini et al. 1993; Decitre et al. 2002). Ion yields of ⁷Li were normalised to 30Si. An NIST SRM-610 glass containing 484.6 ± 21.7 (1 σ) μ g/g Li was used as standard (Pearce et al. 1997). ³⁰Si and ⁷Li peaks were measured for 2 and 8 s respectively. Longterm reproducibility of the SRM-610 standard is better than 10%, including the variations in the instrumental setup (e.g. caused by the change of samples).

The samples

A total of 33 eclogite samples was investigated from a number of localities world-wide (Table 1). About half of the samples originate from collisional belts, including the Central European Hercynides (Bohemian Massif), the Caledonides (Western Gneiss Region, Norway), the Pyrenees (Lherz), the Betic-Rifean orogen (Beni Bousera, Morocco), the Central and Eastern Alps (Alpe Arami and Trescolmen, Switzerland; Pohorje Mts., Slovenia) and the Hellenides (Syros, Greece). Four of these samples are spatially associated with peridotite bodies of mantle origin (Table 1). The other half of the samples are eclogite and garnet clinopyroxenite xenoliths from several kimberlite localities in South Africa (Roberts Victor, Jagersfontein, Bultfontein, Lester), Siberia (Obnazhënnaya), the Eastern Finland Kimberlite Province, and from alkali basaltic vents in the East African Rift System (Marsabit, Kenya). Three of the xenolith samples are diamondiferous (Table 1). Equilibration temperatures for these samples, determined using the garnet-clinopyroxene thermometer of Krogh (1988), are listed in Table 1. We assume equilibration pressures consistent with published estimates for a particular locality or, in the case of the diamond-bearing xenoliths, with the stability field of diamond.

The eclogites from the Münchberg Complex (Bohemian Massif) have been the subject of numerous investigations (e.g. Matthes et al. 1975; Franz et al. 1986; Stosch and Lugmair 1990; Okrusch et al. 1991; O'Brien 1993). The bulk compositions of these kyanite-bearing and kyanite-free eclogites are consistent with a derivation from plagioclase-rich gabbros and MORB-type basalt respectively (Stosch and Lugmair 1990). All samples studied here (notation FG, Table 1) contain

Table 1. Locations, mineral assemblages and estimated equilibration temperatures at assumed pressures of eclogites. *Grt* Garnet, *cpx* clinopyroxene, *opx* orthopyroxene, *dia* diamond, *phe* phengite, *pg* paragonite, *am* Amphibole, *ky* kyanite, *rt* rutile, *qtz* quartz, *pl* plagioclase, *crn* corundum, *sp* spinel, *cc* calcite, (*s*) secondary

Sample	Location	Mineral assemblage	$T (^{\circ}C)^{a}$	P (GPa)	Reference ^b
Eclogite and ga	arnet clinopyroxenite xenoliths				
E Î	Lahtojoki, Finland	Cpx, grt	$1,299 \pm 30$	6.0	1, 2
E 2	Lahtojoki, Finland	Cpx, grt	$1,371 \pm 20$	6.0	1, 2
L 78	Lahtojoki, Finland	Cpx, grt, dia	$1,242 \pm 23$	6.0	1, 2
L 80	Lahtojoki, Finland	Cpx, grt, dia	$1,231 \pm 25$	6.0	1, 2
RV 1	Roberts Victor, South Africa	Cpx, grt, dia	$1,045 \pm 42$	5.0	1
JA 1	Jagersfontein, South Africa	Cpx, grt	1.353 ± 11	5.0	1
JA 4	Jagersfontein, South Africa	Cpx, grt	$1,065 \pm 6$	5.0	1
JA 7	Jagersfontein, South Africa	Cpx, grt	1.038 ± 7	5.0	1
LE 1	Lester, South Africa	Grt, cpx, phl (s)	$1,195 \pm 9$	5.0	1
LE 3	Lester, South Africa	Cpx, grt, cc (s) , phl (s)	$1,126 \pm 10$	5.0	1
LE 4	Lester. South Africa	Cpx. grt. cc (s)	1.228 ± 15	5.0	1
BU 98-2	Bultfontein. South Africa	Grt. cpx	1.271 ± 5	5.0	1
OB 2	Obnazhënnava, Russia	Cpx. grt	977 ± 29	5.0	1
KE 771/1	Marsabit, Kenya	Cpx, grt, opx, am (s)	887 ± 35	2.0	1
KE 771/3	Marsabit, Kenya	Cpx, grt, opx, am (s)	878 ± 40	2.0	1, 3, 4
Metabasaltic ed	clogites				
FG 1	Weissenstein, Germany	Cpx, grt, qtz, rt, phe, am (s)	730 ± 13	1.5	1, 5
FG 3	Autengrün, Germany	Cpx, grt, qtz, phe, ky, rt	568 ± 36	1.5	1, 5
FG 97-1	Weissenstein, Germany	Cpx, grt, qtz, rt	759 ± 14	1.5	1
FG 139	Silberberg, Germany	Cpx, grt, phe, qtz	710 ± 25	1.5	1
FG 158	Hof. Germany	Cpx, grt, gtz, ky, rt, phe	691 ± 13	1.5	1
FG 2208	Silberberg, Germany	Cpx, grt, qtz, ky, phe, rt	609 ± 16	1.5	1
FG 85916	Weissenstein, Germany	Grt, cpx, qtz, rt, ky, $am + pl$ (s)	751 ± 16	1.5	1
FG 85930	Weissenstein, Germany	Cpx, grt, qtz, phe, rt, ky	615 ± 45	1.5	1
SM 43	Almklovdalen, Norway	Grt, cpx, qtz, rt, ky, $am + pl$ (s)	741 ± 45	2.0	1, 9
TC 1	Trescolmen, Switzerland	Cpx, grt, rt, qtz, am (s)	705 ± 36	2.0	1, 7
PM 95-9	Pohorje Mts., Slovenia	Cpx, grt, qtz, ky, rt	717 ± 13	1.5	1, 8
PM 95-19	Pohorie Mts., Slovenia	Grt. cpx. gtz. rt. ky. $am + pl$ (s)	784 ± 15	1.5	1.8
SY 109	Syros, Greece	Grt, cpx, gln, phe, pg, ep, rt, tit, qtz	470 ± 30	1.5	14
SY 323	Syros, Greece	Grt, cpx, gln, pg, ep, rt, tit, qtz	470 ± 30	1.5	14
Eclogites and g	arnet clinopyroxenites associated y	vith mantle peridotites			
MĔ 2	Meidling, Austria	Cpx, grt	$1,223 \pm 25$	2.5	1, 6
AA 1	Alpe Arami, Switzerland	Cpx, grt, rt, ky	691 ± 31	2.0	1, 10
BB 1	Beni Bousera, Morocco	Cpx, grt, crn, sp	900 ± 50	5.0	11, 12
PY 36	Lherz, France	Grt, cpx, sp	901 ± 15	1.5	1, 13

^aTemperature estimates ($\pm 1 \sigma$) are based on the Fe–Mg garnetclinopyroxene exchange thermometer of Krogh (1988) and are given for assumed pressures

^bReferences: *1* this study, *2* Kukkonen and Peltonen (1999), *3* Henjes-Kunst and Altherr (1992), *4* Seitz et al. (1999), Seitz and

garnet, clinopyroxene (omphacitic) and quartz and may contain accessory rutile, kyanite, phengite or amphibole. Samples FG 1, FG 97-1 and FG 139 are kyanite-free. The minimum peak metamorphic conditions of the eclogites from the Münchberg Complex (i.e. samples from Autengrün, Weissenstein, Silberberg, Hof; Table 1) were estimated by O'Brien (1993) to be 650 ± 60 °C and ≥ 1.4 GPa (possibly as high as 2.5–2.8 GPa).

Sample ME 2, from Meidling in Lower Austria (Bohemian Massif), is a garnet clinopyroxenite occurring in association with garnet peridotites (e.g. Carswell and Jamtveit 1990; Carswell 1991). Meidling eclogites are richer in Mg and have significantly higher equilibration temperatures than those reported for the eclogites from the Münchberg Complex (Table 1).

Eclogite sample SM 43 from the Western Gneiss Region (Almklovdalen, Sunmøre district, Norway) contains mainly garnet and omphacitic clinopyroxene Woodland (2000), 5 O'Brien (1993), 6 Carswell and Jamtveit (1990), 7 Meyre and Puschnig (1993), 8 Visona et al. (1991), 9 Medaris (1980), 10 Becker (1993), 11 Kornprobst et al. (1990), 12 Alaoui et al. (1997), 13 Woodland et al. (1996), 14 Trotet et al. (2001)

with accessory quartz, phlogopite, rutile, amphibole and kyanite. Garnet and clinopyroxene grains are essentially homogeneous and display only limited compositional variations. The eclogites occur as interbedded pods in gneiss, and a crustal protolith has been suggested by numerous workers (e.g. Brueckner 1977; Medaris 1980; Griffin and Brueckner 1980; Krogh 1982; Mørk 1985).

Samples from Trescolmen and Alpe Arami in the Central Alps originate from the Adula and Cima Lunga nappes respectively. The metamorphic evolutions of these eclogites were described in detail by Heinrich (1986), Trommsdorff (1990), Gebauer et al. (1992), Becker (1993), Meyre and Puschnig (1993), Gebauer (1996), Meyre et al. (1997), Pfiffner and Trommsdorff (1998), Tappert et al. (1999) and Trommsdorff et al. (2000). Samples consist mainly of omphacitic clinopyroxene and garnet along with accessory rutile. A trace of kyanite is present in the Alpe Arami sample and a trace

Table 2. Representative mineral analyses and estimated whole-rock Li contents of eclogite and garnet clinopyroxenite xenoliths (major

Sample	E 1		E 2		L 78		L 80		RV 1		JA 1		JA 4		JA 7	
Mineral	Grt	Срх	Grt	Срх	Grt	Срх	Grt	Срх	Grt	Срх	Grt	Срх	Grt	Срх	Grt	Срх
SiO ₂	42.95	55.43	41.64	54.20	41.88	54.94	41.43	55.39	42.18	55.44	41.55	54.63	41.33	54.70	41.11	54.88
TiO ₂	0.49	0.15	0.45	0.14	0.62	0.23	0.60	0.55	0.45	0.35	0.93	0.28	0.09	0.14	0.09	0.15
Al_2O_3	21.29	2.09	22.22	6.88	21.56	3.47	22.30	7.79	22.62	3.00	21.51	2.63	23.57	4.12	24.05	5.57
Cr_2O_3	1.55	0.51	0.43	0.26	1.09	0.60	0.03	0.03	0.23	0.18	0.57	0.17	0.20	0.30	0.17	0.23
FeO	7.19	3.53	8.43	3.01	9.43	4.50	13.54	4.72	9.70	3.35	10.12	6.64	10.60	3.57	10.88	3.28
MnO	0.29	0.13	0.16	0.02	0.28	0.15	0.33	0.07	0.37	0.06	0.25	0.14	0.45	0.09	0.29	0.07
NiO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.03	0.10	0.01	0.05	n.d.	n.d.
MgO	21.81	19.77	16.15	13.69	20.99	17.74	16.48	11.96	20.34	16.62	20.67	21.27	19.61	15.26	19.61	14.09
CaO	4.39	16.69	10.29	17.59	3.96	15.00	5.47	13.78	3.86	18.82	4.14	11.97	3.95	18.62	3.79	17.32
Na ₂ O	0.05	1.51	0.12	3.78	0.08	2.58	0.15	5.28	0.05	1.84	0.10	1.69	0.06	2.78	0.06	3.84
Total	100.01	99.80	99.89	99.57	99.89	99.21	100.33	99.57	99.80	99.66	99.87	99.52	99.87	99.63	100.10	99.43
Mg# ^a	84.4	90.9	77.4	89.0	79.9	87.5	68.5	81.9	78.9	89.8	78.5	85.1	76.7	88.4	76.3	88.4
Li mean ^b	0.087	0.516	0.138	0.77	0.155	0.73	0.209	0.96	0.122	0.370	0.206	1.03	0.76	10.7	0.177	1.63
(1 <i>σ</i>)	0.008	0.036	0.017	0.10	0.028	0.13	0.018	0.08	0.001	0.033	0.012	0.06	0.05	0.4	0.009	0.04
Li min	0.066	0.427	0.106	0.67	0.121	0.57	0.178	0.84	0.122	0.334	0.181	0.97	0.73	10.1	0.162	1.56
Li max	0.097	0.568	0.161	1.02	0.234	0.82	0.229	1.06	0.123	0.415	0.218	1.15	0.82	11.3	0.185	1.67
WR Li ^c	0.30		0.45		0.45		0.58		0.27		0.92		9.2		1.1	

^a Mg#=100*Mg/(Mg+Fe_{tot})

^bLi mean (1σ) is arithmetic mean with standard deviation of all values measured; Li min and Li max refer to the lowest and highest ^cWR Li is estimated whole-rock Li content

of quartz is present in the Trescolmen sample. The mineral grains of the Alpe Arami eclogite display homogeneous cores and retrograde rims (Tappert et al. 1999) whereas those from the Trescolmen sample are strongly zoned. A gabbroic protolith is inferred for the eclogites from the Alpe Arami (e.g. Gebauer et al. 1992; Gebauer 1996) and Trescolmen localities (e.g. Meyre and Puschnig 1993).

Eclogites from the Pohorje Mts. (Eastern Alps, Slovenia) are interpreted to be the metamorphic products of subducted ocean-floor basalts with N-MORB affinity (Hinterlechner-Ravnik et al. 1991a, 1991b; Visona et al. 1991). They are composed of essentially homogeneous omphacitic clinopyroxene and lesser garnet with variable amounts of quartz, kyanite, rutile and secondary amphibole. Visona et al. (1991) suggested peak metamorphic conditions of 750–800 °C at 1.5–1.6 GPa.

The paragonite-bearing eclogites from Syros (Aegean Sea, Greece) occur as blocks within a high-pressure metamorphic ophiolitic mélange, in spatial association with lawsonite-bearing mafic blueschists and metasediments (Okrusch and Bröcker 1990; Trotet et al. 2001).

Sample BB 1 from Beni Bousera (Morocco) is a corundum-bearing garnet clinopyroxenite with a layering defined by the presence or absence of corundum. The detailed petrology and geochemistry is reported in Kornprobst et al. (1990). The high temperature obtained from the garnet-clinopyroxene thermometer (Table 1) is likely an artifact due to the high Ca content of the garnet, and a metamorphic equilibration temperature of ~850 °C is considered to be a more reasonable estimate (Alaoui et al. 1997). Based upon detailed petrological and geochemical criteria, Kornprobst et al. (1990) interpreted this pyroxenite to have formed by high-pressure recrystallisation of a plagioclase-rich gabbro under mantle conditions. A similar origin was assumed for Alrich garnet clinopyroxenites from Ronda (Spain) by Morishita et al. (2001). Alternatively, Pearson et al. (1993) suggested that the pyroxenite could represent partially melted, subducted oceanic crust.

Another garnet clinopyroxenite analysed in this study, PY-36, was taken from a dike crosscutting the Lherz peridotite massif (French Pyrenees). This dike is slightly discordant to the prevailing foliation in the host peridotite. It is predominantly composed of clinopyroxene and garnet along with rare aluminous spinel, and is considered to have crystallised from a volatile-poor tholeiitic melt traversing the upper mantle (Bodinier et al. 1987; Vétil et al. 1988). This dike is relatively unaffected by post-intrusion metasomatism (Woodland et al. 1996).

The 15 xenolith samples from various localities are essentially bimineralic eclogites and garnet clinopyroxenites. Late-stage secondary minerals (e.g. phlogopite and calcite veinlets) are present in samples from Jagersfontein and Lester. Three samples, one from Roberts Victor (RV 1) and two from the Eastern Finland Kimberlite Province, are diamond bearing (L 78 and L 80), constraining their minimum equilibration pressure to be \sim 5.0 GPa. However, Kukkonen and Peltonen (1999) consider the Eastern Finland eclogites to have equilibrated at ~ 6.0 GPa. Descriptions of the two garnet clinopyroxenites from Marsabit (Kenya) can be found in Henjes-Kunst and Altherr (1992). These samples are interpreted to be of magmatic origin, having re-equilibrated under conditions within the spinel peridotite facies of the upper mantle. Equilibration temperatures calculated for the xenolith samples (1,370– 880 °C) are in most cases significantly higher than those

elements (oxide wt%) were analysed by electron microprobe, Li (µg/g) by SIMS). n.d. not detected, n.a. not analysed

LE 1		LE 3		LE 4		BU 98-2	2	OB 2		KE 771	/1		KE 771/3		
Grt	Срх	Grt	Срх	Grt	Срх	Grt	Срх	Grt	Срх	Grt	Срх	Opx	Grt	Срх	Opx
40.48	53.84	40.46	54.46	40.16	53.58	40.47	54.56	42.52	54.57	41.55	54.63	41.33	42.38	54.11	56.10
0.08	0.23	0.10	0.25	0.06	0.16	0.12	0.30	0.15	0.27	0.93	0.28	0.09	0.05	0.47	0.08
23.34	8.47	22.52	7.43	23.33	9.73	22.73	14.93	22.73	2.79	21.51	2.63	23.57	23.93	6.05	3.13
0.07	0.08	0.07	0.07	0.05	0.05	0.09	0.15	0.57	0.32	0.57	0.17	0.20	0.30	0.33	0.12
12.76	3.53	12.89	3.60	11.59	3.17	12.80	2.57	9.27	2.56	10.12	6.64	10.60	9.60	2.36	7.00
0.25	0.03	0.41	0.03	0.41	0.03	0.26	0.02	0.31	0.05	0.25	0.14	0.45	0.44	0.07	0.13
n.d.	n.d.	0.02	0.02	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	0.03	0.10	0.01	n.a.	n.a.	n.a.
11.84	11.44	10.82	12.20	10.84	10.70	11.80	7.13	19.20	16.59	20.67	21.27	19.61	19.58	14.47	33.67
12.13	17.47	12.50	17.93	14.13	17.04	11.55	11.48	5.27	22.21	4.14	11.97	3.95	4.25	20.08	0.32
0.04	4.70	0.08	4.07	0.02	5.01	0.07	8.30	0.01	0.95	0.10	1.69	0.06	n.d.	2.63	0.06
100.99	99.79	99.87	100.06	100.59	99.47	99.89	99.46	100.03	100.31	99.87	99.52	99.87	100.50	100.60	100.60
62.3	85.2	59.9	85.8	62.5	85.7	62.2	83.2	78.7	92.0	78.5	85.1	76.7	78.4	91.6	89.5
0.075	0.94	0.088	0.80	0.171	1.60	0.236	2.47	0.169	0.97	0.164	1.46	0.85	0.117	1.18	0.96
0.016	0.07	0.019	0.04	0.022	0.09	0.087	0.07	0.017	0.11	0.041	0.08	0.08	0.004	0.04	n.a.
0.052	0.88	0.054	0.72	0.146	1.48	0.143	2.37	0.152	0.82	0.103	1.34	0.72	0.112	1.14	0.92
0.097	1.06	0.121	0.85	0.198	1.76	0.393	2.56	0.190	1.15	0.302	1.62	0.93	0.120	1.24	0.99
0.29		0.43		0.85		1.3		0.61		0.87			0.74		

measured values respectively

calculated for the eclogites from the orogenic massifs (900–470 °C), with the exception of sample ME 2 from Meidling which records a very high temperature (\sim 1,220 °C; Table 1).

Results and discussion

Major-element compositions of garnet and clinopyroxene

Major-element compositions of garnet and clinopyroxene vary considerably in our suite of samples, which reflects in part the different settings from which the eclogites originate (Tables 2, 3, 4). Phases in most of the xenolith samples are relatively homogenous, with only minor zoning observable. The eclogitic samples from collisional belts exhibit greater degrees of mineral zoning which can be attributed to the complex exhumation histories of these samples and in part to lower maximum temperatures during metamorphism. In particular, the garnets from the low-T eclogites from Syros (samples SY 109 and SY 323) show pronounced prograde zonations, and clinopyroxenes from these samples are also heterogeneous (Table 3).

Garnet compositions cover all of the three fields (groups A, B and C) defined by Coleman et al. (1965), when plotted in terms of their pyrope, almandine+spessartine and grossular+andradite components (Fig. 1). Two compositional trends are apparent which broadly coincide with the metabasic and ultrabasic trends identified by Helmstaedt and Schulze (1989). Garnets from the samples which are clearly high-pressure metabasalts are characterised by fairly constant Ca/ (Fe+Mn) ratios and highly variable Mg contents, and define the metabasic trend. On the other hand, the ultrabasic trend is defined by the garnets from eclogite xenoliths and from three eclogites which are associated with orogenic peridotites (BB 1, ME 2, PY 36). Garnet from sample AA 1 (Alpe Arami), however, is relatively rich in Fe and follows the metabasic trend (Fig. 1). Except for the samples from the Lester and Bultfontein Mines, garnets in the eclogite xenoliths are confined to group A.

Clinopyroxenes from our sample suite display a very large range in Na₂O and MgO contents (Fig. 2). A number of samples (e.g. FG 85916, FG 97-1, BU 98-2) are inconsistent with the classification scheme of Taylor and Neal (1989), which is supposed to mirror the behaviour of the co-existing garnet compositions. This is not surprising in light of the fact that the incorporation of Na in clinopyroxene as a jadeite component is not only a function of bulk composition but also of pressure and temperature (e.g. Holland 1983). The Al contents of clinopyroxene are also very variable (Tables 2, 3, 4). Although a crude correlation exists between Al and Na, it is imperfect, reflecting the additional incorporation of Al via Tschermak-type substitutions, which is independent of the Na content. Clinopyroxene from sample SY 323 shows oscillatory zoning with alternating Na-rich and Na-poor compositions (Table 3).

Li distribution

Mineral phases in the samples of high-T eclogites are characterised by relatively constant Li abundances. On the other hand, the mineral grains of the low-T and medium-T eclogites may show considerable variations in their Li contents. In order to visualise the degree of Li

Table 3. by SIMS.	Represen n.d. not	tative n detecte	nineral <i>ɛ</i> d, <i>n.a</i> . n	analyses ot anal	and est yzed, <i>c</i>	imated v core, r r	vhole-rc im, (s)	ock Li con secondar	itents of y. Cpx	metaba 1 and cr	isaltic ec px 2 (sai	clogites. mple SY	Major e 323) re	elements efer to N	[oxide w Va-rich a	∕t%] we nd Na-j	re analy poor do	sed by e mains of	lectron f omphi	micropr acites, re	robe, Li espectiv	[µg/g] ely
Sample	FG 1			FG 3			FG 97.	-1	FG 13	6		FG 158	~		FG 220	8		FG 859	16		FG 859	30
Mineral	Grt	Cpx	Phe	Grt	Cpx	Phe	Grt	Cpx	Grt	Cpx	Phe	Grt	Cpx	Phe	Grt	Cpx	Phe	Grt	Cpx	Am (s)	Grt	Cpx
0:5	Lt ot	55 40	51 20	00.00	LC 33	51 70	21 06	12 22	10 50	69 33	51 72	20.60	55 05	51.40	10.07	US 75	51 57	20 AD	06 75	10 01	11 22	06 23
TiO,	0.04	0 10	0.58	0 11	0.08	0.44	0.09	0.12	40.00 104	0 11	05.0	0.03	0.11	0.67	, p u	0.10	0.50	0.05	0.13	1 21	77:14 1 J	0.00
Al ₂ O ₂	21.55	10.02	27.98	22.16	9.37	28.05	21.38	9.66	22.23	10.71	27.97	21.95	11.15	28.93	22.46	9.10	29.01	21.29	10.05	15.46	22.45	10.25
Cr,0,	0.04	0.04	0.01	0.08	0.17	0.05	n.d.	0.03	0.01	0.07	0.05	0.10	0.12	0.01	0.05	0.05	0.04	0.04	n.d.	0.03	0.12	0.29
FeO	24.48	5.18	1.97	16.05	1.35	0.71	25.40	6.17	18.68	2.64	1.06	18.83	2.43	1.08	15.89	1.69	0.48	25.26	5.93	12.12	13.71	1.44
MnO	0.65	0.01	0.03	0.31	0.06	0.03	0.39	0.07	0.33	0.06	n.d.	0.35	0.08	n.d.	0.46	0.02	n.d.	0.59	0.02	0.08	0.23	0.03
MgO	6.84	8.67	3.11	12.80	11.64	4.06	5.68	8.11	9.77	9.75	3.85	10.44	9.48	3.70	13.15	11.63	3.99	5.39	7.97	11.08	16.15	10.78
CaO	8.02	14.03	0.02	8.18	16.98	0.01	8.54	13.14	9.02	15.09	0.02	8.49	14.83	n.d.	7.42	16.93	0.03	9.02	13.09	8.59	5.71	15.84
Na_2O	0.43	6.26	0.67	0.05	4.82	0.34	0.02	6.78	0.05	5.73	0.50	n.d.	5.88	0.60	0.02	4.69	0.43	0.03	6.58	4.63	0.01	5.31
P ² C	n.a.	n.a.	9.83	n.a.	n.a.	56.9 50	n.a.	n.d.	n.a.	n.a.	10.10	n.a.	n.a.	C0.2	n.a.	n.a.	9.48	n.a.	n.a.	0.40	n.a.	n.a.
10tal Ma#a	23.7 23.7	08.66 74.0	04.06 8.67	58 7 58 7	93.04	1 10	06.66 28.5	99.69 70.1	C0.66	99.19 86.8	86.64 86.6	00.70 01.7	67.42 67.4	90.04 85.0	100.40 50.6	07.5	UC.CV 7 20	10.001	10.001	90.42 62.0	6C.66	4. 60 10 00
I i mean ^b	0.109	211 2	2.75	0.262	28.4	3.60	0.093	8.64	0.160	23.2	6.30	0.134	24.9	5.56	0.165	8.84	1.17	0.013	14.2	0.450	0.57	56.2
(1 d)	0.032	1.4	2.97	0.064	2.6	0.26	0.087	1.23	0.053	4.1 1.4	1.15	0.042	5.3	3.15	0.025	1.02	1.33	0.002	1.9	0.311	0.22	17.4
Li min	0.057	7.8	0.47	0.147	24.9	3.36	0.013	6.83	0.098	13.8	5.35	0.079	15.2	3.18	0.132	7.63	0.40	0.009	12.0	0.104	0.32	10.7
Li max WR Li ^c	0.170 5.3	12.5	8.52	0.366 13.0	33.1	3.88	0.290 3.9	11.77	$0.250 \\ 13.0$	29.0	8.14	0.201 16.2	31.1	12.79	0.195 5.5	9.88	3.86	0.015 5.6	17.0	0.840	1.09 30.9	89.8
Sample	SM 43		TC 1			PM 95-	6.	PM 95-1	6	SY 109							SY 323					
Mineral	Grt	Cpx	Grt	Cpx	Am (s)	Grt	Cpx	Grt	Cpx	Grt c	Grt r	Cpx c	Cpx r	Gln	Phe	$\mathbf{P}_{\mathbf{g}}$	Grt c	Grt r	Cpx 1 ^d	Cpx 2		
SiO_2	38.89	54.81	39.21	54.82	53.16	40.14	54.86	38.66	54.90	37.17	37.31	57.19	55.68	55.86	50.40	48.55	36.45	36.89	55.57	54.88		
TiO ₂	0.04	0.0	0.07	0.11	0.10	0.07	0.14	0.07	0.12	0.18	0.08	0.00	0.11	0.00	0.14	0.11	0.16	0.10	0.04	0.05		
AI203	21.45 0.00	10./	00.22	9.52	/1/	87.22	9.00	21.09 0.00	70.6	20.19	96.61	11.22	11.41	9.40	/0.02	4.86 4.00	20.02	20.40	C8.4	00.0		
Cr2O3 FeO	0.08 21 46	0.0/ 4 23	0.00 20.26	0.10 3 78	0.10 4 56	0.0 17 40	cn.n	20.0 77.77	80.0 202	10.0	0.00 33 40	7.81	0.00	0.00	0.00 4 68	cu.u 0 93	24.89	00.0 27.92	0.00 7 40	0.04 8 10		
MnO	0.42	0.01	03.07	0.03	ост- р и	0.47	n d	0.49	0.05	1 69	0.76	0.13	0 11	0.06	00.0	00.0	10.26	1 34	0.75	0.76		
MgO	7.60	10.69	9.63	10.44	19.33	11.06	10.77	7.59	9.20	0.74	1.77	1.41	3.55	5.99	2.35	0.26	0.87	2.30	7.00	9.27		
CaO	9.63	16.76	7.77	15.91	9.81	8.33	16.53	8.88	14.94	10.29	7.03	3.17	8.02	0.16	0.01	0.12	6.99	8.27	11.80	15.87		
Sample	FG 1			FG 3			FG 97-	1	FG 139	-		FG 158			FG 2208	8		FG 8591	16		FG 859	30
Mineral	Grt	Cpx	Phe	Grt	Срх	Phe	Grt	Cpx	Grt	Cpx	Phe	Grt	Cpx	Phe	Grt	Cpx	Phe	Grt	Cpx	Am (s)	Grt	Cpx
Na_2O	0.05	4.69	0.04	4.98	2.56	n.d.	4.81	0.05	5.44	0.06	0.02	12.69	9.83	7.36	0.43	6.51	0.00	0.03	7.81	5.38		
K ₂ U Total	n.d. 99.60	n.d. 98.96	n.d. 99.45	n.a. 99.57	n.a. 96.85	n.d. 99.80	n.d. 99.47	n.d. 100.22	n.d. 99.27	00.00 99.66	10.0 99.86	0.00 99.63	0.01 09.73	0.02 97.28	10.21 94.89	1.44 96,40	0.01 09.72	00.0 11.99	09.73	0.01 99.45		
$Mg\#^a$	38.7	81.8	45.9	83.1	88.3	53.1	87.9	37.3	76.6	4.3	8.6	24.3	59.3	36.7	47.2	32.8	5.8	12.1	62.8	67.1		
Li mean ^b	0.127	28.6 2	0.124	17.1	0.500	0.042	31.6	0.080	21.8	0.34	0.28	8.10		7.21	2.57	4.91	3.81	3.88	83.3			
(1 d)	0.040	9.6 4.6	0.077	6.1	0.067	0.015	14.3	0.033	10.2	0.06	0.06	0.37		0.27	0.34	1.51	0.71	0.55	18.5			
Li max	0.070	41.7	0.040	7.4 25.8	0.518	0.067	14.2 51.9	0.135	8.7 37.8	0.24 0.44	0.37	دد./ 8.73		0.79 7.64	2.14 3.60	8.70 8.70	2.04 5.12	5.08 4.71	40./ 114.0			
WR Li ^c	8.6		12.1			20.9		10.2		5.0							43.7					
${}^{a}Mg\# = 1($	$00^{*}Mg/(1 \sigma)$ is :	Mg + Fe arithmet	t _{tot}) tic mean	ı with s	tandard	deviatio	on of all	values n	ieasured	l; Li miı	n and L	i max re	efer to t	he lowe	st and hi	ghest m	easured	values 1	espectir	vely		
	+		1000	+ + + + + + + + + + + + + + + + + + + +	1																	

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^oWR Li is estimated whole-rock Li content ^dCpx 1 and cpx 2 (sample SY 323) refer to Na-rich and Na-poor domains of omphacites respectively

Table 4. Representative mineral analyses and estimated whole-rock Li contents of eclogites and garnet clinopyroxenites associated with peridotites (major elements (oxide wt%) were analysed by electron microprobe, Li (μ g/g) by SIM-S). *n.d.* not detected

Sample	BB 1		ME 2		AA 1		PY 36	
Mineral	Grt	Срх	Grt	Cpx	Grt	Cpx	Grt	Срх
SiO ₂	41.73	45.89	41.23	52.08	39.77	56.20	41.61	51.12
TiO_2	0.09	0.23	0.07	0.14	0.03	0.08	n.d.	0.20
Al_2O_3	23.46	18.54	22.99	7.46	22.11	11.02	23.12	7.14
Cr_2O_3	0.10	0.21	0.20	0.21	0.04	n.d.	0.25	0.24
FeO	8.68	2.04	7.78	2.60	19.99	2.72	10.38	2.69
MnO	0.13	0.08	0.24	0.06	0.50	0.04	0.29	0.06
NiO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	16.96	9.06	15.78	14.24	8.81	9.40	17.36	14.14
CaO	8.48	21.28	11.63	21.62	8.78	14.00	6.50	21.82
Na ₂ O	0.03	2.11	n.d.	1.52	0.01	6.18	n.d.	1.32
Total	99.60	99.40	99.90	99.90	100.00	99.60	99.50	98.70
Mg# ^a	77.6	88.8	78.3	90.7	44.0	86.0	74.9	90.4
Li mean ^b	0.060	8.22	0.050	1.34	0.009	9.73	0.081	1.45
(1σ)	0.010	1.17	0.030	0.35	0.003	0.10	0.016	0.10
Li min	0.043	6.14	0.012	0.577	0.006	9.57	0.057	1.28
Li max	0.076	9.40	0.720	2.180	0.013	9.89	0.100	1.59
WR Li ^c	5.3		0.8		6.8		0.7	

 $^{a}Mg\# = 100*Mg/(Mg + Fe_{tot})$

^b Li mean (1 σ) is arithmetic mean with standard deviation of all values measured; Li min and Li max refer to the lowest and highest measured values respectively

^cWR Li is estimated whole-rock Li content

heterogeneity, minimum and maximum Li concentration values are given in addition to average values and standard deviations (Tables 2, 3, 4). In sample SY 109, cpx grains display significant chemical zoning with respect to major elements, but their Li contents are rather constant (7.5–8.1 mg/g; Table 3) and do not show any systematic variation from core to rim. Since the lateral resolution of the ion beam is $20-25 \mu m$, we were not able to resolve the fine, oscillatory chemical zoning of cpx grains in sample SY 323. We found no correlations between any chemical parameter measured by electron microprobe (e.g. Mg# or Na) and the abundances of Li (Table 3).

In all samples, Li is preferentially incorporated into clinopyroxene, ranging from ~0.4 to 80 μ g/g (Tables 2, 3, 4; Fig. 3). By contrast, co-existing garnet contains only minor amounts of Li (~0.01 to 3.7 μ g/g). In low-temperature metabasaltic eclogites (SY 109, SY 323), Li contents of glaucophane are similar to those of cpx, but phengite and paragonite contain significantly less Li (Table 3). Additional phases, such as Ca-rich amphibole, quartz,

Fig. 1. Major-element compositions of garnet expressed in terms of their pyrope, almanidine + spessartine and grossular + andradite components. Subdivision into group A, B and C eclogites according to Coleman et al. (1965)





Fig. 2. Na₂O vs. MgO systematics of clinopyroxene. Subdivision into group A, B and C eclogites according to Taylor and Neal (1989)

clinozoisite and kyanite, are generally characterised by low Li concentrations (< 1 μ g/g). Thus, clinopyroxene is the principal carrier of Li in eclogitic parageneses. Our suite of eclogites can be subdivided into two groups on the basis of the Li concentrations in clinopyroxene (Fig. 3) – those with > 8.6 μ g/g Li (hereafter high-Li group), and those with < 2.5 μ g/g Li (hereafter low-Li group). For the most part, this subdivision coincides with the mode of origin of the samples; the metabasaltic eclogites have Lirich clinopyroxenes and the xenolith eclogites tend to have low Li contents. Sample JA 4 is an exception and could be grouped with the metabasaltic eclogites on the basis of the Li content in clinopyroxene. The samples from eclogites and garnet clinopyroxenites which are associated with orogenic peridotites fall into both groups (Fig. 3).

Figure 3 clearly indicates that the partitioning of Li between garnet and clinopyroxene is not constant but



Fig. 3. Li abundances in coexisting clinopyroxene and garnet. Hatched *field* represents data for six garnet peridotite and six garnet websterite xenoliths (Seitz and Woodland 2000; Olker, unpublished data)

varies by a factor of ~ 400 . This could result from disequilibrium between these two phases with respect to Li, or because the partition coefficient varies as a function of temperature or some chemical parameter. Assuming equilibrated Li concentrations, we can compute a partition coefficient D_{Li} (grt/cpx) for each of our samples. Calculated $\ln D_{Li}$ (grt/cpx) values are plotted as a function of reciprocal temperature in Fig. 4. It is obvious that there is no systematic variation of $\ln D_{Li}$ (grt/cpx) with temperature, neither within the high-Li nor within the low-Li groups of samples. Note that the range of $\ln D_{Li}$ (grt/cpx) values shown by the low-Li group is similar to that of garnet lherzolites and garnet websterites reported by Seitz and Woodland (2000) and Olker (unpublished data). We therefore conclude that ln $D_{Li}\ (grt/cpx)$ values are not controlled by temperature (and pressure; data not shown). Furthermore, no significant correlation is apparent between the Li contents and major-element compositions of clinopyroxene or garnet (Tables 2, 3, 4; Fig. 5a, b), and ln D_{Li} (grt/cpx) does not show any systematic variation with Na₂O and MgO in clinopyroxene (Fig. 5c, d).

Li behaviour during subduction of oceanic crust

The eclogite samples which unequivocally represent basalts metamorphosed under high pressures (Table 1) provide important insights into the behaviour of Li during subduction of oceanic crust. However, as a starting point, an assessment of the Li content of the mid-ocean ridge basalt protolith is necessary. Studies of fresh MORB from various ridges and fracture zones yield whole-rock Li contents ranging from 3.6 to 16.6 μ g/ g, with an average value of about 6 μ g/g (Humphris and Thompson 1978; Taylor and McLennan 1985; Ryan and Langmuir 1987; Chan et al. 1992, 1993; Niu and Batiza



Fig. 4. Plot of $\ln D_{Li}$ (grt/cpx) values vs. reciprocal equilibration temperatures for the investigated eclogites and garnet clinopyroxenites. Hatched *field* represents data for six garnet peridotite and six garnet websterite xenoliths (Seitz and Woodland 2000; Olker, unpublished data)

1997; Regelous et al. 1999; Niu et al. 1999). The Li content and Li isotopic signature of altered basaltic oceanic crust is variable depending on the type of alteration. Low-temperature alteration can lead to a strong bulk enrichment of Li, presumably due to the formation of Li-bearing sheet silicates such as clays, chlorite and serpentine (Humphris and Thompson 1978; Chan et al. 1992; You et al. 1996; Decitre et al. 2002). On the other hand, an experimental study by Seyfried et al. (1998) indicates that higher-temperature hydrothermal alteration (e.g. at 350 °C, 500 bar) can efficiently leach Li from weathered basalt. This supports the observation of Chan et al. (1996) who reported bulk Li contents as low as 0.6 μ g/g in hydrothermally altered, sheeted dikes at ODP site 504B.

Arc volcanics tend to be enriched in Li relative to MORB (Ryan and Langmuir 1987; Moriguti and Nakamura 1998; Chan et al. 1999). This implies that a certain amount of Li must be retained in the subducted rocks during the initial stages of metamorphism when a series of dehydration reactions are expected to take place, in spite of the apparent mobility of Li in aqueous fluids (Chan et al. 1996; Chan and Kastner 2000).

Whole-rock Li contents of our eclogites can be estimated by multiplying the measured Li concentrations in mineral phases by their respective modal fractions in each sample and summing their contributions (Tables 2, 3, 4). Since Li may be enriched in interstices, along grain boundaries or in retrograde minerals, our approach should result in a minimum value for the whole-rock Li abundances at peak metamorphic conditions. Wholerock Li contents of the metabasaltic eclogites estimated in this way range from about 4 to 31 μ g/g (Tables 3), which is remarkably similar to the range found in fresh and low-T altered MORB described above. This indicates that retention of Li in subducting basalts is significant even to depths in excess of ~40 km (~1.2 GPa) where eclogitic parageneses become stable (e.g. Carswell 1990; Peacock 1996). The implication is that a significant amount of the Li budget of the (altered) oceanic crust is capable of being recycled into the mantle by subduction, rather than being completely removed by fluids generated by dehydration reactions within the slab. Near-surface processes such as low- and high-temperature hydrothermal alteration and submarine weathering appear to be the most important influences on Li addition and removal respectively (e.g. Chan and Kastner 2000; Decitre et al. 2002).

Li in eclogites and garnet clinopyroxenites associated with peridotites

Four samples studied are derived from eclogites or garnet clinopyroxenites associated with orogenic peridotites of mantle origin (Table 1). The garnet clinopyroxenite BB 1 occurs within the Beni Bousera massif and is considered to represent a plagioclase-rich gabbro of (oceanic) crustal origin which was subsequently subducted and recrystallised at high pressures in the upper mantle (Kornprobst et al. 1990). Although the Alpe Arami eclogites are spatially associated with a peridotite body of very deep origin (150–180 km; Brenker and Brey 1997; Paquin and Altherr 2001a, 2001b), they are also interpreted to have had a gabbroic protolith (Gebauer et al. 1992; Gebauer 1996, 1999). Measured Li in clinopy-

Fig. 5a–d. Average Li abundances in clinopyroxenes and ln D_{Li} (grt/cpx) values do not show a systematic variation with major-element composition of clinopyroxene. a Li vs. Na₂O, b Li vs. MgO, c ln D_{Li} (grt/cpx) vs. Na₂O, d ln D_{Li} (grt/cpx) vs. MgO



roxene and estimated whole-rock Li contents for both of these samples fall within the range defined by our high-P metabasalt samples (high-Li group), and are thus consistent with a crustal protolith (Fig. 3, Tables 3, 4).

By contrast, the garnet clinopyroxenite sample PY 36 from Lherz, which has a high-P magmatic origin, falls into the group with low Li concentrations in clinopyroxene (1.5 μ g/g and an estimated whole-rock content of only 0.7 µg/g Li; Table 4). Such low Li contents were also found in the garnet clinopyroxenite xenoliths from Kenya (Table 2). It appears that mafic cumulates formed by crystal fractionation at high pressures tend to have quite low Li contents, except when a significant fraction of trapped melt is present. Consideration of the crystal/melt partitioning behaviour of Li supports this interpretation (Seitz and Woodland 2000). The high-T eclogite sample from Meidling (ME 2) has similarly low Li contents (Fig. 3, Table 4), which suggests that it may have formed in the same fashion. The fact that the Li contents in these high-P metacumulate samples are significantly lower than in any of the high-P metabasalt samples by more than a factor of five suggests a link between Li concentration and the mode of origin. This possibility is further explored below.

The low-Li suite

Estimated whole-rock Li contents of the 13 eclogite xenoliths from kimberlites reveal that all but sample JA 4 contain $\leq 1.3 \ \mu g/g$ Li, with most samples having $< 1 \ \mu g/g$ Li (Table 2). On this basis, it is tempting to suggest that these samples have an origin similar to sample PY 36 and the two garnet clinopyroxenites from Kenya, namely that they are high-P cumulates from a mafic magma. It is noteworthy that essentially identical Li concentrations were measured in clinopyroxenes from a number of mantle-derived garnet lherzolites and garnet websterites, including several peridotite xenoliths from the Eastern Finland Kimberlite Province (Fig. 3; Seitz and Woodland 2000; Olker, unpublished data), further supporting a link with high-P mantle processes.

Developing a viable model for the origin and evolution of the low-Li eclogite samples is not straightforward and a number of alternative models must be considered. However, any plausible model must be consistent with the samples' bimineralic character, the observed majorand minor-element compositions of garnet and clinopyroxene, their high equilibration temperatures and, most importantly, be able to explain the differences in the abundances of Li in clinopyroxene which exist between this suite and the metabasalt samples (Fig. 3). Following from models proposed in the literature, possible modes of origin for these low-Li samples include (1) subducted oceanic gabbros affected by high-T hydrothermal alteration and leaching of Li prior to subduction and recrystallisation at high pressures, (2) remnants of subducted oceanic crust which have undergone partial

melting and melt extraction, (3) recrystallised high-P cumulates from melts derived by partially melting subducted crustal material, and (4) high-P cumulates from migrating mafic melts originating in the mantle.

The possibility that the low-Li samples represent subducted lithospheric gabbros which underwent hightemperature hydrothermal leaching of Li prior to metamorphism is an attractive hypothesis, since deeper portions of the oceanic lithosphere must also be subducted along with the uppermost-lying basalts. Modelling of the high-T hydrothermal alteration of gabbro indicates only minor changes in composition relative to a fresh gabbro, with only a modest increase in Mg content (McCollom and Shock 1998). The implication is that high-temperature alteration of gabbro would have efficiently removed Li but left the major-element compositions of the eclogitic minerals essentially unchanged. However, the compositions of garnet and clinopyroxene from the low-Li suite samples are distinctly different from those in the metabasalt samples (Figs. 1, 2, 3, Tables 2, 3, 4). Except for the samples from the Lester and Bultfontein Mines, the garnets in the low-Li suite are group A in character (Fig. 1). It is also unlikely that the resulting bulk composition from high-temperature alteration could yield essentially bimineralic eclogites upon metamorphism. In addition, it would be expected that samples with varying degrees of hydrothermal alteration and a large spectrum of Li contents would be encountered. This is inconsistent with our observed bimodal distribution of Li. Although high-temperature hydrothermal leaching is a realistic mechanism for Li removal, it does not provide a viable explanation for the origin of our low-Li suite of samples.

A second possibility is that the eclogite xenoliths represent the residuum of subducted oceanic metabasalts which have undergone partial melting at high pressures while residing in the mantle. This hypothesis has been recently elaborated upon by Barth et al. (2001) for a suite of low-MgO eclogites from the Koidu Kimberlite Complex, Sierra Leone (Fung and Haggerty 1995). Minerals in the three samples from the Lester Mine do have broadly similar major-element compositions compared with the low-MgO Koidu eclogites (Table 2), so this hypothesis deserves a more detailed assessment.

During high-pressure partial melting, Li will moderately partition into the melt, thus depleting the residuum (e.g. Hart and Dunn 1993; Blundy et al. 1998; Brenan et al. 1998; Blundy and Dalton 2000). This is the basis for the observed enrichment in Li in MORB relative to the mantle (e.g. Seitz and Woodland 2000). The degree of partial melting necessary to arrive at the Li contents of the low-Li suite can be estimated using the Li contents in our metabasaltic eclogites as a starting point and the mathematical relations given by Shaw (1970). We begin by conservatively assuming that the protolith (already at high pressure) is composed of 50% clinopyroxene and 50% garnet, and that the clinopyroxene contains 10 μ g/g Li. Using a conservative clinopyroxene/melt partition coefficient of D_{Li}=0.1 (Blundy and Wood 1994; Blundy et al. 1998; Brenan et al. 1998; Blundy and Dalton 2000) and assuming that the resulting melt is generated by melting garnet and clinopyroxene in a ratio of 6 to 4, the Li content in the residual clinopyroxene can be computed as a function of melt fraction for the cases of ideal batch and fractional melting. Higher values of D_{Li} would yield lower rates of depletion for a given melt fraction. The relative proportion of clinopyroxene and garnet contributing to the melt is a sensitive function of P, T and initial bulk composition (Rapp and Watson 1995), making it difficult to unambiguously model the melting reaction. As illustrated in Fig. 6, a minimum of 30% batch melting or 10% fractional melting is required before the Li content of the residual clinopyroxene would drop below the threshold of 1.5 μ g/g, representative of the low-Li suite. Our conservative assumptions mean that these values should be viewed as minimum degrees of partial melting. At such high degrees of partial melting, significant changes in the co-existing mineral compositions would be expected, such as a depletion in Na and Al in cpx and an increase in Mg content in both grt and cpx. However, Li contents in cpx are essentially independent of Na and Mg content (Fig. 5a, b), arguing against such a mechanism for producing the low-Li suite of eclogites. Furthermore, an implication from Fig. 6 is that clinopyroxene in eclogites which underwent lesser degrees of partial melting should have Li contents spanning the range from 10 μ g/g down to values similar to those of the low-Li suite. This behaviour is inconsistent with our data (Fig. 3). One way to reconcile the Li data would be to invoke a minimum degree of melting for melt extraction to occur. Below this threshold of at least 10% melting, melt extraction would not take place and the overall Li budget would remain unperturbed. Above this threshold, Li depletion



Fig. 6. Calculated depletion of Li in residual clinopyroxene as a function of melt fraction during ideal batch and fractional partial melting of eclogite. A conservative cpx/melt partition coefficient D_{Li} of 0.1 and a melting reaction of 0.6 grt+0.4 cpx=melt were assumed

would be effective. Such a model seems unlikely based upon the necessarily high degree of partial melting which is required before any melt extraction is permitted, as well as the lack of correlation between Li and Na or Mg contents noted above.

Melts generated by partially melting metabasalt at high pressures have intermediate compositions and are referred to as adakites (e.g. Defant and Drummond 1990; Martin 1999; Defant and Kepezhinskas 2001). Given the fact that garnet and clinopyroxene are residual phases during production of such partial melts (Stern and Wyllie 1978; Rapp and Watson 1995; Rapp et al. 1999), it is conceivable that an eclogitic cumulate assemblage could be generated as these melts traversed the mantle. However, adakite melts are alkali-rich and would produce Na-rich clinopyroxene (Rapp and Watson 1995; Martin 1999; Rapp et al. 1999), whereas the clinopyroxene in most of the low-Li suite of eclogites has much lower Na. The exception is sample BU 98-2 from Bultfontein, which has clinopyroxene with 8.3 wt% Na₂O (Table 2; Fig. 2). This sample also has the highest estimated whole-rock Li content in the low-Li suite (Table 2). However, the major-element composition of the co-existing garnet is significantly richer in Ca and poorer in Fe compared to garnets produced in the experiments of Rapp and Watson (1995) and Rapp et al. (1999). As the number of their experiments in the eclogite field were limited, the difference in garnet composition is attributable to effects of P, T and/or bulk composition. The composition of adakite melt changes significantly upon interaction with surrounding peridotite, driving the melt and co-existing garnet to become more Mg-rich (Rapp et al. 1999). In this situation orthopyroxene becomes a stable liquidus phase along with garnet, so that an eclogitic assemblage can not be produced through adakite melt-peridotite reaction. This implies that, if sample BU 98-2 does indeed represent a high-P cumulate from an adakite melt, the melt could not have interacted very much with adjacent mantle peridotite before crystallising.

The possibility that most of our low-Li suite represents high-P cumulates from migrating mafic melts in the mantle is supported by the generally high values of Mg# of the co-existing garnet and clinopyroxene in these samples (Tables 2 and 4), as well as their high, calculated equilibration temperatures (Table 1). The garnet compositions in this suite of samples are consistent with the ultrabasic trend of Helmstaedt and Schulze (1989), who interpreted such compositions as having originated as veins or dikes in the upper mantle. Except for the three samples from the Lester mine, all of the low-Li suite samples are classified as group A as defined by Coleman et al. (1965). This evidence is, however, not unequivocal. For example, garnet in the aluminous garnet clinopyroxenite from Beni Bousera (BB 1) also plots in the group A field even though this sample has an unusual paragenesis and there is much evidence for its origin as a low-P gabbro. On the other hand, the similarly low Li content of clinopyroxenes in these samples, the garnet clinopyroxenite samples from Kenya as well as the dike sample PY 36 suggests a similar origin for these different samples. This interpretation is reinforced by the observed low Li contents in clinopyroxenes and other minerals in unmetasomatised mantle peridotites and websterites (Fig. 3; Seitz and Woodland 2000; Olker, unpublished data). The similarity in Li content of clinopyroxene in mafic cumulates and peridotite is expected, based upon the low partition coefficient D_{Li} ($0.1 \le D_{Li} \le 0.2$) between clinopyroxene and melt (e.g. Blundy and Wood 1994; Blundy et al. 1998; Brenan et al. 1998; Blundy and Dalton 2000).

One xenolith sample from Jagersfontein, JA 4, contains Mg-rich phases (it is a group A eclogite, Figs. 1 and 2) but has a Li content similar to the metabasalt samples (Tables 2, 3; Fig. 3). The calculated partition coefficient $(\ln D_{Li} (gt/cpx) = -2.65)$ is consistent with the other high-temperature samples, suggesting an equilibrium Li distribution between these two phases (Fig. 4). The question remains as to why this sample contains such high Li when other samples with phases of similar major-element composition belong to the low-Li suite. One possibility is that this is a cumulate sample which contains a certain proportion of trapped melt, leading to elevated Li contents. Such a hypothesis was proposed by Seitz and Woodland (2000) to explain the equilibrated but elevated Li contents in clinopyroxene and orthopyroxene in several pyroxenite samples. A second possibility is that the high Li content reflects a metasomatic overprint which was annealed long enough for an equilibrium distribution of Li to be attained. Although this is certainly feasible, the metasomatism must have been of "cryptic" character, as there is virtually no mineralogical expression of such an event. Further traceelement data are required to help constrain the exact origin of this xenolith.

Concluding remarks

Eclogitic rocks occur in a variety of geologic settings. In some cases their mineralogy and spatial association with other rock types in metamorphosed massifs provide strong evidence for their origin as basaltic oceanic crust which was recrystallised at high pressures. Clinopyroxene in such samples can contain appreciable Li, and whole-rock concentrations can be essentially identical to MORB. Some samples exhibit a notable enrichment of Li in clinopyroxene, suggesting that they represent oceanic crust which underwent low-T alteration and addition of Li prior to subduction. Comparison of estimated bulk Li contents of our metabasaltic eclogites with data for fresh and weathered MORB (e.g. Ryan and Langmuir 1987; Chan et al. 1992, 1993; Niu and Batiza 1997) indicates that a significant amount of the original Li budget was retained during subduction.

The origins of other eclogites which are essentially bimineralic and occur as xenoliths in kimberlite pipes and alkali basaltic vents are less well constrained. Our study indicates that the abundances of Li in minerals as well as in the bulk rock provide further important constraints, in addition to major-element and isotopic criteria, on how a particular eclogite sample may have formed. In this regard, clinopyroxene is the most important carrier of Li in eclogitic assemblages. With the exception of one sample (JA 4), clinopyroxene in our suite of eclogite xenoliths has much lower Li contents than those measured in the metabasaltic eclogites (Fig. 3). The similarity in Li concentration between these samples and magmatic pyroxenites and mantle peridotites suggests a different mode of origin for this low-Li suite, namely that they are high-P cumulates from mafic melts percolating through the mantle.

Although certain eclogite xenoliths have a demonstrated affinity to subducted oceanic crust which subsequently underwent high-pressure recrystallisation (Helmstaedt and Doig 1975; Helmstaedt and Schulze 1979, 1989), this is not to say that all eclogite xenoliths must have formed in the same way. In agreement with the conclusions of Helmstaedt and Schulze (1989) and Snyder et al. (1997), our Li data further emphasise that all eclogites cannot be considered to have originated from a single geologic process. It is likely that some eclogites analysed in the future will have Li contents intermediate to the two groups identified in this pilot study, and that these may have formed by one or other of the processes discussed above. However, it is clear that the behaviour of Li is an important parameter to be considered when assessing the origin and evolution of eclogites.

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ERRATUM

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Li abundances in eclogite minerals: a clue to a crustal or mantle origin?

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In the printed version of the article Table 3 was printed with errors. The correct Table 3 is printed below.

 Table 3. Representative mineral analyses and estimated whole-rock Li contents of metabasaltic eclogites. Major elements [oxide wt%] (sample SY 323) refer to Na-rich and Na-poor domains of omphacites, respectively

Sample		FG 1			FG 3		FG 9	97-1]	FG 139)	I	FG 158	;	F	G 2208		F	G 8591	6	FG 8	85930
Mineral	Grt	Срх	Phe	Grt	Срх	Phe	Grt	Срх	Grt	Срх	Phe	Grt	Срх	Phe	Grt	Срх	Phe	Grt	Срх	Am (s)	Grt	Срх
SiO ₂	38.37	55.49	51.20	39.39	55.37	51.70	38.46	55.61	39.52	55.63	51.23	39.69	55.85	51.40	40.97	56.52	51.53	38.40	56.30	42.82	41.22	55.38
TiO ₂	0.04	0.10	0.58	0.11	0.08	0.44	0.09	0.12	0.04	0.11	0.50	0.03	0.11	0.67	n.d.	0.10	0.52	0.05	0.13	1.21	n.d.	0.09
Al_2O_3	21.55	10.02	27.98	22.16	9.37	28.05	21.38	9.66	22.23	10.71	27.97	21.95	11.15	28.93	22.46	9.10	29.01	21.29	10.05	15.46	22.45	10.25
Cr ₂ O ₃	0.04	0.04	0.01	0.08	0.17	0.05	n.d.	0.03	0.01	0.07	0.05	0.10	0.12	0.01	0.05	0.05	0.04	0.04	n.d.	0.03	0.12	0.29
FeO	24.48	5.18	1.97	16.05	1.35	0.71	25.40	6.17	18.68	2.64	1.06	18.83	2.43	1.08	15.89	1.69	0.48	25.26	5.93	12.12	13.71	1.44
MnO	0.65	0.01	0.03	0.31	0.06	0.03	0.39	0.07	0.33	0.06	n.d.	0.35	0.08	n.d.	0.46	0.02	n.d.	0.59	0.02	0.08	0.23	0.03
MgO	6.84	8.67	3.11	12.80	11.64	4.06	5.68	8.11	9.77	9.75	3.85	10.44	9.48	3.70	13.15	11.63	3.99	5.39	7.97	11.08	16.15	10.78
CaO	8.02	14.03	0.02	8.18	16.98	0.01	8.54	13.14	9.02	15.09	0.02	8.49	14.83	n.d.	7.42	16.93	0.03	9.02	13.09	8.59	5.71	15.84
Na ₂ O	0.43	6.26	0.67	0.05	4.82	0.34	0.02	6.78	0.05	5.73	0.50	n.d.	5.88	0.60	0.02	4.69	0.43	0.03	6.58	4.63	0.01	5.31
K ₂ O	n.d.	n.d.	9.83	n.d.	n.d.	9.93	n.d.	n.d.	n.d.	n.d.	10.16	n.d.	n.d.	9.65	n.d.	n.d.	9.48	n.d.	n.d.	0.40	n.d.	n.d.
Total	99.99	99.80	95.40	99.13	99.84	95.32	99.96	99.69	99.65	99.79	95.34	99.88	99.93	96.04	100.40	100.70	95.50	100.07	100.07	96.42	99.59	99.44
$Mg\#^a$	33.2	74.9	73.8	58.7	93.9	91.1	28.5	70.1	48.2	86.8	86.6	49.7	87.4	85.9	59.6	92.5	93.7	27.6	70.6	62.0	67.7	93.0
Li mean ^b	0.109	11.2	2.75	0.262	28.4	3.60	0.093	8.64	0.160	23.2	6.30	0.134	24.9	5.56	0.165	5 8.84	1.17	0.013	3 14.2	0.450	0.57	56.2
(1 <i>σ</i>)	0.032	1.4	2.97	0.064	2.6	0.26	0.087	1.23	0.053	4.1	1.15	0.042	5.3	3.15	0.025	5 1.02	1.33	0.002	2 1.9	0.311	0.22	17.4
Li min	0.057	7.8	0.47	0.147	24.9	3.36	0.013	6.83	0.098	13.8	5.35	0.079	15.2	3.18	0.132	2 7.63	0.40	0.009) 12.0	0.104	0.32	10.7
Li max	0.170	12.5	8.52	0.366	33.1	3.88	0.290	11.77	0.250	29.0	8.14	0.201	31.1	12.79	0.195	5 9.88	3.86	0.015	5 17.0	0.840	1.09	89.8
WR Li ^c		5.3			13.0		3	.9		13.0			16.2			5.5			5.6		30).9

^a Mg#=100*Mg/(Mg+Fe_{tot})

^b Li mean (1σ) is arithmetic mean with standard deviation of all values measured; Li min and Li max refer to the lowest and highest ^cWR Li is estimated whole-rock Li content

^dCpx 1 and cpx 2 (sample SY 323) refer to Na-rich and Na-poor domains of omphacites respectively

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were analysed by electron microprobe, Li [µg/g] by SIMS. n.d. not detected, n.a. not analyzed, c core, r rim, (s) secondary. Cpx 1 and cpx 2

SM	1 43		TC 1		PM	95-9	PM 9	5-19				SY 109					SY	323	
Grt	Срх	Grt	Срх	Am (s)	Grt	Срх	Grt	Срх	Grt c	Grt r	Cpx c	Cpx r	Gln	Phe	Pg	Grt c	Grt r	Cpx 1 ^d	Cpx 2
38.89	54.81	39.21	54.82	53.16	40.14	54.86	38.66	54.90	37.17	37.31	57.19	55.68	55.86	50.40	48.55	36.45	36.89	55.57	54.88
0.04	0.09	0.07	0.11	0.10	0.07	0.14	0.07	0.12	0.18	0.08	0.00	0.11	0.00	0.14	0.11	0.16	0.10	0.04	0.05
21.43	7.61	22.00	9.32	7.17	22.28	9.66	21.69	9.52	20.19	19.98	17.22	11.41	9.46	26.67	38.44	20.06	20.46	9.85	5.60
0.08	0.07	0.08	0.18	0.16	0.05	0.05	0.02	0.08	0.01	0.00	0.01	0.00	0.00	0.00	0.03	0.03	0.00	0.00	0.04
21.46	4.23	20.26	3.78	4.56	17.40	2.65	22.77	5.02	29.33	33.40	7.81	11.01	18.35	4.68	0.93	24.89	29.72	7.40	8.10
0.42	0.01	0.39	0.03	n.d.	0.47	n.d.	0.49	0.05	1.69	0.26	0.13	0.11	0.06	0.00	0.00	10.26	1.34	0.25	0.26
7.60	10.69	9.63	10.44	19.33	11.06	10.77	7.59	9.20	0.74	1.77	1.41	3.55	5.99	2.35	0.26	0.87	2.30	7.00	9.27
9.63	16.76	7.77	15.91	9.81	8.33	16.53	8.88	14.94	10.29	7.03	3.17	8.02	0.16	0.01	0.12	6.99	8.27	11.80	15.87
0.05	4.69	0.04	4.98	2.56	n.d.	4.81	0.05	5.44	0.06	0.02	12.69	9.83	7.36	0.43	6.51	0.00	0.03	7.81	5.38
n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.01	0.00	0.01	0.02	10.21	1.44	0.01	0.00	0.01	0.01
99.60	98.96	99.45	99.57	96.85	99.80	99.47	100.22	99.27	99.66	99.86	99.63	99.73	97.28	94.89	96.40	99.72	99.11	99.73	99.45
38.7	81.8	45.9	83.1	88.3	53.1	87.9	37.3	76.6	4.3	8.6	24.3	59.3	36.7	47.2	32.8	5.8	12.1	62.8	67.1
0.127	28.6	0.124	17.1	0.500	0.042	31.6	0.080	21.8	0.34	0.28	8.	.10	7.21	2.57	4.91	3.81	3.88	83	.3
0.040	9.4	0.077	6.1	0.067	0.015	14.3	0.033	10.2	0.06	0.06	0.	.37	0.27	0.34	1.51	0.71	0.55	18	.5
0.070	20.7	0.040	7.4	0.397	0.025	14.2	0.039	8.7	0.24	0.18	7.	.53	6.79	2.14	3.19	2.64	3.08	46	5.7
0.183	41.7	0.292	25.8	0.518	0.067	51.9	0.135	37.8	0.44	0.37	8.	.73	7.64	3.60	8.70	5.12	4.71	114	1.0
	8.6		12.1		2	20.9	1	0.2				5.0					4	3.7	

measured values respectively