

Trace Element Partitioning and Accessory Phase Saturation during H₂O-Saturated Melting of Basalt with Implications for Subduction Zone Chemical Fluxes

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Experimental phase equilibrium and trace element partitioning data are reported for H₂O-saturated mid-ocean ridge basalt at 2.5 GPa, 750–900°C and oxygen fugacities at the nickel–nickel oxide buffer. Garnet, omphacite and rutile are present at all temperatures. Amphibole and epidote disappear as residual phases above 800°C; allanite appears above 750°C. The Na–Al-rich silicate glass present in all run products is likely to have quenched from a supercritical liquid. Trace element analyses of glasses demonstrate the important control exerted by residual minerals on liquid chemistry. In addition to garnet, which controls heavy rare earth elements (HREE) and Sc, and rutile, which controls Ti, Nb and Ta, allanite buffers the light REE (LREE; La–Sm) contents of liquids to relatively low levels and preferentially holds back Th relative to U. In agreement with previous experimental and metamorphic studies we propose that residual allanite plays a key role in selectively retaining trace elements in the slab during subduction. Experimental data and analyses of allanite-bearing volcanic rocks are used to derive a model for allanite solubility in liquids as a function of pressure, temperature, anhydrous liquid composition and LREE content. The large temperature dependence of allanite solubility is very similar to that previously determined for monazite. Our model, fitted to 48 datapoints, retrieves LREE solubility (in ppm) to within a factor of 1.40 over a pressure range of 0–4 GPa, temperature range of 700–1200°C and for liquids with anhydrous SiO₂ contents of 50–84 wt %. This uncertainty in LREE content is equivalent to a temperature uncertainty of only ±27°C at 1000 K, indicating the potential of allanite as a geothermometer. Silicic liquids from either basaltic or sedimentary

protoliths will be saturated in allanite except for Ca-poor protoliths or at very high temperatures. For conventional subduction geotherms the low solubility of LREE (+ Th) in liquids raises questions about the mechanism of LREE + Th transport from slab to wedge. It is suggested either that, locally, temperatures experienced by the slab are high enough to eliminate allanite in the residue or that substantial volumes of H₂O-rich fluids must pass through the mantle wedge prior to melting. The solubility of accessory phases in fluids derived from subducted rocks can provide important constraints on subduction zone thermal structure.

KEY WORDS: subduction; experimental petrology; allanite; solubility; supercritical liquid; eclogite

INTRODUCTION

Subduction recycles oceanic lithosphere into the mantle. Dehydration reactions and partial melting selectively release chemical components from the subducting slab into the overlying wedge. This chemical contamination of wedge peridotite by slab components imparts a characteristic chemical signature on subduction zone magmas. It is widely accepted that two slab components play a key role in contaminating the wedge: the altered oceanic basalt crust, and its thin veneer of sediment (e.g. Poli & Schmidt, 2002). The sediment is volumetrically less

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abundant than the basalt, but has substantially higher trace element concentrations, hence sedimentary contributions to the flavour of arc magmas are more striking (Elliott *et al.*, 1997). In many arcs there is a clear correlation between the composition of the actively subducting sediment and that of the magmas erupted from the overlying volcanic arc for many trace elements (Plank & Langmuir, 1993, 1998; Plank, 2005). The chemical contribution of the oceanic crust is rather more cryptic, and is restricted to just a few trace elements, most notably Pb and the large alkalis (Rb, Cs) and alkaline earths (Sr, Ba, Ra). For these reasons, there is a general consensus that the sediment contributes its flavour to the wedge via a silicate melt, whereas the basalt makes its contribution via an aqueous fluid (Elliott *et al.*, 1997). Thus, arc magma sources can be considered geochemically as a tripartite mixture of wedge peridotite, basaltic ocean crust and sediment. These three components are, to a large extent, geochemical constructs, in that their participation in subduction zone magmatism is based on chemical arguments. A key question is the extent to which physical conditions within the subduction zone shape the way in which sediment and basalt make their chemical contributions.

Except in the unlikely case of total fusion, the trace element signature of melts and fluids derived from the slab will be governed by trace element partitioning between melts or fluids and the solid residuum. Consequently, to make the link between physical conditions in the subduction zone and the chemical signature imparted to the mantle wedge, we require information on the mineralogy of the solid residue for different slab lithologies as subduction proceeds (Poli & Schmidt, 2002), and on the solid–fluid trace element partitioning characteristics of these residues (Kogiso *et al.*, 1997; Johnson & Plank, 1999). This includes not only the major mineral phases, such as garnet and clinopyroxene, but also minor, or accessory, minerals whose predilection for certain trace elements (e.g. Nb and Ta in the case of rutile) renders their chemical contribution out of all proportion to their low modal abundance. The aim of this study is to investigate experimentally the behaviour of trace elements during H₂O-fluxed partial melting of a hydrated mid-ocean ridge basalt (MORB) at 2.5 GPa. Such a situation is likely to arise when H₂O is released from the underlying serpentinized peridotite portion of the slab (e.g. Grove *et al.*, 2006). The pressure and temperature were chosen to be close to those along the top of a slab for subduction of young oceanic crust (Van Keken *et al.*, 2002) under conditions at or close to previously determined solidi for basalt and sediment (Fig. 1). In this regard our study is complementary to the recent experimental work of Green & Adam (2003) and Kessel *et al.* (2005a) on trace element partitioning between fluids and residual minerals in hydrated MORB-like compositions at 3 and 4–6 GPa, respectively (Fig. 1).

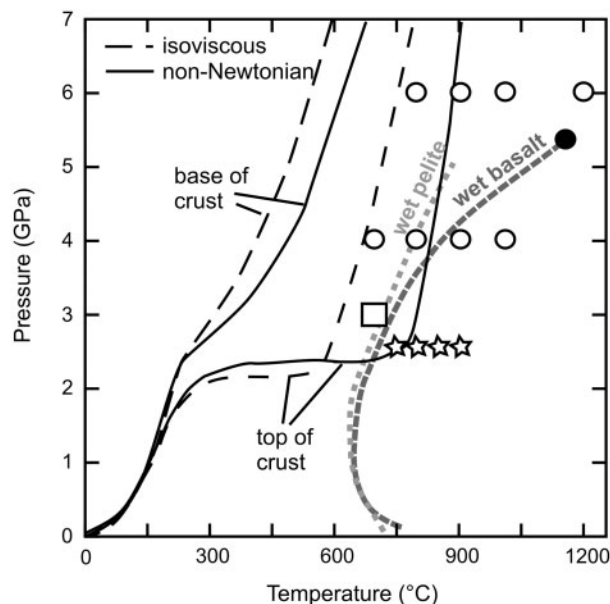


Fig. 1. *P*–*T* diagram showing geotherms for the top and base of a hot subducted slab according to the calculations of van Keken *et al.* (2002) using isoviscous and non-Newtonian rheologies for the mantle wedge. Solidus of wet basalt (dark grey dashed line) after Poli & Schmidt (1998) and Kessel *et al.* (2005b). The filled circle represents the second critical endpoint in the system MORB + H₂O as determined by Kessel *et al.* (2005b). Solidus of pelite (light grey dashed line) after Poli & Schmidt (1998). Experimental conditions (this study) are shown as open stars; those of Kessel *et al.* (2005a) as open circles and those of Green & Adam (2003) as an open square.

EXPERIMENTAL METHODS

As a starting material we selected a bulk composition (KBI) that represents an average of compositions that have been used previously to determine partial melting processes involving subducted oceanic crust (Liu *et al.*, 1996; Schmidt & Poli, 1998; Prouteau *et al.*, 2001; Forneris & Holloway, 2003) and that is close to estimates of altered MORB composition (Staudigel *et al.*, 1996; Table 1). The starting material consisted of a mechanical mixture of synthetic oxides (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO) and carbonates (CaCO₃, K₂CO₃, Na₂CO₃). A second glass (KBloT) without TiO₂ but with the same concentrations of the other elements of KBI was synthesized in the same way. Al₂O₃ and MgO were dried at 1000°C for 24 h to drive off any residual moisture. The other oxides and carbonates were stored in a drying oven at 120°C prior to mixing. Reagents were mixed in appropriate proportions and homogenized by dry grinding in an agate mortar. The mixture was decarbonated at 700–1000°C for 6 h in alumina crucibles. Trace elements were added as inductively coupled plasma (ICP) standard nitrate solutions (see Table 1) using a micro-syringe and dried under a heat lamp. The resulting mixture was again homogenized in an agate mortar and denitrified at 450°C for 1 h.

Table 1: Compositions of starting materials in this and other experimental studies of hydrated basalt melting

	This study				LBE ¹	FH ²	SP ³			PSPM ⁵	SPWS ⁶	
	KB1		KB1oT				KB750	LTCB	TB-1 ⁴			KMB-7
	n = 10	σ	n = 5	σ								
wt. %												
SiO ₂	49.95	0.48	50.19	0.23	53.83	50.3	50.3	52.7	51.7	50.7	50.5	48.6
TiO ₂	1.17	0.07	–	–	0.81	1.3	2.0	–	1.5	–	2.3	1.3
Al ₂ O ₃	16.14	0.20	16.85	0.11	16.13	14.9	13.8	17.0	16.7	19.0	13.9	16.8
FeO	11.68	0.23	11.89	0.24	9.19	12.5	13.0	9.6	10.0	9.9	12.9	9.7
MnO	0.10	0.03	0.10	0.03	0.06	0.2	0.2	–	–	–	–	0.2
MgO	7.16	0.12	7.14	0.05	7.35	7.0	6.6	7.4	7.0	6.9	6.9	6.5
CaO	10.21	0.21	10.39	0.23	8.47	11.1	10.9	10.1	9.9	10.1	10.7	13.5
Na ₂ O	3.31	0.06	3.15	0.04	3.71	2.6	3.1	3.2	3.2	2.9	2.5	2.3
K ₂ O	0.28	0.02	0.29	0.00	0.45	0.1	0.2	–	–	0.5	0.3	1.1
total	100.00		100.00		100.00	100.0	100.0	100.0	100.0	100.0	100.0	100.0
mg#	0.52		0.52		0.59	0.50	0.55	0.47	0.56	0.52	0.49	0.57
ppm												
Li	92		91						247			
Sc	83		69						148			
Ti	–		67						–			
V	48		62						–			
Sr	36		48						113			
Y	40		35						102			
Zr	145		140						151			
Nb	120		128						135			
Ba	9		49						97			
La	158		174						131			
Ce	167		178						137			
Nd	176		186						176			
Sm	163		181						180			
Eu	207		261						192			
Yb	143		155						249			
Lu	133		143						143			
Hf	39		46						231			
Ta	36		35						120			
Th	268		240						229			
U	257		244						241			

¹Liu *et al.* (1996). Mixture of glass + crystals²Forneris & Holloway (2004). Mixture of glass + crystals³Schmidt & Poli (1998). Mixture of glass + crystals⁴Doped oxide mix (also includes Be, B, Cs, Rb, Gd, Dy, Er, Pb) used by Kessel *et al.* (2005a).⁵Prouteau *et al.* (2001). Glass.⁶Staudigel *et al.* (1996). Average of altered MORB.

Doping levels for each element were of the order of 200 ppm or less and were chosen to be sufficient to ensure detectability in run products by ion-microprobe analysis.

The decarbonated, denitrified trace element-doped mixture was pressed into pellets and equilibrated in a

CO–CO₂ gas mixing furnace at an oxygen fugacity (f_{O_2}) corresponding to the nickel–nickel oxide buffer (NNO) at 1000°C for 2 h. The colour of the pellet changed from red to grey, indicating that most of the Fe³⁺ in the starting material had been reduced to Fe²⁺. Using the method of

Kress & Carmichael (1991) the $\text{Fe}^{3+}/\text{Fe}^{2+}$ is estimated to be ~ 0.3 for $f\text{O}_2 = \text{NNO}$ and 1000°C . This approach was used to obtain an $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in the starting glass corresponding to the estimated $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio under the desired experimental conditions. To test homogeneity of the starting material (KBl and KBlOT) a total of three pieces from different parts of the pellets were melted to a glass in a Pt crucible in air for 15 min at 1600°C and 1 atm. The glasses were mounted into araldite resin, diamond polished and analysed by electron microprobe analysis (EMPA) and ion-microprobe for major and trace element concentrations, respectively (Table 1).

Subduction zone melting occurs under relatively oxidizing conditions (Carmichael, 1991). To simulate realistic trace element behaviour, especially for polyvalent elements such as U and Eu, it is necessary to buffer experiments appropriately. We controlled the $f\text{O}_2$ using a conventional double capsule technique with a solid metal-metal oxide mixture in the outer capsule (Chou, 1987). Approximately 10 mg of the starting materials were sealed together with 20 wt % of H_2O , added with a micro-syringe, into $\text{Ag}_{70}\text{Pd}_{30}$ capsules (o.d. 2.2 mm; thickness 0.1 mm) using an oxyacetylene welder. $\text{Ag}_{70}\text{Pd}_{30}$ was chosen to minimize Fe loss from the glass to the capsule and to provide a good permeability to H_2 to quickly obtain $f\text{O}_2$ equilibration with the buffer. The capsules were wrapped in wet tissues and frozen in liquid nitrogen to avoid H_2O loss during welding. The capsules were weighed before and after welding and only capsules that showed almost no weight loss were used in the experiments. The sealed AgPd capsules were then enclosed in Au capsules (o.d. 3 mm; thickness 0.15 mm), together with a mixture of Ni, NiO and small quantities of H_2O , and arc-welded shut. Again, the capsules were wrapped in wet tissues and frozen in liquid nitrogen to avoid any H_2O loss during welding. Both Ni and NiO were detected in the outer capsule at the end of each run. It should be noted that because both the inner and outer capsules are H_2O -saturated in the experiments the $f\text{O}_2$ is buffered close to NNO; the true $f\text{O}_2$ may be slightly lower than NNO because of the dissolved silicate components in the fluid at run conditions (e.g. Klimm *et al.*, 2003).

The experiments were carried out in a 1.27 cm diameter (half-inch) end-loaded piston-cylinder apparatus at Bristol University at a pressure of 2.5 GPa and temperatures between 750 and 900°C . Using the double-capsule technique with AgPd capsules and NNO buffer it was not possible to perform experiments at temperatures $>900^\circ\text{C}$ because Ni diffuses into the capsule wall and forms an alloy with Pd. At $T \geq 950^\circ\text{C}$ this reaction results in leakage of the capsule after only 1 day. The minimum experimental temperature was chosen to be just above the H_2O -saturated solidus at 2.5 GPa (i.e. 720°C), based upon the experiments of Liu *et al.* (1996) on a chemically similar

basalt (Table 1). The pressure medium was NaCl. Crushable alumina was used only to protect the thermocouple. The double capsule was pressed into NaCl and loaded into the graphite furnace. The low-friction NaCl assembly requires a friction correction of $\sim 3\%$ (McDade *et al.*, 2002). The runs were performed using the hot 'piston-in' routine. First, a pressure of 1 GPa was applied. The sample was heated to 500°C and temperature and pressure were then raised simultaneously. Upon reaching the final experimental temperature the last 0.1 GPa of pressure was applied. Pressure was kept constant during runs to ± 0.05 GPa, by manual adjustment when necessary. Temperatures were measured with calibrated $\text{W}_{95}\text{Re}_{5}$ – $\text{W}_{75}\text{Re}_{25}$ thermocouples inserted axially into the assembly using four-bore, high-purity Al_2O_3 tubing. Run durations were 3–7 days to ensure maximum equilibration (Liu *et al.*, 1996; Forneris & Holloway, 2003), although Kessel *et al.* (2005a, 2005b) showed that shorter run durations are sufficient to obtain chemical equilibrium in similar H_2O -rich systems. Experiments were quenched isobarically by manually adjusting the pressure during cooling.

After quenching, the capsules were cleaned in H_2O to dissolve any remaining NaCl and reweighed. Capsules showed no weight loss after the experiments. The entire capsules, inner and outer, were mounted in araldite and carefully polished with abrasive paper. When reaching the buffer assemblage in the outer capsule, or the sample in the inner capsule, H_2O was released, indicating that excess H_2O was present during the experiments in both capsules. The run products were extremely brittle because of the high H_2O content of the charges and further araldite had to be added to avoid loss of the run products. The final polishing was performed with a series of diamond pastes in the absence of additional water.

ANALYTICAL METHODS

Compositions of crystalline phases (except epidote group minerals and rutile) were determined by EMPA on a Cameca SX100 at Bristol University with 15 kV acceleration voltage, 15 nA sample current and focused electron beam. To minimize the migration of alkalis during analysis of hydrous, sodium-rich glasses the analytical conditions were 15 kV, 4 nA and 5 s total counting time for Na (measured first) and the beam was defocused to $15\text{ }\mu\text{m}$ (lowest value was $5\text{ }\mu\text{m}$ for Run 12 because of the small size of the glass pools). Under these conditions Na loss has been shown to be minimal (Humphreys *et al.*, 2006). Allanite and rutile were analysed using a 20 kV and 20 nA beam with a focused spot. Major elements were calibrated on natural and synthetic mineral, metal and oxide standards. Trace element contents of rutile and epidote group minerals were also analysed for the following trace elements using EMPA: V, Sr, Y, Nb, La, Ce, Nd, Sm, Ta, Th, U. Oxides, SrTiO_3 and rare earth element (REE)-doped

glasses were used as calibrants. Minimum detection limits under these conditions were as follows: 50 ppm for Y; 200 ppm for U and Th; 820 ppm for Sr; 1400 ppm for La; 1200 ppm for Ce; 1000 ppm for Nd and Sm; 900 ppm for Ta; 520 ppm for V; 330 ppm for Nb.

Trace element analysis of garnet and quenched glasses in selected runs was carried out using a Cameca IMS-4f ion-microprobe at the University of Edinburgh with a nominal 10 kV primary beam of O⁺ ions. Positive secondary ions were accelerated to 4.5 keV, with an offset of 75 ± 10 eV to reduce the transmission of molecular ions. Beam current was 2–5 nA, resulting in a spot size at the sample surface of *c.* 20 µm diameter. Analysis of relatively small crystals by ion-microprobe carries the risk of contamination by adjacent glass and vice versa. All ion-microprobe pits were examined by scanning electron microscopy (SEM) after analysis, to select only those that showed no evidence of cross-contamination. The masses ⁷Li, ³⁰Si, ⁴²Ca, ⁴⁴Ca, ⁴⁵Sc, ⁴⁷Ti, ⁵¹V, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ¹³⁸Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴³Nd, ¹⁴⁹Sm, ¹⁵¹Eu, ¹⁷¹Yb, ¹⁷³Lu, ¹⁷⁸Hf, ¹⁸¹Ta, ²³²Th and ²³⁸U were counted and ratioed to ³⁰Si, as determined by EMPA of an adjacent spot. Molecular ion interferences (e.g. ²⁹Si¹⁶O on ⁴⁵Sc) were removed by conventional peak stripping. In the case of light REE (LREE) oxide interferences on heavy REE (HREE), Hf and Ta, and BaO on Eu, these are greatly minimized in our experiments by the careful choice of elements and their doping levels. This is not possible when using natural, undoped starting materials. Ion yields were calibrated on NIST standard reference material (SRM) 610 (Hinton, 1990). Garnet DD1 (Irving & Frey, 1978) was analysed as a secondary standard. There are small, but systematic differences in ion-yield between SRM 610 and natural silicate minerals and glasses (both hydrous and anhydrous). We have made no corrections to our data for these effects, which largely serve to cancel each other out when calculating partition coefficients. The effect should, however, be borne in mind when comparing EMPA and ion-microprobe values for CaO and TiO₂, which the ion-microprobe consistently underestimates by 21% and 15% (Green *et al.*, 2000), respectively, relative to EMPA for both minerals and glasses.

EXPERIMENTAL RESULTS

Experimental conditions, run products and their phase proportions, obtained by least-squares mass balance, are listed in Table 2. All runs contained large (20–50 µm diameter) euhedral garnets (Fig. 2), typically with small clinopyroxene inclusions (Fig. 2b), small groundmass clinopyroxene (<10 µm), rutile (typically 1–2 µm; up to 5 µm at 750°C; Fig. 2d) and angular vesicular shards of silicate glass (quenched liquid) of trondhjemitic to haplogranitic composition up to 100 µm in length (Fig. 2e). Glass occurs throughout the capsules, but a slight concentration of the glass at the top of the capsule as a result of

thermal gradients is observed. Runs at 750°C (Fig. 2d) showed significantly smaller, more vesicular glass pockets than runs at >750°C (Fig. 2b), indicating that the water content in the liquid was higher and that a significant melt-producing reaction occurs between 750 and 800°C (see below). Runs at 750°C contained, in addition, REE-poor epidote (~10 µm) and staurolite. Runs at >750°C contained REE-rich epidote (allanite) as small grains ~5 µm across. Staurolite, in equilibrium with silicate melt, has been observed in several previous studies of H₂O-saturated melting of basalt at very similar pressures and temperatures (Hellman & Green, 1979; Poli & Schmidt, 2002; Forneris & Holloway, 2003; Green & Adam, 2003).

Aqueous fluid, hydrous melt or supercritical liquid?

The quenched glass is highly vesicular (Fig. 2d and e) and has textures similar to the porous aggregates of quench solute in experiments at 3 GPa and 650–700°C described by Green & Adam (2003). The porous textures of the glass indicate that at the end of the experiments, during isobaric cooling ('quenching'), the liquid in the capsule separated into a fluid or vapour phase and a hydrous melt or glass. Thus, during the experiment the liquid had higher H₂O contents than the quenched glass. This suggests that a separate H₂O-rich fluid phase may have been absent at run conditions, indicating 'supercritical' behaviour; that is, a complete miscibility between the melt and the fluid. In the following discussion we compare our experimental glasses with recent experimental studies on the critical curves in several silicate–H₂O systems.

Our experiments confirm that partial melting of basalt at high pressure and slightly above the basalt solidus forms H₂O- and silica-rich liquids of trondhjemitic to haplogranitic composition (e.g. Ernst & Liu, 1998; Prouteau *et al.*, 2001). It has been shown experimentally that at high pressures H₂O-rich silicic liquids of similar composition may cross the second critical endpoint, beyond which the conventional designation of solidus, melt and vapour is lost (e.g. Bureau & Keppler, 1999; Manning, 2004; Hermann *et al.*, 2006). The exact pressure depends on the bulk chemical composition (Bureau & Keppler, 1999). The second critical endpoint corresponds topologically to the intersection of the melt–vapour critical curve and the H₂O-saturated solidus, both of which are constrained for haplogranite compositions from the work of Bureau & Keppler (1999) and Holtz *et al.* (2001), respectively (see also Hermann *et al.*, 2006). In Fig. 3 we show the available experimental data for the haplogranite critical curve with our extrapolation to the second critical endpoint in this system (2.5 GPa and 640°C). Our experiments lie above the critical curve and thus, for the sub-system H₂O–haplogranite, are likely to involve a miscible liquid rather than a melt plus fluid phase, in agreement with our interpretation of the

Table 2: Experimental results and calculated proportion of phases (wt %) at 2.5 GPa and $\log f_{O_2} = NNO$

Run	<i>T</i>	Duration	H ₂ O _{in} ¹	cH ₂ O ²	Results ³							Σ <i>r</i> ² ⁴
	(°C)	(days)	(wt%)	(wt%)	gl/ <i>liquid</i>	grt	cpx	rt	ep/aln ⁵	am	other	
<i>KB1</i>												
12	750	7	20.2	17.1	8.3	21.8	27.0	0.9	14.9	27.0	st	0.7
				<i>74.7</i>	<i>26.2</i>	<i>17.4</i>	<i>21.5</i>	<i>0.7</i>	<i>12.1</i>	<i>22.1</i>		
16	800	6	20.2	19.7	20.6	46.6	32.1	0.6	0.8	—	—	0.6
				<i>55.1</i>	<i>36.6</i>	<i>37.2</i>	<i>25.6</i>	<i>0.5</i>	<i>0.8</i>			
13	850	4	19.3	15.9	23.4	50.0	26.4	0.2	0.6	—	—	0.3
				<i>50.5</i>	<i>38.2</i>	<i>40.4</i>	<i>21.3</i>	<i>0.2</i>	<i>0.6</i>			
20	900	3	19.8	23.2	27.4	51.1	21.4	0.1	0.5	—	—	0.9
				<i>47.4</i>	<i>41.8</i>	<i>41.0</i>	<i>17.2</i>	<i>0.1</i>	<i>0.5</i>			
<i>KB1oT</i>												
19	850	4	19.4	23.2	24.8	54.2	21.0	—	0.6	—	—	0.8
				<i>49.3</i>	<i>39.4</i>	<i>43.7</i>	<i>16.9</i>		<i>0.6</i>			
<i>KB1 + omph</i> ⁶												
18	850	4	21.3	—	x	x	x	x	x	—	—	
<i>KB750</i> ⁷												
15	750	12	20.8	22.4	X	x	x	x	x	x	st	

¹Water loaded in the capsule (in wt%).²Water contents of residual glasses determined following the difference method. Numbers in italics indicate calculated water content in a liquid assuming miscibility between fluid and melt at run conditions and that all the added H₂O_{in} is concentrated in that liquid (except for run 12, cH₂O is reduced taking into account the high abundance of hydrous epidote and amphibole with 1.5 and 2 wt% H₂O, respectively).³Phases present in run products. When present, amount of crystals/glass was calculated by mass-balance calculation with least-squares minimization on anhydrous and hydrous basis (numbers in italics). In runs with insufficient microprobe analysis presence of phase is indicated with x. fl, fluid; gl, glass; grt, garnet; cpx, clinopyroxene (omphacite); rt, rutile; ep, epidote; am, amphibole; aln, allanite; st, staurolite. Fluid was present in all runs.⁴Sum of residual squares obtained by the mass-balance calculations.⁵Abundance of aln in runs 16, 13, 20 and 19 calculated on the basis of Ce concentration in the aln, glass and starting material.⁶Starting composition for this run was KB1 + 10 wt% omphacite crystals separated from a natural eclogite (Naxos, Greece).⁷Starting composition for this run was KB1 + 10 wt% oxide mixture compositional identical to glass composition of Run 12 (see Table 1).

glass texture. At lower pressure, below the critical curve (Fig. 3), a hydrous melt, hydrous melt + aqueous fluid or an aqueous fluid with dissolved granitic solute is present, depending on the H₂O content in the system (Bureau & Keppler, 1999). It should be noted that our glass composition is trondhjemitic and therefore also chemically close to the albite–H₂O system. In this system Paillat *et al.* (1992) and Bureau & Keppler (1999) have shown that the second critical endpoint is expected to occur at even lower pressures of ~1.5 GPa and temperatures of ~670°C. Spandler *et al.* (2007) studied the pelite–H₂O system and from fluid or melt inclusions trapped during the experiments they concluded that at 700–750°C and 2.2 GPa fluid + melt (close to haplogranite composition) is present and thus, these *P–T* conditions are below the critical curve, thereby

bracketing the critical curve between 2.2 and 2.5 GPa at 750°C (Fig. 3). This is not in agreement with Bureau & Keppler (1999) and can be explained by (1) the fact that Spandler *et al.*'s melt is not strictly haplogranitic and contains additional FeO, MgO and CaO, or (2) the *P–T* calibration of Bureau & Keppler (1999) in the diamond anvil cell is not precise and the critical curve may be shifted to higher pressures, or (3) the presence of phosphorus as an additional volatile in the experiments by Spandler *et al.* (2007) changes the fluid composition and reduces the water activity in the fluid in a fashion similar to CO₂ + H₂O such that they determined the second critical endpoint in pelite + H₂O + P rather than pelite + H₂O.

It should also be noted that our bulk system is MORB–H₂O, for which the second critical endpoint proposed by

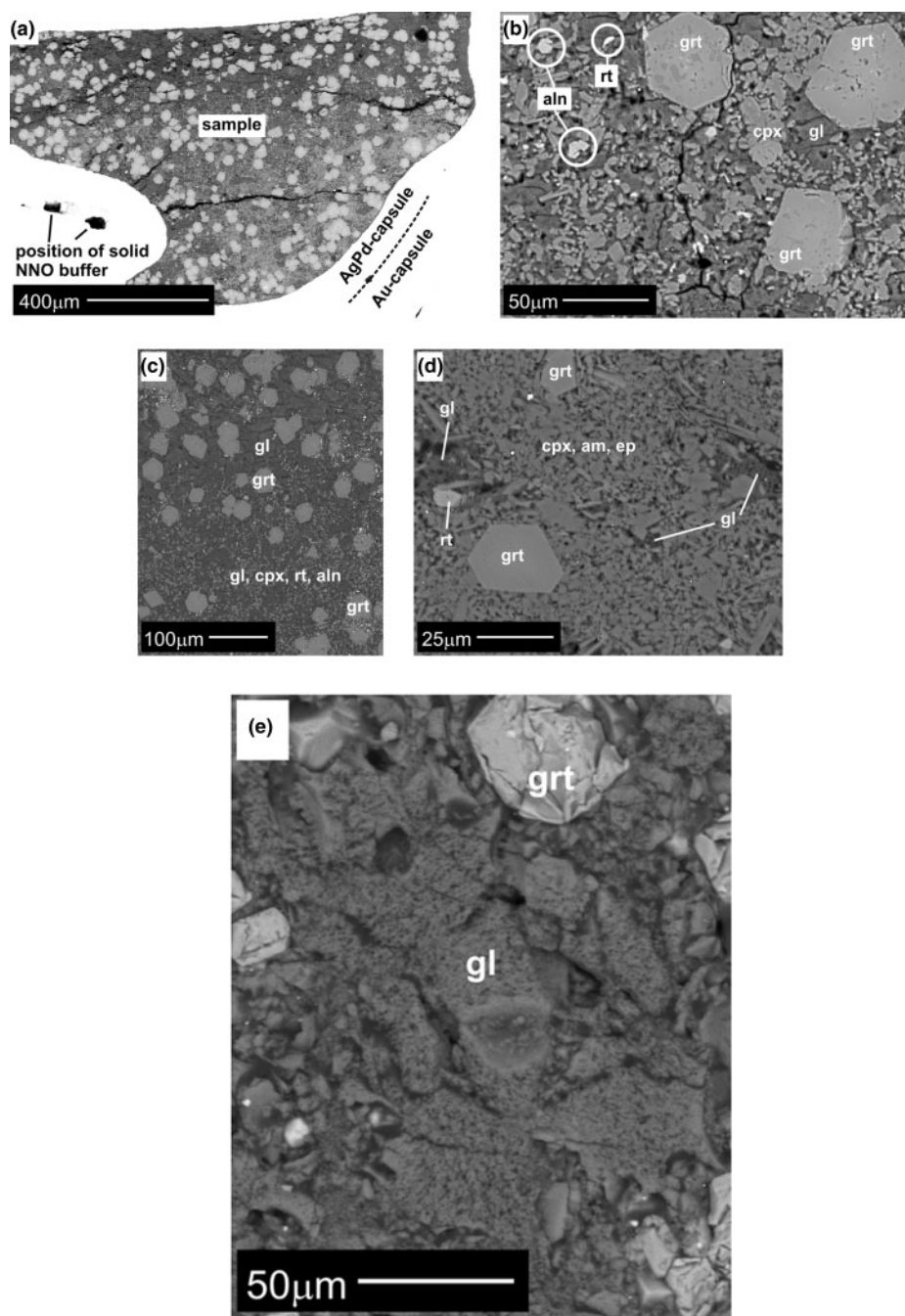


Fig. 2. Backscattered SEM images of experimental run products. (a) R13 (850°C), representative image of the double capsule assemblage after the experiment showing a homogeneous distribution of all phases. The liquids are slightly concentrated to the top of the capsule. (b) R13 (850°C), close-up of the eclogitic residue consisting of grt, cpx, rt and aln set in vesicular glass matrix. (c) R20 (900°C). (d) R12 (750°C), highly crystalline sample containing grt, rt, cpx, am, ep and interstitial vesicular glass. Ep in the matrix appears slightly brighter than cpx and am. (e) R16 (800°C), representative close-up of the highly vesicular glass. Image was taken before the sample was impregnated with resin and repolished for analysis.

Kessel *et al.* (2005b) is at a substantially higher pressure of 6 GPa. Their determination of the second critical endpoint is based on the evolving chemistry of the melt and fluid phase in diamond trap experiments; this marks the point

at which the H₂O in the liquid gradually decreases and the concentration of all oxides gradually increases. At pressures below 6 GPa, Kessel *et al.* (2005b) observed a concentration step of all oxides in the liquid as a function of

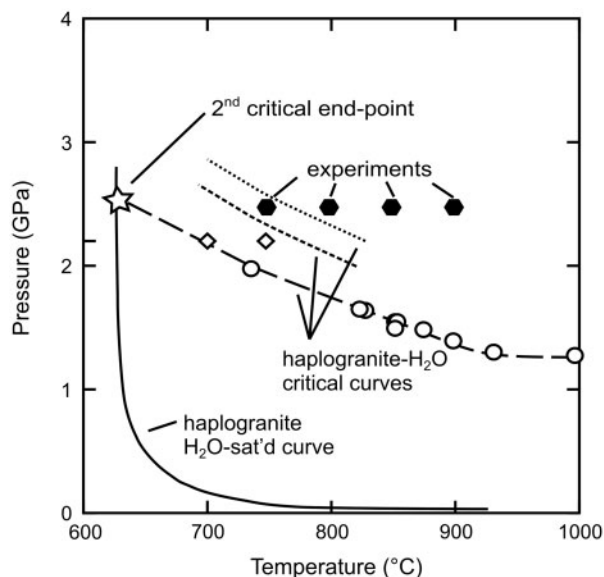


Fig. 3. Projected second critical endpoint (open star) based on intersection of haplogranite critical curve (open circles and long-dashed curve; Bureau & Keppler, 1999) and the haplogranite solidus (Holtz *et al.*, 2001). Experiments of this study are shown as filled hexagons. Open diamonds: Spandler *et al.* (2007), pelite–H₂O system with coexisting melt of granitic composition and fluid. This may shift the haplogranite–H₂O critical curve to higher pressures (short-dashed line). However, the presence of phosphorus may have an influence on the fluid composition, and thus the short dashed curve could represent the minimum pressures of the critical curve in the system pelite–H₂O–P. Because melting is not completed at 750°C as a result of the presence of epidote and amphibole, the critical curve for our liquids may be above 750°C at 2.5 GPa (dotted curve).

temperature defining the solidus in the MORB–H₂O system. These steps occur between 850–900 and 1000–1050°C at 4 and 5 GPa, respectively. However, it remains unclear from Kessel *et al.*'s textural descriptions and liquid composition above the solidus, especially at 5 GPa, if that liquid consisted of a single phase or an immiscible mixture of melt + fluid. At 2.5 GPa the H₂O-saturated solidus for MORB is at ~720°C (Liu *et al.*, 1996) and we would expect only a fluid phase present in our system below this temperature according to Kessel *et al.* (2005b). It is difficult to clarify from our experimental textures if the liquid in the run at 750°C quenched from a single-phase liquid because of the rather small size of the glass pools. The glass composition is different from that in the runs at higher temperature (more FeO, MgO and CaO; see below) and the glass appears to be even more vesicular (Fig. 2d). Thus, at 750°C a melt + fluid may have been stable, indicating that for this melt composition the *P*–*T* conditions fall below the critical curve (Fig. 3).

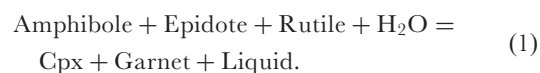
It is clear that the issue of supercritical behaviour in natural systems is far from being resolved and more systematic studies are required. In the subsequent discussion we refer to the hydrous silica-rich phase in our experiments as a 'supercritical liquid' and its quench product as 'glass'. It is

important to note that the key conclusions of our work, regarding residual phase stability and trace element transport out of the basalt during H₂O-fluxing, are not materially affected by the exact nature of the liquid in our experiments.

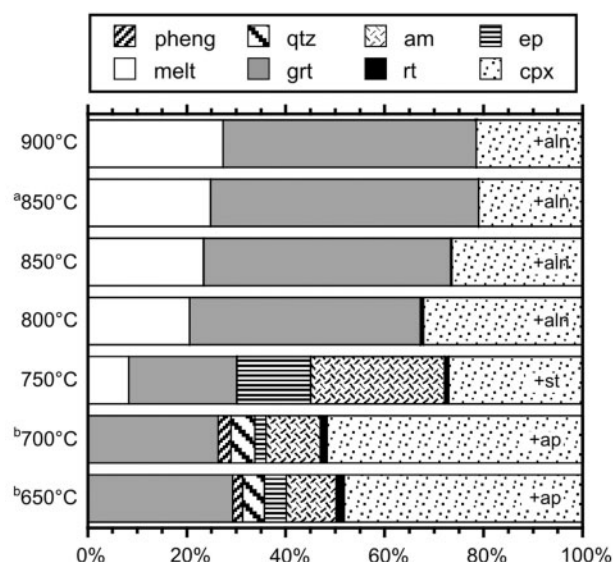
Phase proportions

It is important to note that, because the liquid in our experiments is likely to be supercritical, the calculated glass fractions in Table 2 are not the same as the liquid fractions as a result of exsolution of H₂O-rich vapour during quench. As a consequence, the liquid fraction at any given temperature is greater than the calculated glass fraction (Table 2). It is a feature of supercritical liquid production that the amount of liquid at any given temperature depends primarily on the H₂O content of the starting material. This is in strong contrast to conventional hydrous melting, where the liquid composition and proportion are controlled by the solubility of H₂O. It is useful to bear this important distinction in mind when we discuss the implications of our results in a later section.

Phase proportions show systematic changes with temperature, as shown in Fig. 4. In this figure we have supplemented our data with modes from the experiments of Forneris & Holloway (2004) on a very similar basalt (Table 1) at 650°C, 2.6 GPa and 700°C, 2.4 GPa, to show better the full evolution with temperature. Below 750°C the assemblage comprises predominantly garnet and omphacitic clinopyroxene with lesser epidote, amphibole, phengite, quartz and rutile, but no quenched glass. Glass appears between 700 and 750°C, in agreement with the experimental determination of Liu *et al.* (1996). It is difficult to constrain the glass-producing reaction that occurs between 700 and 750°C because of the minor differences in bulk composition between our experiments and those of Forneris & Holloway (2004). This may account for the higher amphibole proportion in our 750°C experiment than the 700°C experiment of Forneris & Holloway (2004). Nonetheless, the absence of phengite in our experiments suggests that this phase plays a key role at temperatures below 700°C. At 750°C staurolite joins the silicate assemblage. The glass fraction increases dramatically from 8 to 21 wt % between 750°C and 800°C. This increase coincides with the total disappearance of amphibole and REE-poor epidote and a small reduction in the rutile mode. There is a corresponding increase in omphacitic clinopyroxene and, to a greater extent, garnet, suggesting that the predominant liquid-producing reaction is a peritectic of the form



The appearance of trace amounts of allanite at 800°C suggests that the liquid-producing reaction is also peritectic



^a Ti-free starting material

^b Data from Forneris & Holloway (2004)

Fig. 4. Phase proportions (in wt%) as given in Table 2, augmented with data of Forneris & Holloway (2004) at 650°C, 2.6 GPa and 700°C, 2.4 GPa for comparison. Accessory phases are allanite (aln), staurolite (st) and apatite (ap).

with respect to epidote, such that during melting REE become progressively concentrated in epidote, forming allanite via the reaction



This aspect of the melting behaviour will be discussed in more detail below.

From 800 to 900°C there is relatively little change in phase proportions. The glass fraction increased from 21 to 27 wt % and there is a progressive increase in the ratio of residual garnet to clinopyroxene from 1.5 to 2.4. Rutile and allanite persist across this temperature interval, although the proportion of both diminishes. In the case of rutile this is a combination of the increasing solubility of TiO₂ in the liquid and the increasing partitioning of TiO₂ into garnet with increasing temperature (see Klemme *et al.*, 2002). There is minimal difference in phase assemblage between the Ti-bearing and Ti-free runs at 850°C, apart from the fact that the latter lacks rutile.

Major element phase chemistry

Glasses

Glasses have been analysed successfully in experiments at all temperatures (Table 3). Glasses are consistently trondhjemitic in composition with very high contents of alkalis, especially Na₂O, and low contents of MgO and FeO, despite being in equilibrium with garnet and clinopyroxene. The shortfall from 100% totals is of the order of

20 wt %, but we attach very little significance to this as regards the original H₂O content of the glasses given the evidence for vesiculation and H₂O loss during quenching. It has to be noted that no quench crystals have been identified within the glass shards, indicating that the glass composition has not been significantly modified by crystallization upon quenching.

Glasses show systematic chemical variations with temperature. In Fig. 5 we compare our glass analyses with those of Prouteau *et al.* (2001) and Ernst & Liu (1998), who also performed H₂O-saturated experiments on MORB-like starting materials at pressures of 2.2–2.4 and 3 GPa, respectively. We have selected only those glasses that are in equilibrium with an eclogite assemblage of garnet + omphacite ± amphibole ± rutile. When recalculated on an anhydrous basis, glasses show smoothly decreasing SiO₂ and increasing Al₂O₃ with increasing temperature. TiO₂ also increases steadily, consistent with increasing rutile solubility at higher temperature (Ryerson & Watson, 1987). Our data compare remarkably well with Ryerson & Watson's (1987) rutile solubility model, despite the fact that our experimental temperatures are well below the range used for their calibration (1000–1300°C). In our experiments TiO₂ increases from 0.12 ± 0.01 wt % at 750°C to 0.52 ± 0.03 at 900°C. Using Ryerson & Watson's melt compositional parameter, *FM*, from our experiments we calculate TiO₂ contents (on an anhydrous basis), at rutile saturation, of 0.16 wt % at 750°C and 0.48 wt % at 900°C.

The Na₂O content of the glass appears to show a marked peak at ~800°C, probably corresponding to the total consumption of amphibole at around this temperature. At temperatures above 800°C Na₂O starts to fall, as a result of dilution with other components. [We note that Ernst & Liu (1998) used a highly focused electron beam to analyse their glasses, which may have lost significant Na₂O as a consequence.]

Garnets

Garnets comprise sub-equal proportions of grossular, almandine and pyrope components, with subordinate (<8 mol%) andradite (Table 3). In each experiment garnets show zoning from Fe-rich cores to Mg-rich rims, as previously observed in experiments on H₂O-saturated basalts in which garnet seeds were used (Schmidt & Poli, 1998; Forneris & Holloway, 2003). The overall change in mg-number from core to rim is 0.05–0.10. In Table 3 we list the global average composition of all garnets analysed, together with the average of the 2–7 points closest to the outermost rim. For mass-balance purposes we used the global average; when discussing chemical trends with increasing temperature we take the rim composition.

Garnet chemistry varies systematically with temperature. In Fig. 6 we show the composition of garnet rims

Table 3: Major element composition of experimental run products (except rutile and allanite)

Run	Phase	<i>n</i>	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Total	
12	gl	2	62.92 (44)	0.10 (1)	12.42 (12)	0.26 (5)	0.00 (0)	0.12 (1)	1.42 (10)	3.33 (21)	1.44 (5)	81.99	
	grt	bulk	21	39.03 (68)	0.69 (20)	21.39 (47)	24.19 (182)	0.27 (12)	5.94 (133)	9.66 (46)	0.06 (6)	0.01 (1)	101.23
		rim	6	39.82 (39)	0.50 (9)	21.80 (10)	21.93 (52)	0.17 (2)	7.64 (31)	9.50 (47)	0.12 (11)	0.01 (1)	101.48
	cpx	5	54.27 (59)	0.27 (7)	10.08 (49)	9.36 (84)	0.10 (4)	8.43 (39)	14.09 (47)	4.65 (60)	0.03 (5)	101.28	
	am	2	49.39 (28)	0.41 (0)	12.38 (20)	12.51 (121)	0.08 (3)	11.64 (53)	6.20 (122)	3.13 (5)	0.30 (12)	96.04	
	st	2	28.66 (28)	1.24 (15)	52.15 (165)	9.93 (18)	0.05 (4)	5.01 (26)	0.44 (27)	0.24 (13)	0.00 (1)	97.74	
16	gl	4	58.41 (44)	0.31 (6)	12.47 (53)	0.20 (9)	0.00 (0)	0.05 (1)	0.22 (3)	7.07 (23)	1.02 (7)	79.74	
	grt	bulk	9	38.58 (31)	0.83 (14)	21.93 (64)	19.86 (156)	0.19 (4)	7.27 (135)	11.63 (114)	0.06 (2)	0.00 (0)	100.35
		rim	3	38.50 (57)	0.72 (5)	22.15 (46)	19.12 (38)	0.15 (4)	8.49 (23)	11.24 (24)	0.06 (2)	0.01 (0)	100.43
	cpx	4	53.60 (26)	0.32 (5)	8.75 (22)	5.46 (43)	0.01 (3)	11.51 (39)	16.68 (13)	4.40 (23)	0.02 (1)	100.75	
13	gl	6	60.59 (70)	0.23 (7)	13.38 (30)	0.43 (12)	0.01 (2)	0.04 (2)	0.73 (11)	7.77 (26)	0.99 (16)	84.17	
	grt	bulk	29	38.48 (79)	1.58 (32)	20.86 (67)	20.44 (204)	0.26 (13)	7.68 (177)	11.25 (88)	0.14 (14)	0.01 (1)	100.69
		rim	7	39.01 (21)	1.19 (20)	21.53 (13)	18.06 (33)	0.15 (5)	9.92 (56)	10.41 (89)	0.11 (5)	0.01 (1)	100.39
	cpx	4	53.21 (73)	0.50 (7)	8.20 (44)	5.09 (58)	0.03 (3)	12.04 (20)	17.52 (27)	4.18 (23)	0.01 (1)	100.78	
20	gl	4	55.75 (129)	0.41 (3)	13.65 (39)	0.47 (23)	0.02 (3)	0.05 (7)	0.67 (25)	6.91 (32)	0.96 (24)	78.90	
	grt	bulk	19	37.98 (66)	1.86 (16)	20.01 (66)	20.30 (151)	0.25 (10)	7.01 (109)	12.06 (60)	0.08 (3)	0.00 (0)	99.55
		rim	2	38.26 (26)	1.63 (9)	20.31 (29)	17.58 (31)	0.11 (1)	9.35 (81)	11.43 (52)	0.10 (1)	0.01 (1)	98.78
	cpx	4	53.16 (36)	0.34 (7)	4.92 (67)	6.06 (12)	0.03 (2)	13.86 (85)	19.68 (23)	2.20 (24)	0.00 (0)	100.25	
19	gl	4	54.34 (90)	0.00 (0)	12.09 (21)	0.38 (8)	0.00 (0)	0.01 (1)	0.80 (13)	7.48 (25)	1.04 (3)	76.13	
	grt	bulk	19	39.25 (131)	0.02 (2)	21.39 (170)	19.15 (150)	0.15 (7)	7.77 (145)	12.05 (140)	0.15 (26)	0.01 (1)	99.93
		rim	4	39.60 (57)	0.01 (1)	22.51 (20)	18.16 (36)	0.09 (3)	9.82 (31)	10.13 (30)	0.05 (2)	0.01 (1)	100.39
	cpx	7	53.55 (104)	0.00 (0)	6.63 (68)	6.50 (84)	0.03 (1)	11.95 (33)	18.31 (39)	2.79 (34)	0.02 (1)	99.78	
18	cpx	rim	4	54.30 (104)	0.11 (7)	6.57 (84)	4.08 (40)	0.15 (8)	11.60 (82)	17.59 (134)	4.41 (125)	0.01 (1)	98.81
15	am	4	48.15 (116)	0.63 (6)	12.41 (54)	12.47 (50)	0.07 (4)	13.62 (62)	6.29 (65)	3.80 (23)	0.33 (5)	97.78	
	st	2	29.54 (35)	0.70 (14)	52.98 (91)	10.33 (55)	0.04 (2)	4.36 (11)	0.22 (16)	0.03 (5)	0.01 (1)	98.21	

Abbreviations as in Table 2; *n*, number of analyses; numbers in parentheses are the standard deviation (σ) $\times$ 100.

from our experiments together with the garnet compositions from the long-duration 2.4–2.6 GPa runs of Pawley & Holloway (1993), Poli (1993) and Forneris & Holloway (2004), using similar basalt starting compositions. With increasing temperature the garnet mg-number increases progressively, corresponding to an increase in pyrope component from ~15 mol% at ~700°C to 36 mol% at 900°C. Over the entire temperature interval the grossular component remains at 24 ± 2 mol%. The TiO₂ content of garnet rims increases systematically with increasing temperature from 0.50 wt % at 750°C to 1.63 wt % at 900°C.

Clinopyroxenes

Average clinopyroxene compositions are reported in Table 3. Unlike garnets they show no evidence of compositional zoning and little inter-grain variation within a run. In an additional experiment at 850°C (Run 18) we added omphacite seeds from a Naxos eclogite to the KBl starting

material in an attempt to reproduce clinopyroxenes grown in the seedless experiments. Analyses of the chemically distinct rims grown on the seeds match exactly the small clinopyroxenes grown from both KBl (Run 13) and KBlot (Run 19) at the same temperature (Table 3, Fig. 7), providing evidence that these are equilibrium compositions.

All clinopyroxenes are omphacites with 0.15–0.30 Na atoms per formula unit (a.p.f.u.). There is exactly the same range in octahedral Al (Al^{VI}) content, indicating that Na is almost exclusively incorporated via the jadeite component, rather than acmite. With increasing temperature Na (and Al^{VI}) contents decrease systematically (Fig. 7b), whereas Ca contents increase (Fig. 7a). Clinopyroxenes from the experiments of Pawley & Holloway (1993), Poli (1993), Schmidt & Poli (1998) and Forneris & Holloway (2004) at 2.4–2.6 GPa lie at the low-temperature extrapolation of these trends (Fig. 7). TiO₂ contents are consistently low (≤ 0.5 wt %).

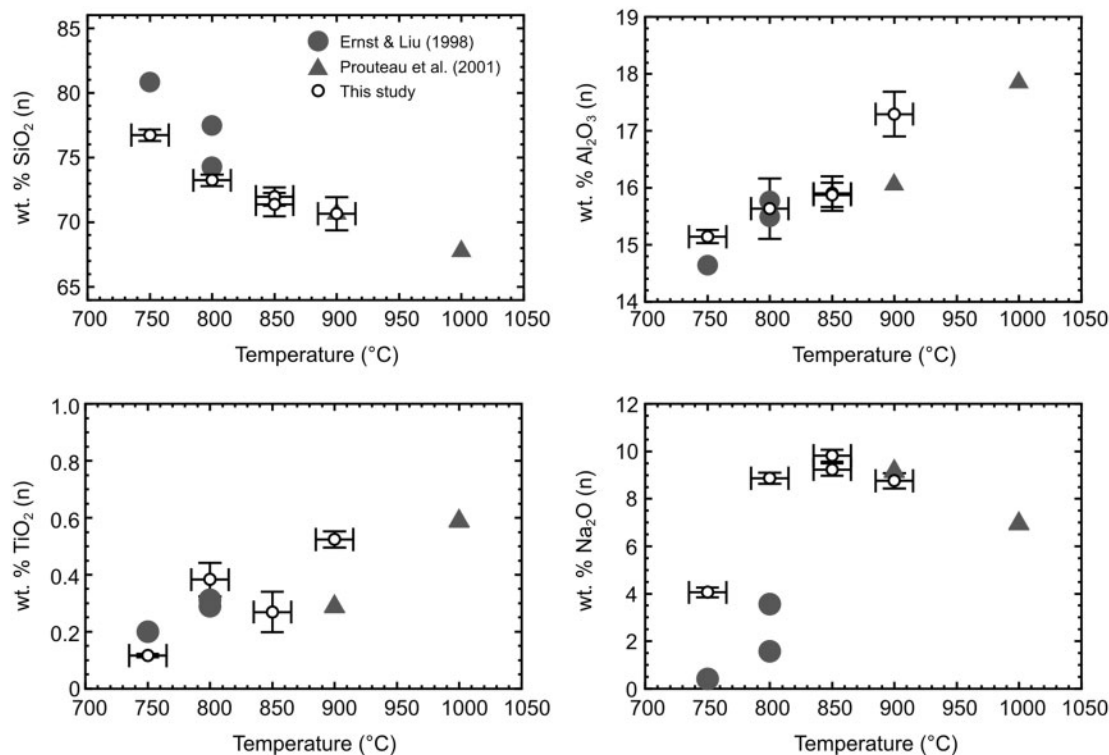


Fig. 5. Major element chemistry of quenched glasses (on anhydrous basis) from the experiments augmented with data from runs of Prouteau *et al.* (2001) and Ernst & Liu (1998) at 2.0 and 2.4 GPa, respectively, in equilibrium with eclogite residues. Error bars (1 SD) are shown for data from this study only.

Amphiboles

Amphiboles are confined to two experiments at 750°C (Table 2). In both cases the grains are very small and difficult to analyse even with a focused beam. There is a corresponding variability in composition in both runs, which may in part be a consequence of contamination by surrounding silicate phases. Conversely, it may be a reflection of the fact that our experiment was run very close to the upper stability pressure of amphibole. In the experiments of Forneris & Holloway (2003), for example, amphibole is no longer stable in the presence of glass above 2.5 GPa and over the pressure range 2.4–2.6 GPa it undergoes a dramatic change in composition at constant temperature. The experiments of Liu *et al.* (1996) show an upper pressure stability of 2.4 GPa for amphibole.

Despite the evidence for chemical heterogeneity in our amphiboles we have identified a dominant compositional population in both runs and this is reported in Table 3. In both runs the amphiboles are barroisite with approximately sub-equal amounts of Na and Ca on the M4 site [amphibole formulae were calculated using the method of Holland & Blundy (1994)]. These amphiboles are very similar in composition (Fig. 8) to those produced in experiments at 2.2–2.5 GPa by Poli (1993), Ernst & Liu (1998) and Forneris & Holloway (2003), but distinct from the

glaucophanic amphiboles produced at 2.6 GPa by Forneris & Holloway (2003). There is a weak covariation in Na^{M4} and octahedral Al (Al^{VI}; Fig. 8a) and stronger covariation in the temperature-sensitive exchange involving A-site cations and tetrahedral Al (Al^{IV}; Fig. 8b).

Epidote-group minerals

Epidote-group minerals are present in all runs. The epidotes in runs above 750°C are consistently fine-grained and difficult to analyse with the high electron beam currents required to determine REE, Th and U accurately. For that reason there is some compositional variability in each run as a result of contamination by adjacent phases, including glass. We have screened the epidote analyses from these runs for those with the lowest Na contents and closest approximation to ideal stoichiometry. It should be noted that Eu was not determined by EMPA, but based on partitioning arguments (see below) is likely to be present at concentrations of 1–2 wt % Eu₂O₃. The Eu₂O₃ contents listed in Table 4 are calculated from the liquid Eu concentration, as determined by ion-microprobe, and the Eu partition coefficient for epidote–liquid, D_{Eu} , extrapolated from D_{Sm} (see below).

There is a marked compositional change from REE-poor epidote at 750°C to REE-rich epidote at higher

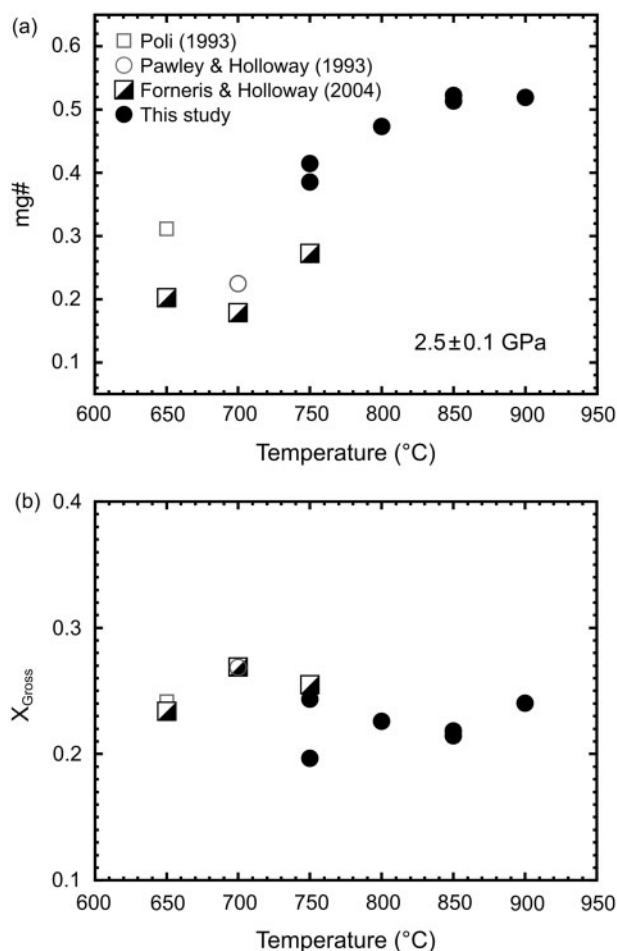


Fig. 6. Garnet chemistry as a function of temperature expressed in terms of (a) mg-number and (b) mole fraction grossular. Experimental data from this study are augmented with data at 2.5 ± 0.1 GPa from Pawley & Holloway (1993; open circles), Forneris & Holloway (2004; half-filled squares) and Poli (1993; open squares).

temperatures (Table 4). Epidotes at 750°C have negligible REE content, as determined by EMPA, and lie close to the epidote end-member. Higher temperature epidotes have 10–13 wt % total LREE₂O₃, 4–7 wt % ThO₂ and ~1 wt % UO₂. The REE-rich epidotes have ~0.4 LREE (La–Sm) a.p.f.u., and therefore lie midway between epidote and allanite. Because the total REE + Th + U contents amount to >0.5 a.p.f.u., they are, following Armbruster *et al.* (2006), members of the allanite subgroup. The incorporation of 3+ and 4+ cations onto the A-sites requires charge-balancing 2+ cations to substitute for Al and Fe³⁺ on the M-sites. All of the allanites produced above 750°C have high MgO contents (≤3 wt %). If estimated from stoichiometry, the Fe³⁺ contents of these allanites are negligible, such that FeO is of the order of 6–7 wt %. Thus these allanite subgroup minerals are

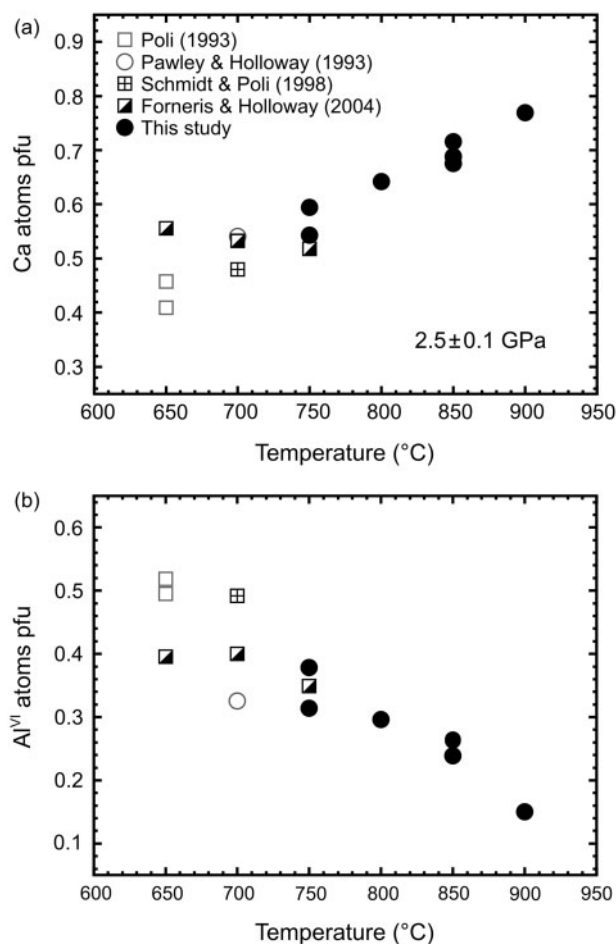
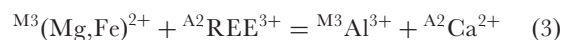
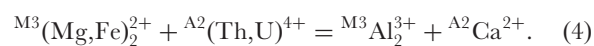


Fig. 7. Clinopyroxene chemistry as a function of temperature expressed in terms of (a) Ca atoms per formula unit (a.p.f.u.) and (b) octahedral Al a.p.f.u. Experimental data from this study are augmented with data at 2.5 ± 0.1 GPa from Pawley & Holloway (1993; open circles), Forneris & Holloway (2004; half-filled squares), Schmidt & Poli (1998; square with cross) and Poli (1993; open squares).

mixtures of allanite and dissakisite in which the dominant charge balancing mechanism for REE is



whereas for Th and U it is



In the discussion below we shall refer to the REE-rich epidotes in our experiments simply as ‘allanite’.

Substitution mechanisms (3) and (4) are consistent with the variation in natural REE-epidotes and allanites in rhyolitic volcanic rocks and high-grade metamorphic rocks (Fig. 9), which shows clearly that there is continuous solid solution from epidote-clinozoisite (0 REE a.p.f.u.) to allanite-dissakisite (1 REE a.p.f.u.). There is some non-stoichiometry in our experimental allanites as previously

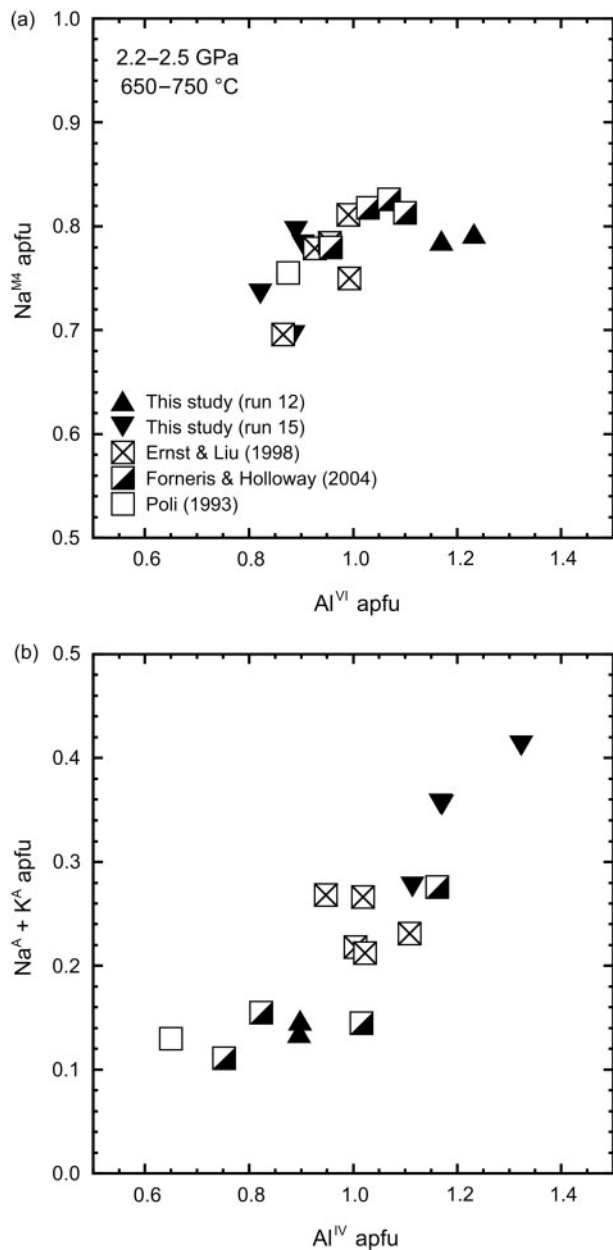


Fig. 8. Amphibole chemistry from runs 12 and 15 expressed as (a) Na on M4 site vs octahedral Al and (b) A-site occupancy vs tetrahedral Al. Multiple grains from each run are plotted to illustrate the chemical variation. Experimental data from this study are augmented with data at 2.2–2.5 GPa, 650–750 °C from Ernst & Liu (1998; square with cross), Forneris & Holloway (2004; half-filled squares) and Poli (1993; open squares).

observed in metamorphic REE-epidotes by Spandler *et al.* (2003) and in some rhyolitic allanites (Mahood & Hildreth, 1983; Chesner & Ettlinger, 1989). This non-stoichiometry is manifest as >3 Si a.p.f.u. on an eight-cation basis and a total charge of >25 with all Fe as Fe²⁺. Armbruster *et al.* (2006) suggested that, poor analysis

Table 4. Composition of experimental epidote-group minerals

Run:	12	σ	16	σ	13	σ	20	σ	19	σ
T (°C):	750	$n=3$	800	$n=2$	850	$n=2$	900	$n=2$	850	$n=2$
SiO ₂	43.53	1.67	36.73	1.26	34.07	0.38	33.24	1.24	36.05	0.89
TiO ₂	0.63	0.50	0.29	0.02	0.66	0.16	0.72	0.07	0.02	0.01
Al ₂ O ₃	25.82	1.36	21.43	0.21	19.10	0.74	17.89	0.71	19.57	0.71
FeO	8.32	0.13	5.61	0.01	6.52	0.32	6.81	0.43	6.07	0.25
MnO	0.05	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	1.79	0.39	2.65	0.06	2.74	0.09	3.10	0.16	2.69	0.04
CaO	16.45	1.69	12.77	0.03	12.81	0.72	12.37	0.45	10.55	0.72
Na ₂ O	1.23	0.63	0.59	0.11	0.63	0.14	0.31	0.06	2.23	0.85
K ₂ O	0.15	0.03	0.08	0.03	0.06	0.04	0.05	0.02	0.11	0.02
SrO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Y ₂ O ₃	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
La ₂ O ₃	0.13	0.00	2.59	0.25	3.38	0.29	3.92	0.00	4.07	0.52
Ce ₂ O ₃	0.13	0.04	2.33	0.28	3.00	0.23	3.58	0.05	3.25	0.46
Nd ₂ O ₃	0.10	0.05	2.12	0.37	2.73	0.09	2.71	0.01	2.47	0.32
Sm ₂ O ₃	0.09	0.01	1.70	0.18	1.66	0.06	1.04	0.03	1.10	0.13
Eu ₂ O ₃ ¹	—	—	2.05	0.08	1.92	0.19	0.77	0.05	1.14	0.13
ThO ₂	0.20	0.07	3.96	0.43	5.42	0.02	5.79	0.01	6.11	1.05
UO ₂	0.10	0.03	1.48	0.22	0.99	0.04	0.88	0.19	0.91	0.05
Total	98.71		96.35		95.70		93.18		96.30	
Σ REE ₂ O ₃	0.45		10.79		12.70		12.02		12.02	
La/Th			0.635	0.008	0.605	0.050	0.657	0.001	0.649	0.029

¹Estimated from Eu content of melt and D_{Eu} extrapolated using lattice strain model.

notwithstanding, the most likely causes of partial non-stoichiometry are the presence of A-site vacancies, or substitution of O²⁻ by F⁻ on the O4-site (dollaseite substitution). However, in our study the non-stoichiometry is probably caused by the uncertainty on Fe³⁺/Fe²⁺ rather than the presence of fluorine (F-free starting material).

The change from epidote to allanite coincides with the disappearance of residual amphibole and a marked increase in glass fraction (Fig. 3). We suggest that during melting epidote is progressively consumed, but its LREE + Th + U budget becomes concentrated in the residue to form allanite, as shown in reaction (2) above. The fact that allanite has not been reported in other experiments on basaltic starting compositions can be explained by the fact that these were not doped with LREE. Although our doping levels are ~ 500 ppm total LREE allanite is rare and requires painstaking location by SEM. For a 'normal' MORB with LREE content of 25–150 ppm, allanite, if present, would be substantially less abundant in the run products and therefore virtually impossible to spot. We consider that the presence of allanite in our

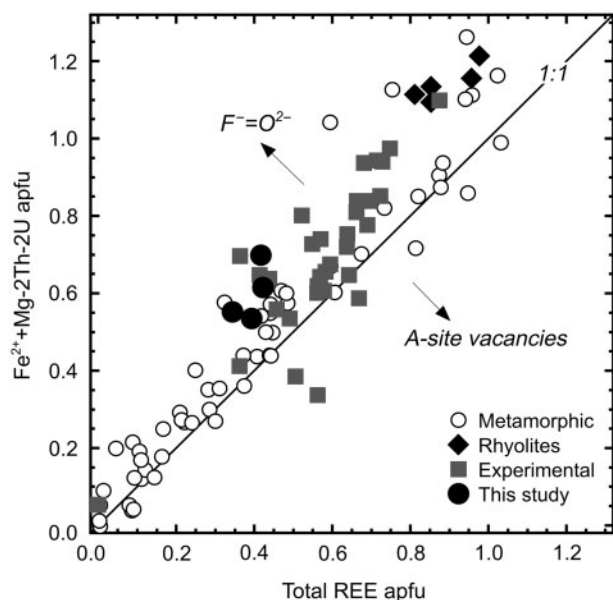


Fig. 9. Compositions of natural and experimental epidote group minerals expressed in terms of allanite–dissakisite coupled substitution [equation (3)] after allowing for Th and U [equation (4)]. Deviations from the 1:1 line may be attributed to the presence of fluorine or A-site vacancies as indicated by the arrows. Experimental data are taken from Hermann & Green (2001), Hermann (2002) and unpublished data of T. H. Green given in the supplementary dataset. Other data sources are given in the text.

experiments is related to its finite solubility in LREE-bearing silicic liquids. Thus its presence is not a consequence of the doping levels in our experiments, although its abundance is. In this regard it is directly analogous to rutile saturation in silicic liquids during basalt melting. At 800°C, for example, the solubility of TiO_2 is ~ 0.2 wt %. In a bulk system with just enough TiO_2 to saturate the liquid there will be sparingly little residual rutile. For exactly the same bulk system, but with five times as much TiO_2 initially, appreciable residual rutile will be present. In both experiments, however, the TiO_2 content of the liquid will be fixed at 0.2 wt %. We develop the issue of allanite solubility below.

Although absent from hydrous basalt melting experiments, REE-epidotes and allanites, with very similar composition to those in our experiments, have been synthesized from more silica-rich, trace element-doped starting materials by Hermann & Green (2001) and Hermann (2002). REE-epidotes and allanites have also been reported from several paleosubduction-related high-pressure metamorphic terranes, including the Sanbagawa Belt, Japan (Sakai *et al.*, 1984), Catalina Schist, USA (Sorensen, 1991), Tauern Window, Austria (Finger *et al.*, 1998), Dora Maira Massif, Italy (Hermann, 2002); New Caledonia (Spandler *et al.*, 2003) and New England, USA (Wing *et al.*, 2003). The chemistry of the REE-rich epidotes, in particular their high MgO contents and the apparent occurrence,

Table 5: Electron microprobe analysis of rutile (R13, 850°C)

	wt%	σ ($n=5$)
SiO_2	0.20	0.05
TiO_2	90.55	0.26
Al_2O_3	0.66	0.03
Nb_2O_5	2.39	0.21
V_2O_3	0.02	0.02
Fe_2O_3	2.58	0.15
Ta_2O_5	0.64	0.06
Total	97.04	

based on stoichiometry, of A-site vacancies, is similar in these rocks to those in our experiments (Fig. 9). The occurrence of allanite and REE-rich epidotes in experiments and in natural metabasic rocks strongly suggests that REE-rich epidote is an important mineral during the high P – T metamorphism of basaltic rocks. In that case, its presence can account for a substantial portion of the LREE + Th + U budget of such rocks, as pointed out by Sorensen & Grossman (1989), Tribuzio *et al.* (1996), Hermann (2002) and Spandler *et al.* (2003).

Other minerals

Staurolite analyses from two runs at 750°C are reported in Table 3. They are relatively TiO_2 -rich (≥ 0.7 wt %) and have mg-numbers in the range 0.43–0.47. Their compositions are similar to those reported by Poli & Schmidt (2002).

The composition of a single rutile grain large enough for EMPA is reported in Table 5. In addition to TiO_2 the rutile contains significant Al_2O_3 , Fe_2O_3 , Nb_2O_5 , and Ta_2O_5 .

Trace element chemistry

The trace element contents of garnets and quenched glasses were analysed by ion-microprobe. Analyses and calculated mineral–liquid partition coefficients are given in Table 6. Partition coefficients are also reported for allanite and rutile based on EMPA of selected trace elements.

Glasses are relatively homogeneous in trace element composition as evidenced by multiple analyses showing standard deviations of typically $\leq 20\%$ relative (Table 6). This is not true for garnets, which show considerable within-run variability. We screened the raw ion-microprobe garnet analyses for those that have Ti and Ca contents consistent with values determined by EMPA, taking into account ion-yield differences described above. Analyses that showed clear physical evidence (from SEM) of glass contamination have been eliminated. For each run, however, even after screening, significant trace element

Table 6: Trace element composition (ppm) of experimental glasses and garnets and calculated partition coefficients (on anhydrous basis)

<i>n</i>	Li	Sc	Ti	V	Sr	Y	Zr	Nb	La	Ce	Nd	Sm	Eu ¹	Yb	Lu	Hf	Ta	Th	U	U/ Th	Zr/ Hf	Nb/ Ta	La/ Th
<i>Glass</i>																							
16	5	236 (38)	2.4 (6)	882 (270)	5.3 (27)	93 (10)	0.42 (17)	76 (7)	90 (16)	7.8 (21)	8.9 (25)	9.2 (30)	11.7 (44)	16.7 (48)	0.46 (21)	0.34 (15)	51 (14)	18 (5)	26 (10)	140 (48)	5.4 (4)	1.6 (6)	5.0 (5)
13	5	205 (45)	4.3 (21)	1169 (436)	3.6 (19)	67 (5)	0.61 (8)	69 (7)	91 (6)	17.8 (24)	19.5 (30)	20.0 (37)	17.1 (33)	20.8 (37)	0.86 (22)	0.73 (31)	35 (3)	16 (1)	52 (6)	143 (17)	2.7 (1)	2.0 (1)	5.7 (3)
20	7	161 (55)	3.8 (5)	2193 (560)	7.3 (50)	65 (11)	1.20 (18)	120 (14)	212 (19)	43.1 (77)	48.7 (81)	43.2 (91)	32.9 (44)	36.5 (58)	1.76 (34)	1.44 (24)	62 (7)	37 (6)	122 (22)	369 (58)	3.0 (1)	1.9 (2)	5.8 (6)
19	4	265 (19)	2.0 (2)	30 (4)	3.9 (4)	127 (5)	0.53 (4)	57 (3)	314 (16)	29.5 (35)	29.8 (44)	27.4 (53)	15.3 (23)	15.0 (18)	0.65 (9)	0.66 (8)	37 (5)	75 (5)	97 (14)	199 (19)	2.1 (3)	1.5 (1)	4.2 (1)
<i>Garnet</i>																							
12	4	12 (2)	167 (39)	6002 (2414)	44 (6)	4.1 (22)	92 (16)	170 (32)	64 (61)	17 (13)	18 (12)	25 (17)	44 (16)	80 (17)	589 (260)	553 (271)	35 (3)	13 (14)	25 (21)	24 (19)	1.0 (2)	4.8 (6)	5.6 (18)
16	5	12 (1)	128 (20)	7304 (1628)	44 (3)	2.6 (10)	67 (18)	310 (38)	41 (16)	11 (12)	13 (15)	18 (13)	39 (19)	90 (30)	445 (76)	435 (64)	53 (9)	10 (4)	22 (29)	16 (9)	1.9 (13)	5.8 (4)	4.4 (12)
13	6	13 (2)	166 (60)	8348 (1000)	55 (8)	4.5 (38)	80 (25)	303 (75)	63 (27)	21 (21)	24 (23)	32 (22)	62 (27)	130 (40)	524 (258)	556 (264)	49 (12)	14 (5)	29 (36)	35 (24)	1.9 (9)	6.2 (5)	4.6 (8)
20	5	13 (1)	145 (41)	9559 (433)	62 (5)	2.3 (6)	100 (28)	303 (69)	73 (19)	7 (5)	11 (6)	37 (10)	114 (20)	250 (29)	443 (232)	388 (221)	53 (11)	22 (6)	15 (11)	56 (6)	5.7 (37)	5.7 (3)	3.4 (3)
19	6	6 (3)	196 (31)	131 (30)	58 (9)	5.5 (13)	114 (27)	436 (89)	202 (62)	36 (15)	42 (17)	54 (20)	96 (26)	207 (46)	724 (220)	712 (217)	88 (13)	62 (17)	50 (22)	65 (27)	1.6 (8)	5.0 (4)	3.2 (2)
<i>D_{grt/melt}</i>																							
16		0.051 (10)	54 (16)	8.3 (31)	8.5 (44)	0.027 (11)	159 (78)	4.0 (6)	0.46 (20)	1.4 (16)	1.5 (17)	2.0 (16)	3.4 (21)	5.4 (24)	967 (470)	1277 (584)	1.05 (33)	0.52 (26)	0.83 (115)	0.11 (8)	0.35 (23)	3.6 (13)	0.89 (26)
13		0.066 (17)	39 (24)	7.1 (28)	15.1 (85)	0.066 (57)	130 (44)	4.4 (12)	0.69 (30)	1.2 (12)	1.2 (12)	1.6 (12)	3.7 (18)	6.2 (22)	613 (339)	765 (489)	1.42 (36)	0.86 (29)	0.56 (69)	0.25 (17)	0.71 (35)	3.1 (3)	0.79 (14)
20		0.084 (29)	38 (12)	4.4 (11)	8.5 (58)	0.036 (11)	83 (27)	2.5 (6)	0.35 (9)	0.2 (1)	0.2 (1)	0.9 (3)	3.5 (8)	6.9 (13)	252 (141)	270 (160)	0.86 (20)	0.58 (18)	0.13 (10)	0.15 (3)	1.88 (124)	2.9 (4)	0.59 (7)
19		0.022 (11)	99 (19)	4.4 (12)	14.9 (27)	0.043 (11)	216 (54)	7.7 (16)	0.64 (20)	1.2 (5)	1.4 (6)	2.0 (8)	6.3 (19)	13.8 (35)	1117 (373)	1084 (358)	2.36 (47)	0.83 (24)	0.52 (24)	0.32 (14)	0.75 (42)	3.2 (3)	0.77 (5)
<i>D_{all/melt}</i>																							
16			1.94 (61)							2819 (792)	2245 (697)	1980 (742)	1254 (491)	794					1331 (517)	97 (36)	0.028 (7)		2.02 (33)
13			3.38 (149)							1619 (261)	1309 (227)	1169 (217)	839 (163)	602					908 (112)	64 (8)	0.140 (36)		1.78 (18)
20			1.97 (53)							775 (138)	628 (104)	538 (113)	272 (37)	138					416 (74)	22 (6)	0.061 (3)		1.86 (11)
19			4.03 (29)							1178 (205)	931 (191)	771 (180)	617 (121)	495					555 (126)	42 (5)	0.072 (12)		2.12 (15)
<i>D_{rut/melt}</i>																							
13			394 (120)							183 (20)									327 (39)			0.56 (4)	

¹ D_{Eu} for allanite is calculated from lattice strain model fit to other D_{LREE} . This value is used to calculate Eu_2O_3 of allanites. Uncertainties (standard deviation of the mean, 1 σ) are given in parentheses as last significant digits. For example, 7.8 (21) must be read as 7.8 ± 2.1 and 0.01 (2) as 0.01 ± 0.02 .

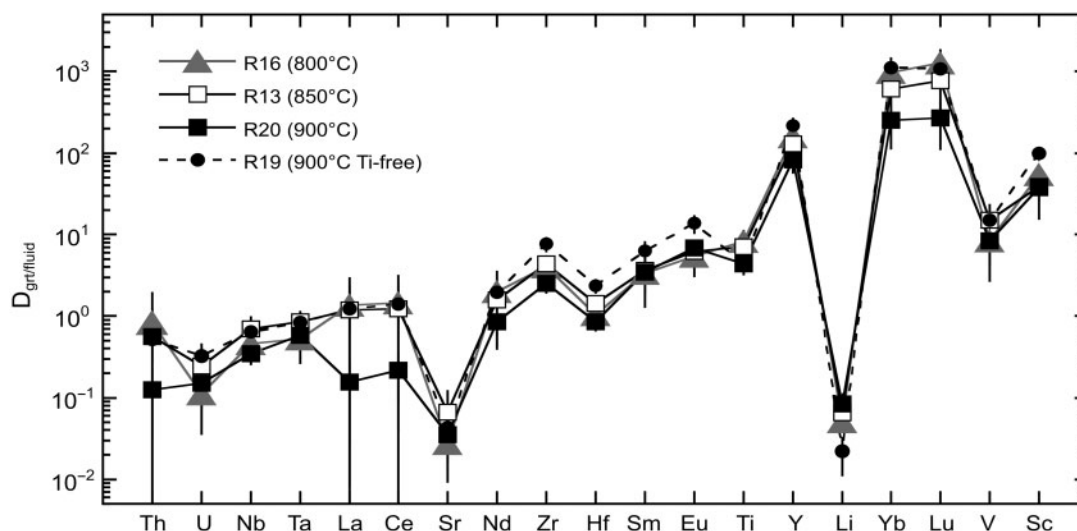


Fig. 10. Garnet–melt partition coefficients for the trace elements studied. 1 SD errors bars are shown for selected runs. Partition coefficients for the LREE, HREE and Th are subject to large analytical uncertainties (see text).

heterogeneity persists in the garnets. This is most clearly manifest in the highly compatible elements (i.e. HREE) and highly incompatible elements (i.e. LREE, Sr). The moderately compatible elements, such as Sm, Eu, Ti, Zr, Sc and V, show much less variability. We consider that these observations reflect the magnitude of bulk solid–liquid partition coefficients (D^{bulk}) during growth of the large garnets in our experiments. The closer that D^{bulk} is to unity, the less variation will occur in the liquid phase during garnet growth. Thus, for HREE the variability is a consequence of the very high partition coefficients for these elements (≥ 200 ; Table 6) such that even modest amounts of crystallization of a garnet-rich assemblage lead to substantial depletion in the liquid. If solid-state diffusion is too slow to fully re-equilibrate garnet trace elements on experimental timescales (Van Orman *et al.*, 2002) then a trace element-zoned garnet results. For example, just 5% fractional crystallization of an assemblage with $D^{\text{bulk}}_{\text{HREE}} = 100$ leads to a 160-fold depletion of HREE in the liquid. In terms of garnet growth this corresponds to a zone only 1 μm wide on a 50 μm diameter crystal. Therefore in the course of an experiment involving modest garnet growth, substantial zonation in HREE is unavoidable. When dealing with highly compatible elements in low-temperature experiments it is simply not possible to generate crystals that are both trace element-unzoned and large enough for ion-microprobe analysis. For that reason we calculated mean and standard deviation for entire populations of screened garnets from each run and used these for partition coefficient determinations. As noted previously (Wood *et al.*, 1999) the relative variation in element ratios from grain to grain in an experimental run product is considerably less than the relative variation in concentration for any single element. For key element ratios

(U/Th, Zr/Hf, Nb/Ta) partition coefficient ratios (e.g. $D_{\text{U}}/D_{\text{Th}}$, etc.) have been calculated and are reported in Table 6, with their associated small errors.

TRACE ELEMENT PARTITIONING Garnet

Garnet–liquid partition coefficients are plotted for a range of trace elements in Fig. 10. Several key features are evident. First, there is no difference in partitioning behaviour at the 1 SD level between the Ti-free and Ti-bearing experiments at 800–900°C, for all elements except Li, which is a factor of three lower in the Ti-free experiments. Our data suggest that small amounts of TiO_2 (≤ 1.2 wt %) in the garnet structure have little effect on trace element partitioning behaviour, in agreement with the predictive model for garnet–liquid partitioning by Van Westrenen & Draper (2007). In contrast, based on garnet–liquid partitioning experiments in anhydrous eclogite, Pertermann *et al.* (2004) showed that Ti-poor garnets (0.5 wt % TiO_2) have 2–5 times higher partition coefficients than Ti-rich garnets for highly charged cations such as Nb, U and Zr (1.5–2.0 wt % TiO_2). Second, partition coefficients for HREE are extremely high (≥ 200), which is consistent with the low temperature of our experiments and the large enthalpy of fusion for the fictive REE–garnet component as derived by Van Westrenen *et al.* (2001a) and Van Westrenen & Draper (2007). Despite significant analytical variability in D_{HREE} there is an apparent increase in D_{HREE} with decreasing temperature. In H_2O -saturated experiments involving basaltic bulk compositions at pressures (3–4 GPa) and temperatures (700–900°C) similar to those in our experiments, Green & Adam (2003) and Kessel *et al.* (2004) also obtained very high D_{HREE} , in the

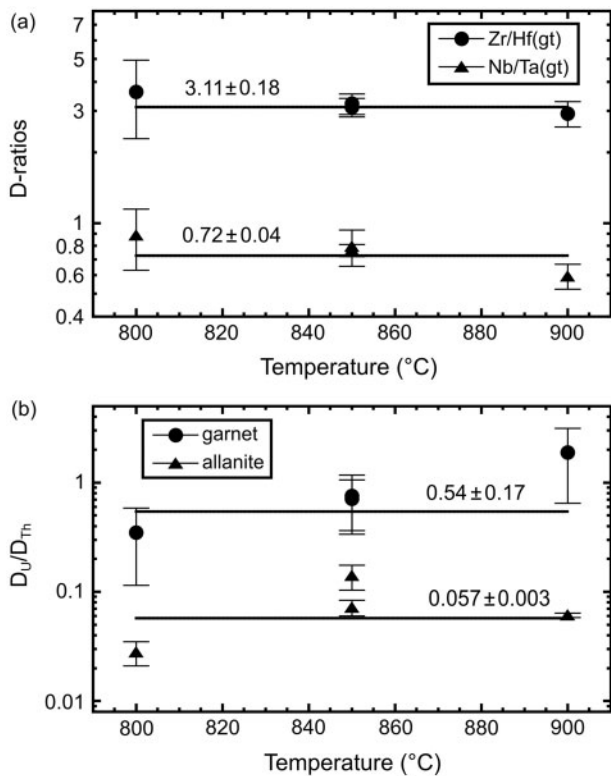


Fig. 11. Partition coefficient ratios for (a) Zr/Hf and Nb/Ta in garnet and (b) U/Th in garnet and allanite. Error bars are 1 SD. Horizontal lines are weighted mean values.

range 200–600, with a marked increase with decreasing temperature. Rubatto & Hermann (2007) reported lower D_{HREE} (10–100) and a significantly smaller increase of D_{HREE} with decreasing temperature in the presence of zircon in experiments at 2 GPa and 800–1000°C. In this case, zircon–melt partition coefficients for HREE in zircon are extremely high (10–1000). Variability in our values of D_{LREE} is masked by the large analytical uncertainties for the garnets; the values given in Table 6 are almost certainly overestimates. D_{Li} and D_{Sr} are very low in garnet, in keeping with most previous determinations (Van Westrenen *et al.*, 1999, 2000; Adam & Green, 2006). D_{Zr} is consistently greater than D_{Sm} , which in turn is greater than D_{Hf} . There is no evidence of any appreciable anomaly in D_{Eu} , in keeping with the relatively oxidizing nature of the experiments (NNO) and the low $\text{Eu}^{2+}/\text{Eu}^{\text{tot}}$ ratio (~ 0.1) in the liquid under these conditions (Aigner-Torres *et al.*, 2007).

D_{Zr} and D_{Hf} vary little with temperature. The partitioning ratio $D_{\text{Zr}}/D_{\text{Hf}}$ is remarkably constant between runs (Fig. 11a). A weighted average of the four determinations yields a mean of 3.11 ± 0.18 . This constancy is probably a function of the near-constant grossular contents of our garnets (24 ± 2 mol%); at constant pressure and temperature, $D_{\text{Zr}}/D_{\text{Hf}}$ has been shown to correlate positively with

grossular content (Van Westrenen *et al.*, 2001b). However, the magnitude of the $D_{\text{Zr}}/D_{\text{Hf}}$ ratio in our experiments is considerably greater than at higher temperatures for the same grossular content (e.g. $D_{\text{Zr}}/D_{\text{Hf}} \approx 1.25$ at 1340–1390°C; Pertermann *et al.*, 2004). For a hydrous tholeiitic bulk composition, similar to KBI, run at 1200°C and 3 GPa, Green *et al.* (2000) found $D_{\text{Zr}}/D_{\text{Hf}} = 1.76 \pm 0.16$ for a slightly less grossular-rich garnet (17 mol%). This is intermediate in temperature between the experiments of Pertermann *et al.* (2004) and ours, suggesting that temperature, as well as grossular content, plays a role in determining $D_{\text{Zr}}/D_{\text{Hf}}$.

$D_{\text{Nb}}/D_{\text{Ta}}$ is tightly constrained by our experiments to be 0.72 ± 0.04 (Fig. 11a). The Green *et al.* (2000) experiment at 3 GPa yields a rather low value (0.22 ± 0.13), whereas the seven higher temperature, dry eclogite experiments of Pertermann *et al.* (2004) yield a weighted mean value of 0.58 ± 0.09 for garnets of similar grossular content. It may be that these minor variations in $D_{\text{Nb}}/D_{\text{Ta}}$ are a consequence of variations in the composition of the liquid phase, as proposed by Linnen & Keppler (1997) and Schmidt *et al.* (2004). In any event, it would appear that garnet-induced fractionation between Zr and Hf is much more sensitive to temperature (at a given garnet composition) than is fractionation between Nb and Ta.

$D_{\text{U}}/D_{\text{Th}}$ is less well constrained by our data and does show a small increase with temperature (Fig. 11b), although this is not significant at the 2 SD level. The weighted mean $D_{\text{U}}/D_{\text{Th}}$ is 0.54 ± 0.17 . The $D_{\text{U}}/D_{\text{Th}}$ ratios obtained by Pertermann *et al.* (2004) are considerably larger than this (>5) because of the lower $f\text{O}_2$ in their graphite-buffered experiments and the consequent absence from their liquids of U^{5+} and U^{6+} species, which are much less compatible in garnet than U^{4+} . We emphasize that during subduction the relatively high $f\text{O}_2$ means that Th is preferentially retained in the garnet-bearing residue relative to U. This is the opposite sense of fractionation to that which occurs during lower $f\text{O}_2$ melting of garnet peridotite beneath mid-ocean ridges (Beattie, 1993).

Partition coefficients for Sc and the REE show a parabolic pattern consistent with the lattice strain models of Van Westrenen *et al.* (2001a), with a peak at the HREE (Fig. 12). The parabolic nature of the patterns is masked to a large degree by the uncertainties in D_{HREE} and D_{LREE} . However, as D_{Sm} , D_{Eu} and D_{Sc} are subject to considerably less uncertainty than heavier or lighter REE, weighted least-squares fitting can be used to derive the fit parameters $r_{0(\text{X})}$ (optimum radius of the X-site), E_{X} (apparent Young's Modulus of the X-site) and D_0 (the partition coefficient for a cation of radius $r_{0(\text{X})}$ entering the X-site). [For a fuller description of these terms see Blundy & Wood (2003).] An example of a fitted parabola to Run 20 is shown in Fig. 12. Because of the highly correlated nature of the fit parameters D_0 and E_{X} (Wood & Blundy, 1997)

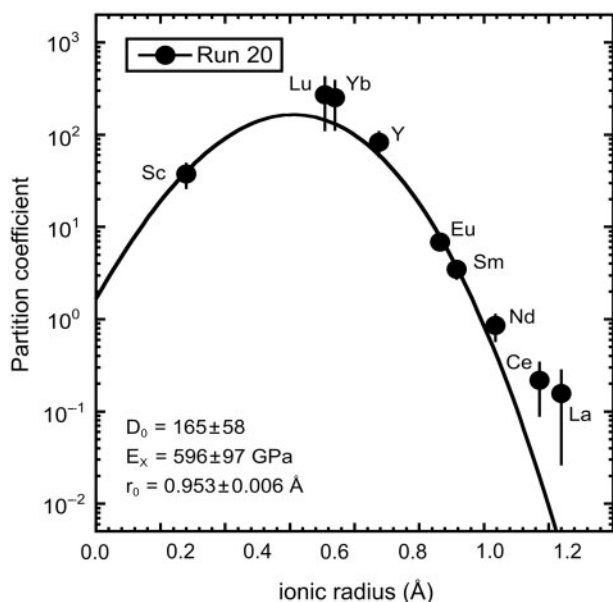


Fig. 12. Lattice strain parabola for REE, Y and Sc in garnet from Run 20. Best-fit curve is shown as a continuous line. Error bars on partitioning data are 1 SD. (See Table 7 for fit parameters.)

Table 7: Lattice strain fit parameters

Run:	R16	σ	R13	σ	R20	σ	R19	σ
E^1 (fixed)	656.5		628.8		612.6		638.7	
D_0 (fitted)	305	62	245	70	176	32	557	67
r_0 (fitted)	0.951	0.004	0.953	0.005	0.954	0.004	0.953	0.002
r_0^2	0.950		0.950		0.951		0.953	
r_0^1	0.904		0.908		0.912		0.910	

¹Van Westrenen & Draper (2007).

²Van Westrenen *et al.* (2001a).

it proved difficult to fit simultaneously for all three parameters in the other experiments. For this reason we have elected to fix E_X for each run using the values of Van Westrenen & Draper (2007), and to fit for $r_{0(X)}$ and D_0 only. In Table 7 the fitted values are compared with the calculated values from Van Westrenen *et al.* (2001a) and Van Westrenen & Draper (2007). Both the fitted values and model values of D_0 are very large, but there is a sizeable discrepancy because our experiments lie well outside the calibrant dataset of either model. However, our values of $r_{0(X)}$ are in excellent agreement, at 1 SD level, with those of Van Westrenen *et al.* (2001a), but somewhat lower than those of Van Westrenen & Draper (2007). This discrepancy results from the much greater temperature dependence of $r_{0(X)}$ in the latter model, which, when extrapolated to very low temperatures, results in a very small $r_{0(X)}$.

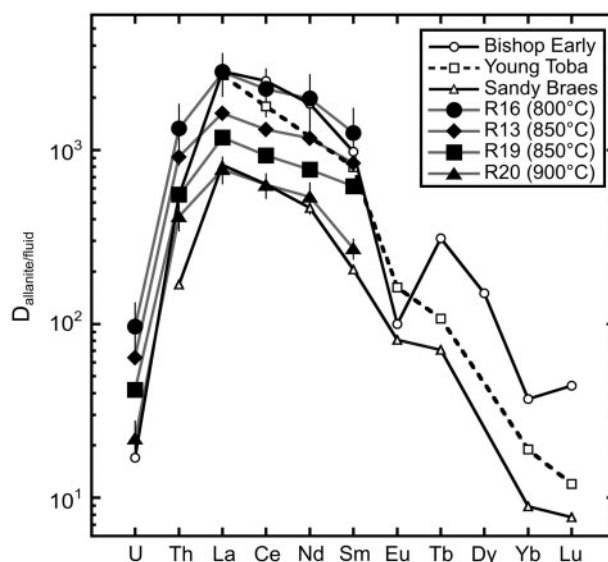


Fig. 13. Allanite-melt partition coefficients for LREE, U and Th from experiments compared with those from natural rhyolites from the Bishop Tuff (Mahood & Hildreth, 1983), Toba Tuff (Chesner & Ettlinger, 1989) and Sandy Braes (Brooks *et al.*, 1981).

The fit parameters in Table 7 can be used to derive partition coefficients for all REE + Y + Sc in our experiments. We suggest that this approach is more reliable for obtaining D_{HREE} and D_{LREE} than the raw garnet-liquid partitioning data (Table 6) themselves.

Allanite

Partition coefficients for allanite in experiments at 800–900°C are presented in Table 6. In contrast to garnet, the allanite trace element analyses are by EMPA, rather than ion-microprobe. We have not corrected the glass ion-microprobe data for any ion-yield differences. However, this would affect the partition coefficients by at most 20% relative, which is negligible compared with their overall magnitude and element to element variability.

D_{LREE} decreases by a factor of 2–3 from La to Sm, defining a parabolic variation centred on an ionic radius slightly larger than La (Fig. 13). D_{Th} is consistently less than D_{La} , and in most cases comparable with D_{Sm} . D_U is ~20 times less than D_{Th} ; the weighted mean D_U/D_{Th} is 0.057 ± 0.003 (Fig. 11b). This is a consequence of both the smaller size of U^{4+} compared with Th^{4+} (Wood *et al.*, 1999) and the presence of some U^{6+} at NNO. The extrapolated values of D_{Eu} (Table 6), which were used to calculate the Eu_2O_3 contents of allanites (Table 4), assume that there is no Eu anomaly, as also observed for garnets (Fig. 12). It should be noted that Sr in the allanites was consistently below detection by EMPA (815 ppm), which constrains D_{Sr} to be less than 6–12. This is consistent with the relatively low values for D_{Ca} , which are in the range 13–58. T. H. Green

(unpublished data) obtained D_{Sr} values for allanite in the range 0.5–1.0.

The variation in partition coefficients for LREE, U and Th is very similar to that observed in natural allanites from rhyolites (Brooks *et al.*, 1981; Mahood & Hildreth, 1983; Chesner & Ettlinger, 1989) crystallized at comparable temperatures to the experiments (700–800°C), but at much lower (sub-volcanic) pressures. The rhyolitic allanites have ~1 REE a.p.f.u. (Fig. 9) rather than the 0.4 in our experimental allanites. Despite these differences in mineral chemistry, the similarity in partitioning behaviour, both in terms of absolute magnitude and inter-element variation, is striking. The partitioning behaviour we observe is consistent with the experimental zoisite–melt and zoisite–fluid partition coefficients of Frei *et al.* (2003) and Feineman *et al.* (2007), respectively, and Frei *et al.*'s (2003) modelling of allanite–melt partitioning in terms of lattice strain on the XI-coordinated A2-site. Using their value of E_{A2} for allanite (166 GPa), taken from Dollase (1971), and taking interpolated XI-coordination ionic radii for La–Sm from Shannon (1976), we obtain a weighted mean fitted value for $r_{0(A2)}$ of 1.299 ± 0.007 Å for all four experiments. This is in remarkable agreement with Frei *et al.*'s (2003) calculated value of $r_{0(A2)} = 1.309$ Å. These observations give us confidence that our allanite–liquid partition coefficients represent a close approximation to equilibrium. Conversely, our data do not support the experimentally determined allanite–melt partition coefficients of Hermann (2002), which are essentially constant ($\pm 10\%$ relative) from La to Dy, decreasing then by only a factor of two to Yb. These patterns are wholly inconsistent with lattice strain models of partition coefficients, which predict a marked size preference for LREE relative to middle REE (MREE) and HREE. We concur with Frei *et al.* (2003) and Gieré & Sørensen (2004) that the Hermann (2002) allanite–melt partition coefficients are somehow in error.

Rutile

Rutile–liquid partition coefficients from a single experiment at 850°C (Run 13) are given in Table 6. Again, trace elements in rutile were measured by EMPA and no correction has been made for small ion-yield differences.

D_{Nb} is less than D_{Ta} ($D_{Nb}/D_{Ta} = 0.56 \pm 0.04$) as observed in all previous studies of rutile–liquid partitioning (Green & Pearson, 1987; Jenner *et al.*, 1993; Green & Adam, 2003; Bennett *et al.*, 2004; Schmidt *et al.*, 2004; Xiong *et al.*, 2005). Although there has been recent discussion of liquid compositional effects on Nb–Ta fractionation by rutile (Linnen & Keppler, 1997; Schmidt *et al.*, 2004), the weighted least-squares fit to the entire dataset of 41 experimental data points, including the rutile–aqueous fluid partitioning data of Brennan *et al.* (1994), gives D_{Nb}/D_{Ta} of 0.513 ± 0.010 (Fig. 14). This value holds across an overall variation in D_{Nb} from ~10 to >2000,

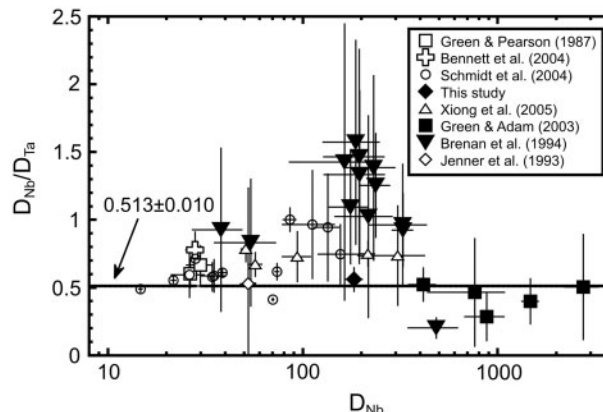


Fig. 14. Nb/Ta partition coefficient ratio for rutile as a function of D_{Nb} from this study and published experimental studies involving melts (Green & Pearson, 1987; Jenner *et al.*, 1993; Green & Adam, 2003; Bennett *et al.*, 2004; Schmidt *et al.*, 2004; Xiong *et al.*, 2005) and fluids (Brennan *et al.*, 1994). Error bars are 1 SD. The horizontal line is a weighted mean of all the data.

a temperature range of 650–1330°C and a pressure range of 0.4–3 GPa. Thirty-six of the 41 data points lie within 2 SD of 0.513. Although we acknowledge that subtle liquid compositional effects do exist, we suggest that for the purposes of subduction zone modelling, where major element fluid or melt compositions are rarely well constrained, a fixed value of D_{Nb}/D_{Ta} of 0.51 be adopted for rutile.

Hf and Zr were not determined. Following Xiong *et al.* (2005) and Bennett *et al.* (2004) we adopt $D_{Zr}/D_{Nb} = 0.058 \pm 0.004$ (weighted mean of six values) and $D_{Zr}/D_{Hf} = 0.87 \pm 0.07$ (five values). This results in calculated rutile–liquid $D_{Zr} = 10.7$ and $D_{Hf} = 12.2$ for Run 13.

Bulk residues

Partition coefficients between the bulk solid residues at $T \geq 800^\circ\text{C}$ (i.e. rutile + allanite-bearing eclogites) and the quenched glass can be calculated using the glass fractions determined by mass balance (Table 2), and the compositions of the starting material (Table 1) and the glasses (Table 6). Because both were determined by ion-microprobe analysis no correction for minor ion-yield differences is required. These solid–glass partition coefficients are calculated on the basis of the anhydrous glass fraction. Assuming that all the H₂O is dissolved in a supercritical liquid at experimental conditions the liquid fraction has to be increased to determine appropriate solid–liquid partition coefficients (see Table 2). This results in a systematic increase of the solid–liquid partition coefficients by a factor <2 compared with the solid–glass partition coefficients. These solid–liquid partition coefficients underestimate H₂O soluble elements in the liquid fraction because of exsolution of H₂O-rich vapour during quenching. We consider this approximation to be valid for all but the most H₂O-soluble species (K, Li, Sr and Ba)

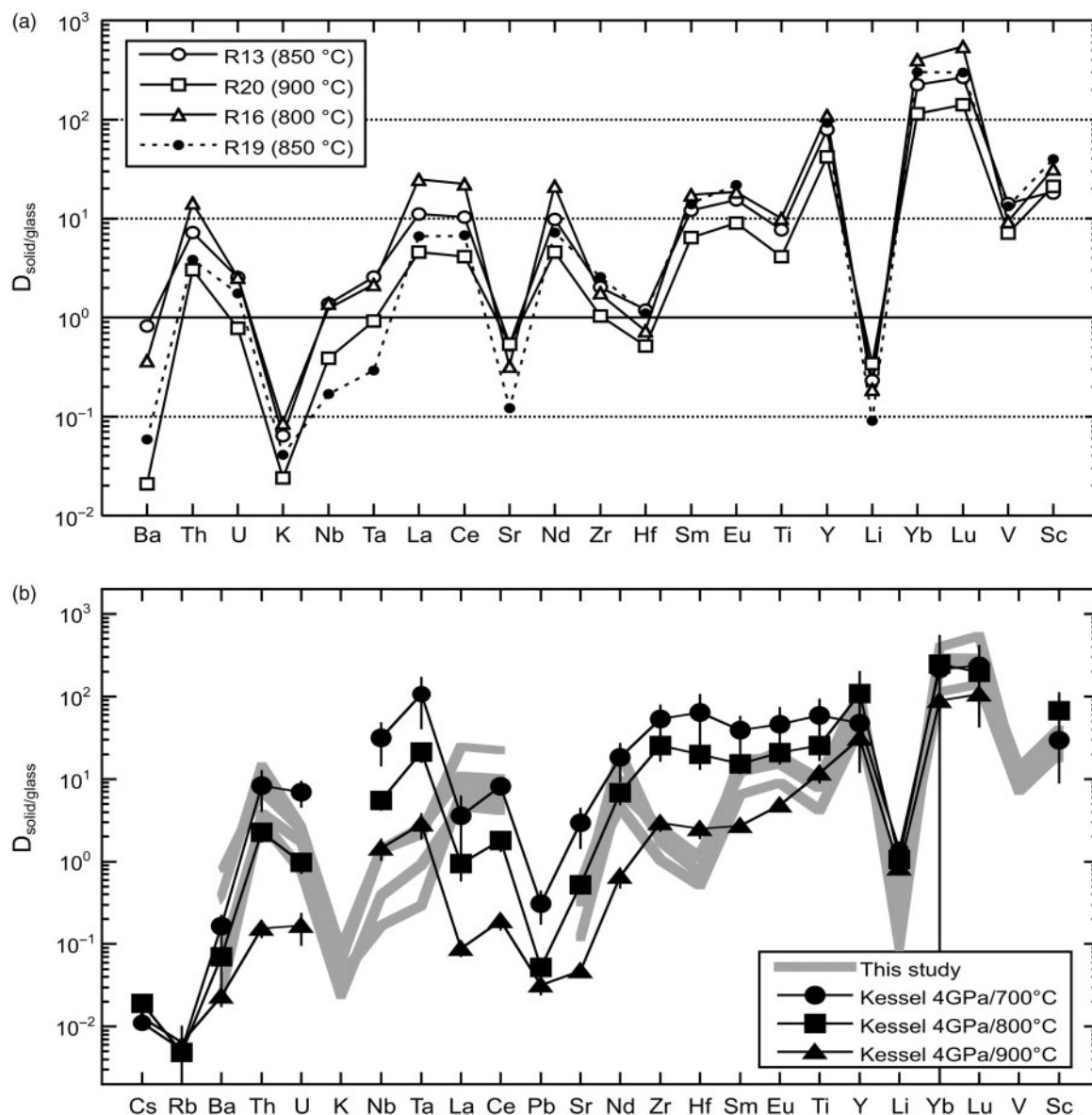


Fig. 15. (a) Bulk solid–glass partition coefficients from this study calculated using the anhydrous modal proportions in Table 2 and the glass compositions. (b) Bulk solid–fluid data from three experiments of Kessel *et al.* (2005a) compared with data from this study (shaded region) from (a). Error bars are 1 SD.

in agreement with experimental fluid compositions in pelitic systems (Spandler *et al.*, 2007).

Bulk solid–glass partition coefficients are shown in Fig. 15a. Values for HREE resemble those of garnet, whereas those for U, Th and LREE resemble those of allanite. Likewise, rutile controls the Nb, Ta and Ti budget. In the absence of residual zircon a mixture of garnet and rutile control Zr and Hf. Although we did not measure clinopyroxene–liquid partition coefficients in our experiments, because the crystals were too small, it is apparent from Fig. 15a and mass-balance considerations that clinopyroxene exerts negligible control on the trace element

composition of the liquid because, for any of the elements considered here, its partition coefficients are appreciably less than those of garnet, allanite or rutile.

A consequence of having three residual phases with very large individual partition coefficients is that almost all bulk partition coefficients are significantly greater than unity. Elements that are essential structural components, such as Ti in rutile and LREE in allanite, are buffered at their solubility levels for the pressure–temperature–composition conditions of the experiments. The high activity of these components in the liquid means that they no longer obey Henry's Law. Conversely, elements that are not essential

constituents, but still have very large partition coefficients, such as HREE in garnet, Nb and Ta in rutile, and U and Th in allanite, have bulk partition coefficients that are controlled by the abundance of their host mineral in the solid residue. These elements do obey Henry's Law. Thus there is an important distinction to be made between trace elements whose bulk partition coefficients are solubility-controlled (i.e. LREE, Ti) and therefore sensitive only to the presence of a particular residual phase, irrespective of bulk composition, and those whose bulk partition coefficients are controlled by the abundance of a phase in the residue and are therefore sensitive to bulk composition (e.g. HREE, Th, U, Nb, Ta). For example, TiO₂-rich materials will yield large quantities of residual rutile at a given pressure and temperature, resulting in high $D_{\text{Nb}}^{\text{bulk}}$ and $D_{\text{Ta}}^{\text{bulk}}$. A similar starting material with much lower TiO₂, but enough to saturate with rutile, will buffer TiO₂ at the same level, but have much lower bulk $D_{\text{Nb}}^{\text{bulk}}$ and $D_{\text{Ta}}^{\text{bulk}}$. By the same token, a TiO₂-free system will have very low bulk $D_{\text{Nb}}^{\text{bulk}}$ and $D_{\text{Ta}}^{\text{bulk}}$ (Figure 15a).

The only trace elements with consistently very low bulk partition coefficients in our experiments are K, Sr, Ba and Li (Fig. 15a). Consequently Li, K, Sr and Ba are the only traces to be significantly enriched in the liquid relative to the starting materials. At the highest temperatures (900°C) bulk $D_{\text{Nb}}^{\text{bulk}}$ and $D_{\text{Hf}}^{\text{bulk}}$ also fall below unity and a small enrichment in the liquid over source occurs. In the case of Nb this is simply a consequence of the greater solubility of TiO₂ in liquid and garnet at higher temperatures, such that the mode of residual rutile (X_{rut}) is reduced, thereby reducing $D_{\text{Nb}}^{\text{bulk}} \approx X_{\text{rut}} \times D_{\text{Nb}}^{\text{rut}}$. The reduction of $D_{\text{Hf}}^{\text{bulk}}$ is caused by a reduction in X_{rut} , combined with a small decrease in $D_{\text{Hf}}^{\text{gt}}$ (and $D_{\text{Zr}}^{\text{gt}}$) at higher temperature (Fig. 10). There is no evidence from mass balance that zircon became saturated in any of our experiments. Using the liquid Zr concentrations and liquid compositions from Tables 6 and 3, respectively, zircon saturation temperatures for each experiment, using the model of Watson & Harrison (1983), lie between 670 and 749°C. This is consistently below the experimental temperatures, corroborating the fact that our experiments were zircon-undersaturated. It has to be noted that Rubatto & Hermann (2007) determined lower Zr concentration in liquids coexisting with zircon than predicted by Watson & Harrison (1983), indicating that increasing pressure may decrease Zr-saturation temperatures. The presence of zircon in an eclogitic residue would impart a marked negative Zr–Hf anomaly, relative to adjacent MREE, on extracted melts or fluids. However, in our bulk composition and in altered MORB zircon would disappear from the solid residue at or close to the solidus. Only a much more Zr-rich lithology (i.e. $\gg 150$ ppm) would have residual zircon persisting well above the solidus.

It is useful to compare our experimentally determined bulk partition coefficients with those of Kessel *et al.*

(2005a) for a K-free basalt at slightly higher pressure (4 GPa) and similar temperatures (700–900°C; Fig. 15b). Kessel *et al.* used a wholly different experimental set up from ours. They trapped the fluid phase in diamond aggregates during the run, froze it in liquid N₂ after quenching, and analysed the mixture of diamonds and frozen fluid by laser-ablation ICP-MS. Thus their analysis of the fluid phase does not suffer the possible loss of H₂O-soluble elements during quench and their bulk partition coefficients for these elements more closely approximate true solid–fluid values. Nonetheless, their bulk partition coefficients are strikingly similar to ours in several respects. First, they also observed $D_{\text{HREE}} > 100$ and a strong negative D_{Li} anomaly relative to D_{Y} . Second, the lowest bulk partition coefficients in their experiments are for Li, Sr and Ba, as well as for Pb, Cs and Rb (absent from our experiments).

The first striking difference between the data of Kessel *et al.* (2005a) and ours lies in the HFSE (Zr, Nb, Hf, Ta), for which their partition coefficients are systematically higher (Fig. 15b). This is again a simple consequence of the reduced solubility of rutile in their experiments relative to ours and the slightly higher TiO₂ in their starting materials (1.43 wt %) compared with ours (1.17 wt %), leading to a greater proportion of residual rutile. Their lower rutile solubility results from the higher pressure in their experiments and, more importantly, from the very high H₂O content of their fluids (~80 wt % in the experiments at 700–900°C). We have calculated the anhydrous rutile solubility for each of their experiments using the Ryerson & Watson (1987) expression and, as with our experiments, find remarkable agreement ($\pm 30\%$ relative) with the measured anhydrous TiO₂ contents of their fluids. Although Ryerson & Watson (1987) did not explicitly consider the role of H₂O, it would appear that it acts as an inert diluent in terms of TiO₂ solubility, a finding entirely in keeping with the very low solubility of rutile in pure H₂O at high pressure and temperature and the intermediate rutile solubility in fluid + silicate–solute systems (Audetat & Keppler, 2005; Manning *et al.*, 2007; Spandler *et al.*, 2007).

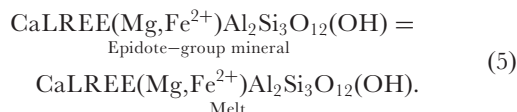
The second difference between the bulk partition coefficients of Kessel *et al.* (2005a) and ours is in terms of LREE (Fig. 15b). We argued above that $D_{\text{LREE}}^{\text{bulk}}$ is controlled by allanite solubility. Although Kessel *et al.* (2005a) did not report allanite in any of their original experimental papers, subsequent examination of the run products, combined with mass-balance calculations, has shown that the runs at 4 GPa and 700–900°C do indeed contain residual epidote-group minerals (P. Ulmer, personal communication, 2007). As we show below, the LREE contents of their fluids at these conditions are entirely consistent with them being allanite-saturated at slightly higher pressure and for slightly different fluid compositions than in our runs. We conclude that the bulk partition coefficients for MORB in the experiments of Kessel *et al.* (2005a) and the experiments

presented here are in excellent agreement despite radically different experimental techniques. This close agreement reinforces our view, expressed above, that the exact nature of the liquid (supercritical liquid or H₂O-rich melt) does not materially affect our conclusions regarding the trace element chemistry of subduction zone fluids

ALLANITE SOLUBILITY

A critical issue in the interpretation of our experiments and their implications for subduction zones is the solubility of allanite. Our experiments, and those of Hermann & Green (2001) and Hermann (2002), were doped with LREE, and it is reasonable to ask to what extent this facilitated allanite saturation in a way that would not occur in nature. We argued above that allanite solubility is controlled by intensive parameters, and therefore independent of bulk composition, such that the only consequence of doping is to increase the abundance of residual allanite and hence make it easier to identify and analyse. Analysis of LREE in other experimental glasses in equilibrium with allanite (Fig. 16a) confirms that there is a strong temperature control on the LREE contents of allanite-saturated liquids and that at low temperature the solubility is rather low; for example, 25 ppm total LREE (La–Sm) at 700°C. If the presence of allanite in residues of fluid or melt extraction from eclogites is controlled by its solubility in hydrous silicic liquids then this has important implications for the flux of LREE from subducted basaltic crust into the mantle wedge. If the solubility of allanite is sufficiently low at subduction zone temperatures that all liquids leaving the basalt have very little LREE, then generating the observed enrichments of LREE in the source regions of arc volcanic rocks will require either sustained fluxes over long periods of time or subjecting subducted crustal rocks to much higher temperatures than generally assumed. To test this possibility we have developed a model for allanite saturation in silicic melts and fluids similar to that used by Montel (1986, 1993) for monazite solubility. Monazite is an LREE-phosphate that, as we shall show, is remarkably similar to allanite in the temperature dependence of its solubility.

The equilibrium for the solubility reaction we will use is



Within the LREE we include La, Ce, Pr, Nd and Sm. We make no distinction between the different LREE end-members, nor between dissakisite and allanite, which constitutes an implicit assumption that mixing is ideal between these various components. To our knowledge there is no geochemical evidence to the contrary. The equilibrium constant K for equilibrium (5) is denoted K_5 .

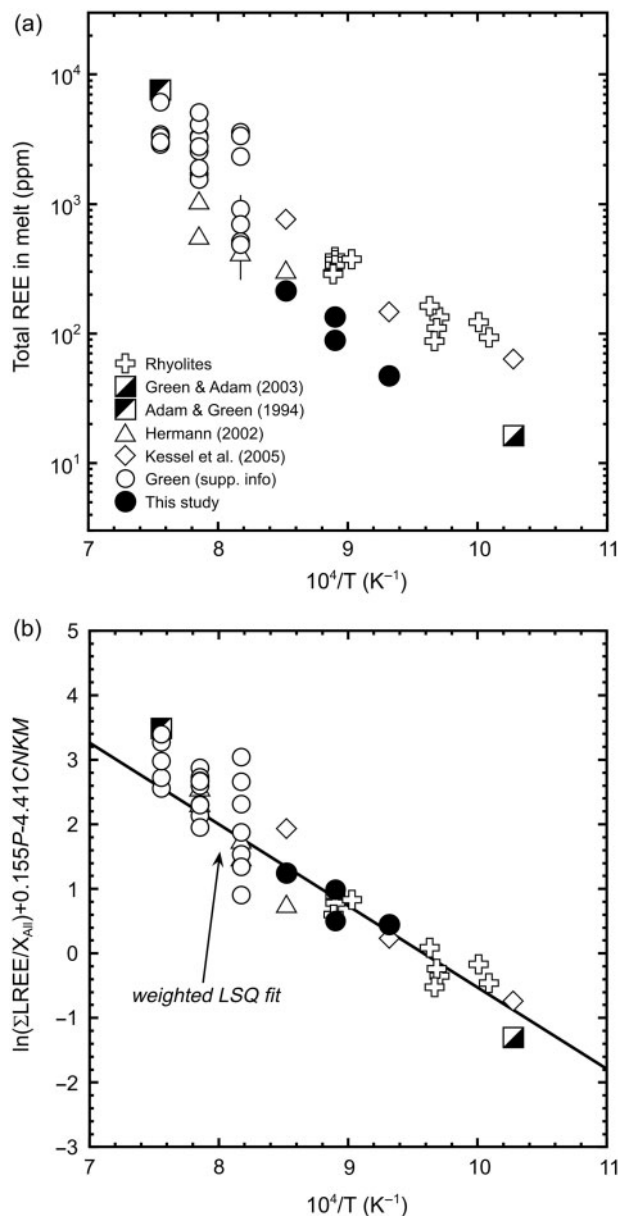


Fig. 16. (a) Solubility of allanite in melts and fluids from this study as a function of $10^4/T$ (K^{-1}) compared with published experimental data and natural rhyolites. (b) Modelled allanite solubility expressed in terms of $10^4/T$. The additional terms in the ordinate account for the pressure and composition terms in equation (9). The continuous line shows the temperature dependence from equation (9).

Following Montel (1993), we also make an allowance for impurity in the dissolving mineral, in this case allanite. We assume that the activity of allanite in an epidote-group mineral is simply the number of LREE a.p.f.u.:

$$a_{\text{allanite}}^{\text{epidote}} = X_{\text{LREE}}^A \quad (6)$$

Again, implicit in equation (6) is the assumption that mixing between epidote-group minerals is ideal and that

there is substantial short-range order between LREE substitution on the A-site and Mg or Fe²⁺ substitution on the M-site in keeping with the lack of any apparent compositional break in Fig. 9. This assumption can be modified should more thermodynamic data become available for this system.

We express the activity of allanite in the liquid in terms of the summed atomic fractions (see Montel, 1993):

$$a_{\text{allanite}}^{\text{fluid}} = \sum_{\text{La-Sm}} \left(\frac{\text{LREE}_{\text{ppm}}}{\text{LREE}_{\text{AW}}} \right) \quad (7)$$

where LREE_{ppm} is the ppm concentration of a given LREE in the liquid and LREE_{AW} is its atomic weight. This form of summation gets around the problem of selective doping of experiments with LREE of differing atomic numbers.

As all of the liquids and melts in our dataset contain H₂O, consideration must be given to the effect of this component on solubility. Following the observation that the model of TiO₂ solubility of Ryerson & Watson (1987) reproduces the TiO₂ contents of hydrous melts and aqueous fluids on an anhydrous basis, we have adopted the same approach here. This is consistent with the low solubility of monazite in aqueous fluids compared with silicate melts (Ayers & Watson, 1991). Thus LREE_{ppm} in equation (7) is the concentration of LREE in the liquid, recalculated on an anhydrous basis. For example, if a concentration of 32 ppm LREE is measured in a hydrous liquid with 20 wt % H₂O, then LREE_{ppm} = 40. Fits that attempted to use the hydrous solubility, coupled with the dissolved H₂O content were not only subject to the considerable uncertainty in H₂O contents, but also yielded substantially higher residuals, supporting our contention that, as in the case of Ti, H₂O acts primarily as an inert diluent in the supercritical liquid phase.

Parameters used for initial fitting are temperature, pressure and a compositional term. This term is largely empirical in the absence of activity–composition relations for the allanite component in the liquid. We investigated various possibilities, including the *D* parameter of Montel (1996), but found that the most robust term was simply the *CNKM* parameter:

$$\text{CNKM} = \text{molar} \frac{\text{Ca}}{(\text{Na} + \text{Mg} + \text{Ca} + \text{K})}. \quad (8)$$

The dataset used for fitting includes experimental data for which (1) allanite is reported and analysed in the run products, and (2) major elements and LREE are reliably determined in the melt or fluid phase. The data are weighted according to 1 SD uncertainties on measured LREE concentrations. With the exception of our study and that of Hermann (2002) there are no published analyses of allanite in any other experiments. For that reason we have augmented our dataset with unpublished allanite

analyses of T. H. Green from published experiments (Green & Pearson, 1985*a*, 1985*b*, 1986, 1988) provided as Supplementary Data (available for downloading at <http://www.petrology.oxfordjournals.org>). These data cover pressures of 1.2–3.5 GPa and temperatures of 900–1000°C in addition to a very wide compositional range, and are therefore extremely useful in tying down the compositional dependence of solubility.

We have supplemented our experimental dataset with analyses of rhyolitic glasses in equilibrium with allanite (Bacon *et al.*, 1981; Izett, 1981; Leeman & Phelps, 1981; Mahood & Hildreth, 1987; Chesner & Ettlinger, 1989). We have used only trace element analyses of glass separates or bulk analyses of obsidians with <0.001% phenocrysts (i.e. Bacon *et al.*, 1981). We have also confined ourselves to volcanic rocks where there are good independent constraints on eruption temperature ($\pm 20^\circ\text{C}$) from Fe–Ti oxide thermometry (e.g. Chesner, 1998; Manley & Bacon, 2000) and modest constraints on pressure (± 0.15 GPa), from volatile-saturation or other means (e.g. Wallace *et al.*, 1999). In all of these studies compositional data for allanite by EMPA were provided, allowing us to determine $a_{\text{allanite}}^{\text{epidote}}$. Where glass analyses did not include Pr, this element was interpolated from adjacent chondrite-normalized LREE.

The full calibrant dataset consists of 48 analyses, of which 25 are experimental and 23 volcanic. The data cover a range in pressure of 0–4 GPa, a range in temperature of 700–1200°C and include fluids or melts with 50–84 wt % SiO₂ on an anhydrous basis. The data were fitted by weighted least-squares regression. The weighted best fit, with 1 SD uncertainties, is

$$\begin{aligned} \ln K_5 &= \frac{\sum_{\text{La-Sm}} (\text{LREE}_{\text{ppm}}/\text{LREE}_{\text{AW}})}{X_{\text{LREE}}^{\text{A}}} \\ &= 12.13 \pm 0.13 - \frac{12657 \pm 136}{T(\text{K})} \\ &\quad - 0.155 \pm 0.010P(\text{GPa}) + 4.41 \pm 0.12 \text{ CNKM}. \end{aligned} \quad (9)$$

This expression has an absolute average deviation of 0.335, which means that it fits every allanite-saturated experiment to a factor of 1.40 in atomic LREE concentration over a range of more than two orders of magnitude. In terms of temperature, this translates to an uncertainty (1 SD) of only $\pm 27^\circ\text{C}$ at 1000 K, demonstrating the thermometric potential of allanite solubility. Interestingly, the temperature dependence of allanite solubility in equation (9) (i.e. $-12657 \pm 136 \text{ K}^{-1}$) is very similar to that for monazite derived by Montel (1993), -13318 K^{-1} . His intercept is lower for monazite solubility, 9.50 vs 12.14, indicating that monazite is slightly less soluble than allanite in systems that contain sufficient phosphorus to form monazite. These observations raise the interesting possibility that LREE become saturated in silicate melts or fluids at relatively

low concentrations regardless of whether Ca + Si + (Al or Fe³⁺) + (Mg or Fe²⁺) (allanite) or P (monazite) are present in the system. It is unclear if, or how, LREE would saturate in the absence of either of these groups of components (e.g. in carbonate systems).

Undoubtedly, equation (9) would benefit from additional experimental data, or data from very high temperature allanite-saturated rhyolites. In the absence of such data, however, our expression clearly demonstrates that allanite saturation is strongly controlled by temperature and that even for relatively modest (i.e. undoped) levels of LREE in a silicate rock allanite (or monazite) saturation is inevitable at relatively low temperatures. Given that partial melts of sedimentary rocks have broadly similar silica- and alkali-rich, Ca-poor major element chemistry (i.e. haplogranitic) to the liquids discussed here (Johnson & Plank, 1999), it is likely that they too will saturate in allanite (or monazite). It should be noted that, according to equation (9), allanite solubility increases with increasing Ca content of the liquid. However, all slab-derived fluids have low Ca as observed experimentally by us and others (Johnson & Plank, 1999; Green & Adam, 2003; Kessel *et al.*, 2005b) and therefore should be allanite-saturated. This raises some interesting questions about the LREE efflux from subducted materials.

DISCUSSION

The importance of accessory phases

A key finding of our experiments is the very low concentrations in the liquid of all trace elements except those not readily accommodated in garnet, allanite or rutile. In our experiments the excluded elements are the large ion lithophile elements (LILE), Ba and Sr, and the alkali metals, Li and K. By inference, based on their geochemical behaviour and on the experiments of Kessel *et al.* (2005a), Cs, Ra and Pb would also be excluded. The net result is that our silicate-rich supercritical liquid has the classic geochemical attributes of an 'aqueous fluid' as invoked by many workers to account for the contribution of selected trace elements from the subducted oceanic crust to the mantle wedge. We have shown that this signature is not so much a result of very high solubility of certain trace elements in aqueous fluids, as generally believed, but of the presence of residual garnet, rutile and allanite holding back all other trace elements. This will be true over the wide range of pressure–temperature conditions prevailing during subduction. The selective retention of a large suite of trace elements, and the release of rather few, will persist until the temperature is high enough to destroy one or more of the residual phases. This is unlikely to ever be garnet, so HREE in the fluid will always be vanishingly low, as is widely acknowledged (e.g. Stolper & Newman, 1994; Eiler *et al.*, 2000; Grove *et al.*, 2002; McDade *et al.*, 2003). However, only for very Ti- or LREE-poor

lithologies, or at very high temperatures (>900°C), can rutile or allanite be consumed. It is unlikely that for a conventional subduction geotherm such high temperatures will ever be encountered in the basaltic portion of the slab. We conclude that a 'fluid' signature consisting predominantly of Li, K, Na, Rb, Cs, Sr, Ba, Ra and Pb is an inevitable consequence of the subduction of H₂O-bearing or H₂O-fluxed rocks.

The apparent ubiquity of high-partition coefficient residual phases for many trace elements raises the question of how enrichments of these elements can occur in the source regions for arc magmas. This is not a new problem. It has long been recognized that accessory minerals play a key role in controlling the trace element budgets in a variety of rocks, including granites (e.g. Sawka *et al.*, 1984; Beard *et al.*, 2006) and metamorphic rocks, with or without partial melting (e.g. Sorensen & Grossman, 1989; Tribuzio *et al.*, 1996; Spandler *et al.*, 2003). Given that subduction zone metamorphism involves hydrous fluids, silica-rich melts and relatively low temperatures it is not surprising that accessory phases are important in this setting too (e.g. Green, 1981; Ryerson & Watson, 1987; Ayers & Watson, 1991).

Traditionally, residual rutile has been favoured as the means of holding back Nb and Ta and, to a lesser extent Zr and Hf, in subduction zones (e.g. Brenan *et al.*, 1994; Elliott *et al.*, 1997). Rutile is relatively soluble in silicate melts (Ryerson & Watson, 1987), but highly insoluble in aqueous fluids (Audetat & Keppler, 2005). Zircon may also play a role in retaining Zr and Hf. It is widespread in deeply subducted rocks and is highly insoluble in aqueous fluids (Ayers & Watson, 1991). Like rutile, zircon is relatively soluble in silicate melts (Watson & Harrison, 1983), but Zr is much less abundant than Ti in most rocks. Consequently, zircon is likely to be an important residual phase only at relatively low temperatures, and absent at or above the solidus. This is consistent with absence of zircon in our relatively high-temperature experiments, although we note that Johnson & Plank (1999) inferred the persistence of residual zircon up to 900°C at 2 GPa in their sediment melting experiments. The presence or absence of sizeable negative Zr–Hf anomalies in arc volcanic rocks consistent with the presence of residual zircon may provide a useful means of thermometry. Finally, this study and the work of Hermann (2002) have drawn attention to the role of allanite in holding back LREE and Th during subduction.

Clearly, the complex relationship between the initial abundances of some trace elements in subducted protoliths, the *P–T* conditions encountered during subduction and the solubility of accessory phases play a key role in generating the signature of arc volcanic rocks. In fact, it appears that understanding the solubility of accessory phases is at least as important as the mineral–fluid partitioning of more

abundant phases such as garnet and clinopyroxene. The influence of accessory phases is further strengthened by their production during incongruent melting, as in the case of allanite via reaction (2), or in the case of rutile during eclogite melting (Klemme *et al.*, 2002). Klemme *et al.* argued that because accessory phases are melting reaction products, wherever liquid is produced so too are accessory phases ensuring widespread saturation. This circumvents any questions about how a drop of melt formed in one part of a subducted slab knows that there is an accessory phase nearby and adjusts its composition accordingly.

Klemme *et al.* (2002) provided calculations to illustrate the behaviour of TiO₂ during melting of anhydrous eclogite at high temperature. Below the solidus TiO₂ is dissolved in silicate minerals $\pm$ rutile depending on the bulk TiO₂ content of the rock. At temperatures just above the solidus the concentration of TiO₂ in the liquid is controlled by the solubility of rutile. TiO₂ in the liquid attains its maximum value at the point that rutile is exhausted from the residue, following a dilution curve thereafter until it reaches the bulk TiO₂ value at 100% melting. The same principles will apply to the case of supercritical liquid extraction, although the marked change in behaviour across a solidus will not be observed. We illustrate this behaviour schematically in Fig. 17a. At low temperatures, the accessory phase may or may not be present in the solid residue depending on bulk composition. If absent, then the liquid concentration of the relevant species (i.e. LREE for allanite, Ti for rutile) will lie below saturation. Once the accessory phase saturates in the residue then the liquid composition will be buffered along the solubility curve. If both allanite and rutile are present, as in our experiments, the LREE/Ti ratio in the liquid will be buffered. Finally, at some higher temperature the accessory phase may be exhausted from the residue. Whether or not this happens depends on the bulk LREE or Ti content and the temperature. Beyond the point of elimination LREE and Ti will not be buffered in the liquid, which will show a dilution trend. Thus, we can anticipate three regimes, denoted A, B and C in Fig. 17a, corresponding to the different scenarios above. In regime B, the LREE/Ti ratio of the liquid is buffered at a value determined by the relative solubility of allanite and rutile, whereas in regimes A and C, buffering will not occur. The temperature extent of these three regimes is not well known. All of our experiments over 750°C pertain to regime B, whereas regime C will be relevant only at very high temperatures or for very LREE- and Ti-poor lithologies. The likelihood of low-temperature regime A is currently unknown. Klemme *et al.* (2002) argued that except for very low-Ti mafic lithologies rutile will be stable down to very low temperatures; in such low-Ti rocks ilmenite may be the key Ti-bearing phase. Similarly, in a recent study of allanite and monazite

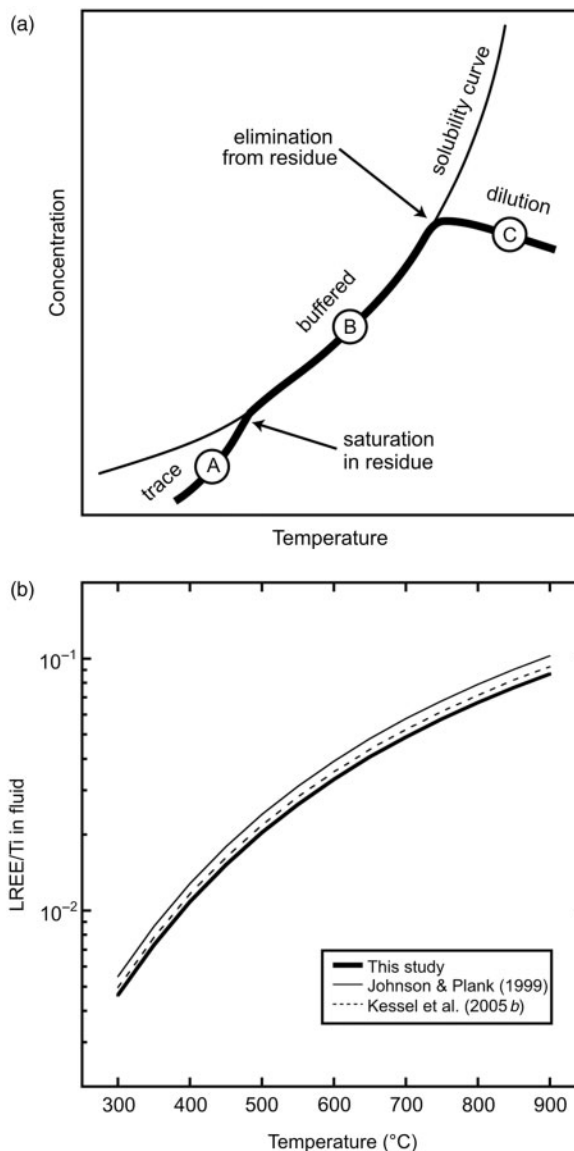


Fig. 17. (a) Schematic sketch illustrating the change of LREE and/or Ti concentration of a fluid as a function of temperature (at fixed pressure), modified after Klemme *et al.* (2002). In the course of melting the fluid becomes allanite and rutile saturated, irrespective of whether they were present before melting (regime A). The LREE and Ti in the fluid are buffered by allanite and rutile for a limited T range (regime B) until allanite and/or rutile are eliminated from the residue (regime C) because the solubility of LREE and Ti in the fluid exceeds the initial concentration in the protolith. (b) calculated LREE/Ti concentration ratios for allanite- and rutile-saturated fluids at 3 GPa as a function of temperature from fluid compositions from Johnson & Plank (1999), Kessel *et al.* (2005b) and this study, using the compositional parameters given in the text. The very strong temperature dependence of the LREE/Ti ratio should be noted.

stability in a pelite with 0.88 wt % CaO and $\sim$ 700 ppm LREE, Janots *et al.* (2007) calculated that allanite is stable at temperatures of 250–550°C and 0.1–1.5 GPa, whereas monazite is stable at all other conditions.

Janots *et al.* (2007) argued that for rocks with higher CaO content, allanite stability will be increased. Thus it seems likely that an LREE phase (allanite or monazite) will be stable in all subducted lithologies down to very low temperatures. As monazite and allanite have broadly similar solubilities, their buffering capacity for LREE in liquids will be similar. In the discussion below we focus on the case of allanite and rutile saturation, although the arguments could equally well be applied to a rock saturated with residual monazite and/or ilmenite.

For the case of allanite and rutile saturation (regime B) the LREE/Ti content of the extracted supercritical liquid will be buffered by their respective solubilities. As the solubilities of both allanite and rutile are reasonably well constrained, from equation (9) and Ryerson & Watson (1987), respectively, it is possible to model the LREE/Ti ratio of the liquid as a function of temperature, at fixed pressure and anhydrous liquid composition. Although we are dealing with a supercritical liquid of unknown H₂O content, the solubility relationships for allanite and rutile have been shown above to work well for the anhydrous component of the liquid, largely because of the diluent behaviour of H₂O. Consequently, our calculations do not require *a priori* assumptions about the H₂O content of the source rock, the extent of fluid fluxing through the rock or the evolution of fluid fraction with temperature, none of which are well constrained.

We have used equation (9) for allanite and the expression of Ryerson & Watson (1987) for rutile to calculate LREE/Ti in liquids as a function of temperature. Both expressions require knowledge of the anhydrous composition of the liquid phase. In the case of allanite this is the *CNKM* parameter in equation (8), whereas for rutile this is the *FM* parameter of Ryerson & Watson (1987). Both parameters are likely to vary with pressure and temperature, but for the purposes of illustration we will assume constant values based on experimental data from this study for liquid derived from basalt, from Kessel *et al.* (2005b) for fluid from K-free basalt, and from Johnson & Plank (1999) for fluid from pelagic clay. In each case we have calculated the *CNKM* and *FM* parameters for the lowest temperature liquids reported in each study. For our experiments these are *CNKM*=0.13 and *FM*=1.6; for Johnson & Plank (1999) they are 0.13 and 0.5; and for Kessel *et al.* (2005b) they are 0.28 and 5.5. As we shall show, the exact values are not hugely important to the results. We have adopted a pressure of 3 GPa for our calculations as this corresponds approximately to the depth of the slab beneath the volcanic front. The biggest unknown is X_{all} ; we have adopted a value of 0.4, a typical value for our experiments. It is clear from equation (9) that LREE solubility scales linearly with X_{all} . A better understanding of allanite–epidote solid solutions and the variation in X_{all} with pressure and temperature (see Janots *et al.*, 2007) is required.

The results of the calculations are shown in Fig. 17b. The LREE/Ti ratio of the liquid is consistently less than one because of the much lower solubility of allanite than rutile. It should be noted that, as Ti is much more abundant in the Earth than LREE, this does not mean that on normalized concentration plots subduction zone magmas will be enriched in Ti relative to LREE; quite the contrary in fact. LREE/Ti is very temperature sensitive (Fig. 17b), because rutile and allanite solubilities have different temperature dependences, and thus has the potential to constrain temperatures in the subducting slab for any arc where the LREE/Ti ratio of the slab fluid input can be calculated or estimated.

Implications for slab fluids

Our experiments and model calculations raise some interesting points about the flux of H₂O and trace elements from slab to wedge. First, the trace elements released from all slab lithologies consist of those not retained to any significant degree in any residual phase. At temperatures of $\geq 700^\circ\text{C}$ our experiments and those of Kessel *et al.* (2005a) suggest that these elements are K, Rb, Cs, Sr, Ba, Li and Pb. At lower temperatures and/or higher pressures the presence of residual mica may reduce the flux of these elements (e.g. Bebout *et al.*, 2007). Other trace elements are likely to be controlled by residual phases whose presence depends on a combination of bulk composition, pressure and temperature. In some cases (e.g. LREE, Ti) the trace elements will be buffered by solubility; in other cases (e.g. HREE, Th, U, HFSE) the concentration in the fluid will be controlled by a combination of partition coefficients and modal abundance. In the case of buffered trace elements the concentration ratio of an element buffered by one phase (e.g. LREE in allanite) to that buffered by another (e.g. Ti in rutile) will be very temperature sensitive and could potentially provide a means of constraining the temperatures of slab fluids (Fig. 17b). The case of unbuffered trace elements is less tractable as it requires knowledge of residual phase proportions. However, certain features can be discerned. Where residual allanite is present, fluid U/Th ratios will be very high, not so much because of the high solubility of U⁶⁺ in aqueous fluids, as often presumed, but because allanite has $D_{\text{Th}} \approx 1000$ and $D_{\text{Th}}/D_{\text{U}} > 10$. The ratio of LREE to Th, which has been pioneered as a monitor of sediment recycling by Plank (2005), will be sensitive to a combination of pressure and temperature and the mode of residual allanite. We note that for all of the experimental and volcanic allanites in Fig. 13 $D_{\text{La}}/D_{\text{Th}} \approx 2$. Ratios of HFSE, such as Nb/Ta and Zr/Hf, will be strongly influenced by the presence of rutile and garnet, although the exact ratio is dependent on garnet composition and temperature, especially for Zr/Hf.

The second point is that the absolute concentrations of trace elements in aqueous liquids, or more specifically the ratio of trace element to H₂O, will be very low for all but

the most strongly excluded elements (e.g. alkalis, Sr, Ba, Pb). HREE contents of fluids, although not strictly buffered by garnet, will be vanishingly low in all subduction zone fluids derived from a garnet-bearing residue. It is clear that a balance exists between the temperature of fluid release, the amount of fluid fluxed into the mantle wedge and the total enrichment of the wedge in certain trace elements. Although detailed flux calculations are beyond the scope of this study, we suggest that supplying the requisite quantities of trace elements such as LREE or Th to the source regions of arc magmas at normal subducted slab temperatures will require considerable fluxes of H₂O because of the low solubility of allanite (or monazite). This is broadly in accord with the flux-melting model of Grove *et al.* (2006) for mantle wedge peridotite. Our solubility data for allanite suggest that some quantification of the H₂O flux may now be possible.

An alternative scenario to adding all trace elements to the wedge via dilute H₂O-rich liquids is to mechanically incorporate fragments of subducted crust into the mantle wedge during subduction, either by mechanical imbrication near the trench or as ascending diapirs from the slab–wedge interface (e.g. Kelemen *et al.*, 2003; Gerya & Stockert, 2006). In this case the various subducted lithologies will be subjected to much higher temperatures than is possible within the slab itself. Such high temperatures provide not only scope for generating melts with much higher solubilities of the trace elements retained in accessory phases, but may also lead to the selective elimination of such phases from the residue (region C in Fig. 17a). For example, it is possible to envisage a situation in which temperatures are high enough to eliminate allanite or monazite, releasing copious amounts of LREE, but not high enough to eliminate rutile, thereby maintaining low Ti, Nb and Ta. Because of the very high initial trace element content of subducted sediment, relatively small amounts of mechanically incorporated sediment could produce much greater enrichments in trace elements such as LREE and Th than is possible with dilute fluids alone. We suggest tentatively that a combination of physical sediment incorporation, via diapirs or imbrication, with fluxing of the wedge with dilute LILE-rich aqueous fluids, driving partial melting, is entirely consistent not only with our experimental data, the model of Grove *et al.* (2006) and the numerical simulations of Gerya & Stockert (2006), but also accords with the longstanding tripartite distinction of materials in the mantle source regions of arc basalts as discussed in the Introduction.

CONCLUSIONS

We have performed phase equilibrium and trace element partitioning studies of H₂O-saturated MORB at a pressure of 2.5 GPa and temperatures of 750–900°C with $f_{\text{O}_2} = \text{NNO}$. Amphibole and epidote were present below

800°C; garnet, omphacitic clinopyroxene and rutile are present under all conditions. Allanite is a residual phase above 750°C. Under the experimental conditions the trondhjemitic Na–Si–Al-rich glass in the experiments is likely to have quenched from a supercritical liquid.

Our trace element analyses of glasses demonstrate the important control exerted by residual minerals on the trace element compositions of fluids released from subducted basalts. In addition to garnet, which controls HREE, and rutile, which controls Ti, Nb and Ta, allanite buffers the LREE contents of fluids to relatively low levels and preferentially holds back Th and, to a much lesser extent, U. In agreement with previous experimental (Hermann & Green, 2001; Hermann, 2002; Spandler *et al.*, 2003) and metamorphic (Sorensen, 1991; Tribuzio *et al.*, 1996) studies we conclude that allanite plays a key role in selectively retaining trace elements in the slab during subduction.

We have used our new and published experimental data and analyses of allanite-bearing volcanic rocks to derive a model for allanite solubility in silicic liquids as a function of pressure and temperature and LREE (La–Sm) content. The model reproduces, to within a factor of 1.4, bulk LREE contents across more than two orders of magnitude. The temperature dependence of allanite solubility is very similar to that previously determined for monazite (REE-phosphate) by Montel (1993) and indicates the geothermometric potential of allanite solubility. Silicic liquids from either basaltic or sedimentary protoliths will be allanite- (or monazite-) saturated except at very high temperatures. For conventional subduction zone geotherms the low solubility of LREE (+ Th) in liquids derived from allanite-saturated basalts and their sedimentary veneer raises questions about how the flux of these elements from slab to wedge is effected. We suggest either that, locally, temperatures experienced by the slab lithologies are substantially higher than normally assumed, as a result of mechanical incorporation into the wedge, or that considerable volumes of H₂O-rich liquids, carrying their modest budget of LREE + Th, must pass through the mantle wedge for sustained periods. The solubility of accessory phases in liquids derived from subducted rocks, coupled with reactive transport modelling of such liquids through the mantle wedge, can provide important petrological constraints on the thermal structure of subduction zones.

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SUPPLEMENTARY DATA

Supplementary data for this paper are available at *Journal of Petrology* online.

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