A Partial Record of Mixing of Mantle Melts Preserved in Icelandic Phenocrysts

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RECEIVED FEBRUARY 15, 2011; ACCEPTED MAY 10, 2011
ADVANCE ACCESS PUBLICATION JUNE 29, 2011

The record of mixing of mantle melts in magma chambers has previously been observed in the compositions of olivine-hosted melt inclusions from Borgarhraun, a primitive basalt flow from the Theistareykir volcanic system, northern Iceland. Borgarhraun also contains high Mg-number (85–92) clinopyroxenes, which exist in polycrystalline nodules and as phenocrysts. Coincident major and trace element analyses were made in compositional zones of these clinopyroxenes, and Ce/Yb ratios of the melts in chemical equilibrium with each of the clinopyroxene zones were calculated using carefully selected crystal–melt partition coefficients. These calculations allow direct comparison of clinopyroxene compositions with existing melt inclusion data. The range of Ce/Yb ratios in the crystals and in the equilibrium melts cannot be accounted for by crystallization alone, requiring simultaneous mixing and crystallization of compositionally variable mantle melts. However, the range in Ce/Yb ratios in the crystals is larger than that of melts generated at shallower depths, which is smaller than that of melt inclusions hosted by olivines with equivalent Fo contents. Also, the mean composition of the melts from which clinopyroxene grew has significantly lower Ce/Yb than the olivine-hosted melt inclusions. The record of mantle melt variability in clinopyroxenes is thus biased towards more depleted Ce/Yb ratios in the enriched melts, compared to the olivine-hosted melt inclusions. The record of mantle melt variability in clinopyroxenes is thus biased towards more depleted (low Ce/Yb) melt compositions. This bias can be understood if the trace element variation in the Borgarhraun parental melts is coupled to major element variation, as expected from petrological parameterizations of mantle melting. The major element variation influences the phase relationships and controls the appearance of liquidus phases during fractional crystallization in near-Moho magma chambers. Small-degree, deep melts, formed in the presence of garnet, have high Ce/Yb ratios. On cooling, these melts have a longer olivine-only crystallization path than melts derived from the shallow mantle. When these deep-sourced melts eventually become clinopyroxene saturated, they have low Mg-numbers to crystallize high Mg-number clinopyroxenes such as are found in Borgarhraun. In contrast, shallow, depleted melts saturate in clinopyroxene at high Mg-number. The delayed onset of clinopyroxene crystallization in the enriched melts, coupled with concurrent mixing and crystallization of melts generated at a range of depths in the mantle, can account for the difference in the distribution of the trace element composition of high Mg-number melts saturated in olivine and clinopyroxene. The trace element compositions of high Mg-number clinopyroxenes in Borgarhraun therefore provide only a partial and biased record of the mixing of mantle melts. As well as showing that melt mixing may be preserved in phenocryst compositions, the results illustrate that trace element disequilibrium between crystals and carrier melt can be a consequence of magma mixing, rather than necessitating a xenocrystic origin for the crystals. Furthermore, care must be taken when using clinopyroxene separates from primitive basalts to examine compositional heterogeneity, as they provide a record of the chemical evolution of the magmatic system that is biased towards depleted compositions and therefore incomplete.

KEY WORDS: clinopyroxene; Iceland; mid-ocean ridge; mixing; trace elements

INTRODUCTION

Melting of the upwelling mantle under mid-ocean ridges by adiabatic decompression is thought to be near-fractional (e.g. Kelemen et al., 1997, and references therein). Over the depth range of melting, instantaneous fractional melts may vary hugely in their major and trace element compositions. For example, the small volumes of melt produced near the base of the melting region have high light rare earth element (LREE) concentrations, whereas larger melt fractions from shallow melting have relatively low

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LREE concentrations. After separating from the solid residue, melts formed by adiabatic decompression may rise in channels (Kelemen et al., 1995). Within such channels the compositional diversity of melts sourced from different depths may be preserved (Spiegelman & Kelemen, 2003) without fully mixing. Light/heavy REE ratios (LREE/HREE, e.g. La/Yb) and other incompatible trace element ratios are changed little during fractional crystallization in the crust, and so variation in these ratios between whole-rock, glass or melt inclusion analyses may in some instances be interpreted as reflecting variation in primary mantle melt compositions (e.g. Gast, 1968).

It has been proposed that the record of chemically variable primary melts can be preserved in the compositions of melt inclusions found in early crystallizing phases; for example, forsteritic olivine (Sobolev & Shimizu, 1993; Gurenko & Chausidon, 1995; Kamensky et al., 1998; Shimizu, 1998; Sobolev et al., 2000; Maclennan et al., 2003b; Laubier et al., 2007; Maclennan, 2008) or anorthitic plagioclase (Nielsen et al., 1995; Sours-Page et al., 1999). Variability in melt inclusion compositions reflects incomplete homogenization of fractional mantle melts before the onset of crystallization. Furthermore, compositional variation in the whole-rock or glass compositions of erupted basalt flows is commonly much less than that of the melt inclusions hosted in phenocrysts in the flow, indicating that extensive melt mixing and compositional homogenization has taken place between inclusion entrapment and eruption. These differences in compositional variability have been highlighted in a study by Maclennan et al. (2003a), which used over 100 olivine-hosted melt inclusion compositions from the Borgarhraun basaltic flow, northern Iceland, to show that primary mantle melts entering the Icelandic lower crust undergo concurrent melt mixing and crystallization. The ranges in key geochemical indices of the melt inclusions (e.g. La/Yb) were shown to be greatest in melts hosted by olivines with a composition of 90 mol % forsterite (Fo90), and the variability of inclusion compositions decreased as the Fo content of the host olivine decreased. The average La/Yb of the melt inclusions, reflecting the composition of the homogenized product of mixing, was shown to be near-identical to the whole-rock La/Yb of the erupted Borgarhraun basalt.

Although mixing of compositionally diverse melts may vary in its extent and depth, it is likely that melt mixing is a ubiquitous process in sills or magma chambers beneath much of the global mid-ocean ridge system.

A caveat in the interpretation of melt inclusion compositional variability is that the influence of processes in the crust must first be excluded. Processes that may affect melt inclusion compositions include pre-entrapment crustal melt assimilation (e.g. Yaxley et al., 2004), more complex dissolution–reaction–mixing (DRM) processes (Danyushevsky et al., 2004), and post-entrapment diffusion through the host crystal (Gaetani & Watson, 2000; Gaetani et al., 2002; Michael et al., 2002; Danyushevsky et al., 2003). Although the effects of assimilation and DRM processes may be assessed by careful investigation of geochemical indices (e.g. Maclellan, 2008), diffusion has so far been more difficult to rule out. This is because estimates of diffusion rates through olivine vary by several orders of magnitude. Spandler et al. (2007) and Spandler & O’Neill (2010), using the equations of Qin et al. (1992), estimated that complete re-equilibration times for REE in a 50 μm diameter, spherical melt inclusion within a 1 mm diameter olivine held in melt at 1300°C are of the order of ~10^10 to ~10^11 years (the diffusion coefficient for REE under these conditions being DREE ~10^{-15} m^2 s^{-1}). On the other hand, Cherniak (2010) measured diffusion coefficients ofREE in olivine that suggest re-equilibration times under the same conditions of >10^4 years.

The potential problems of fast diffusion rates through olivine can be obviated by analysis of different crystal phases. For example, compositions of clinopyroxene phenocrysts from erupted basalts may also preserve a record of the heterogeneous melts from which the phases crystallized. Rates of diffusion of key trace elements are much slower in clinopyroxene than in olivine (DREE ~10^{-18} to 10^{-20} m^2 s^{-1}; Sneeringer et al., 1984; Van Orman et al., 2001). Melt inclusions in clinopyroxene may also preserve such a record, although post-entrapment crystallization (e.g. Danyushevsky et al., 2002; Magnani et al., 2006; Streck & Wacaster, 2006) and syn-entrapment alteration (Nakamura & Shimakita, 1998) may change the original compositions.

Several recent studies have indicated the usefulness of clinopyroxene phenocryst compositions in examining processes and melt heterogeneity in magmatic systems (e.g. Kamensky et al., 1998; Wade et al., 2008; Jackson et al., 2009). This study focuses on an investigation of coincident major and trace element analyses from compositional zones in clinopyroxene crystals found in the Borgarhraun flow, northern Iceland. These crystals are present in wehrlitic and gabbric nodules and as phenocrysts. Clinopyroxene trace element compositions are converted into equilibrium liquid compositions using suitable partition coefficients, allowing the compositions of the liquids from which clinopyroxene crystallized to be compared with published olivine-hosted melt inclusion data. The results show that the Borgarhraun clinopyroxenes crystallized from melts with a range of compositions. This variability is particularly well displayed in trace element ratios such as Ce/Yb. These findings support the interpretation of compositional variation in olivine-hosted melt
inclusions from Borgarhraun as reflecting diversity in mantle melt compositions (Slater et al., 2001; Maclellan et al., 2003a, 2003b). These diverse melts then concurrently mix and crystallize in near-Moho magma chambers. Although melt mixing has previously been inferred from phenocryst compositions—including the presence of highly anorthitic plagioclase in mid-ocean ridge basalts (MORB; Elthon & Casey, 1983; Sinton et al., 1993; Kohut & Nielsen, 2003) and isotopic heterogeneity between phenocrysts and host-rock (Halldorsson et al., 2008; Jackson et al., 2009)—this study is the first to demonstrate that phenocryst trace and major element compositions can be used to track the process of mixing during fractional crystallization.

In detail, the observations highlight differences in the distribution of the trace element composition of melts that were trapped in olivines as inclusions, and the melts that crystallized clinopyroxene phenocrysts. The maximum and mean Ce/Yb ratios of melts that crystallized clinopyroxene are lower than those of the olivine-hosted inclusions. This bias is likely to arise from the coupled variation of the major and trace element composition of mantle melts generated at different depths under northern Iceland. This major element variation controls the appearance of clinopyroxene as a liquidus phase, such that the distribution of crystallizing clinopyroxene compositions is biased towards recording trace element-depleted, high-fraction mantle melts produced near the top of the melting region.

**Geological and petrological context of the Borgarhraun flow, northern Iceland**

The Thieisareykir volcanic system in the Northern Volcanic Zone of Iceland (Fig. 1) is the most northerly on-land system in Iceland. It lies ~100 km north of the putative plume centre (the NW of the Vatnjökull icecap), and it has been shown that melt generation beneath this system can be explained by passive mantle upwelling driven by plate separation alone (Maclellan et al., 2000). Variability in major element, trace element and isotopic compositions of Thieisareykir whole-rock samples and melt inclusions has been attributed to variation in mantle melt compositions, controlled both by source heterogeneity and the melting process under Thieisareykir (Elliott et al., 1991; Hemond et al., 1993; Skovgaard et al., 2001; Slater et al., 2001; Maclellan et al., 2003b; Stracke et al., 2003; Thirlwall et al., 2004). The bulk of erupted postglacial basalts from Thieisareykir form a lava shield, Storaviti (~30 km³, labelled 'C' in Fig. 1), but a number of separate flows have been described by Slater (1996) and Slater et al. (2001). Borgarhraun is one of the early postglacial flows from Thieisareykir (12–7 ka BP), covering ~20 km², and is basaltic to picritic in composition (9–7–9 wt. % MgO; Hemond et al., 1993; Slater, 1996; Sigurdsson et al., 2000). It is variably olivine-, plagioclase- and clinopyroxene-phryic. The flow also contains gabbroic, wehrlitic, dunitic and troctolitic nodules of up to ~2 cm diameter. These nodules were described in detail by Maclellan et al. (2003a). Importantly, the variability in the trace element compositions of melt inclusions hosted by olivine phenocrysts in Borgarhraun is far greater than the variability observed amongst different whole-rock samples from this flow (Maclellan et al., 2003b). Melt inclusions in chromian spinel phenocrysts also preserve significant major element compositional variability, particularly in CaO contents (Sigurdsson et al., 2000).

**SAMPLE COLLECTION AND PREPARATION**

New sampling of gabbroic and wehrlitic nodules from the Borgarhraun flow was carried out in July 2007; all samples came from within a few tens of metres of 65°51'05"N, 16°59'-39"W. Polycrystalline nodules containing clinopyroxene and large (up to ~1 cm) clinopyroxene phenocrysts were made into 500-μm-thick sections or mounted in epoxy resin. Maclellan et al. (2003a) reported similar major element compositions for clinopyroxenes in the nodules and those existing as phenocrysts, and noted that some Borgarhraun phenocrysts probably represent the disaggregated remnants of nodules. Some samples were remounted for ion probe analyses; in these cases, care was taken to preserve the previously studied sample surface when setting in epoxy resin and polishing.

**ANALYTICAL METHODS**

To assess compositional zonation within clinopyroxene crystals, backscattered electron images were obtained using a JEOL JSM-820 scanning electron microscope, with an accelerating voltage of 15 kV and beam current of 6–10 nA. The concentrations of major and minor elements in clinopyroxene crystals, and also of several olivine crystals in wehrlitic or gabbroic nodules, were analysed using a Cameca SX100 electron microprobe at the Department of Earth Sciences, University of Cambridge, UK. Reed (2005) has provided a review of the methods involved. Both single point analyses and profiles across crystals were performed. Elements were analysed in wavelength-dispersive mode using five spectrometers, an accelerating voltage of 15 kV and a beam current of 10 nA for major elements or 100 nA for minor elements. The beam was focused to a 2 μm spot. Typical peak counting times were 20 s for major elements and 40 s for minor elements, and background counting times were 10 s. A set of natural silicate and metal standards was used at the start of each session for calibration of elemental concentrations, as follows: Na on jadeite, Mg on periclase, Si and Ca on diopside, Fe on fayalite, K on feldspar, Ti on rutile, Al on corundum, and Cr, Mn and Ni on pure metals. Analyses with oxide totals outside the range 98.5–101.5 wt. % or
with poor stoichiometry were discarded. In general, accuracy and precision for elements present at >1 wt % is ~1 % (1σ relative precision) and 5 % for elements at <1 wt %. Semi-quantitative element maps were made for several samples, which highlighted some of the more complex textural features (e.g. sector and patchy/turbulent zonation) within crystals and were used to guide placement of ion microprobe points during subsequent analyses.

Trace element concentrations were determined within the compositional zones recognized in backscattered electron images. Concentrations were analysed both by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and secondary ionization mass spectrometry (SIMS). LA-ICP-MS spots were picked so as to sample the larger compositional zones, reducing the chance of contamination from adjacent zones. SIMS analyses were typically performed within the thinner compositional zones.

For LA-ICP-MS analyses, concentrations were measured using a New Wave UP213 Nd:YAG laser ablation system interfaced to a Perkin-Elmer Elan DRC II ICP-MS system at the University of Cambridge. The diameter of the laser beam was 100–120 μm, the laser repetition rate was 10 Hz and the laser power was ~5 J cm⁻². Sample pit depth was around 50 μm. The ablated material was carried to the mass spectrometer from the ablation cell in a helium–argon gas mixture. Data acquisition settings for the ICP-MS system were one sweep per reading, one replicate,
40 readings per replicate, with a rinse-through time between analyses of 60 s. Dwell times were typically 10–50 ms, but were dependent on the isotope and concentration of each element. CaO concentrations of the compositional zones, determined by electron microprobe, were used for internal standardization of elemental concentrations. Intra-zone variability in these electron microprobe determined CaO concentrations is negligible, with standard errors on the means of repeat spot analyses <0.17 wt %. NIST SRM610 was used for calibration of elemental sensitivities, and accuracy was assessed by analysing NIST SRM612 and the international rock standards BIR-1, BHVO-2 and BCR-2. Recovered values were typically 90–110% of published values (Pearce et al., 1997). For the elements analysed, matrix-matching of standards to unknowns for calibration of LA-ICP-MS signals was not necessary, as calibration using the NIST SRM610 glass produces concentrations with accuracies of 5–10% (reviewed by Pettke, 2006; Joachum & Stoll, 2008; Sylvester, 2008; see also Heinrich et al., 2005). External precision was monitored using an in-house clinopyroxene standard, and precision values are reported in Electronic Appendix 1 (available for downloading at http://www.petrology.oxfordjournals.org). Intra-session ICP-MS drift was not detected in the repeat analyses of the clinopyroxene standard. Data reduction was carried out using Glitter Software (GEMOC, Australia), which allows selection of signals, visualization of data quality and corrections for isobaric interferences. Because concentrations in the samples are close to detection limits for some trace elements, 1σ errors from counting statistics are reported in the instances where these are greater than the external precision. However, repeat analyses within zones were often achievable, thus errors in Electronic Appendix 1 are predominately standard errors on the mean concentration of an element in a recognized clinopyroxene zone. Most repeat analyses in clinopyroxene zones are within 5–10% of each other; where there are larger differences, this may be due to the ablation either of portions of adjacent compositional zones at depth within a laser pit, or of small melt inclusions.

SIMS analyses were performed at the NERC Ion Microprobe Facility, University of Edinburgh, UK, using a Cameca IMS-4f ion microprobe. Analytical procedures have been described by Shimizu & Hart (1982). The samples were gold coated and bombarded by a beam of O⁺ ions. The primary accelerating voltage was 10 kV, and the secondary ion accelerating voltage was 4-5 kV. A 75 eV energy offset was used, with a 40 kV window, to suppress molecular ion interferences (Shimizu & Hart, 1982). Internal standardization was carried out using known Si concentrations from electron microprobe analyses. Spot size was ~25–35 μm, and the contrast aperture was set to 25 μm. Each analysis comprised 10 scans, each lasting ~2-5 min. Dwell times varied depending on elemental abundance, but ranged from 2 to 8 s per scan. Element abundances were calculated from secondary ion intensities (ratioed to 30Si) using the in-house JCION-5 software. Molecular interferences were corrected for in this software and further possible interferences were investigated with the aid of major element and LA-ICP-MS trace element concentrations. Accuracy was determined from daily analyses of the NIST SRM610 glass, and small corrections were applied to the data consistent with the daily SRM610 concentrations for each element. Precision was estimated using repeat analyses on the KH-1 clinopyroxene (Irving & Frey, 1984). For clinopyroxene, ion yield patterns and efficiency relative to Si are similar to NBS SRM610, therefore no corrections were made for matrix effects. Precision from repeat analyses of standards is generally <5%. Because of long analysis times, no repeat measurements were made in clinopyroxene zones. Several zones were analysed both by LA-ICP-MS and SIMS, and there is good agreement between the concentrations of elements measured by the two methods. As with the LA-ICP-MS analyses, when the errors from counting statistics are greater than those from repeat analyses on standard material, these are reported as the precision estimates. Electronic Appendix 1 provides trace element data for each clinopyroxene zone, which are tabulated along with the major element concentrations in each zone. In total, 73 distinct zones in 21 clinopyroxene crystals were analysed for both major and trace elements, in four xenoliths and six phenocrysts.

CLINOPYROXENE ZONATION AND MAJOR ELEMENT CHEMISTRY

Zoning in Borgarhraun clinopyroxenes is clear in backscattered electron images. Spatial variations in major element concentrations match observed zonation patterns in these images. Crystals show normal or reverse concentric zoning (Fig. 2a), and sector zoned crystals are common (Fig. 2b). Some crystal cores and/or rims (especially those with Mg-number ~90) show evidence for resorption by the melt, with embayments and rounded-off edges to zones (Fig. 2b). Cores are occasionally complexly zoned. Intra-crystal variability in major elements is often small (<2 Mg-number units, even between zones of sectored crystals), except in the nodule shown in Fig. 2a, where simply zoned clinopyroxenes have Mg-number ~85 cores and Mg-number ~90 rims. Mg-number of clinopyroxene is calculated throughout as 100 × Mg/(Mg + Fe), assuming all Fe is present as Fe²⁺.

Electron microprobe analyses of Borgarhraun clinopyroxenes and olivines from gabbroic and wehrlitic nodules are listed in Electronic Appendices 1 and 2 respectively.
Often, several major element analyses were performed in each recognized clinopyroxene zone; the values listed are averages with standard errors on the mean. Xenolith and phenocryst compositions are very similar to those reported by Maclellan et al. (2003a). The highest Mg-number Borgarhraun clinopyroxenes have high Cr$_2$O$_3$ contents (up to $\sim$1.9 wt%), consistent with their deep green colour in hand specimen; these can be termed Cr-diopsides.

**CLINOPYROXENE THERMOBAROMETRY**

Pressure and temperature estimates of clinopyroxene crystallization were revised from those of Maclennan et al. (2001b, 2003a) using the crystal–melt barometer and thermometer of Putirka et al. (1996). These methods are suitable for anhydrous mafic compositions and are therefore applicable to depleted Icelandic basalts such as those of Borgarhraun, which are likely to contain <0.15 wt% H$_2$O (Saal et al., 2002; Nichols & Wysoczanski, 2007). The method also ignores clinopyroxene components containing Fe$^{3+}$. Fortunately, Fe$^{3+}$/ΣFe ratios are likely to be low in Borgarhraun clinopyroxenes (melt Fe$^{3+}$/ΣFe $= 0.1$; Maclellan et al., 2003a). Errors for the thermometer and barometer are $\pm 27$ K and $\pm 1.4$ kbar respectively.

Accurate thermobarometry using the Putirka et al. (1996) models is heavily dependent on identifying a suitable liquid composition in equilibrium with each clinopyroxene composition. For these liquids, rather than simply using Borgarhraun whole-rock compositions, which are not necessarily in major and trace element equilibrium with the clinopyroxene, a compilation of 1000 whole-rock and glass analyses was used, consisting of Icelandic basalts for which major element and REE data exist. These compositions were used as potential equilibrium liquids in the Putirka et al. (1996) model, and tested for both Mg–Fe and trace element equilibrium, as described below. Whole-rock compositions with $>12$ wt% MgO were excluded from the database of potential equilibrium liquids, as they are likely to be affected by significant proportions of accumulated olivine.

Suitable equilibrium liquids were investigated by comparing the major element composition of each analysed clinopyroxene zone with every Icelandic basalt composition in the compilation, to obtain $\sim$1000 initial clinopyroxene–liquid pairs for each clinopyroxene zone. These pairs were first tested for equilibrium Mg–Fe partitioning.
This was achieved by using the Mg-number of each clinopyroxene zone and equation [35] of Wood & Blundy (1997) to calculate a predicted value of the clinopyroxene–liquid equilibrium constant for Fe–Mg exchange, $\Delta G_{\text{dcpx-liqu}}^{\text{Fe-Mg}}$, for each zone. If the observed clinopyroxene–liquid $\Delta G_{\text{dcpx-liqu}}^{\text{Fe-Mg}}$ value was within 0.03 of this predicted value, the liquid was accepted as potentially suitable equilibrium liquid.

The accepted crystal–liquid pairs were further assessed for crystal–liquid trace element equilibrium. Predicted liquid trace element concentrations, calculated using 3+ element partition coefficients calculated from Wood & Blundy (1997) and the trace element data for the clinopyroxene zone (from this study), were compared with the concentrations in the selected Icelandic melt compositions. For comparison of predicted and observed concentrations, three trace elements (Ce or La, Nd or Sm, and Yb, Dy or Y, depending on the available liquid trace element data) were used. If the observed trace element concentrations were within 20% of the predicted values, the Icelandic melt composition was considered to be a suitable equilibrium liquid for use in the Putirka et al. (1996) thermometer and barometer. This method of selecting equilibrium clinopyroxene–liquid pairs is believed to be more robust than those used in previous studies (Maclean et al., 2001b, 2003a), and thus the resulting pressures are likely to be more accurate. Because several Icelandic basalt compositions were typically found to be in equilibrium with each clinopyroxene compositional zone, multiple pressure estimates were often found for each clinopyroxene zone, resulting in a range of pressures for each zone (shown by the black bars in Fig. 3). These ranges are always less than 2 kbar and are typically comparable with the 1σ calibration error of ±14 kbar associated with the Putirka et al. (1996) barometer.

All pressures determined from clinopyroxene zones in this way range from 4.9 to 11.0 kbar. Temperatures range from 1208 to 1286°C. Excluding the outermost ~100 μm wide zone of one crystal in sample B6 (Mg-number = 85-4), which gives pressures of 4.9–5.2 kbar, the pressure range is 6.4–11.0 kbar, with a mean of 8.1 ± 1.4 kbar (1σ). Likewise, the mean temperature is 1249 ± 14°C. Pressure of crystallization does not correlate with the Mg-number of the clinopyroxene zones ($r^2 = 0.03$).

Many of the highest-Mg-number (90–92) clinopyroxene zones are not in equilibrium with any of the Icelandic whole-rock or glass compositions from the compilation. This may be because, as shown below, such high Mg-number clinopyroxene crystallizes from mantle melts with extreme trace element depletion that are rarely erupted. These clinopyroxene zones are, however, very similar in terms of major element compositions to the clinopyroxene formed in experimental crystallization run TS137 of Skulski et al. (1994). The starting composition for this experiment was a Baffin Island picrite, PD-27, and conditions were 1300°C, 10 kbar. Pressures of crystallization of the Mg-number 90–92 Borgarhraun clinopyroxene zones were thus calculated by using the resultant glass composition from this experiment as the liquid composition in the Putirka et al. barometer. Again, crystal–liquid pairs were checked by comparing predicted and observed $\Delta G_{\text{dcpx-liqu}}^{\text{Fe-Mg}}$ values. The range of pressures calculated for the Mg-number 90–92 zones is 6.5–10.5 kbar, similar to that of the lower Mg-number clinopyroxene zones. Pressures calculated in this way are shown in Fig. 3 as triangles.

The pressure ranges for all the zones indicate that crystallization of all Borgarhraun clinopyroxenes took place in the lower crust and uppermost mantle under Theistareykir, where the Moho depth is 20–25 km (Staples et al., 1997). This result is in agreement with crystallization pressures of around 10 kbar estimated for Borgarhraun whole-rock compositions (Maclean et al., 2001b) using the predicted position of the olivine–plagioclase–augite–melt saturation boundary (Yang et al., 1996). Furthermore, some wehrlitic and gabbronorite nodules from this study show evidence for crystallization of clinopyroxene before plagioclase, similar to those of Maclean et al.
The new pressure estimates are thus in keeping with the results of crystallization experiments (Bender et al., 1978) and modelling (Weaver & Langmuir, 1990), which indicate that MORB-like compositions start to crystallize clinopyroxene before plagioclase at pressures > 8 kbar.

**CLINOPYROXENE TRACE ELEMENT CHEMISTRY**

Trace element analyses were made within the clinopyroxene zones recognized in backscattered electron images. Trace element variability between clinopyroxene crystals in nodules is present, as well as trace element zonation within crystals. Examples of variability of Ce/Yb and Mg-number in clinopyroxene are shown for two crystals in Fig. 2. Representative trace element concentrations from Borgarhraun clinopyroxene zones are reported in Electronic Appendix 1 alongside major element data for the same zones. Where LA-ICP-MS and SIMS analyses of the same zone were performed, SIMS data (generally higher precision) are tabulated. Clinopyroxene data, from this study and from Maclennan et al. (2003a), are shown in Fig. 4a, normalized to the primitive mantle (PM) values of McDonough & Sun (1995).

**Trace element variability in Borgarhraun clinopyroxene**

Incompatible trace element concentrations in Borgarhraun clinopyroxene increase as the Mg-number of the clinopyroxene drops from 92 to 85. Notably, Ce concentrations vary approximately 10-fold from 0.05 to 0.51 and Yb concentrations from 0.18 to 0.96. Incompatible trace element ratios (e.g. Ce/Yb) also vary markedly from 0.16 to 0.99.

The ranges in trace element concentrations and ratios of Borgarhraun clinopyroxene are too great to be explained by fractional crystallization with constant crystal–melt partition coefficients (D values). Therefore, these ranges must arise either during crystallization from a single liquid composition with varying partition coefficients, or by crystallization of variable liquid compositions. These two possible controls on the final clinopyroxene compositions were therefore investigated.

**Trace element fractionation during crystal growth**

Variable growth rates of clinopyroxene can cause large ranges in crystal concentrations of trace elements. For instance, in experimentally formed clinopyroxene, partition coefficients for REE increase roughly six-fold over cooling rates of 5–1000°C h⁻¹ (Loßgren et al., 2006). This effect is due to growth rates increasing relative to the diffusion rates of REE away from the boundary layer that develops at the crystal–melt interface. Nonetheless, ratios of partition coefficients (e.g. D_yb/D_ce) in the Loßgren et al. (2006) study remained roughly constant across the range of cooling rates. The large ranges in Ce/Yb in the Borgarhraun clinopyroxenes cannot therefore be attributed to variable crystal growth rates. This statement is further supported by noting that sector-zoned crystals in Borgarhraun, which probably formed at relatively rapid growth rates (e.g. Nakamura, 1973), vary only modestly in Ce/Yb ratios (<0.05) between adjacent crystal sectors.

**Partition coefficient variability**

Pressure and temperature of crystallization may influence crystal–melt partition coefficients of trace elements in clinopyroxene. Using the method of Wood & Blundy (1997), the effect of these two parameters over the pressure...
Francis & Minarik (2008) reported a three-fold increase in $D_{\text{REE}}$ as $A_{\text{IV}}$ increases from 0.05 to 0.45 cations per formula unit. This $A_{\text{IV}}$ range is essentially identical to the variability observed in Borgarhraun clinopyroxenes.

However, despite the influence of pressure and temperature on partition coefficients, the effect of these factors on ratios of REE partition coefficients is small, and cannot explain the observed ranges in REE ratios in Borgarhraun. For instance, varying pressure from 5 to 11 kbar at 1260°C changes the mean calculated $D_{Yb}/D_{Ce}$ ratio for Borgarhraun clinopyroxene only from 3.20 ± 0.20 to 3.26 ± 0.20 (1σ range). Varying temperature from 1210 to 1310°C at 8 kbar causes this value to change from 3.39 ± 0.22 to 3.09 ± 0.48. Similarly for $A_{\text{IV}}$, the results of Francis & Minarik (2008) suggest near-constant $D_{\text{HREE}}/D_{\text{LREE}}$ ratios over the range of $A_{\text{IV}}$ contents in their clinopyroxene phenocrysts. The small variability in $D_{\text{HREE}}/D_{\text{LREE}}$ ratios in the clinopyroxene crystallization experiments of Gaetani & Grove (1995) also suggests that $A_{\text{IV}}$ variation cannot be responsible for the range in LREE/HREE observed in Borgarhraun clinopyroxenes.

**GEOCHEMICAL VARIABILITY AND MIXING OF MELTS**

The arguments presented above imply that crystal growth rates and partition coefficient variability are unlikely to be the causes of the variability in trace element concentrations and ratios in the Borgarhraun clinopyroxenes. Compositional variability of the crystallizing melts is therefore likely to be responsible for the ranges. To allow comparison of these melts with existing melt inclusion data from the Borgarhraun flow, it is desirable to calculate the trace element compositions of the liquids that were in equilibrium with each clinopyroxene zone as it crystallized. Previous work concerning Borgarhraun melt inclusions used La/Yb vs olivine Fo content systematics in its arguments (Maclennan et al., 2003a), as La/Yb is a useful index for the investigation of melt compositional heterogeneity. However, La concentrations in Borgarhraun clinopyroxenes are typically very low and are generally measured at lower precision than Ce, a similarly behaving LREE. Thus, the Ce/Yb ratios of clinopyroxene are used here in calculations of equilibrium melt compositions.

The partition coefficients used for calculating the Ce/Yb ratios of the equilibrium melts were determined using the methods of Wood & Blundy (1997). The major element composition of each clinopyroxene zone was used to calculate a unique set of REE partition coefficients for each zone, at a temperature of 1260°C and a pressure of 8 kbar. These partition coefficients were used for plotting equilibrium liquid Ce/Yb data in Fig. 5. The mean $D_{Ce}$ value calculated for the clinopyroxene zones was 0.145 ± 0.009 (1σ range), and that for Yb was 0.469 ± 0.016.

Although several different trace element ratios would be of use for investigating melt compositional variability, calculation of melt Sr/Y and Zr/Y ratios was found to involve more uncertainties and assumptions than calculation of melt Ce/Yb ratios. Thus only Ce/Yb ratios of equilibrium liquids are calculated. Details on the selection of partition coefficients and calculations can be found in the Appendix.

The range in Ce/Yb of the melts calculated to be in equilibrium with clinopyroxene compositional zones is 0.51–2.99. The causes of this large range in the parental melts of the clinopyroxene zones may be related to shallow-level effects such as assimilation–fractional crystallization (AFC) or DRM processes. Alternatively, the range may arise from variation in the primary mantle melt compositions. These scenarios are investigated further below.

**Causes of geochemical variation in Borgarhraun parental melts**

AFC processes have previously been invoked to explain the increase in La/Sm of Theistareykir whole-rock samples with decreasing whole-rock Mg-number (Eiler et al., 2000). However, it was argued by Maclennan et al. (2003a) that the observed trace element heterogeneity in melt inclusions hosted by magnesian olivines (up to 92 mol% Fo) from the Borgarhraun flow could not easily be explained by AFC processes. Importantly, it was shown that the AFC trend proposed by Eiler et al. (2000) could explain neither the trends of La concentrations and La/Yb ratios in the melt inclusions with the Fo content of the host crystal, nor the disparity between La/Sm vs CaO/Na2O systematics of melt inclusions and whole-rock compositions, even if initially low Fo olivines had undergone complete Mg–Fe re-equilibration with high Mg-number melts. Furthermore, it is worth noting that the close match between the average trace element composition of Borgarhraun olivine-hosted melt inclusions and the average whole-rock composition of the flow suggests that AFC processes have not significantly affected the whole-rock compositions. As for several other primitive basalt flows from Iceland, this relationship indicates a simple relationship between Borgarhraun olivines and their host lava, involving mixing of mantle melts (as explained below) but little or no interaction with the crust (Maclennan, 2008a). Because the Borgarhraun clinopyroxenes studied here have co-crystallized with high-Fo olivine crystals (Maclennan et al., 2003a), it is unlikely that AFC processes control the Ce/Yb variation seen in these crystals.

It has also been suggested that a significant proportion of the variable or anomalous melt inclusion compositions reflects localized, grain-scale DRM processes (Danyushevsky et al., 2004) rather than variation in...
mantle melt compositions. In particular, inclusion compositions showing anomalously high Sr/Y may have been affected by dissolution of Sr-rich plagioclase by high Mg-number, plagioclase-undersaturated melts (Danyushevsky et al., 2003, 2004). Although Sr/Y ratios are strongly influenced by plagioclase dissolution, it is important to note that this is not an effective mechanism for generating the range in REE patterns observed in the Borgarhraun melt inclusions (Maclennan, 2008a). The maximum Sr/Y in Borgarhraun olivine-hosted melt inclusions is 10-4, about twice the mean value (5-7). The highest Sr/Y in these inclusions could be generated if the mean melt composition bulk assimilates 25% plagioclase with 250 ppm Sr and 0·2 ppm Y (typical of /C24An70^80 plagio-
class phenocrysts from the September 1984 flow of the Krafa volcanic system, northern Iceland; B. Winpenny, unpublished data). This large extent of assimilation of plagioclase with 1ppm Ce and 0·01ppm Yb has very little influence on the Ce/Yb of the melt, raising it from 2-97 to 3-17. In contrast, the maximum Ce/Yb observed in Borgarhraun melt inclusions is >7. Furthermore, Maclennan (2008b) showed that correlations between Pb isotopic ratios and incompatible trace element ratios (e.g. Nb/Y) in olivine-hosted melt inclusions from high-Mg Icelandic basalts are difficult to explain by crustal processes. DRM processes were therefore considered to be of only minor importance in controlling the variation in LREE/HREE ratios in crystals and melt inclusions from primitive Icelandic basalts such as Borgarhraun.

Magma chamber processes are therefore not considered to be the cause of Ce/Yb variation in the melts in equilibrium with Borgarhraun clinopyroxenes. The preferred explanation, in keeping with the results of Maclennan et al. (2003a) and Maclennan (2008a) is that the range in melt Ce/Yb results from compositional variation in the primary mantle melts that begin to crystallize under Theistareykir. This variation arises from the range of melt compositions in the average olivine MI composition (grey dot-dash line). The average Ce/Yb of the Theistareykir picrites (see Fig. 1 and Slater, 1996) is shown as a black dotted line. (b) Normalized cumulative probability distributions of Ce/Yb in the melts in equilibrium with clinopyroxene (black lines: thick line uses Wood & Blundy (1997) partition coefficients; thin line uses Skulski et al. (1994) coefficients), the eight Borgarhraun clinopyroxene-hosted melt inclusion (MI) data of Slater (1996) (step-like, dark grey line), and the olivine-hosted MI data of Slater (1996) and Maclennan et al. (2003a, 2003b) (pale grey line). The Kolmogorov–Smirnov statistics D and significance levels p comparing olivine MIs with clinopyroxene MIs, and olivine MIs with clinopyroxene equil. melts (Wood & Blundy partition coefficients) are shown. Use of the Skulski et al. partition coefficients does not significantly affect the statistics (see the Appendix). The p values are small, suggesting that clinopyroxene and olivine crystallize from sets of melts with different trace element ratio distributions. Clinopyroxene appears to have crystallized from a set of melts with low average Ce/Yb.
that can be produced during incremental fractional melting of the mantle.

**Mantle melt mixing**

Variability in incompatible trace element ratios of Borgarhraun melt inclusions has been the subject of several studies (Slater, 1996; Slater et al., 2001; Maclellan et al., 2003a, 2003b). Notably, Maclellan et al. (2003a) observed a large range in La/Yb of melt inclusions hosted in Fo90 olivines. This range narrows, and approaches the average of all the melt inclusion compositions, as the Fo content of the host crystal reduces. This average was observed to be very close to the average whole-rock composition of the Borgarhraun flow. Maclellan et al. (2003a) interpreted the decreasing range in inclusion La/Yb with decreasing host Fo content in terms of the mixing of mantle melts during fractional crystallization, with the whole-rock composition representing a final well-mixed composition. The variability in La/Yb of the melt inclusions was shown to reflect the variability in composition of incremental fractional mantle melts. These melts were interpreted to have risen to the top of the mantle in channels (e.g. Spiegelman & Kelemen, 2003), only fully mixing once they approached or reached the lower Icelandic crust (after the onset of crystallization). The distribution of melt compositions that reach the Icelandic lower crust in channels is thought to be roughly bimodal (Maclellan, 2008).

The term 'enriched' is used subsequently when referring to melts with high LREE concentrations and LREE/HREE ratios. 'Depleted' melts are defined in the opposite sense. It is important to note that the compositions of melts generated under Theistareykir result both from melting processes and from variability in the composition of the mantle source, as shown by correlations of indices of enrichment (e.g. high LREE/HREE) with isotopic indicators in whole-rock samples from Theistareykir (Stracke et al., 2003).

**Comparison of olivine- and clinopyroxene-hosted melt inclusions**

Using Ce/Yb as an index of mantle melt compositional variability, differences between the compositions of olivine-hosted melt inclusions, clinopyroxene-hosted melt inclusions and the melts calculated to be in equilibrium with clinopyroxene zones were investigated (Fig. 5).

To plot Borgarhraun clinopyroxene Mg-number and olivine Fo content on the same axis in Fig. 5a, their equilibrium liquidus values were determined using equation [3] of Wood & Blundy (1997) for calculating the constant for Mg–Fe exchange between clinopyroxene and melt, $K_{\text{eq}} = \text{Mg} / \text{Fe}$, and the equivalent olivine equation of Ford et al. (1983). This formulation (dot–dash line in Fig. 6) provides a good fit to the average Mg-number of clinopyroxene and Fo content of olivine crystals found in gabbroic and wehrlitic nodules from this study and that of Maclellan et al. (2003a), shown as black squares and grey circles, respectively, in Fig. 6. In particular, coexisting clinopyroxene and olivine in samples from this study form a linear array with clinopyroxene Mg-number slightly higher than the coexisting olivine Fo content, similar to the relationship between primitive olivines and clinopyroxenes observed in gabbroic sills in the Moho transition zone of the Oman ophiolite (Korenaga & Kelemen, 1997). It is worth noting that intra-crystal Mg-number variation indicates that Mg-Fe diffusion has not been significant for clinopyroxene. Additionally, the positive correlation of Mg-number of clinopyroxene with Fo for the nodules indicates that olivine is unlikely to have undergone significant Mg-Fe re-equilibration with lower Mg-number melts, which may occur over time scales of several hundred years (Jurewicz & Watson, 1988; Dimanov & Sautter, 2000). The Fo content of olivine and Mg-number of clinopyroxene crystals in the Borgarhraun nodules from this study are thus likely to reflect liquidus compositions, and the linear array in Fig. 6 is explained well by the Wood & Blundy (1997) and Ford et al. (1983) formulations.

Ce/Yb ratios of Borgarhraun olivine- and clinopyroxene-hosted melt inclusions analysed by Maclellan et al. (2003a, 2003b) and Slater (1996) are plotted in Fig. 5a versus the Mg-number or Fo content of their respective host crystal. The REE concentrations in the melt inclusions are illustrated in Fig. 4b. The large range in Ce/Yb ratios of olivine-hosted melt inclusions at ~Fo90 is apparent (Fig. 5a). Similar to the variation observed in La/Yb ratios noted by Maclellan et al. (2003a), this range narrows as the Fo content of the host olivine reduces, indicative of melt mixing during fractional crystallization.

Although there are only eight analyses of clinopyroxene-hosted melt inclusions (from Slater, 1996), all of their Ce/Yb ratios are lower than both the average Ce/Yb of the olivine-hosted melt inclusions (2.31 ±1221σ range) and the average Ce/Yb of Borgarhraun whole-rocks. Figure 5b shows normalized probability distributions of Ce/Yb in clinopyroxene- and olivine-hosted melt inclusions. Also shown are the statistics from a two-sample Kolmogorov–Smirnov test comparing the Ce/Yb ratios of the two sets of melt inclusion data. This is a non-parametric test, with the Kolmogorov–Smirnov statistic, D, indicating the maximum separation between the relevant cumulative histogram lines in Fig. 5b. The probability, $p$, is the likelihood that sample sets are taken from the same distribution. The $p$ value comparing olivine- and clinopyroxene-hosted melt inclusions is 0.048, a low value that suggests strongly that the sets of melts crystallizing either clinopyroxene or olivine have different distributions of Ce/Yb ratios, with clinopyroxene having crystallized, on average, from more depleted melts.
Comparison of liquids in equilibrium with clinopyroxene and melt inclusions

The Ce/Yb ratios of liquids calculated to be in equilibrium with each clinopyroxene zone (Ce/Yb_{eq-melt}) are also shown in Fig. 5a, plotted against zone Mg-number. These include Ce/Yb ratios calculated from the clinopyroxene data of Maclennan et al. (2003a). Similar to the clinopyroxene-hosted melt inclusion data, it is noticeable that most equilibrium liquids have lower Ce/Yb_{eq-melt} ratios than the average of the olivine-hosted melt inclusions. Averages and standard deviations of all Ce/Yb_{eq-melt} values and of Ce/Yb ratios of olivine-hosted melt inclusions are 1.24 ± 0.54 and 2.31 ± 1.22 respectively.

Total ranges are 0.51–3.05 and 0.27–7.53 respectively. A two-sample Kolmogorov–Smirnov test comparing the Ce/Yb_{eq-melt} ratios with the Ce/Yb ratios of olivine-hosted melt inclusions gives a very low p value of 7.0 × 10^{-14}.

It is also important to note the general increase in Ce/Yb_{eq-melt} with decreasing Mg-number in Fig. 5a, mimicking the lower part of the range in Ce/Yb of the olivine-hosted melt inclusion data. The Ce/Yb_{eq-melt} values of the lowest Mg-number (~85) clinopyroxene zones are close to the average value for Borgarhraun olivine-hosted melt inclusions. These features suggest that the liquids that formed the clinopyroxene zones underwent mixing with more enriched melts during fractional crystallization. The data displayed in Fig. 5a indicate that these enriched melts are trapped in olivine-hosted inclusions but did not crystallize clinopyroxene. The clinopyroxene with the lowest observed Mg-number is thus interpreted as having crystallized from the fully mixed melts, in the same manner as the low Fo content olivines in Borgarhraun. The correlation between the Mg-number of the melts and the variance of the trace element composition of the melts can be understood in terms of a model of concurrent mixing and crystallization (Maclennan, 2008).

The data in Fig. 5 therefore suggest that clinopyroxene phenocryst compositions, as well as melt inclusion compositions, can record mixing of mantle melts during fractional crystallization in or below the Icelandic lower crust. The reason for the smaller range in Ce/Yb ratios and lower average Ce/Yb of clinopyroxene equilibrium liquids (and clinopyroxene-hosted melt inclusions) compared with the range and average of the olivine-hosted melt inclusion data is examined below.

Owing to poorer constraints on crystal–melt partition coefficients (see the Appendix), it was not possible to calculate accurately the Sr/Y ratios of melts in equilibrium with clinopyroxene for comparison with the melt inclusion data. However, it is unlikely that this geochemical index can offer further information on the mixing of mantle melts, as Sr/Y is highly sensitive to crustal processes (e.g. Danyushevsky et al., 2003). The poor correlations of Sr concentrations and Sr/Y ratios with Pb isotopes in melt inclusions from SW Iceland highlight this problem (Maclennan, 2008). Melt Ce/Yb ratios are unlikely to be altered by such magma chamber processes; it is further worth noting that the differences in Ce/Yb systematics between the olivine and clinopyroxene data cannot be easily achieved by AFC or DRM processes: if a single batch of primary mantle-derived melt with a homogeneous composition was affected by such processes, the distributions of melt Ce/Yb ratios recorded in each of the two co-crystallizing phases would be very similar.
HIGH Mg-NUMBER CLINOPYROXENE: PHASE RELATIONSHIPS

The data presented in Fig. 5 and the accompanying interpretation indicate that the mean Ce/Yb ratio of the melts in equilibrium with clinopyroxene is lower than that of the olivine-hosted melt inclusions. This difference can be accounted for by a simple model of the phase relationships of the compositionally variable mantle melts from which these phases crystallize. The fractional melts are sourced from different depths in the melting region and their trace element variation will therefore be coupled to major element variability. As these melts begin to crystallize and mix in the lower crust and uppermost mantle under northern Iceland this major element variability causes them to follow different evolutionary paths.

To demonstrate the influence of depth and degree of melting on the subsequent crystallization behaviour of mantle melts in near-Moho magma chambers, a simple model of melting of a uniform peridotite source was constructed. The possible role of compositional and lithological variation in the mantle source is addressed in the discussion.

Melt generation under Theistareykir has been successfully modelled by passive mantle upwelling and plate separation alone, with small degree melting beginning by adiabatic decompression melting at ~100 km depth (Maclennan et al., 2001a). Small fraction melts that form within the garnet stability field of the mantle beneath Iceland will have very high LREE concentrations but relatively low HREE concentrations. Melts formed shallower in the melting column at greater extents of melting will have much lower LREE/HREE ratios. Figure 7 shows schematic crystallization paths of mantle melts sourced from two depths in the melting region, equivalent to pressures of 30 and 15 kbar, in the system olivine–diopside–SiO₂. These paths begin on the loci of the peridotite eutectics of Takahashi & Kushiro (1983) and end on the 10 kbar basalt phase boundaries of Stolper (1980). The contrasting lengths of the two paths show that, because of expansion of the olivine primary phase field as pressure decreases from 30 to 15 kbar, shallower-sourced melts will undergo less olivine-only crystallization than deeper-sourced melts. Because prolonged olivine crystallization significantly reduces melt MgO content relative to FeO, only shallower-derived melts will saturate in clinopyroxene at high enough Mg-number to produce the highest Mg-number clinopyroxene. This logic fits the observed pattern in Fig. 5a: Mg-number 87–92 clinopyroxene zones are almost exclusively crystallized by low Ce/Yb (<~2.5), shallow-derived mantle melts. These high Mg-number zones must have formed during the early stages of fractional crystallization, implying that clinopyroxene joined the liquidus shortly after olivine for the depleted melts. Deeper-sourced, higher Ce/Yb melts saturate in clinopyroxene only after extensive fractional crystallization of olivine, so enriched signatures cannot be recorded in high Mg-number clinopyroxene. The logic of the simple phase diagram in Fig. 7 also indicates that olivine is the first crystallizing silicate phase for liquids generated over the full depth range of melting. Therefore, highly forsteritic (Fo90)
olivine can crystallize from both enriched and depleted melts, in agreement with the data shown in Fig. 5.

During crystallization, the compositions of all melts can be modified by melt mixing. For Borgarhraun, mixing causes the general narrowing of the range of Ce/Yb ratios of olivine-hosted melt inclusions as the Fo content of the host olivine falls. Mixing also causes the overall increase in Ce/Yb of liquids in equilibrium with clinopyroxene as the Mg-number of the clinopyroxene falls. This increase arises because at high Mg-number the range of clinopyroxene-saturated melts is biased towards the depleted compositions and at low Mg-number (~88) the most depleted trace element signature has been removed by mixing with more enriched melts. Significantly, mixing is complete by the time that Mg-number 88 clinopyroxene and Fo87 olivines are crystallized. Accordingly, high Ce/Yb melts, as preserved in some Fo90 melt inclusions, do not evolve independently to become saturated in low Mg-number clinopyroxene because they mix with depleted melt compositions. Therefore, all clinopyroxene equilibrium liquid compositions in Fig. 5 have Ce/Yb < 3.

Using the schematic crystallization paths in Fig. 7, the approximate Mg-number of the first clinopyroxene crystallized from melts sourced from different depths in the mantle can be estimated. Assuming that 30 kbar melts and 15 kbar melts under Théistareykir are in equilibrium with Fo90 olivine and Fo92 olivine respectively (Macalennan et al., 2003a), ~50% and ~18% crystallization respectively is needed to reach the olivine + clinopyroxene cotectic in each case. Using equation (6) of Macalennan et al. (2003a), and converting Fo into equilibrium Mg-number using the Ford et al. (1983) and Wood & Blundy (1997) formulations (dot–dash line in Fig. 6), this gives first liquidus clinopyroxene Mg-number values of 70.5 and 90.5 for the 30 kbar and 15 kbar melts respectively.

In an attempt to validate the theoretical basis of this interpretation, the fractional crystallization paths of Icelandic basalt compositions and synthetic melts of depleted peridotite were examined, to determine the predicted compositions of clinopyroxene that crystallize from parental melts with a wide range of Ce/Yb.

HIGH Mg-NUMBER CLINOPYROXENE CRYSTALLIZATION IN MODELS

Icelandic melt compositions

The fractional crystallization paths of whole-rock and glass compositions of basalts from the Théistareykir and adjacent Krafá volcanic systems (Elliott et al., 1991; Nicholson & Latin, 1992; Hemond et al., 1993; Slater, 1996; Sigurdsson et al., 2000; Macalennan et al., 2003a; Macalennan, 2008a), plus high-MgO glasses from Kistufell (Breddam, 2002) were examined using the programs MELTS (Ghiorso & Sack, 1995; Asimow & Ghiorso, 1998) and PETROLOG (Danyushevsky, 2001). The adiabat.lph front-end (Smith & Asimow, 2005) was utilized for MELTS calculations. For all modelling, a constant pressure of 8 kbar was used, with fO2 fixed at 1 log unit below the quartz–fayalite–magnetite buffer (Óskarsson et al., 1994). Olivine, clinopyroxene and plagioclase were allowed to crystallize in PETROLOG following the methods of Danyushevsky (2001). In MELTS, all phase crystallization was allowed and crystallization runs were started at 1410°C. For each incremental melt composition output during the crystallization runs, the Ce/Yb ratio of the melt and the Mg-number or Fo content of any crystallizing clinopyroxene or olivine was monitored. Most importantly, the Mg-number of the first crystallizing clinopyroxene was recorded.

Results from MELTS are shown in Fig. 8a. In this diagram, the forsterite values on the x-axis are for olivine calculated to be in equilibrium with the crystallizing melt using the approach of Ford et al. (1983), as the output from MELTS occasionally involves orthopyroxene crystallization rather than olivine. The equilibrium olivine Fo content at which each melt starts to crystallize clinopyroxene is marked by an open circle. The Mg-number of clinopyroxene in equilibrium with the liquid and olivine was calculated using the expressions from Ford et al. (1983) and Wood & Blundy (1997), the same formulation as used for the calculation of the black dot–dash line in Fig. 6. Equilibrium Mg-number values are used on the x-axis in preference to the Mg-number of liquidus clinopyroxene output by MELTS, as MELTS clinopyroxene Mg-number values are consistently lower than the Mg-number of clinopyroxene expected to be in equilibrium with high-Fo olivine, and never reach values as high as those observed in Borgarhraun clinopyroxene (see ‘MELTS’ line in Fig. 6). However, Mg-number values from PETROLOG are more consistent with the expected equilibrium Fo–Mg-number relationship and predict the high Mg-number values seen in Borgarhraun (Fig. 6). Despite the disparity between the two programs, PETROLOG crystallization results give a very similar distribution of crystallization paths and initial liquidus clinopyroxene Mg-number to those in Fig. 8a.

The natural samples have clearly experienced variable extents of fractional crystallization, and therefore some of the liquid compositions (especially Krafá basalts, with moderately high Ce/Yb) are initially clinopyroxene-saturated and can crystallize only low Mg-number clinopyroxene. However, high-MgO (up to 11.95 wt % MgO) basalts from the table mountain Grasafjöll (‘B’ in Fig. 1) have high Ce/Yb ratios (mean = 8.84 ± 0.2), and yet do not crystallize clinopyroxene with Mg-number >88.
The results from modelling the crystallization of Icelandic basalt compositions using MELTS and PETROLOG suggest that high Mg-number clinopyroxene can appear on the liquidus of low Ce/Yb melts, whereas the first clinopyroxene crystallized from higher Ce/Yb melts has significantly lower Mg-number. This variability in Mg-number of the first clinopyroxene crystallized agrees with the likely phase relations of mantle melts sourced from different depths in the melting region, as suggested above. For the modelled melt compositions, the approximate region (in clinopyroxene Mg-number-Ce/Yb space) where clinopyroxene is present on the liquidus is shown by the shaded region in Fig. 8a.

**Synthetic mantle melt compositions from pMELTS**

Figure 8b compares the compositions of Borgarhraun olivine-hosted melt inclusions and liquids in equilibrium with clinopyroxene with the phase relations of crystallizing mantle melt compositions (lines) generated using the program pMELTS (Ghiorso et al., 2002). These fractional mantle melts were produced assuming a mantle potential temperature, \( T_P \) of 1480°C under northern Iceland (Maclellan et al., 2001a) and were calculated every 1 kbar along an adiabat. The range of pressures of melt generation shown in (b) is 12−31 kbar. The small black crosses show the maximum Mg-number of clinopyroxene that each of these synthetic melts may crystallize, plotted as in (a). The region where olivine + clinopyroxene is predicted to be crystallized is shaded and labelled. This region is roughly similar to that in (a), and also agrees fairly well with the observed Ce/Yb and Mg-number of Borgarhraun clinopyroxene zones, supporting the proposition that high Mg-number clinopyroxene can be crystallized only from low Ce/Yb melts.
observed occurrence of Borgarhraun clinopyroxenes, with higher Mg-number clinopyroxene being crystallized from mantle melts with lower Ce/Yb.

All the sets of modelled fractional crystallization paths support the argument based on phase relations (Fig. 7) that low Ce/Yb (<2.5) melts, formed by high-fraction melting of the uppermost mantle, are capable of crystallizing high Mg-number (~67 to ~92) clinopyroxene such as is found in Borgarhraun. Higher Ce/Yb melts, sourced from deeper in the mantle, have long stretches of crystallization with olivine as the only liquidus phase such that the first clinopyroxene to crystallize from these enriched parents has a relatively low Mg-number. Highly forsteritic Fo90 olivine can be produced from the whole spectrum of melts sourced from throughout the depth range of melting. An overview of the melt compositions entering and the mixing and crystallization processes occurring within the Theistareykir volcanic system is shown in Fig. 9.

**DISCUSSION**

**Mantle source heterogeneity and low pressure crystallization paths**

The trace element compositions of Borgarhraun clinopyroxene indicate that high Mg-number (>67) clinopyroxene crystallization in Icelandic basalt compositions is limited to trace element-depleted, low LREE/HREE melts from the shallow mantle (Fig. 9). The model of mantle melting used above to explain this phenomenon is based upon fractional melting of a single peridotitic mantle source composition, and so the following inferences drawn from the Borgarhraun clinopyroxenes are likely also to be valid for mid-ocean ridges in general.

Nevertheless, observations of correlations between the trace element and isotopic compositions of whole-rock samples from Theistareykir (Stracke et al., 2003) and from melt inclusions in single hand specimens of Icelandic picrites (Maclennan, 2008b) indicate that compositional heterogeneity is likely to be present in the mantle source regions of the Borgarhraun melts. Enriched eruptions in the Theistareykir system tend to have low SiO2 when compared with depleted eruptions at the same Mg-number. For example, the major element composition of basalts from Gæsafjöll, a trace element enriched subglacial table mountain shown in Fig. 1, can be produced from a parent melt similar in composition to experimental melts of KG2, a fertile peridotite produced by mixing peridotite KLB-1 with average MORB in 2:1 proportions (Kogiso et al., 1998). If these experimental melt compositions are crystallized using the same approach as outlined above for the model peridotite melt compositions from pMELTS, olivine appears on the liquidus with a composition of Fo90. Clinopyroxene first appears on the liquidus with an Mg-number of 86. This result is broadly in agreement with the systematics displayed in Fig. 8, where both Theistareykir whole-rock compositions (Fig. 8a) and model melts of depleted peridotite (Fig. 8b) saturate in clinopyroxene at lower Mg-number for trace element enriched melt compositions than they do for depleted ones. Therefore, although the presence of source heterogeneity may alter the details of the boundary between the olivine-only and the olivine+clinopyroxene fields in Fig. 8b, the conclusion that trace element enriched melts first saturate in clinopyroxene at lower Mg-number than depleted melts is robust for Iceland.

**A biased record of primitive melt compositions in phenocrysts?**

If mixing of compositionally variable mantle melts occurs after or during the onset of fractional crystallization, as is the case for Borgarhraun, then the average composition of all clinopyroxene crystals found in a basalt flow will be systematically biased towards the more depleted (low Ce/Yb) compositions entering the volcanic system. This is because these depleted melt compositions become saturated in clinopyroxene (with high Mg-number) earlier than more enriched (high Ce/Yb) melts (Fig. 9). If melt mixing occurs before any clinopyroxene crystallization, then the clinopyroxene will at best record the history of the mixed magma. Thus, compositions of clinopyroxene resulting from fractional crystallization of primary mantle melts may be biased, reflecting only shallow mantle melting under mid-ocean ridges. High Mg-number clinopyroxenes do not record the existence and compositions of the deepest-sourced, most enriched melts.

Clinopyroxene phenocrysts, although relatively rare in MORB, are occasionally present in Icelandic basalts. They are present in several depleted picritic lavas from the Western Volcanic Zone (Hemond et al., 1993; Gurenko & Chaussidon, 1995), which have Ce/Yb ratios similar to or lower than the average Borgarhraun whole-rock value. The findings in this study indicate that high Mg-number clinopyroxene may be found in these picrites; indeed, clinopyroxenes from the Midfell picrites (mean Ce/Yb of all glasses = 2.16 ± 0.30; Gurenko & Sobolev, 2006) have Mg-number values up to 90-2.

Looking further afield to other mid-ocean ridges, clinopyroxenites with average Mg-number of up to 90-99 were dredged from the Southwest Indian Ridge (Dantas et al., 2007). In agreement with the observations and inferences from Borgarhraun, these were found to be relatively depleted in highly incompatible elements, and it was proposed that they corresponded to the shallowest, incremental melt fractions produced during decompression melting of a normal MORB mantle source. High Mg-number clinopyroxene phenocrysts have also been found in primitive MORB from the Mid-Atlantic Ridge. For instance, a sample from 43°N (Kamenetsky et al., 1998, and references therein) was found to contain clinopyroxene phenocrysts.
with Mg-number up to 92·0. Although no clinopyroxene trace element data are available, a similarity to Borgarhraun is that these clinopyroxenes were found to co-exist with high-Fo olivines whose melt inclusions are extremely variable in their incompatible trace element ratios. This variability was interpreted as resulting from the diverse melt compositions produced by fractional melting of the mantle. The findings of our current study are also in keeping with those of Coogan et al. (2000), who observed that clinopyroxene (Mg-number up to 90) in primitive gabbros from Ocean Drilling Program Hole 923A displayed slightly lower LREE/HREE ratios than MORB from the same region. Their magnesian compositions led those workers to suggest that the major element composition of the parent melt was different from that of normal MORB, requiring that an array of mantle melt compositions had become homogenized only once the melts began to crystallize in crustal magma chambers. High CaO/Al₂O₃ melts, which may be formed by fractional melting near the top of the melting region, were shown

Fig. 9. Schematic illustration of crystallization of clinopyroxene (cpx) under Theistareykir. Initial crystallization of high Mg-number clinopyroxene (\(~87–92\)) occurs in magma chambers or sills at \(~6–11\) kbar. Only the most depleted, low Ce/Yb, primary mantle melts may crystallize such clinopyroxene. More enriched primary melts may crystallize only lower Mg-number clinopyroxene, after significant olivine fractionation. However, Fo₉₀ olivine may crystallize from depleted or enriched mantle melts. Mixing of depleted and enriched mantle melts occurs at similar depths, along with concurrent fractional crystallization. This mixing is recorded in the compositions of clinopyroxene phenocrysts, with lower Mg-number clinopyroxene recording higher equilibrium melt Ce/Yb values. The Borgarhraun flow whole-rock composition is a typical result of such mixing. As a result of mixing, the flow contains olivine and clinopyroxene with variable Fo and Mg-number and variable Ce/Yb in their melt inclusions or compositional zones respectively. Relatively unmixed magmas may also be erupted (indicated by arrows), forming, for example, the depleted Theistareykir picrites (mean Ce/Yb = 1·67) or the enriched Gasafjöll subglacial eruption (mean Ce/Yb = 8·86; see Fig. 1).
to crystallize the highest Mg-number clinopyroxene. The present of high Mg-number, trace element-depleted clinopyroxene, and similar crystal assemblages to Borgarhraun at mid-ocean ridge settings outside Iceland, suggest that the concepts presented here may be applicable to mid-ocean ridge magmatism in general.

An important observation from the Borgarhraun clinopyroxenes is that many of their compositions are not in trace element equilibrium with the carrier melt. The average Borgarhraun whole-rock composition has a higher Ce/Yb ratio than that of both the clinopyroxene-hosted melt inclusions and the melts in equilibrium with the different clinopyroxene zones. Many of the clinopyroxenes could therefore be described as 'antecrysts' (Davidson et al., 2007): the clinopyroxenes crystallized from various batches of magma, which, although each distinct in composition from the erupted lava, ultimately mixed with each other to form the erupted magma composition. This relationship is in contrast to true xenocrysts, which might be picked up during assimilation of material (e.g. hyaloclastite, Bindeman et al., 2008) from the Icelandic crust.

Crystallization of phenocrysts from certain batches of pre-mixed magma may also explain the observed differences in isotopic composition between phenocrysts and host lavas. Notably, a recent study by Jackson et al. (2009) showed that clinopyroxenes from Samoan lavas often have differing $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios from their carrier melts. All of these clinopyroxenes with Mg-number > 86 have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than their host lavas. A study of the Thjórsá lavas of southern Iceland by Halldorsson et al. (2008) reported lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for calcic plagioclase phenocrysts (up to 90 mol % anorthite, An$_{90}$) than for the groundmass. A similarity between the Thjórsá lavas and the Borgarhraun flow is the presence of disintegrated Ca-diopside crystals. It is possible that these clinopyroxenes and the high-An plagioclase predominantly crystallized from melts with low LREE/HREE ratios and low, depleted MORB mantle (DMM)-like $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, produced by high-degree melting of the shallow mantle. These melts and their crystals then mixed with the daughters of deeper-derived, enriched mantle parent magmas to produce the liquid that carried the depleted phenocrysts to the surface for eruption.

**SUMMARY AND CONCLUSIONS**

High Mg-number (85–92) clinopyroxene crystals are present in gabbric or wehrlitic nodules and as phenocrysts in the Borgarhraun basaltic lava flow, north Iceland. Revised pressure estimates confirm that clinopyroxene crystallization occurs near or just below the seismic Moho in this region, at pressures of 6–11 kbar. Like olivine-hosted melt inclusions from Borgarhraun, these clinopyroxenes preserve evidence for mixing of compositionally heterogeneous melts, resulting from incremental fractional melting of the mantle. The range in Ce/Yb ratios of clinopyroxene can be accounted for by progressive, concurrent mixing and crystallization of compositionally heterogeneous mantle melts in the magmatic system that supplied Borgarhraun. However, comparison of clinopyroxene equilibrium liquids with the compositions of olivine-hosted melt inclusions shows that the Borgarhraun clinopyroxenes crystallized from a more restricted range of melt compositions than olivines. Clinopyroxene crystallized from a set of melts that is biased towards depleted compositions, with lower maximum Ce/Yb and lower mean Ce/Yb than olivine-hosted melt inclusions. This observation can be explained by the phase relationships of the primary mantle melts, sourced from different depths in the melting region, as they undergo fractional crystallization. Deep-sourced, small-degree, high Ce/Yb melts produced in the presence of garnet have a longer olivine-only crystallization path than higher degree, low Ce/Yb, shallow mantle melts. Thus, only the depleted melts can crystallize the high Mg-number clinopyroxenes that are seen in Borgarhraun. Forsteritic olivine, on the other hand, can be crystallized from the entire range of depleted and enriched melt compositions.

Many Borgarhraun clinopyroxenes are in chemical disequilibrium with their host lavas. In this case, disequilibrium is a natural consequence of melt mixing. Because the compositions of the high Mg-number clinopyroxenes are biased towards the compositions of the most depleted, shallow-sourced mantle melts entering the volcanic system, care must be taken when using average clinopyroxene compositions to infer general mantle melting processes and to assess source heterogeneity.

**ACKNOWLEDGEMENTS**

Thanks are due to the staff of the Edinburgh Ion Microprobe facility, particularly Richard Hinton. Jason Day, Martin Walker and Chiara Petrone provided valuable analytical assistance. We also thank Mike Bickle, Marian Holness and Marie Edmonds for useful discussions. We are grateful to Oli Shorttle for compiling many of the Icelandic basalt data for use in the pressure calculations. Supportive reviews of an earlier version of this paper by Rick Carlson, Matthew Jackson and an anonymous reviewer were extremely helpful in helping us to clarify our arguments. Sympathetic and pragmatic editorial handling by Marjorie Wilson is also greatly appreciated.

**FUNDING**

This work was supported by a Natural Environment Research Council studentship to BW (NE/F007183/1), a Natural Environment Research Council young investigator grant to J.M. (NE/E001254/1) and a Natural Environment...
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Research Council Ion Microprobe Facility award (IMF 365/1008).

SUPPLEMENTARY DATA

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

REFERENCES


APPENDIX: SELECTION OF CRYSTAL–MELT PARTITION COEFFICIENTS

To calculate the trace element compositions of liquids in equilibrium with clinopyroxene, the method of Wood & Blundy (1997) was used to calculate crystal–melt partition coefficients for REE in each clinopyroxene zone. A pressure of 8 kbar was selected, and a temperature of 1260°C. Major element concentrations for each calculation were taken from electron microprobe analyses of the crystal zones. This method gives reasonable values for the partition coefficients, but it is noted that experimentally derived partition coefficients vary significantly, especially for LREE, even for experimental runs performed at similar temperatures, pressures and starting compositions (e.g. Hack et al., 1994). Therefore, a set of suitable partition coefficients representing a worst-case scenario for the
arguments presented in this study was also sought; that is, a set that gave the highest ratio of Yb to Ce partition coefficients, $D_{\text{Yb}}/D_{\text{Ce}}$. If this ratio is increased then the calculated values and overall range of Ce/Yb ratios of clinopyroxene equilibrium liquids are modified such that the difference between the compositional distribution of these liquids and that of the olivine-hosted melt inclusions is reduced.

To this end, coefficients for Ce and Yb from experimental run TS137 of Skulski et al. (1994) were considered. This experiment used a starting composition potentially similar to that of the primary melts under Theistareykir (a Baffin Island picrite) and produced clinopyroxene of similar composition to those in Borgarhraun (a Cr-diopside with Mg-number = 90.3, Al$_2$O$_3$ = 5.09, Cr$_2$O$_3$ = 1.38). These Ce and Yb partition coefficients are lower than most published values, but the ratio $D_{\text{Yb}}/D_{\text{Ce}}$ (the factor that acts to increase calculated Ce/Yb eq-melt ratios), is higher than the $D_{\text{Yb}}/D_{\text{Ce}}$ values from calculations using Wood & Blundy (1997) (4.72 vs 3.23 ± 0.20). Whereas equilibrium liquid ratios in Fig. 5a are based on the Wood & Blundy (1997) partition coefficients, cumulative probability profiles for melt Ce/Yb ratios calculated using both the Wood & Blundy (1997) and Skulski et al. (1994) methods are shown in Fig. 5b (thick and thin black lines respectively). Importantly, when comparing the Ce/Yb of equilibrium liquids with the Ce/Yb of olivine-hosted melt inclusions, the Kolmogorov–Smirnov test probability, $p$ (the probability that the datasets are taken from the same distribution), is very small when using either the Skulski et al. (1994) or Wood & Blundy (1997) coefficients ($2.5 \times 10^{-7}$ vs $7.0 \times 10^{-14}$ respectively). This indicates that the conclusions are robust to errors in the partition coefficients.

The models of Wood & Blundy (2001) take account of the effects of cation charge (particularly clinopyroxene Al$^{IV}$ content) on partition coefficients. As such effects are similar for cations of equal charge, Al$^{IV}$ content should not affect the ratios of partition coefficients such as $D_{\text{Yb}}/D_{\text{Ce}}$. However, when calculating partition coefficients for Sr/Y$_{eq}$-melt ratios, varying crystal Al$^{IV}$ content may have significant effects on $D_{\text{Sr}}^{2+}/D_{\text{Y}}^{3+}$ ratios. This is due to the contrasting relationships between Al$^{IV}$ contents and partition coefficients for cations of different charge (Wood & Blundy, 2001). Because Al$^{IV}$ contents in the Borgarhraun clinopyroxenes vary significantly (0.04–0.16 cations per formula unit), a constant $D_{\text{Sr}}^{2+}/D_{\text{Y}}^{3+}$ ratio using the Skulski et al. (1994) dataset cannot be applied. Furthermore, because of the variety of models, uncertainties and more complex calculations involved in obtaining $D_{\text{Sr}}^{2+}$ and $D_{\text{Y}}^{3+}$, errors in $D_{\text{Sr}}/D_{\text{Y}}$ are likely to be significantly larger than those in $D_{\text{Yb}}/D_{\text{Ce}}$. Thus, because Ce/Yb$_{eq}$-melt ratios are better constrained than Sr/Y$_{eq}$-melt (and, for similar reasons, Zr/Y$_{eq}$-melt), only Ce/Yb ratios are calculated for comparisons of clinopyroxene equilibrium liquids with melt inclusion data.