Chemical Geology 239 (2007) 323 – 335

CHEMICAL GEOLOGY INCLUDING ISOTOPE GEOSCIENCE

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Squeezing out the slab — modelling the release of Li, Be and B during progressive high-pressure metamorphism

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Accepted 18 August 2006

Editor: S.L. Goldstein

Abstract

A model for the release of Li, Be and B from progressively dehydrating altered oceanic crust during subduction is presented. Combining clinopyroxene/fluid partition coefficients determined experimentally in an earlier study Brenan et al. [Brenan, J.M., Ryerson, F.J., Shaw, H.F., 1998. The role of aqueous fluids in the slab-to-mantle transfer of boron, beryllium, and lithium during subduction: Experiments and models. Geochim. Cosmochim. Acta 62, 3337–3347] with apparent mineral/clinopyroxene partition coefficients as observed in natural high-pressure metamorphic rocks Marschall et al. [Marschall, H.R., Altherr, R., Ludwig, T., Kalt, A., Gméling, K., Kasztovszky, Zs., 2006a. Partitioning and budget of Li, Be and B in high-pressure metamorphic rocks. Geochim. Cosmochim. Acta 70, 4750–4769] results in a set of mineral/fluid partition coefficients for high-pressure metamorphic minerals. Mineral modes of altered oceanic crust as a function of pressure and temperature along a given subduction path can be derived from thermodynamic calculations using the program PerpleX. Combination of these modes with mineral/fluid partition coefficients results in whole rock/fluid partition coefficients at any stage of the *P–T* path including information on the amount of fluid released at any depth. Based on these data, the concentrations of Li, Be and B in subducting rocks and released fluids along a given *P–T* path can be modelled. The derived information on B concentrations in rocks and fluids are combined with the temperature-dependent fractionation of B isotopes in order to model the B isotopic evolution of subducting rocks and released fluids. Model calculations are performed for two slightly different chemical compositions (hydrous MORB without K and with 0.5 wt.% K_2O), in order to demonstrate the impact of phengite on the boron budget. Provided the necessary input data are available, the concept of such a model could be employed to quantify the trace element release from the slab from any lithology along any reasonable *P–T* path.

Keywords: Lithium; Beryllium; Boron isotopes; Subduction zone; Dehydration

1. Introduction

The light elements Li, Be and B are important tracers for mass transfer in subduction zones. They are readily mobilised by fluids and melts and display strong isotope fractionation (Li and B) in nature. Concentrations of the three elements in the mantle and in fresh oceanic basalts are low, whereas they are enriched in sediments, altered

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0009-2541/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.chemgeo.2006.08.008

oceanic crust and continental crust. Therefore, any input of fluid or melt from the subducting slab into the overlying mantle has a strong impact on the light element budget and isotopic composition of the mantle wedge, and the magmas generated there. Island arc volcanic rocks consequently display enrichments of Li, Be and B with respect to MORB (Ryan and Langmuir, 1987, 1988, 1993; Smith et al., 1997; Sano et al., 2001; Ryan, 2002) and specific isotopic signatures of light elements (Ishikawa and Nakamura, 1994; Ishikawa and Tera, 1997; Clift et al., 2001; Straub and Layne, 2002; Morris et al., 2002; Palmer and Swihart, 2002; Tomascak, 2004). The use of light elements as tracers in subduction zone geochemistry was put forward by studies on subduction-related volcanic rocks by various authors starting with J. Ryan and C. H. Langmuir in the late 1980s (Ryan and Langmuir, 1987, 1988, 1993). Recent reviews on the geochemical behaviour of the light elements and their isotopes are given in the literature for lithium (Tomascak, 2004; Bouman, 2004; Elliott et al., 2004), beryllium (Ryan, 2002) and boron (Palmer and Swihart, 2002; Leeman and Sisson, 2002). Element ratios such as Li/Yb, B/Be and B/Nb and isotope signatures (^{7}Li/^{6}Li, ^{10}Be/^{9}Be, ^{11}B/^{10}B) have been used over the Last ~ 15 years to gain knowledge on slab dehydration and subduction-related melting processes. Apart from the volcanic output of subduction zones information on the light element output has also been deduced from other subduction-related rocks and fluids, such as xenoliths from the mantle wedge (Nishio et al., 2004), orogenic peridotites (Paquin and Altherr, 2002; Paquin et al., 2004), mud volcanoes (Deyhle and Kopf, 2002; Kopf and Deyhle, 2002) and serpentinite diapirs (Benton et al., 2001, 2004).

Another important source of information are exhumed high-pressure metamorphic rocks, such as eclogites (Zack et al., 2003), metasedimentary units (Moran et al., 1992; Bebout et al., 1993, 1999) and serpentinites (Scambelluri et al., 2004). In-situ studies on light element partitioning between high-pressure metamorphic minerals allows for the quantification of the budget of these elements in different lithologies (Domanik et al., 1993; Woodland et al., 2002; Marschall et al., 2006a). Studies on high-pressure metamorphic tourmaline revealed important insights into B isotope fractionation within dehydrating oceanic crust (Nakano and Nakamura, 2001; Bebout and Nakamura, 2003; Marschall, 2005). Experimental data on light element behaviour during fluid/rock or fluid/mineral interaction is available from the literature (Seyfried et al., 1984; You et al., 1995, 1996; Kogiso et al., 1997; Brenan et al., 1998; Johnson and Plank, 1999; Green and Adam, 2003; Kessel et al., 2005). The temperature dependent boron isotopic fractionation has also been determined experimentally (Hervig et al., 2002; Wunder et al., 2005; Schmidt et al., 2005).

Summarising the results of all these studies dealing with the behaviour of light elements in the subduction cycle, some general conclusions can be drawn: Li and B are relatively mobile in hydrous fluids and in silicate melts; Be is relatively immobile in hydrous fluids but mobile in silicate melts; Li and B concentrations in the slab decrease with slab depth, because these elements are released with fluids during dehydration; Preferential loss of the heavier isotopes ^{7}Li and ^{11}B results in decreasing δ^{7}Li and δ^{11}B values in the subducting material.

Within the slab, the most important reservoirs for Li, Be and B are the sediments, the altered oceanic crust (AOC) and serpentinised ultramafic rocks. Fresh mantle and magmatic rocks show very low concentrations and no isotopic anomalies. Sediments, AOC and serpentinites are not only enriched in Li, B and ±Be, but also show δ^{7}Li and δ^{11}B values higher than MORB (or mantle), due to a preferential enrichment in the heavy isotopes during the interaction with seawater. The hydrous portion of the subducting slab therefore introduces large amounts of heavy Li and B into a subduction zone. Be (including ^{10}Be) is enriched in the sedimentary column of the oceanic crust. Detailed knowledge on the budget and partitioning of light elements within different materials of the subducting slab are essential for the modelling of Li, Be and B transfer and isotopic evolution in subduction zones. In order to fully understand the light element signatures of arc volcanic rocks, it is necessary to know the behaviour of these elements during subduction-related progressive metamorphism of slab materials. The elemental and isotopic signatures of the fluids released from a certain portion of the slab will probably not be directly transferred to the arc volcanic rocks, as the fluids will interact with other portions of overlying slab and mantle rocks. This will have a significant influence on the trace element and isotopic compositions of such fluids (Marschall et al., 2006b). In addition, fluids released from deeper portions of the basaltic crust or serpentinised lithosphere may strongly alter the major and trace element composition of the subducting rocks along localised flow channels (e.g. Spandler and Hermann, 2006; Zack and John, 2007). Hence, a holistic model of trace element input into the magma source region will not only consider the trace element release during dehydration of rocks within the slab, but will also include reactive flow processes. Yet, this study is treating the first part of the problem, and presents a model for a quantitative calculation of light element release and B isotope fractionation during dehydration of oceanic crust. The aim is to extract as much information as possible from the data deduced from high-pressure (H*P*) metamorphic rocks — to squeeze out the slab. The consequent interaction of the released fluids with overlying rocks is discussed in detail by Zack and John (2007).

2. Previous attempts to model light element release and isotope fractionation during H*P* metamorphism

Several authors have modelled light element release (Bebout et al., 1993; Brenan et al., 1998) and isotopic fractionation of Li (Zack et al., 2003; Bouman, 2004) and B (Peacock and Hervig, 1999; Bebout and Nakamura, 2003; Rosner et al., 2003) in subduction zones. Bebout et al. (1993) modelled B/Be ratios of rocks and fluid in subducting sediments during progressive dehydration using a Rayleigh fractionation formulation such as commonly applied to modelling trace element distribution during partial melting processes and fluid/rock interaction processes (Nabelek, 1987). Brenan et al. (1998) experimentally determined Li, Be and B partition coefficients between clinopyroxene (and garnet) and aqueous fluid (pure water and 0.5 M HCl) at 2.0 GPa and 900 °C (Table 1). They combined these clinopyroxene/fluid partition coefficients with amphibole/clinopyroxene, lawsonite/clinopyroxene and mica/clinopyroxene partition coefficients determined on natural H*P* metamorphic rocks (Domanik et al., 1993). This resulted in mineral/fluid partition coefficients for five different H*P* minerals (garnet, clinopyroxene, lawsonite, amphibole and mica). Brenan et al. (1998) then calculated whole rock/fluid partition coefficients by combining the mineral/fluid partition coefficients with data on the modal composition of MORB + H_2O during progressive subduction (Poli and Schmidt, 1995). Both H_2O-content and whole rock/fluid partition coefficients change due to the change in modal composition of the subducting rock, but can be calculated from the data set. Using this method, Brenan et al. (1998) were able to calculate B/Be ratios of rocks and fluid in subducting hydrous MORB. Peacock and Hervig (1999) used literature data on the temperature dependence of B isotope fractionation to calculate the B isotopic composition of rocks and fluids in a system where B is progressively released from the rocks as temperature increases from 25 to ~700 °C. Their model includes neither mineral/fluid partition coefficients nor modal compositions of the rocks. Instead, it is based on the assumption of B being steadily released from the rock during increasing temperature. The same kind of calculation was performed by Bebout and Nakamura (2003). These authors assumed a constant fractionation of 10‰ between silicate rocks and fluid and calculated fluid and rock B isotopic compositions for batch and Rayleigh devolatilisation as a function of the amount of B remaining in the rock. The model of Rosner et al. (2003) is also similar to that of Peacock and Hervig (1999), and assumes B loss from the slab as a linear function of temperature, decreasing the original B concentration to a value of 20% at a temperature of 750 °C. The thermal structure of the subducting slab was taken from geophysical data and modelling (Springer, 1999). Boron isotope evolution of rocks and fluids were then calculated using the temperature dependency of isotope fractionation given by Williams et al. (2001).

Table 1
Partition coefficients of Li, Be and B between 13 silicates, clinopyroxene and fluid

	Li		Be		B	
	min/*Cpx**	min/fluid	min/*Cpx**	min/fluid	min/*Cpx**	min/fluid
Cld	$1.5\ 10^{-4}$	$2.41\ 10^{-5}$	$2.2\ 10^{-2}$	$3.89\ 10^{-2}$	$4.6\ 10^{-3}$	$7.39\ 10^{-5}$
Ttn	$9.1\ 10^{-4}$	$1.46\ 10^{-4}$	$1.3\ 10^{-3}$	$2.38\ 10^{-3}$	$4.1\ 10^{-2}$	$6.56\ 10^{-4}$
Grt	$3.0\ 10^{-2}$	$4.80\ 10^{-3}$	$2.0\ 10^{-3}$	$3.60\ 10^{-3}$	$3.7\ 10^{-2}$	$5.92\ 10^{-4}$
Czo	$1.1\ 10^{-2}$	$1.76\ 10^{-3}$	$3.2\ 10^{-2}$	$5.76\ 10^{-2}$	0.20	$3.20\ 10^{-3}$
Lws	$8.2\ 10^{-5}$	$1.31\ 10^{-5}$	0.55	0.990	0.11	$1.76\ 10^{-3}$
Cam	$4.0\ 10^{-2}$	$6.40\ 10^{-3}$	2.3	4.14	2.0	$3.20\ 10^{-2}$
Gln	1.2	0.192	0.84	1.51	2.4	$3.84\ 10^{-2}$
Chl	1.6	0.256	0.30	0.540	0.77	$1.23\ 10^{-2}$
Tlc	0.21	$3.33\ 10^{-2}$	$1.8\ 10^{-2}$	$3.24\ 10^{-2}$	1.9	$3.08\ 10^{-2}$
Phe	0.33	$5.28\ 10^{-2}$	2.8	5.04	45	0.720
Pg	0.51	$8.16\ 10^{-2}$	10	18.0	70	1.12
Ab	$1.8\ 10^{-4}$	$2.88\ 10^{-5}$	2.7	4.86	0.35	$5.60\ 10^{-3}$
Qtz	$1.1\ 10^{-3}$	$1.76\ 10^{-4}$	$2.0\ 10^{-3}$	$3.60\ 10^{-3}$	$5.9\ 10^{-2}$	$9.44\ 10^{-4}$
Cpx**		0.16		1.8		$1.6\ 10^{-2}$

*min/*Cpx* data from Marschall et al. (2006a). ** *Cpx*/fluid data from Brenan et al. (1998).

Zack et al. (2003) and Bouman (2004) calculated similar models in order to explain observed δ^7Li values of eclogites and island arc basalts (IAB). In both studies, Rayleigh fractionation with constant isotopic fractionation factors and partition coefficients between rocks and fluids are used, together with "typical AOC" Li contents and isotopic signatures as initial values for the subducting slab. The results allow for a prediction of Li contents and isotopic compositions of subducting AOC at any stage of dehydration (Bouman, 2004), or for Li contents and isotopic composition of an eclogite's possible protolith (Zack et al., 2003).

3. The model

The model presented in this study combines the different methods discussed above. A procedure similar to that of Brenan et al. (1998) is used for the calculation of trace element fractionation, which is then combined with a method similar to that of Peacock and Hervig (1999) for the calculation of B isotopic fractionation. Fig. 1 displays the principles of the model.

It is assumed that a protolith with a given modal composition, trace element content and isotopic signature is progressively dehydrating with increasing P and T as it is subducting. The H_2O-content is calculated from the stoichiometric H_2O-contents and weight fractions of all hydrous minerals in the rock. The P–T path, the changing modal composition (metamorphic reactions) and the H_2O-contents are calculated using PerpleX (Connolly, 1990, 2005). The second set of input parameters are mineral/clinopyroxene partition coefficients $D_i^{\min/Cpx}$, determined on natural HP metamorphic rocks (Marschall et al., 2006a) and defined as the concentration ratio of an element i in any mineral ($c_i^{\min}$) in equilibrium with clinopyroxene (c_i^{Cpx}):

$$D_i^{\min/Cpx} = \frac{c_i^{\min}}{c_i^{Cpx}}. \tag{1}$$

For calculating the behaviour of trace elements during dehydration reactions, mineral/fluid partition coefficients are required. Brenan et al. (1998) provide

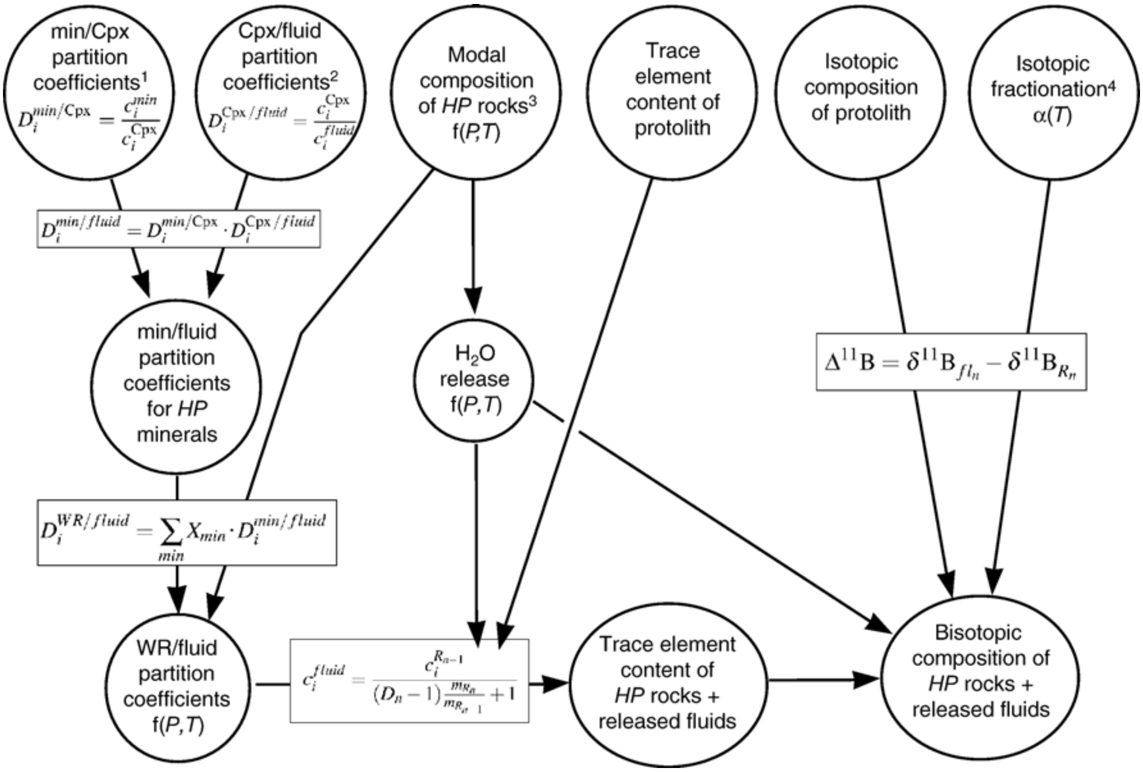

Fig. 1. Flowchart displaying the calculation used for modelling of trace element behaviour and isotope fractionation in dehydrating crust. Input data are: [1]mineral/clinopyroxene partition coefficients from Marschall et al. (2006a); [2]clinopyroxene/fluid partition coefficients from Brenan et al. (1998); [3]modal composition of the HP metamorphic rocks as a function of P and T from calculations with PerpleX; [4]boron isotopic fractionation as a function of T from Hervig et al. (2002).

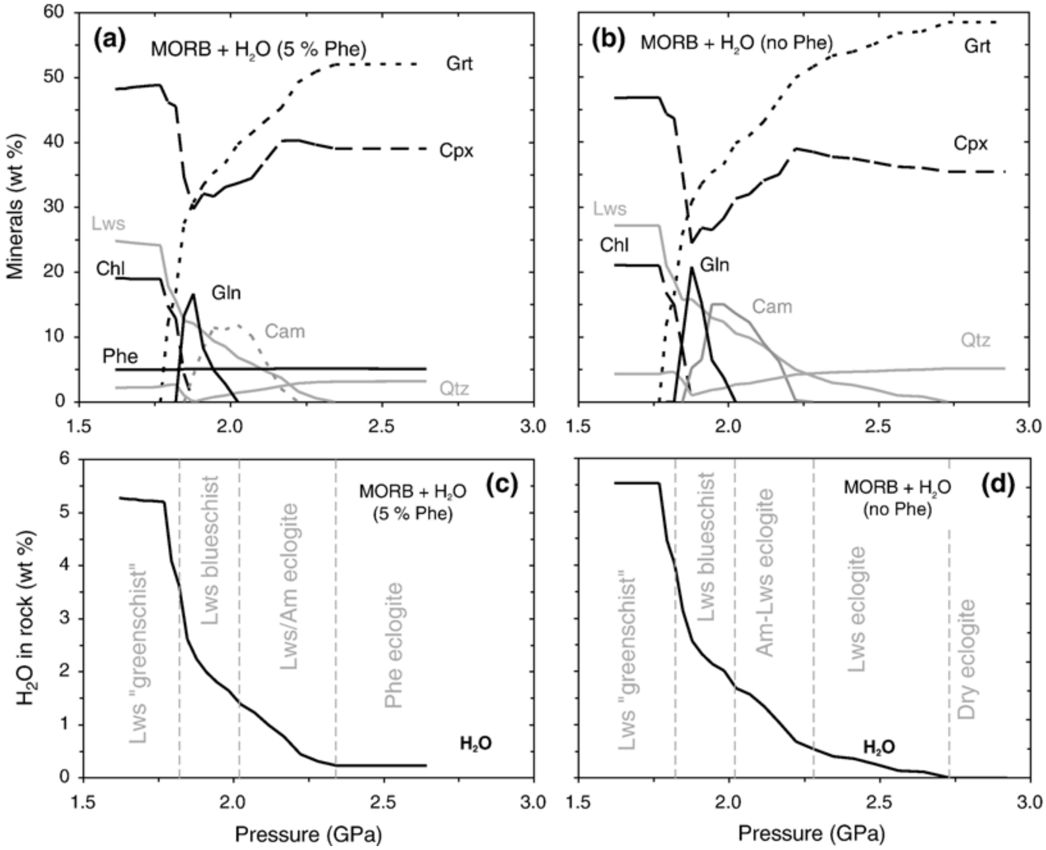

Fig. 2. (a) Modal composition of MORB+H_2O as a function of P along the calculated P–T path. (b) Same as in Fig. a for the composition K_2O-free MORB+H_2O, which does not contain Phe. (c) H_2O-content of rock for which the modal composition is displayed in Fig. (a) as a function of P. (d) H_2O-content of rock for which the modal composition is displayed in Fig (b) as a function of P. A pressure of 3 GPa corresponds to a depth of ~100 km.

clinopyroxene/fluid partition coefficients $D_i^{Cpx/f}$ for Li, Be and B, determined from experimental studies:

$$D_i^{Cpx/f} = \frac{c_i^{Cpx}}{c_i^f}. \tag{2}$$

These two sets of partition coefficients (Eqs. (1) and (2)) are combined to produce mineral/fluid partition coefficients for a set of 15 HP minerals investigated by Marschall et al. (2006a):

$$D_i^{\min/f} = D_i^{\min/Cpx} \cdot D_i^{Cpx/f}. \tag{3}$$

Whole rock/fluid partition coefficients are derived from the sum of all mineral/fluid partition coefficients multiplied with the mass fractions $X_{\min}$ of the respective minerals in the rock:

$$D_i^{r/f} = \sum_{\min} X_{\min} \cdot D_i^{\min/f}. \tag{4}$$

Starting with any typical light element content of AOC, the evolution of Li, Be and B concentrations in the dehydrating rocks and the released fluids is:

$$c_i^f = \frac{c_i^{r_{n-1}}}{(D_n - 1)\frac{m_{r_n}}{m_{r_{n-1}}} + 1} \tag{5}$$

where $c_i^{r_{n-1}}$ is the concentration of element i in the rock before dehydration step n, D_n is the partition coefficient between dehydrated rock at step n and fluid, and $m_{r_{n-1}}$ and m_{r_n} are the masses of the rock before and after dehydration step n, respectively (see Marschall et al., 2006b, for details). The concentration of element i in the rock after dehydration is calculated from the concentration of the element in the fluid and the whole rock/fluid partition coefficient.

In tourmaline-free HP metamorphic rocks, B is stored predominantly in white mica and amphibole (Domanik et al., 1993; Marschall et al., 2006a). These minerals are generally assumed to contain B in tetrahedral coordination (Hervig et al., 2002; Werding and Schreyer, 2002;

Tonarini et al., 2003). B in acidic hydrous fluids is predominantly trigonally coordinated in $B(OH)_3$ units (Palmer and Swihart, 2002). Recent experiments have shown that this also holds true at pressures ≤2.0 GPa (Schmidt et al., 2005). Experimental studies (Hervig et al., 2002; Wunder et al., 2005; Sanchez-Valle et al., 2005) have investigated the temperature dependence of B isotopic fractionation between phases of different B coordination (e.g. mica, amphibole, melt, fluid, tourmaline). Hervig et al. (2002) demonstrated a systematic decrease of fractionation with increasing temperature, given by the formula

$$1000\ln\alpha = 5.68 - 12290/T \qquad (6)$$

where α is the fractionation factor and T is the temperature (K). Eq. (6) is used for modelling the B isotopic fractionation of dehydrating H*P* metamorphic rocks containing tetrahedrally coordinated B and released fluid containing B in trigonal coordination. Input parameters for the isotope mass balance calculation (see Marschall et al., 2006b, for details) are (i) the B contents of rocks and fluids calculated from Eq. (5) and (ii) a value for the B isotopic composition of the protolith, which may be a value for "typical AOC". As formulated, the model provides a complete description of the light element concentrations and B isotopic compositions of the slab mineralogy and the released fluids during subduction along any specific *P*–*T* path.

4. Results

4.1. P–T path, H_2O-content and modal composition

The model presented above requires a certain *P*–*T* evolution of the subducting material as input data. Any reasonable *P*–*T* path of the top of the subducted oceanic slab would perfectly serve as an input data set and would produce its individual results. As an example, the *P*–*T* path published by Jödicke et al. (2006) was taken as a basis for the calculations presented here. Model calculations were done for K_2O-bearing (Fig. 2a) and K_2O-free (Fig. 2b) MORB compositions, assuming water saturation in both cases. A comparison of the results for both compositions demonstrates the impact of phengite on B concentrations and isotopic signatures. The amount of H_2O in the rocks was calculated for the K_2O-bearing (Fig. 2c) and the K_2O-free MORB (Fig. 2d) from their respective modal compositions.

The modal composition in both cases starts with a lawsonite greenschist, rich in clinopyroxene, chlorite and lawsonite accompanied by quartz±phengite, which contains ~5.5 wt.% H_2O. As temperature increases, garnet grows at the expense of chlorite and the H_2O-content decreases to ~3 wt.%. The transition from this Lws greenschist to a Lws blueschist is marked by the appearance of glaucophane at the expense of clinopyroxene, while the H_2O-content steadily decreases to a value of ~1.5 wt.%. At ~520 °C, the mode of omphacitic clinopyroxene starts to increase, while the abundances of glaucophane and lawsonite decrease. The assemblage consisting of garnet+omphacite+barroisitic amphibole+lawsonite+quartz±phengite can be described as hydrous eclogite or amphibole-lawsonite eclogite. The H_2O-contents continuously decrease together with the modal abundances of hydrous minerals (Fig. 2c and d). The K_2O-bearing MORB reaches a limit of ~0.25 wt.% H_2O as it reaches the stage of phengite eclogite, while in the K_2O-free assemblage an anhydrous eclogite is formed. Note that the mineral assemblage within the slab at any depth depends on the temperature evolution during subduction. A different *P*–*T* path causes the mineral reactions to occur at different depths, and therefore alters

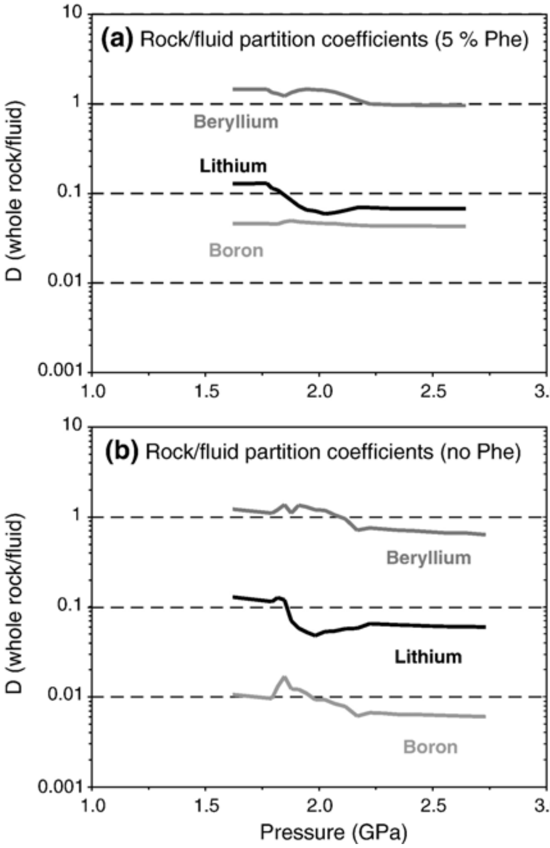

Fig. 3. Calculated partition coefficients of light elements between H*P* metamorphic rocks and released fluids as a function of pressure. The diagrams display two different compositions: (a) MORB+H_2O and (b) K_2O-free MORB+H_2O.

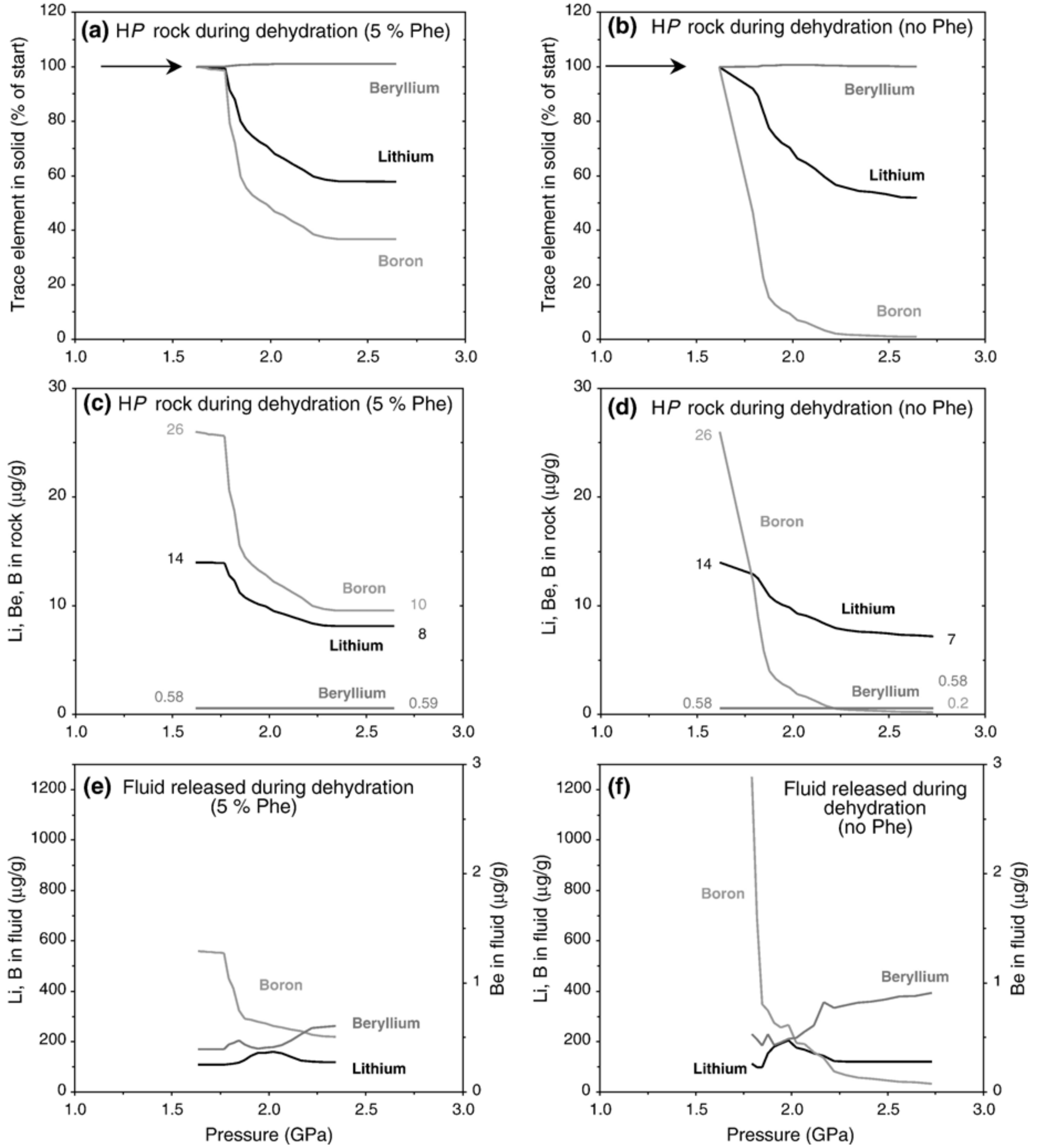

Fig. 4. Results of modelling of light element concentrations in H*P* metamorphic rocks and released fluids as a function of pressure. The diagrams display two different compositions: MORB + H_2O in Figs. a, c and e, and K_2O-free MORB + H_2O in Figs. b, d and f. (a, b) Li (black), Be (dark grey) and B (light grey) concentrations in the dehydrating rocks normalised to the initial concentrations. (c, d) Li, Be and B absolute concentrations in dehydrating rock. (e, f) Li, Be and B absolute concentrations in released fluids. Note different scale for Be.

the trace element and isotope signatures. The colder *P–T* path employed by Brenan et al. (1998), for example, leads to a longer persistence of lawsonite and amphibole in the slab, and to a shift of the dehydration reactions and of the trace element release to higher pressures.

4.2. Calculated whole rock/fluid partition coefficients

For both MORB compositions, Be has a whole-rock partition coefficient close to unity over the entire pressure range (Fig. 3), which is consistent with the relative

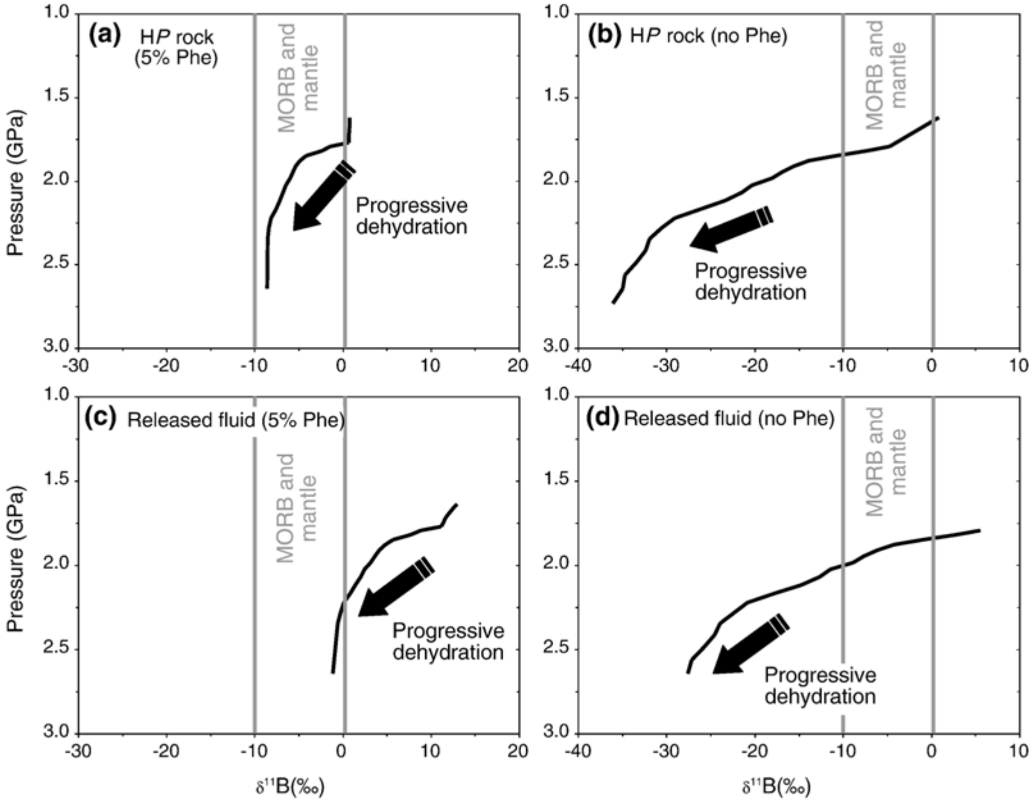

Fig. 5. Results of modelling of B isotope ratios in H*P* metamorphic rocks and released fluids as a function of pressure. The diagrams display the two different compositions discussed in the text and in Figs. 2, 3 and 4. Boron isotope composition of MORB and mantle (Spivack and Edmont, 1987; Chaussidon and Jambon, 1994; le Roux et al., 2004) is shown for comparison. (a) B isotope ratios in the phengite-bearing rock, (b) B isotope ratios in the phengite-free rock, (c) B isotope ratios in the fluids released from the phengite-bearing rock, (d) B isotope ratios in the fluids released from the phengite-free rock.

immobile character of this element. Li shows a decrease of *D* from ~0.13 in the chlorite-rich assemblage to values of ~0.06 for the blueschists and ~0.07 for the eclogites (Fig. 3). Partition coefficients for B are the lowest of the three elements and are strongly dependent on the modal abundance of phengite. For the phengite-bearing composition they are relatively constant at ~0.05, while for the phengite-free composition they are significantly lower and increase from ~0.010 for the Lws greenschist to ~0.012 for the Lws blueschist and then decrease to ~0.006 for the eclogite (Fig. 3).

4.3. Light element concentrations in rocks and released fluids

The abundance of Be is very constant from greenschist to eclogite in both bulk compositions (Fig. 4). Li concentrations decrease to ~55% during subduction from greenschist to eclogite conditions, irrespective of phengite abundance (Fig. 4). The amount of B remaining in the rocks is strongly dependent on the modal abundance of phengite. In the K_2O-bearing MORB (~5% phengite), ~37% of the B remains in the eclogite (Fig. 4a), while the K_2O-free composition preserves only ~1% of the initial B (Fig. 4b).

Absolute concentrations of light elements in the model rocks and fluids can be calculated if typical light element concentrations of AOC are assumed as initial values. Keeping in mind the large variability of Li and B concentrations in AOC, the following values from the literature were used: 14 μg/g Li (Kelley et al., 2003), 0.58 μg/g Be (Kelley et al., 2003) and 26 μg/g B (Smith et al., 1995).

Using these initial values, the concentrations of light elements in the released fluids were calculated (Fig 4c and d). The impact of the phengite abundance on the concentrations of Li and Be in the fluids is very limited (Fig. 4e and f) — as is the case for Li and Be abundances in the rocks. Be concentrations in fluids released from both lithologies range from ~0.4 to ~0.9 μg/g. Li concentrations vary from ~100 μg/g released at ~1.6 GPa from the greenschists, to ~200 μg/g in fluids released at

~2.0 GPa, to ~100 μg/g in fluids released at ~2.3 GPa from the eclogites. B concentrations depend strongly on the amount of phengite in the restitic rock. The phengite-bearing assemblage releases fluids with a B concentration decreasing from ~550 μg/g to ~200 μg/g along the *P*–*T* path (Fig. 4e), while B concentrations of fluids released from phengite-free rocks decrease from >1200 μg/g to <100 μg/g at $P>2.2$ GPa (Fig. 4f).

4.4. B isotopic composition of rocks and released fluids

Depending on fluid/rock ratios, temperature, the extent of alteration and other parameters during sea-floor metamorphism of oceanic crust, the B isotopic composition may vary between −4.3‰ to +24.9‰ (Smith et al., 1995). An average δ^{11}B value of +0.8‰ for layer 2A (uppermost layer) of AOC is given by Smith et al. (1995) with a boron concentration of 26 μg/g. These values are used here for modelling (Fig. 5). The δ^{11}B evolution of the two different rocks is significantly different. The δ^{11}B value of the phengite-bearing rock is lowered to a value of −8.6‰ as it reaches the eclogite stage at ~2.2 GPa, whereas the δ^{11}B value of phengite-free rock is shifted to a much lower value of <-30‰ at the same depth (Fig. 5a and b). Consequently, the fluids released at the blueschist–eclogite transition at 2.2 GPa show the same difference between +0.1‰ and −20.8‰ in the phengite-bearing and the phengite-free compositions, respectively (Fig. 5c and d). It is important to note, that the δ^{11}B value of the phengite-bearing eclogite is within the δ^{11}B range published for MORB and mantle (Spivack and Edmont, 1987; Ishikawa and Nakamura, 1992; Chaussidon and Jambon, 1994; Chaussidon and Marty, 1995; le Roux et al., 2004). The δ^{11}B value of the phengite-free eclogite on the other hand is significantly lower than the values for MORB and mantle. Correspondingly, the fluid released from the phengite eclogite carries a positive δ^{11}B signal, whereas the δ^{11}B value of the fluid released from the phengite-free assemblage is extremely negative.

5. Discussion

5.1. Limitations of the model

The universal applicability and significance of our model is limited by a number of factors. The whole model is based on the assumption of chemical and isotopic equilibrium in the rock, as are comparable models on partial melting processes. Furthermore, the trace element and isotopic composition of the generated fluids are assumed to be in equilibrium with the restitic rock and the fluid is extracted from the rock after each step of dehydration (=batch dehydration, using 10 °C step size). Chemical equilibrium during metamorphism depends on a number of factors, such as grain size, fluid availability, deformation and concurrent recrystallisation, the type of minerals involved and element diffusivities. In the case of Li, Be and B in dehydrating upper oceanic crust during subduction, all these factors are relatively favourable. Firstly, the upper part of the oceanic crust is usually subjected to intense deformation – shearing and isoclinal folding – as documented in many exhumed H*P* terranes. Secondly, increasing temperatures lead to dehydration reactions, providing fluids which in turn accelerate metamorphic reactions within the rocks. Thirdly, the light elements are stored in phases such as chlorite, phengite, amphibole and pyroxene that are likely to react rapidly. Garnet, which is expected to have sluggish reaction kinetics at low temperatures, is only a minor carrier of Li and does not incorporate Be and B in significant amounts (Marschall et al., 2006a). Studies on natural rocks have demonstrated that light element partitioning among different metamorphic phases is highly systematic, suggesting a relatively fast adaptation to equilibrium partitioning (Marschall et al., 2006a).

Another limiting factor for the model is the quality of the partition coefficients used in the calculations. To date, the data base on light element fractionation among different H*P* metamorphic minerals and especially between minerals and hydrous fluid is limited. A detailed investigation on samples from Syros (Marschall et al., 2006a) revealed a basis for inter-mineral partitioning of light elements, but did not decipher possible influence of *P* or *T* on the coefficients. A secondary effect could be generated by a change of the major element composition as a function of *P* and *T* variations, e.g. increasing jadeite content in omphacite as a consequence of increasing pressure. This change in major element composition would affect the crystallographic parameters of the mineral, and could therefore influence trace element partitioning. However, the large variety of clinopyroxene compositions investigated by Marschall et al. (2006a) does not reveal any strong influence of mineral compositions on trace element partitioning.

The mineral/fluid partition coefficient dataset determined experimentally by Brenan et al. (1998) at relatively high *P*–*T* conditions (2 GPa, 900 °C) are probably not perfectly transferable to the metamorphic conditions of the calculated *P*–*T* path. Therefore, future studies on fluid/mineral partition coefficients may enhance our knowledge on this aspect and further improve the quality of the results calculated by our model.

Modal compositions used in our model do not include tourmaline. The impact of this boro-silicate on the B budget and δ^{11}B systematics of metamorphic rocks during subduction was already emphasised (Nakano and Nakamura, 2001). Tourmaline is probably more frequent in metasediments than in metabasites, but it strongly controls the B budget and B isotopic composition of rocks, even if it occurs only as an accessory phase (Marschall et al., 2006a). Nakano and Nakamura (2001) have demonstrated that tourmaline-bearing metasediments are able to retain their entire B budget by incorporating mica-derived boron into newly growing tourmaline. Transferring the presented model to metasediments would therefore require the introduction of tourmaline into the mineral assemblage. Thermodynamic data on the minerals of the tourmaline group, however, are sparse (Garofalo et al., 2000; Anovitz and Hemingway, 2002).

5.2. Implications of the results for the subduction cycle of light elements

The calculations demonstrate that Li concentrations of eclogites still amount to ~50% of the initial value. Despite the fluid-mobile character of this element, the subducting oceanic crust retains more than 50% of its lithium, even in the H_2O-saturated portion of the subducting crust. This finding has already been proposed by Woodland et al. (2002) after investigating Li abundances of natural eclogite samples from several localities. Li concentrations of the released fluids range from ~100 to ~200 µg/g and are highest at intermediate pressures at the transition from blueschist to hydrous eclogite. The results for the behaviour of Li in subducting AOC provide a good database for the modelling of Li isotope fractionation during subduction (Zack et al., 2003).

Be concentrations of the eclogites are almost identical to those in the protoliths. This is due to the fact that the whole rock/fluid partition coefficients are close to unity. It has been demonstrated experimentally that whole rock/fluid partition coefficients for Be between progressively metamorphosed clay-rich sediment and the released fluids range from 2 to 4.5, and drop to 0.7–0.9 at the onset of partial melting (Johnson and Plank, 1999). Natural H*P* metamorphic metabasites also show relatively high Be concentrations of 0.4–3.2 µg/g (Marschall, 2005), which is consistent with the conservative behaviour of Be during dehydration as predicted by our model. However, concentrations of Be in released fluids are still ~0.5 µg/g, i.e. as high as the concentration in the rocks. Hence, despite of the fact that there is no recognisable change in Be concentrations in the slab, the fluids are rich in Be and may be able to generate anomalies within mantle rocks. Fluids with a Be concentration of 0.5 µg/g, corresponding to ~10 times the value of primitive mantle (0.068 µg/g McDonough and Sun, 1995) would probably produce a measurable positive Be anomaly in the depleted mantle wedge. Equivalent to the transportation of Be by fluids generated in dehydrating metabasites, fluids from metasediments are expected to transport Be and especially cosmogenic ^{10}Be in concentrations comparable to the dehydrating whole rocks. Therefore, it is possible that ^{10}Be signals in IAB are generated by metasomatism of the IAB source by hydrous fluids and not exclusively by silicate melts.

The results for B demonstrate the significant influence of phengite on the evolution of B concentration and isotopic composition in rocks and fluids. The hydrous MORB produces a phengite eclogite (5 wt.% Phe) which retains approximately one-third of the original B with an isotopic composition in the range of mantle rocks, while the phengite-free composition produces a dry eclogite with low B concentration (1% of the initial value) and extremely light B. Therefore, deep subduction of phengite eclogite would produce a B-rich fluid with isotopic composition close to the mantle, as it reaches the upper pressure stability of phengite (~10 GPa Schmidt and Poli, 1998). In contrast, deep subduction of dry eclogite would introduce portions of extremely negative δ^{11}B into the deep mantle, but no anomaly in B concentration. Calculated B concentrations for dry eclogite of 0.2 µg/g are similar to those of the primitive mantle (Chaussidon and Jambon, 1994; McDonough and Sun, 1995; Palme and O'Neill, 2003). The results for the two different compositions, containing 5 wt.% phengite (0.5 wt.% K_2O) and 0.0 wt.% K_2O (no phengite) demonstrate the strong impact of white mica on B concentrations and isotope signatures in the subduction zone. Low-temperature alteration of MORB at the ocean floor may enrich K_2O to concentrations of 2 wt.% or even higher (Smith et al., 1995) which would form blueschists and eclogites with higher amounts of phengite (>20 wt.%). These rocks would retain even higher amounts of their initial B and higher δ^{11}B signals to great depths.

Fluids released from the dehydrating AOC show B concentrations in the order of 200–550 µg/g from the onset of dehydration to the eclogite stage. In the case of phengite-free rocks, the first fluids show even higher B concentrations of >1200 µg/g. B/Be ratios of fluids are on the order of ~1000, reflecting the greater mobility of B as compared to Be. δ^{11}B values of fluids released at the onset of dehydration are positive and significantly above the ranges of mantle and MORB, while the fluids released at greater depth rapidly reach negative δ^{11}B values, even lower than those of the mantle. Therefore, the high B concentrations and δ^{11}B values of serpentinite diapirs (Benton et al., 2001), mud volcanoes (Kopf and Deyhle, 2002) and trench fluids (Kopf et al., 2000; Deyhle and Kopf, 2002), fed by shallow dehydration of the slab, are well explained by the modelled fluids. In contrast, high δ^{11}B values of various IAB of −3.8 to + 7.3‰ (Ishikawa and Nakamura, 1994; Ishikawa and Tera, 1997), +4.6 to +12.0‰ (Straub and Layne, 2002) or even higher (Clift et al., 2001) cannot be explained by fluids expelled from subducting AOC at depths of ~100 km (~3 GPa), i.e. fluids that are thought to influence IAB magma generation. Instead, these high δ^{11}B values may be explained by a multi-stage model: Serpentinite which is infiltrated by high-δ^{11}B slab-derived fluids at shallow depth may be dragged down to sub-arc depth by mechanical coupling to the slab. During serpentinite breakdown, B-rich high-δ^{11}B fluids are released and metasomatise the magma source region.

6. Conclusions

In this study, modelling of trace element release from progressively dehydrating metabasites during subduction of AOC was performed for the light elements Li, Be and B. These elements show contrasting behaviour during fluid/rock interaction processes. Clinopyroxene/fluid partition coefficients for Li, Be and B were combined with mineral/clinopyroxene partition coefficients for various H*P* minerals to deduce a set of mineral/fluid partition coefficients. These were combined with the modal compositions of H*P* metamorphic rocks derived from thermodynamic calculations using the program PerpleX. The result is a data set of the modal composition of a rock and its whole rock/fluid partition coefficients for the trace elements of interest at any stage of the *P*–*T* path, including information on the amount of fluid released at any depth. Based on these data, the concentrations of trace elements in the subducting rocks and in the released fluids along a certain *P*–*T* path were modelled. The derived information on boron concentrations of rocks and fluids were combined with the temperature dependent isotopic fractionation of B, in order to model the B isotopic evolution of subducting rocks and of the released fluids.

Light element budgets for two compositions were calculated, (i) MORB + H_2O and (ii) K_2O-free MORB + H_2O. For both compositions, Be concentrations of the dehydrating rocks do not change during dehydration and released fluids also show constant Be concentrations which is similar to that of the rocks. Li concentrations in both assemblages decrease to ~55% between the onset of dehydration and eclogite conditions. Li concentrations of the released fluids range from ~100 to ~200 µg/g and are highest at intermediate pressures at the transition from blueschists to hydrous eclogites. The behaviour of B is strongly dependent on the amount of white mica in the rock. The K_2O-bearing MORB composition, transformed to an eclogite with ~5% phengite retains ~37% of the original amount of B, while the K_2O-free MORB composition, transformed to a phengite-free assemblage retains only ~1%. ^{11}B/^{10}B ratios are also significantly different. The phengite-bearing rocks release fluids with positive δ^{11}B values, reaching the MORB or mantle range as the rocks are transformed to eclogites. In contrast, the phengite-free assemblage produces fluids with strongly negative δ^{11}B values at the blueschist-to-eclogite transition. In both cases, however, fluids with high δ^{11}B values are released at shallow depth, which may migrate into the accretionary wedge or forearc mantle.

Our model is subject to a number of uncertainties and has to be improved by the input of better data, especially on trace element partitioning. However, in principle, this model offers the possibility of a quantification of trace element release and isotope fractionation from the slab in any lithology along any reasonable *P*–*T* path.

Acknowledgements

This paper benefited from discussions with Stefan Prowatke, Jens Paquin, Thomas Zack and Angelika Kalt. Emily Lowe helped to improve the English style. We greatly acknowledge constructive and helpful comments by James Brenan and an anonymous reviewer, and editorial handling by Adam Simon and Robbie King. This study resulted from the Dr. rer. nat. thesis of H.M. and was financially supported by the Deutsche Forschungsgemeinschaft (DFG, grants KA 1023/8-1 and AL 166/15-3), which is greatly acknowledged.

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