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Li abundances in inclusions in diamonds from the upper and lower mantle

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Abstract

Lithium abundances in inclusions in diamonds of peridotitic, websteritic, eclogitic (including garnets with majoritic component) and lower mantle paragenesis were determined with the ion microprobe. The partitioning of Li both between olivine and clinopyroxene and clinopyroxene and garnet appears to be pressure-dependent in peridotites. More importantly, garnets containing a majorite component show a dramatic increase in Li solubility so that even for mildly majoritic garnets $D^{\mathrm{cpx/majorite}}$ is smaller than one. Lower mantle ferropericlase is a sink for lithium, containing several hundred times more Li than coexisting Mg-perovskite. Lithium decreases in olivine inclusions with increasing forsterite content, which we interpret as reflecting a depletion event in the protoliths of the inclusions. We also infer that lithium was not re-enriched in the silicate phases by a metasomatic agent during diamond formation unlike other trace elements like REE and HFSE. Depletion on partial melting and no re-enrichment also seems to hold for the eclogitic suite of inclusions where cpx's (and deduced bulk composition) have similar Li abundances as in the peridotitic suite and are significantly lower than in crustal eclogites. For the lower mantle bulk, lithium estimates give values four to five times higher than primitive mantle. This may relate either to local enrichment through fluid/melt metasomatism similarly as for spinel lherzolites or high Li abundances in lower mantle diamonds sources are inherited from crustal protoliths.

Keywords: Lithium; Inclusions in diamond; Eclogites; Peridotites; Websterites; Majorite

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1. Introduction

Mineral inclusions in diamonds are well kept samples of the Earth's interior. They were incorporated at the time and place of diamond formation and carry information on the chemistry, stratigraphy, age and evolution of the lithosphere and asthenosphere, the transition zone and the upper parts of the lower mantle (e.g., Stachel et al., 2000a,b). Upper mantle inclusions are divided into a peridotitic, an eclogitic and a less common websteritic paragenesis. Garnets with a majorite component may come from as deep as the transition zone (Moore and Gurney, 1985; Sautter

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et al., 1991) and those diamonds which contain ferropericlase, Mg-perovskite and Ca-perovskite come from the lower mantle. Such super deep inclusion parageneses were recovered in diamonds from Brazil (Soa Luiz or Juina area: Wilding, 1990; Harte and Harris, 1994; Harris et al., 1997; Hutchinson, 1997; Harte et al., 1999; Kaminsky et al., 2001), West Africa (Kankan: Stachel et al., 2000a,b) and Canada (Lac de Gras: Davies et al., 1999). A number of studies of major and trace elements and isotopic signatures of diamonds and their inclusions unravelled diamond formation processes, the magmatic, metamorphic and metasomatic evolution of the precursor rocks and possible crust-mantle interaction (e.g., Stachel and Harris, 1997a,b; Jacob and Foley, 1999). Peridotitic inclusions carry in their compatible elements a signature of partial melting at shallow depth but also show re-enrichment of (highly) incompatible elements presumably at the time of diamond formation (e.g., Stachel et al., 2000a,b and references therein).

The history of eclogites and eclogitic inclusions from the cratonic lithosphere has been more complex. Genetic models consider eclogites as either former basalts, gabbros or feldspar-rich cumulates, as high pressure cumulates of mantle melts, or as residues of high pressure melting (e.g., McCulloch, 1989; Jacob and Foley, 1999; Barth et al., 2001 and references therein). Clearly, they are modified rocks that lost part of their inventory of incompatible elements by volatile loss and/or partial melting. Similar to peridotitic inclusions, re-enrichment during diamond formation is documented (Taylor et al., 1996, 1998; Sobolev et al., 1998; Stachel et al., 2000a).

Websterites and websteritic inclusions have recently been interpreted as hybrid products of partial melts from eclogites reacting with peridotite (Aulbach et al., 2002). Lower mantle inclusions (ferropericlase, Mg- and Ca-silicate-perovskites) also do not reflect primitive mantle and show REE enrichment features specifically in Ca-perovskite. Furthermore, positive and negative Eu anomalies in some CaSi-perovskites indicate accumulation and fractionation of plagioclase in a low pressure precursor rock.

There is growing interest in lithium and its isotopes as useful tracers of mantle processes as well as subduction related and alteration processes (e.g., Sywall, 1996; Hoefs and Sywall, 1997; Seitz and Woodland, 2000; Woodland et al., 2002; Tomascak et al., 2002; Chan et al., 2002; Zack et al., 2003). In this work, we extend our previous studies on Li concentrations in mantle samples to inclusions in diamonds from the upper and lower mantle. We used samples which were well characterised having been analysed previously for major and trace elements (Stachel and Harris, 1997a,b; Stachel et al., 1998, 1999, 2000a,b; Viljoen et al., 1999; Aulbach et al.,

Table 1
Li contents in peridotitic and websteric inclusions (wt. ppm)

Diamond no.	ol	opx	cpx	grt	Est. bulk
Peridotitic					
G 50	0.970 ± 15		0.187 ± 21	0.048 ± 18	0.7
G 126	0.915 ± 58			0.014 ± 5	0.6
G 113	0.718 ± 10				not calc.
G 103	0.185 ± 17				not calc.
G127	0.685 ± 51				not calc.
G 201	2.175 ± 70		0.365 ± 7		1.4
G 23	0.886 ± 56		0.309 ± 133		0.7
MW 14–25/26	0.988 ± 76		0.327 ± 62		0.8
MW 14–28/27	1.016 ± 57		0.286 ± 49		0.8
KK 28	1.110 ± 180		0.210 ± 37	0.068 ± 19	0.8
Websteritic					
VE 54		5.733 ± 182	5.687 ± 91	0.888 ± 7	5.7
VE 163	0.539 ± 11		3.245 ± 38	0.454 ± 12	3.1
VE 166			5.870 ± 52	0.472 ± 5	5.8

2002) and compared them with upper mantle xenoliths world wide and with lower mantle inclusions from Brazil. The samples were selected to cover the range of re-enrichment processes as seen in the complex and highly variable REE patterns in garnets and clinopyroxenes and also to cover the depth range down to the lower mantle. The aim of the study is to obtain a first understanding of the partitioning behaviour of Li between mineral phases from the upper to lower mantle pressure regimes and, for the first time, obtain information about bulk Li contents in major mantle reservoirs.

2. Analytical techniques

Major elements were analysed with a JEOL JXA-8900 RL electron microprobe in Frankfurt and trace elements by SIMS (ion microprobe) in Edinburgh; operating conditions and further details were previously given in Stachel et al. (2000a,b). Analyses of Li were carried out using a modified CAMECA 3f-IMS ion microprobe at the Mineralogisches Institut, Universität Heidelberg. Analyses were made using a $^{16}O^-$ primary beam at an acceleration voltage of 12.5 kV. A focused beam with an intensity of 1 nA gives a beam diameter of ~ 10 μm. Samples were coated with a layer of gold ca. 50 nm thick. 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 ~ 1000 to suppress interfering molecules and to minimise matrix effects (Ottolini et al., 1993; their estimated precision and accuracy is better than ± 20% at the ppm level). We normalised ^{7}Li ion yields to ^{30}Si for silicates, to ^{26}Mg for ferropericlase and to ^{27}Al for corundum. ^{30}Si, ^{26}Mg and ^{27}Al were measured for 2 s and ^{7}Li for 8 s. The external precision (over several months) for the SRM-610 standard is about 10%, the daily internal precision is typically 1–2% (1σ). The latter are given in Tables 1–3. Because of the small size of the inclusions only one to three spots could be analysed per grain and the 1σ deviations relate to the counting statistics of a single spot measurement or to the average from up to three spots.

Table 3
Li contents in lower mantle inclusions (wt. ppm)

Diamond no.	Ferropericlase	Mg-perovskite	Est. bulk
KK 16	49.5 ± 1.08	0.068 ± 0.015	6.3–8 see text for details
KK 44	38.7 ± 0.9	0.095 ± 0.02	

3. Samples and their lithium contents

Altogether 44 mineral grains from 20 diamonds (10 with peridotitic, 5 with eclogitic, 3 with websteritic and 2 with lower mantle inclusions) were analysed for their lithium contents. With three exceptions, only diamonds with more than one inclusion species were selected in order to obtain further information on the partitioning behaviour of Li. For this purpose, they were also selected on the basis that mineral compositions indicate equilibrium between the phases found within single diamonds. Analyses in Tables 1–3 are labelled according to locality as in the previous studies (Stachel and Harris, 1997a,b; Stachel et al., 1998, 1999, 2000a,b; Viljoen et al., 1999; Aulbach et al., 2002): KK denotes the Kankan

Table 2
Li contents in eclogitic inclusions (wt. ppm)

Diamond no.	cpx	grt	Majoritic grt	Corundum	Est. bulk
KK 1	2.262 ± 199		2.674 ± 260		2.5
KK 81	3.357 ± 134		3.790 ± 117		3.6
KK 96	10.168 ± 659	1.361 ± 133			5.8
VE 160	15.398 ± 109	2.545 ± 63			9.0
VE 176	2.334 ± 61	0.079 ± 13, 0.078 ± 5, 0.111 ± 12		0.985 ± 125	2.5

district in Guinea, G the Akwatia mine in Ghana, VE the Venetia mine in South Africa and MW the Mwadui mine in Tanzania.

An overview of the present knowledge about Li in mantle lithologies is shown in Fig. 1 taking data from Seitz and Woodland (2000) and Woodland et al. (2002). The most primitive spinel lherzolite SC-1 from San Carlos (Arizona; Jagoutz et al., 1979) contains 1.6 ppm Li in olivine, 1.1 ppm in orthopyroxene and 1 ppm in clinopyroxene, and a calculated bulk composition from modal abundances gives 1.31 ppm. Li-contents in minerals from a garnet peridotite from a rift setting (Vi 313-10; Vitim, Lake Baikal) are 1.28 ppm in olivine, 0.65 ppm in orthopyroxene, 0.75 ppm in clinopyroxene and 0.046 ppm in garnet with a calculated bulk rock composition of 1 ppm. Garnet peridotites from Pali Aiki (Chile) and the Kenya Rift are similar (see Fig. 1 and Seitz and Woodland, 2000). Eclogites from orogenic settings considered to represent metamorphic equivalents of basalts have much higher lithium contents in their clinopyroxenes ranging from 8 to 80 ppm and on average also higher contents of around 0.1 ppm in their garnets. This gives bulk compositions in the range of 4–44 ppm similar to fresh and altered MORB (Woodland et al., 2002; Chan et al., 2002). Lithium contents in eclogitic xenoliths are in general much lower with < 1.31 ppm Li in the bulk.

3.1. Peridotitic paragenesis inclusions

The Li content of one olivine inclusion from Guinea (G 201) exceeds the value for the SC-1 olivine by more than one third (2.2 versus 1.6 ppm). All other olivine inclusions have lower values ranging from 1.1 down to 0.685 ppm and one extremely low value at 0.185 ppm Li. Fig. 2 shows that clinopyroxene inclusions are significantly lower in Li (365–187 ppb) compared to those from primitive xenoliths (e.g., SC-1 with 1 ppm). The two garnet inclusions are in the same range as garnet from the xenolith Vi 313-10 (18 and 48 ppb vs. 46). Bulk compositions estimated by assuming modal amounts of phases appropriate for primitive mantle always give depleted values compared to undepleted mantle xenoliths. The one exception is sample (G 201) with its high Li-olivine that gives a value similar to SC-1.

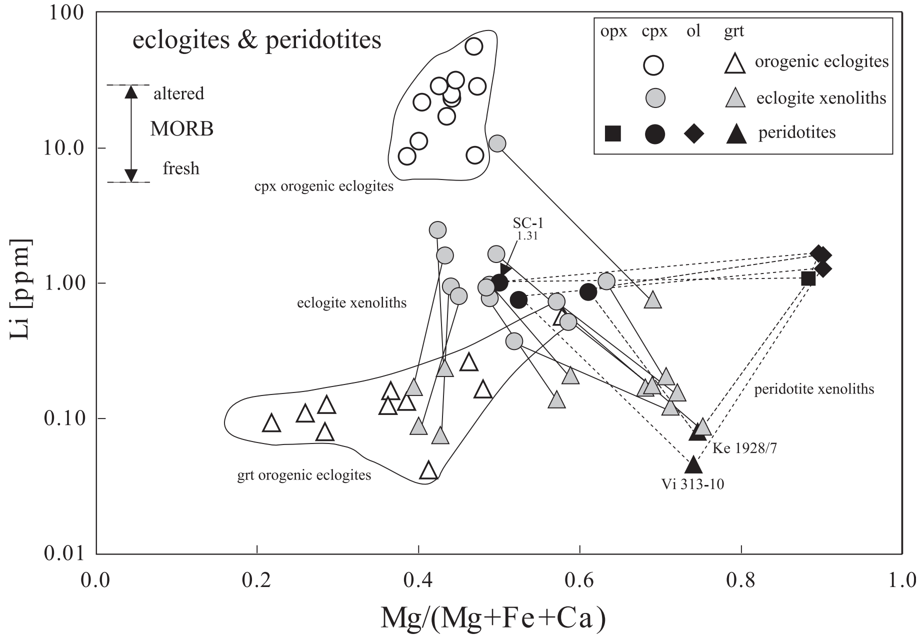

Fig. 1. Li versus Mg/(Mg + Fe + Ca), summarising the data from Seitz and Woodland (2000) and Woodland et al. (2002). Coexisting phases are linked by lines. Estimated bulk lithium abundances for a spinel lherzolite SC-1 from San Carlos, Arizona (Jagoutz et al., 1979) are given in the diagram.

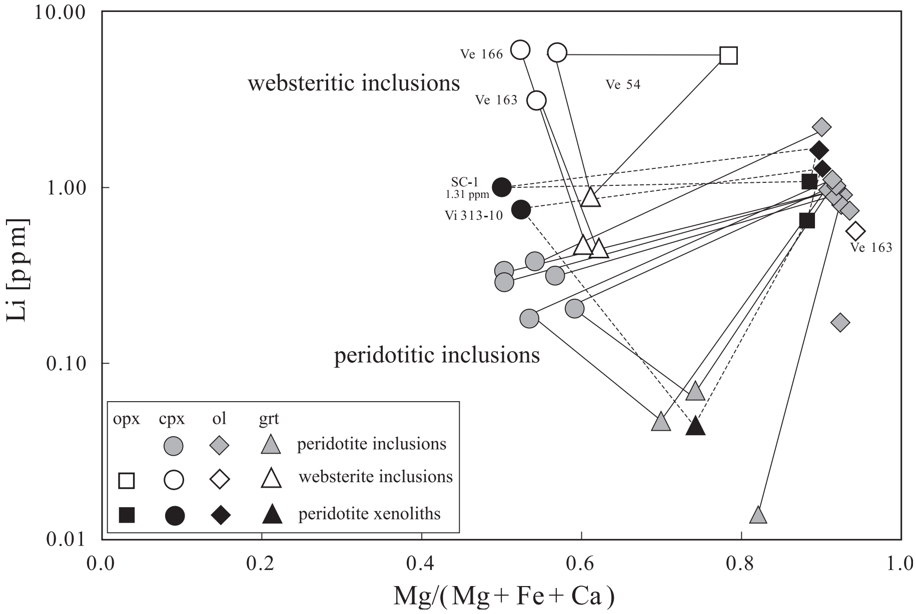

Fig. 2. Li versus Mg/(Mg + Fe + Ca) for peridotitic and websteritic diamond inclusions. Coexisting phases are linked by lines. Abundances in minerals from spinel lherzolite SC-1 and in a fairly primitive garnet peridotite from a rift setting (Vi 313-10; Vitim, Lake Baikal; Ionov et al., 1993) are plotted for comparison.

3.2. Websteritic paragenesis inclusions

Websteritic inclusions in three diamonds from Venetia were analysed. VE 163 contained a forsterite-rich olivine (Fo_{94}) with 0.54 ppm Li typical of highly depleted mantle. Clinopyroxene and garnet also occurring in this diamond have high values of 3.2 and 0.45 ppm, respectively. These two minerals appear to be in equilibrium, but both are not in equilibrium with the olivine. Diamond VE 54 contains opx with very high (within the peridotitic paragenesis) lithium contents. The value is similar to both a coexisting cpx and also similar to a cpx from diamond VE 166. The corresponding garnets, however, are quite different with 0.89 and 0.47 ppm Li, respectively. Clinopyroxene and garnet values lie within the range of both the eclogitic inclusions and estimated bulk compositions (see below) (Fig. 2).

3.3. Eclogitic paragenesis and majorite inclusions

Eclogitic inclusions were analysed from Kankan (3) and from Venetia (2). Two of the Kankan diamonds contain majoritic garnets and thus are distinct in origin from ‘normal’ lithospheric eclogites. It is most remarkable that Li contents of the majoritic garnet inclusions (KK1b and KK81) are very similar to those of the coexisting clinopyroxenes while lithium in “normal” peridotitic and eclogitic garnets is 20–40 times lower. Calculated bulk composition for one normal inclusion set (VE 176) is 1.2 ppm (assuming grt/cpx = 50:50), but for the diamonds containing majoritic garnet it is 2.5 and 3.6 ppm, respectively. The values for both the lithospheric and sublithospheric eclogitic diamond sources are lower than the estimated bulk composition for orogenic eclogites but higher than the more common cratonic eclogite xenoliths. One other cpx-grt pair (VE 160) gives a higher bulk composition of 9.0 ppm similar to eclogite xenolith Ja 4 (Woodland et al., 2002) from the Jagersfontein kimberlite in South Africa (Fig. 3).

3.4. Lower mantle inclusions

Coexisting ferropericlase and MgSi-perovskite inclusions from two diamonds from Guinea show that the ferropericlases are very high in lithium with 39

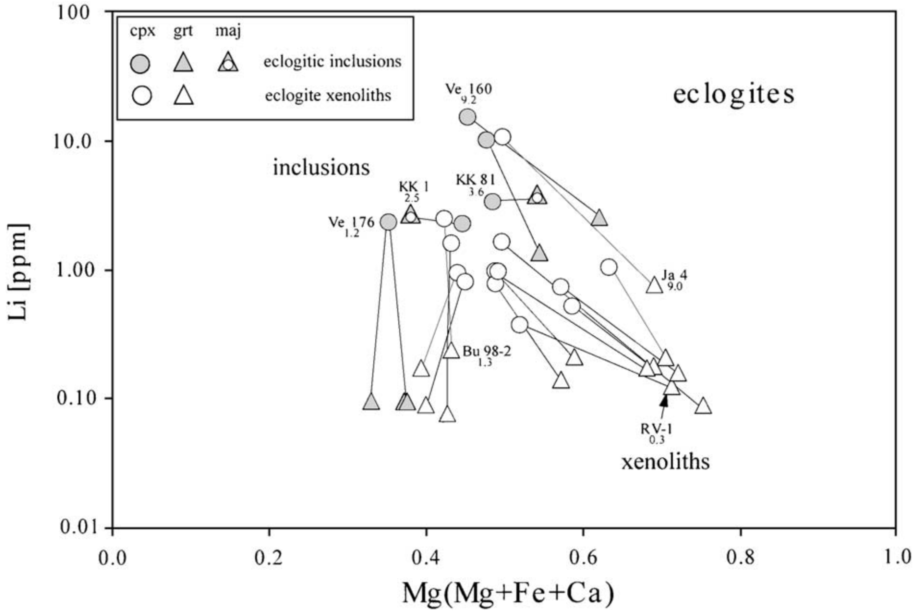

Fig. 3. Li versus Mg/(Mg + Fe + Ca) for eclogitic diamond inclusions. Eclogite xenoliths data from Woodland et al. (2002) are plotted for comparison. Estimated bulk Li abundances of the bulk rock are shown underneath the sample numbers.

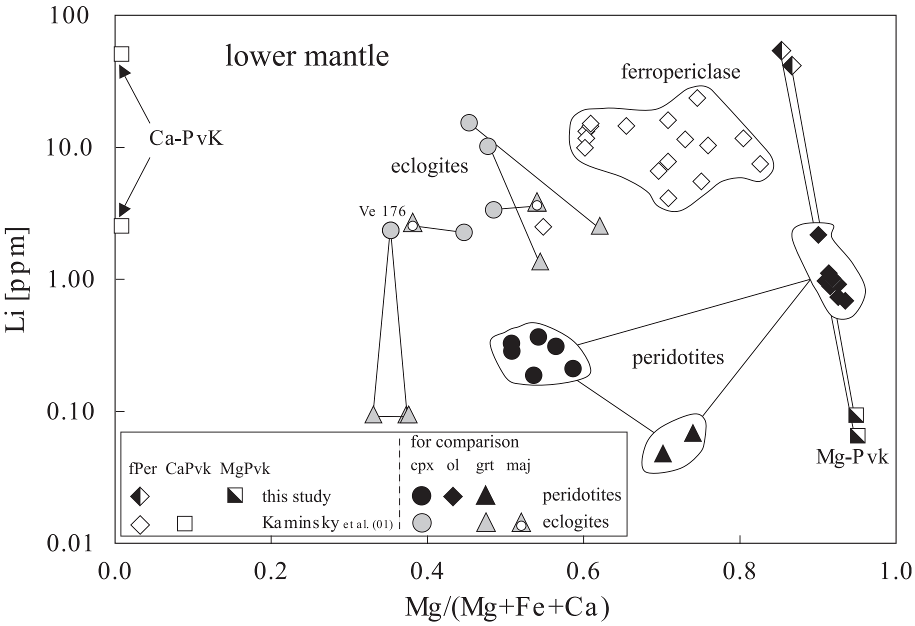

Fig. 4. Li versus Mg/(Mg + Fe + Ca) diagram for lower mantle diamond inclusions. Inclusions from the Juina area Brazil (Kaminsky et al., 2001) as well as eclogite and peridotite inclusions from this study are shown for comparison.

and 50 ppm, while coexisting Mg-perovskites have extremely low values (0.07 and 0.1 ppm) (Fig.4). The ferropericlase values are even higher than those reported by Kaminsky et al. (2001) for similar inclusions. These authors also give values of 2.5 and 50.5 ppm for two Ca-perovskites. For estimations of the lithium content in the bulk composition of the lower mantle, the following assumptions were made:

(a) the lower mantle at Kankan is depleted and consists of only ferropericlase (40 ppm) and Mg-perovskite (0.08 ppm) in proportions of 30:70. This combination gives a lithium value of about 12 ppm.
(b) the lower mantle consists of 15% ferropericlase, 75% Mg-perovskite, 5% Ca-perovskite (with 2.5 ppm Li) and 5% of an aluminous phase with assumed 2.5 ppm Li. This results in a bulk composition of about 6.3 ppm Li.

4. Discussion

The following discussion is based on the assumption that multiple inclusions in diamonds are in chemical equilibrium. This has been shown to be the case for the present set of inclusions (e.g., Stachel et al., 2000a,b) except for the one websteritic diamond (Aulbach et al., 2002). This means that the inclusions were formed in mutual chemical equilibrium and that their composition has not been changed since their incorporation into the diamond, e.g., by diffusional processes. Lithium could be a candidate for high mobility (diffusivity) in diamond yet its correlation with Mg-value in olivine argues against any compositional change subsequent to the incorporation in diamond (see below). Also Bibby (1982) could not detect any lithium in diamond, at least at the detection limit of neutron activation analysis.

4.1. Peridotitic inclusions

Olivine inclusions from all samples except G 201 have lower or similar Li abundances to olivine from undepleted or moderately (melt)-depleted mantle (Fig. 2). Also, except for G 201 and G 103, lithium correlates negatively with the forsterite content in olivine. The latter is an indication of the degree of previous melt depletion experienced by the peridotite host (Fig. 5). Such a correlation was noticed before by Seitz and Woodland (2000) for lherzolites, and inclusions in diamonds now continue this trend to highly depleted harzburgitic compositions. Thus, it appears that Li in olivine inclusions simply reflects earlier melt depletion event(s) in the peridotitic protolith. This may be tested by using the experimentally determined Li partitioning data of Brenan et al. (1998) who derived values of $D^{\mathrm{ol/l}} = 0.2-0.43$ and $D^{\mathrm{cpx/l}} = 0.11-0.18$. Assuming of $D^{\mathrm{opx/l}} = D^{\mathrm{cpx/l}}$ and modal batch melting, lithium depletion can be described as a function of the degree of partial melting (see trend in Fig. 5). The relationship between forsterite in olivine and the percentage of melt extraction is approximately linear and is taken from the experimental work of Hirose and Kushiro (1993). Even this crude estimate clearly shows that lithium abundances in peridotitic parageneses may be explained simply by depletion via melt removal.

Accordingly, lithium is also depleted in clinopyroxene inclusions. In fact, it is even lower than that predicted from $D^{\mathrm{ol/cpx}}$ of 1.6–2 as given by Seitz and Woodland (2000). These authors suggested that the partitioning of lithium between olivine and clinopyroxene is independent of pressure and temperature and therefore concluded that any deviation reflects disequilibrium and different kinds of mantle metasomatism. However, although metasomatic overprint of diamond source regions is well documented in the REE patterns of clinopyroxenes and garnets (e.g., Stachel et al., 2000a), lithium is low and equilibrium between the inclusion phases in individual diamonds is well documented. The $\mathrm{REE_N}$-patterns for the clinopyroxenes and garnets of this study are shown as inserts in Fig. 5, a diagram of Li in olivine versus forsterite content. While Li steadily decreases with increasing Mg-value, the REE patterns of related clinopyroxenes and garnets become more variable and complex. This is clear indication that Li is not transported by the metasomatic agent accompanying or causing diamond growth and also suggests equilibrium partitioning between olivine and clinopyroxene. The high partition coefficients $D^{\mathrm{ol/cpx}}$ observed for the inclusions must then be due to a so far unexpected P,T-dependence of $D^{\mathrm{ol/cpx}}$. We argue that Seitz and Woodland (2000) came to their conclusion of $D^{\mathrm{ol/cpx}}$ being constant and independent of pressure and temperature because of their particular choice of

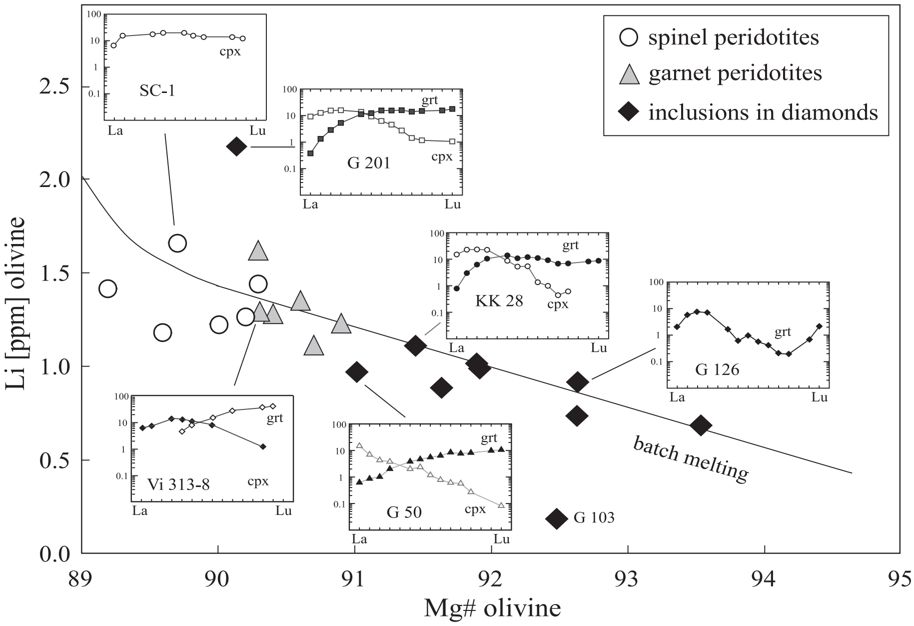

Fig. 5. Li in olivine versus Mg# in olivine for diamond inclusions from this study and from spinel and garnet peridotites from Seitz and Woodland (2000). Lithium decreases with increasing Mg#, suggesting that lithium reflects simple partial melting, similar to Mg#. In contrast, REE patterns for coexisting garnets and clinopyroxenes indicate metasomatic overprint (shown as inlays). As there are no REE data for sample Vi 313-10 we have used REE data from a similar sample (Vi 313-8, Vitim, Lake Baikal; Ionov et al., 1993).

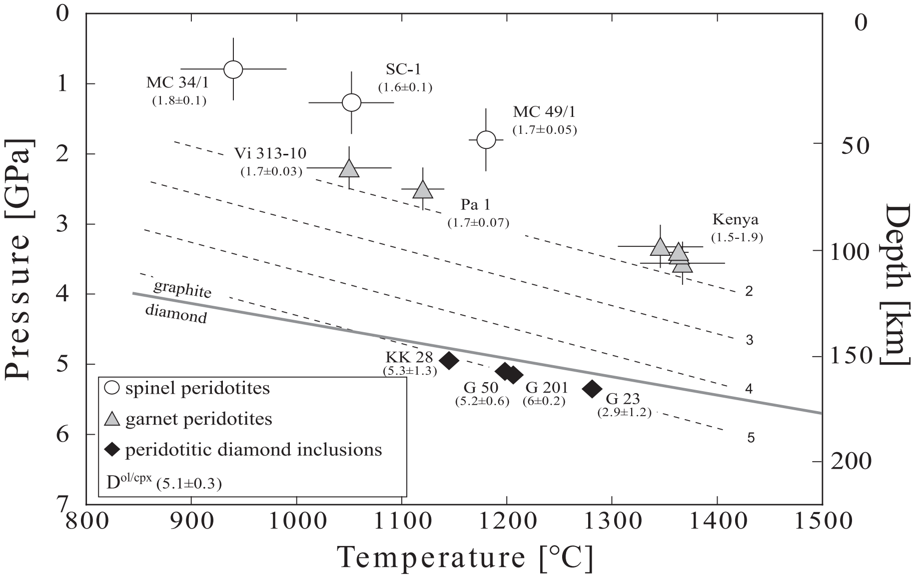

Fig. 6. Pressure and temperature estimates for equilibrated spinel and garnet peridotites are taken from Seitz and Woodland (2000) and for diamond inclusions from Stachel et al. (2000a) and Stachel and Harris (1997a). Hatched lines are tentative lines of constant partition coefficients ($D^{ol/cpx}$). Calculated $D^{ol/cpx}$ are given in parentheses underneath the sample numbers. Also shown is the graphite diamond phase boundary (Kennedy and Kennedy, 1976).

mantle samples. This is demonstrated in Fig. 6, a pressure–temperature diagram in which crystallisation conditions of the equilibrated garnet and spinel peridotites used by Seitz and Woodland (2000) are plotted and the corresponding $D^{\mathrm{ol/cpx}}$ are given in numbers. Also shown are the conditions for coexisting cpx–grt inclusion pairs (pressure cannot be calculated from these pairs and was thus assumed to be close to the graphite–diamond boundary). Their $D^{\mathrm{ol/cpx}}$-values are also given in numbers. It appears that pressure–temperature conditions for the sample set used by Seitz and Woodland (2000) are such that they cancel out each other. This makes $D^{\mathrm{ol/cpx}}$ constant and apparently independent of P and T. Inclusions in diamonds with higher $D^{\mathrm{ol/cpx}}$-values come from significantly higher pressures but similar temperatures. The values imply that partitioning of lithium between olivine and clinopyroxene is dependent on both pressure and temperature with the influence of pressure being dominant. This is shown tentatively in Fig. 6 as lines of constant partition coefficients. They imply that Li may be a useful barometer.

Consequently and because of similar abundance levels of lithium in the two garnets from inclusions and those from Kenya and Vitim (Fig. 2) partition coefficients $D^{\mathrm{cpx/grt}}$ are also lower for the inclusions at around 3 compared to about 11–16 for the samples from Vitim, Pali Aiki and Kenya (Table 4). $D^{\mathrm{ol/grt}}$ remains the same and high at around 20.

4.2. Eclogitic inclusions

One set of clinopyroxene–garnet inclusions (VE 176) has low and very similar Li-abundances and $D^{\mathrm{cpx/grt}}$ in the range of most eclogite xenoliths analysed by Woodland et al. (2002). In their summary and evaluation models for the origin of eclogite xenoliths, Woodland et al. (2002) inclined to the view that they were high pressure cumulates of mafic mantle melts but left the possibility open that they may be residues of partial melting of former subducted oceanic crust. Two other cpx–grt pairs (VE 160 and KK 96) have lithium contents much higher than most eclogite xenoliths and also the websteritic inclusions. Their Li and also $D^{\mathrm{cpx/grt}}$ values are, however, similar to a xenolith from Jagersfontein (Ja 4), which approaches orogenic eclogites in composition (Fig. 1).

Most significant and dramatic is the change in the behaviour of lithium in garnet with a majorite component compared to one with only pure garnet. This is expressed most clearly in the difference between partition coefficients $D^{\mathrm{cpx/grt}}$ (3–8) and $D^{\mathrm{cpx/maj}}$ (around 0.9), see Table 4. The analysis of a single majoritic inclusion by Kaminsky et al. (2001) with about 8 ppm Li (Fig. 4) also indicates that there is a significant change in the partitioning behaviour of Li.

Crystal chemistry may be the reason for this very different behaviour of Li in garnet with and without a majorite component, because lithium will tend to substitute for magnesium in six-fold coordination and mimic its geochemical behaviour. Hence the low lithium contents in garnet compared to pyroxenes and olivine. With a majorite, uptake of lithium takes place via the exchange $(\mathrm{AlAl})^{\mathrm{VI}}$–$(\mathrm{MgSi})^{\mathrm{VI}}$ so that six-fold coordinated Mg is present. Lithium may then be incorporated via a further reaction $\mathrm{Mg}^{\mathrm{VI}}\mathrm{Si}^{\mathrm{IV}}$–$\mathrm{Li}^{\mathrm{VI}}\mathrm{P}^{\mathrm{IV}}$. Since the majoritic component in garnet is strongly pressure dependent, any lithium present would be similarly constrained. This in turn implies that the

Table 4
Partition coefficients

Peridotitic	ol/cpx	cpx/grt	Websteritic	cpx/grt	cpx/majorite	Lower mantle	Fper/Mg-Per
G 50	5.2 ± 0.6	3.9 ± 1.5	VE 54	6.4 ± 0.1		KK 16	728 ± 161
G 201	6.0 ± 0.2		VE 163	7.2 ± 0.2		KK 44	407 ± 87
G 23	2.9 ± 1.2		VE 166	12.4 ± 1.3			
MW 14–25	3.0 ± 0.6		eclogitic				
MW 14–28	3.6 ± 0.6		KK 1b		0.85 ± 0.1		
KK 28	5.3 ± 1.3	3.1 ± 1.0	KK81		0.89 ± 0.05		
			KK 96	7.5 ± 0.9			
			VE 160	6.0 ± 0.2			
			VE 176	26.1 ± 3.0			

partitioning of Li between cpx and grt is a strong function of pressure beginning at a depth where the first molecules of majorite are incorporated into garnet. The change from $D^{\mathrm{cpx/grt}}$ to $D^{\mathrm{cpx/maj}}$ may reflect the change of pressure much better than a majorite component calculated from a microprobe analysis.

4.3. Lower mantle inclusions

The analyses of two inclusion sets of ferropericlase and Mg-perovskite are shown in Fig. 4 together with the data for the eclogitic and peridotitic inclusions and with literature data for ferropericlases and CaSi-perovskites from Brazil. $D^{\mathrm{Fper/MgSi\text{-}Per}}$ is extremely high with values of around 400 and 700 (Table 4). The very different behaviour of Li in ferropericlase and in Mg-perovskite may be explained in a similar way to that in olivine compared to garnet. Magnesium in ferropericlase is in octahedral sites and lithium can substitute for Mg with Al replacing a second Mg for charge balance (analogous to Na). With perovskite, Mg is eight-fold coordinated and Li does not enter this site. Whilst such a mechanism satisfactorily explains low Li in MgSi-perovskites, it fails to explain the high concentrations of Li in CaSi-perovskites (Fig. 4). Clearly, a quite different mechanism operates here. Stachel et al. (2000b) reported the solubility of a small KPO_3-component in Ca-silicate-perovskite inclusions but not in Mg-silicate-perovskites. The lithium, therefore, may be dissolved in $CaSiO_3$ as $LiPO_3$.

4.4. Lithium abundances in the upper and lower mantle

Considerable variations can be observed in the abundances within and between the peridotitic, websteritic and eclogitic groups. Olivine is the major carrier of Li in peridotites and the observed correlation between Fo- and Li-contents establishes Li as a proxy for the degree of previous melt depletion. We have calculated possible bulk rock compositions of the peridotite diamond sources based on ol:opx:cpx:grt abundances of 60:25:10:5 and assuming that the Li-content of un-observed opx is the same as that of cpx. The results of these estimates are given in Table 1 and range from 1.4 to 0.6 ppm. G 201 with 1.4 ppm lithium, therefore, lies close to the abundance of a primitive mantle peridotite (e.g., Jagoutz et al., 1979; McDonough and Sun, 1995; Eggins et al., 1998; Seitz and Woodland, 2000).

Bulk estimates for websterites are based on a rock that contains ortho- and clinopyroxenes in equal amounts and 2% garnet. The estimated lithium abundances are higher than for peridotites with 3.1–5.8 ppm and lie between bulk estimates for orogenic eclogites and estimates for most eclogite xenoliths. These relative amounts are consistent with an origin of the websterites as products of hybridisation of peridotite through a melt from eclogite pods as suggested, for example, by Aulbach et al. (2002).

Bulk estimates for eclogites were made by assuming grt:cpx = 50:50, even if a majoritic garnet was present. The latter show a grt/cpx partition coefficient for Li close to one so that the chosen ratio is not critical. Interestingly, the two inclusion pairs with majoritic garnet from a depth as deep as the transition zone have similarly low bulk lithium to the more common group of eclogite xenoliths. The calculated bulk REE- and trace element budget of the ‘majoritic bulk rock’ is similar to or higher than enriched MORB and KK 81 shows a negative Eu-anomaly (Stachel et al., 2000a). The latter was taken as indication of the involvement of a plagioclase bearing precursor rock.

The lower mantle samples show neither lithium depletion nor abundance levels similar to primitive mantle. If the assumed modal abundances of lower mantle phases are correct, lithium is four to five times enriched relative to primitive mantle. Our data of high Li in ferropericlase are supported by similar values reported by Kaminsky et al. (2001). Quite different to the lithospheric upper mantle, lithium in the lower mantle appears to be transported and enriched by an unspecified agent during the diamond forming process. This also means that lithium does not bear a memory of a depletion event in a former protolith. An alternative scenario envisages Li being enriched by low temperature alteration in some kind of ocean floor environment; this protolith later being subducted into the lower mantle with the Li-signature preserved. A very unlikely hypothesis is that ferropericlase contains the Li-inventory of a primitive mantle. In this case, the consequences would be very low modal abundances of ferropericlase (about 4%) and a correspondingly higher modal amount of Mg-perovskite which would give an unreasonably high Si-content to the lower mantle. Whatever the cause, the fact remains that lithium is highly enriched in the kind of lower mantle material brought up to the earth surface.

5. Conclusions

Lithium seems to display properties in transporting agents (fluids or melts) which lead to a stockwork distribution of lithium abundances in the earth. At the depths of the spinel peridotite field lithium appears to be quite mobile in fluids or melts. Within the deeper lithosphere, in the asthenosphere and the transition zone, lithium does not appear to be introduced during metasomatic events. This may either mean that lithium is not soluble in the transporting agents occurring at great depths or that its partitioning behaviour is very strongly biased in favour of these fluids/melts. At lower mantle conditions, lithium appears to be mobile again. It must be soluble in some kind of transporting agent and also have a high partitioning behaviour towards solids (ferropericlase).

Lithium displays also drastic differences in its distribution behaviour between solids with depth. High partition coefficients $D^{\mathrm{cpx/grt}}$ in the lithosphere change to values of smaller than one in the asthenosphere and transition zone with the development of a majorite solid solution component in garnet. In the lower mantle, ferropericlase acts as a sink for lithium. This dramatically differing partitioning behaviour of Li between solids with depth also implies dramatic changes in the partitioning behaviour between solids and fluids or melts. The chemical and physical properties of fluids or melts also change with temperature, pressure and oxygen fugacity. The combination of these complexities may lead to the observed stockwork behaviour of lithium.

The present work gives only hints in this direction. With the rapidly advancing possibilities to analyse Li and its isotopes accurately on a microscale, much progress will be made in the future and the presently patchy picture will take on clearer forms. Research focuses at present on subduction related processes by studying volcanic products and the precursors of the subducted material. We may contribute to the understanding of these or similar processes in earlier times of the earth by looking at their products at depth.

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