The Distribution of Olivine Compositions in Icelandic Basalts and Picrites

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A number of recent studies have used the compositional relationship between magmatic crystals and their carrier liquids to understand processes within volcanic plumbing systems. Here, an extensive compilation of electron microprobe data for Icelandic olivine and glass compositions is used to examine the distribution of the forsterite content of olivine macrocrysts within single lava flows, and the relationship of these olivines to their carrier basaltic liquids. A dataset of 7836 olivine and 233 glass point analyses was examined and 11 eruptions were identified where glass data and over 60 crystal core compositions were available. In common with many basaltic suites, single olivine crystals typically have uniform core compositions with narrow normally zoned rims. Accordingly, in 10 of the 11 Icelandic eruptions over 90% of the olivines are too forsteritic to be in equilibrium with their carrier basaltic liquids. The sampling density of the dataset permitted statistical investigation of the distribution of olivine compositions that contain information that can be used to provide new constraints on magmatic processes. The results of both kernel density estimates and Gaussian mixture modelling indicate that each of the 11 eruptions contained at least one robust peak in olivine compositions. Out of these 11 eruptions, eight show unimodal distributions of macrocryst olivine forsterite content, two are bimodal and one is polymodal. An important feature of the relationship between the carrier glass compositions and the distribution of olivine forsterite contents is that, for 10 of the 11 flows, a strong peak in the olivine compositional distribution occurs at forsterite contents that are 2–3 mol % higher than those expected for olivines in equilibrium with the carrier liquid. This offset peak is not predicted for olivines generated by simple equilibrium or fractional crystallization models. Instead, the distribution of olivine compositions and its relationship with the carrier liquids can be accounted for using a three-stage model. In the first stage, fractional crystallization and crystal settling generate a mush pile on the floor of a magma chamber. Compositional stratification is present in this mush, with the olivines at its base being more forsteritic than those at its top, reflecting the evolution of liquid compositions during fractional crystallization. The olivines in the uppermost part of the mush are close to equilibrium with basaltic liquid in the interior of the chamber. In the second stage local diffusion acts to homogenize single crystals in the mush, creating the uniform cores observed upon eruption. Concurrently the chemical gradient across the full thickness of the mush pile is altered by diffusion through the interstitial melt phase, reducing the variance of olivine core compositions in the mush. This process never reaches completion in the Icelandic flows but does generate a single peak in olivine compositions close to the mean forsterite content of the olivines in the crystal pile. Finally, the mush is disaggregated into the carrier liquid of the chamber interior shortly before eruption, creating the diffusional rim overprints. Quantitative models of this process indicate that the observed offset peak in olivine compositions can be generated after 42–8000 years of diffusion in a mush pile, depending on the mush thickness. Key features of the compositional distribution of olivines in basalts can therefore be accounted for using a simple model of mush generation and disaggregation.

KEY WORDS: basalt; crystallization; cumulate; igneous petrology; magma chamber

INTRODUCTION

Terminology of liquid–crystal relationships

Understanding of the relationship between crystals and the melts that carry them has long been a preoccupation of igneous petrologists. This relationship provides a record of processes occurring in magmatic systems under volcanic regions and is a pivotal part of investigation into the storage and transport of magma. Estimates of the...
temperatures of crystallization of primitive melts, which have been used to constrain mantle potential temperature variations, have been derived under the assumption that the relationship between olivine macrocrysts and their carrier liquids is well enough understood to allow for robust determination of the composition of primitive liquids in equilibrium with forsteritic olivines (Thompson & Gibson, 2000; Putirka, 2005; Keiding et al., 2011). Although the simplicity of end-member genetic models such as equilibrium or fractional crystallization has pedagogical appeal and pragmatic purpose in the modelling of melt evolution, detailed studies of the textures and compositions of crystals in porphyritic lava samples have uncovered a complex array of genetic links between crystals and their carrier liquids. Such complexity has been clearly demonstrated for plagioclase-phyric andesites, where petrographic and micro-analytical observations preclude genetic interpretation of the crystals as equilibrium phenocrysts or as xenocrysts (Davidson et al., 2007). Unfortunately, the intricacies of the relationship between crystals and the melts that carry them have highlighted inadequacies in the terminology of this field, a problem that has been recognized for decades (Donaldson & Brown, 1977).

The term phenocryst was introduced by Iddings (1889) to denote crystals in a porphyritic igneous rock that were identifiably larger than groundmass crystals in the same rock, with its origin in the Greek phainein 'to show'. However, over the twentieth century petrological practice led to the association of a genetic meaning for the term phenocryst. For example, Cox et al. (1979) described a phenocryst assemblage as 'that group of solid phases which was in equilibrium with the liquid before the quenching phase', and the implication of Davidson et al. (2007) is that a phenocryst is a crystal that has formed from the liquid, frozen to glass or groundmass, in which it is hosted. Xenocrysts were defined by Sollas (1894) as isolated crystals in igneous rocks of 'foreign derivation', accidentally incorporated into the melt (Harker, 1896). The identification of the widespread occurrence of crystals formed either by direct solidification of their carrier liquid nor by accidental incorporation as xenocrysts led to the development of the term antecryst (Charlier et al., 2005; Davidson et al., 2007). In this definition, antecrysts are phases that originate in the magma system but are not true phenocrysts. Although there is much to commend the development of this term and exposure of the limitations of the genetic usage of the terms phenocryst and xenocryst, the devil is in the detail. One problem with the term antecryst is the difficulty in defining what is meant by the magma system, an ambiguity that is particularly pressing in regions such as Iceland where magmatism has continuously been sustained by mantle melting and magma has built the crust for millions of years. In this case it is not easy to determine how the limits of a magmatic system should be defined. This breadth of definition has led to crystals with different genetic relationships to their carrier liquids being referred to as antecrysts (Davidson et al., 2007; Maclennan, 2008a; Wipenny & Maclennan, 2011).

Although the study of Maclennan (2008a) referred to olivine crystals in Icelandic basalts as antecrysts, the genetic relationship between Icelandic olivines and their host lava flows is more tightly circumscribed than the broader definition of antecryst as intended by Davidson et al. (2007). Olivine-hosted melt inclusions in Icelandic basalts and picrites are known to be highly variable in their trace element composition, even in olivines extracted from single hand specimens (Gurenko & Chaussidon, 1995; Slater et al., 2001). Nevertheless, in the 10 eruptions studied by Maclennan (2008a), the mean trace element composition of olivine-hosted melt inclusions is similar to that of the mean composition of whole-rock samples from the host flow. Furthermore, the olivine crystals found in the flows are generally too forsteritic to be in equilibrium with their carrier liquids. These observations indicate that the olivines grew during concurrent mixing and crystallization of diverse mantle melts, and that some of the early formed olivines are retained in the mixed melt. This mixed melt finally carries the olivines to the surface for eruption. This genetic relationship of crystals to their carrier liquid is more specific than the relationship implied by the current definition of the term antecryst (Davidson et al., 2007).

Phenocryst, xenocryst and antecryst are now terms that carry a genetic connotation. As the findings of this paper focus on a specific genesis for the olivine crystals in Icelandic lava flows, we feel it is necessary to avoid any terms with genetic associations. We therefore choose to apply terminology developed for the description of kimberlites, which has so far not been tainted with a genetic association. When describing our results from Iceland, we refer to crystals that are larger than the groundmass and in the size range of ~0.5 mm to 10 mm as macrocrysts (Skinner & Clement, 1979; Le Maitre et al., 1989). Larger crystals, which are extremely rare in Icelandic basalts and picrites, may be referred to as megacrysts.

Olivine–liquid relationships in basaltic magma systems

The relationship between olivine crystals and their carrier melts in basaltic eruptions is pertinent to the study of magmatism in a range of settings, and has received particular attention at ocean islands, mid-ocean ridges and large igneous provinces where the solidified remains of olivine-rich magmas such as picrites and oceanites are found. The range of olivine sizes, textures and compositions found in olivine-rich tholeiites from Mauna Loa and Kilauea on
the island of Hawai‘i has been interpreted as a product of mixing multiple crystal populations (Helz, 1987; Garcia, 1996; Garcia et al., 1996; Vinet & Higgins, 2010). In particular, Vinet & Higgins (2010) suggested that the crystals assigned as phenocrysts grew from a range of magma compositions possibly related by fractional crystallization, whereas the crystals they classified as antecrysts were derived by disaggregation of deformed, olivine-rich cumulates, perhaps similar to the cognate dunite xenoliths described in Mauna Loa eruptions by Garcia (1996). A study of porphyritic lava erupted offshore the island of Fernandina in the Galápagos archipelago found that Fo80–88 olivine macrocrysts are carried in basaltic carrier liquids that have too low an Mg# to be in equilibrium with their olivines (Geist et al., 2006). It was suggested that these olivines have been entrained from an olivine-gabbro crystal mush in the root zones of Fernandina volcano. The disaggregation of olivine-bearing cumulates or mushes has also been proposed as a key part of the genesis of picrite lavas from the island of La Réunion (Upton & Wadsworth, 1972; Albarède & Tamagnan, 1988; Salain et al., 2010).

The relationship between olivine crystals and their carrier liquids has also been examined in basalts and picrites from oceanic spreading centres. The presence of distinct groups of olivine crystals in mid-ocean ridge basalt (MORB) recovered by ocean drilling from the Atlantic Ocean basin was recognized by Donaldson & Brown (1977). In their study, <1 mm olivines with euhedral, hopper or skeletal morphologies were referred to as phenocrysts, and 2–3 mm olivines with round or subhedral shapes were termed megacrysts. In the terminology used in our study both of these sets of olivines are classified as macrocrysts. The large olivines were found to be too forsteritic to be in equilibrium with their host glasses, and their origin was understood to be dominantly as the fractional crystallization products of mixtures of primitive oceanic basalt melts with more evolved tholeiites. The presence of such olivine macrocrysts has been reported across the ocean basins (Rhodes et al., 1979). However, not all forsteritic olivines from the mid-ocean ridges exhibit these characteristics. Picrite samples from the Siqueiros Fracture Zone contain olivines with up to 91.5 mol% forsterite, but the olivine compositions reported in these samples, in the range of Fo87–91, are close to equilibrium with their carrier glasses (Perfit et al., 1996).

Olivine-bearing rocks from large igneous provinces have also been the focus of detailed petrological study to examine the relationship between the olivines and their carrier liquids. Olivine crystals contained in picrites of the Vaigat formation, erupted in West Greenland at ~60 Ma, display a wide range of compositions and morphologies (Larsen & Pedersen, 2000). This olivine population is interpreted as a mixture of phenocrysts and xenocrysts, where olivines generated during crystallization of primitive melts partially re-equilibrated with the evolved liquids remaining after crystallization. Mixing between magmas at different stages in their evolution was proposed as a mechanism for producing the full range of olivine morphologies and zoning patterns observed in these picrites (Larsen & Pedersen, 2000). Importantly, melts that carry olivines to the surface for eruption of the Vaigat picrites are typically in equilibrium with olivines that are less forsteritic than the population of the olivine macrocrysts present in the system. Similar picritic rocks have been described from Baffin Island (Francis, 1985) but their interpretation was predicated on a distinction between kink-banded, highly forsteritic (Fo92–93) olivines described as xenocrysts and less forsteritic euhedral olivine phenocrysts. More recently, Starkey et al. (2012) have identified a compositional continuum in the olivines of the West Greenland and Baffin Island picrites and described highly forsteritic olivines that are free of kink-bands. Clusters of olivine xenocrysts are present in these Baffin Island picrites whose textural relationships and composition indicate that they are formed by the disaggregation of dunite cumulates (Starkey et al., 2012). Complex populations of olivine macrocrysts have also been found in mafic dykes in large igneous provinces, including the Horingbaai dykes of Namibia (Thompson & Gibson, 2000) and the M9 picrite dyke of Rum (Upton et al., 2002). Both of these dykes contain a bimodal distribution of olivine compositions and this bimodality was interpreted to reflect two stages of crystallization. First, crystallization of primitive melts produced highly forsteritic olivines (Fo~95). The liquid remaining after this crystallization was proposed to have been too dense to rise further in the magmatic system. This first generation of olivines was thought to have been subsequently entrained by a more evolved rising liquid that crystallized to generate the less forsteritic (Fo86–90) olivine macrocrysts. In both of these studies, the observed distribution of forsteritic contents of olivine macrocrysts was used to determine the petrological relationships within the system, which in the case of the study by Thompson & Gibson (2000) were critical in the estimation of mantle potential temperatures. Indeed, recent re-evaluation of these relationships has led to substantial downwards revision of mantle potential temperature estimates from these rocks (Keiding et al., 2011).

A large quantity of textural and compositional data exists for olivine crystals from basaltic suites and the widespread occurrence of olivine macrocrysts whose cores are too forsteritic to be in equilibrium with their carrier basalt liquids is well known. In this study, we use a large dataset from Icelandic basalts and picrites to make a statistical investigation of the distribution of olivine compositions and identify robust features of this distribution that can be
used to test models of magmatic processes. However, before this statistical exercise is described, it is necessary to provide a brief description of the current understanding of Icelandic magmatic systems.

**Magmatic plumbing systems of Icelandic basalts**

The study of the composition of olivine-hosted melt inclusions provides a means of understanding the relationships between macrocrysts and their carrier liquids. It is now well established that the melts being supplied from the mantle into the basal parts of the Icelandic volcanic systems are highly compositionally variable, with significant diversity in trace element and Pb isotope compositions of olivine-hosted melt inclusions from single hand specimens (Gurenko & Chauveau, 1995; Slater et al., 2001; Maclellan, 2008a, 2008b). The relationship between melt inclusion trace element variance and the forsterite content of the host olivines was interpreted by Maclellan (2008a) in terms of concurrent mixing and crystallization in Icelandic magma chambers. Petrological barometry calculations indicate that this concurrent mixing and crystallization takes place over a range of depths, between ~12 and 30 km, in the Icelandic lower crust and uppermost mantle (Maclellan et al., 2001a, 2003a, 2003b; Maclellan, 2008a; Winpenny & Maclellan, 2011). The relationship between olivine-hosted melt inclusion compositions and those of their carrier liquids indicates that the olivine macrocrysts grew from diverse parental melts, which then mixed to form the carrier liquid (Maclellan, 2008a). This carrier liquid retains a crystal cargo of macrocrysts that record the progress of mixing and crystallization of melts. The mixing and crystallization of diverse mantle melts is also preserved in the composition of magmatic clinopyroxenes found in several Icelandic flows (Winpenny & Maclellan, 2011).

Whereas the studies of Maclellan (2008a) and Winpenny & Maclellan (2011) emphasized the ability of the carrier liquid to retain crystals formed during earlier mixing and crystallization of diverse parental melts, many other workers have noted the importance of entrainment of liquid–crystal mushes into Icelandic eruptions (Hansen & Grønvold, 2000; Gurenko & Sobolev, 2006; Holness et al., 2007a; Halldorsson et al., 2008; Passmore et al., 2012). The disaggregation of these mushes produces some of the macrocrysts found in Icelandic lavas and mush disaggregation is likely to be important in a range of settings including mid-ocean ridges (Ridley et al., 2006; Costa et al., 2010) and ocean islands (Holness et al., 2007a; Salaul et al., 2010). Recent developments in the modelling of diffusion profiles within macrocrysts in basalts have allowed for estimation not only of the residence time of crystals within the mush, but also the timescales between mush disaggregation and eruption (Costa & Morgan, 2010; Costa et al., 2010). The residence time of plagioclase in a mush under one part of the Mid-Atlantic Ridge has been estimated to be <140 years, whereas the time interval between mush disaggregation and eruption is very short, perhaps less than a year (Costa et al., 2010).

In this study we examine the compositional relationships between olivine macrocrysts and their carrier liquids in a number of Icelandic eruptions. In common with many of the previously described studies from spreading ridges and ocean islands, we find that most of the olivine macrocrysts are too forsteritic to be in equilibrium with the liquids that carried them to the surface. We also examine the details of the distribution of olivine forsterite contents within the products of single eruptions and find that most eruptions contain olivines with a unimodal distribution in forsterite content and that the peak in the distribution is 2–3 mol % higher in forsterite than olivines in equilibrium with the host glasses. These relationships between olivine and their carriers are not consistent with either equilibrium crystallization or fractional crystallization. Neither are they accounted for by models in which the crystals produced during concurrent mixing and crystallization of diverse parental melts are retained in the evolving liquid. However, the systematic relationships between not only the trace element compositions of olivine-hosted melt inclusions and the carrier liquids (Maclellan, 2008a), but also the distribution of forsterite contents of the olivine macrocrysts and the carrier liquid, indicate that the macrocrysts are not simply xenocrysts or produced by the disaggregation of mushes unrelated to the carrier liquid. We propose instead that the olivines initially form by fractional crystallization from parental melts, and these parental melts may have diverse trace element compositions. Ponding, mixing and continued crystallization in magma chambers generates a relatively homogeneous carrier liquid and settling of olivine crystals produces a mushy cumulate layer at the base of the chamber. We demonstrate that Mg–Fe diffusion in the mush pile may modify the distribution of olivine forsterite contents away from their original distribution, generated during fractional crystallization, and lead to the development of a peak in the distribution, which is offset to a higher forsterite content than that of the olivines in equilibrium with the liquid in the open chamber above. Prior to eruption, this basal mush is disaggregated into the main body of the chamber and rapidly carried to the surface for eruption. This model of fractional crystallization of olivines followed by their residence in a mush and subsequent disaggregation can account for the key features of the compositional relationships between olivine macrocrysts and their carrier liquids in almost all of the Icelandic eruptions we have examined. This model has broader applications to basaltic magmatism at mid-ocean ridges, ocean islands and large igneous provinces.
SAMPLE COLLECTION, DESCRIPTION AND ANALYSIS
Lithological and petrographic characteristics of sampled basalts and picrites

To undertake this study we compiled a large quantity of data from Icelandic basaltic lavas from both published and unpublished sources. We also collected and analysed a small number of new samples from two subglacially erupted pillow-mounds, as described below. Despite the huge quantity of data assembled in this database, only 11 units have clean host glass analyses and measurements of more than 60 olivine macrocryst compositions available, a minimum requirement for the statistical investigation described in a later section.

The locations of these 11 units are shown in Fig. 1 and a summary of their petrological characteristics is provided in Table 1. All of the samples come from the active rift zones of Iceland and are tholeiites. A number of these units were produced by eruptions under thick ice during the last glacial period and the composition of the liquid that carried the macrocrysts from the magma chambers to the surface for eruption can be estimated from clean pillow rim glasses. In such eruptions it is straightforward to find glass that is free of significant microlite crystallization. One of the postglacial flows is the large AD 1783 Laki fissure eruption, which produced substantial amounts of tephra with a relatively evolved basaltic composition. Careful examination of the tephra has allowed microlite-poor glass to be found and the compositions of the erupted liquids to be determined. The other postglacial flows are high MgO basalts and picrites from early postglacial times. The extremely high MgO contents of the whole-rock samples of these flows are caused by variable accumulation of olivine macrocrysts. Analysis of clean glass compositions in tephra from these eruptions indicates a maximum liquid MgO of a little over 10 wt %, indicating that the carrier liquids are basaltic in composition.

The petrography of the studied materials is similar to that described for numerous Icelandic basalt and picrite flows (e.g. Jakobsson et al., 1978, 2008; Passmore et al., 2012). The samples are porphyritic, with macrocrysts of olivine ± clinopyroxene ± plagioclase. Some of the more mafic flows such as Borgarhraun and Háleyjabunga also carry macrocrysts of chromian spinel. The distinction between macrocrysts and groundmass is straightforward in these porphyritic samples, as demonstrated in the thin section images shown in Figs 2 and 3. Only a few samples from the interior of thick units of the AD 1783 Laki flow have textures approaching seriate (Passmore et al., 2012). As mentioned above, pillow rims and tephra contain zones of clear glass, almost devoid of quench crystals (Fig. 3a). Skeletal rods of quench olivine, reported by

Fig. 1. Map of Iceland showing the location of eruptions for which there are olivine and melt data, investigated in this study, as labelled triangles. Dark grey zones show the extent of the volcanic systems in the active rift zones. White regions show the stable glaciers on Iceland. NVZ, Northern Volcanic Zone; WVZ, Western Volcanic Zone; EVZ, Eastern Volcanic Zone.
Table 1: Summary of lithological, petrographic and petrological characteristics of the sampled material

<table>
<thead>
<tr>
<th>Eruption</th>
<th>Type</th>
<th>MgO</th>
<th>MgOav</th>
<th>FeOav</th>
<th>FeOmax</th>
<th>Ol (%)</th>
<th>Pl (%)</th>
<th>Cp (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borgarhraun</td>
<td>PG</td>
<td>9.1</td>
<td>11.8</td>
<td>88.6</td>
<td>92.4</td>
<td>8</td>
<td>1</td>
<td>1</td>
<td>1, 2</td>
</tr>
<tr>
<td>Gæsafjöll</td>
<td>GL</td>
<td>7.7</td>
<td>8.7</td>
<td>83.3</td>
<td>89.5</td>
<td>5</td>
<td>1</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Háleyjabunga</td>
<td>PG</td>
<td>10.2</td>
<td>12.0–29.6</td>
<td>90</td>
<td>91.1</td>
<td>&lt;5–60</td>
<td>&lt;1</td>
<td>-</td>
<td>4, 5</td>
</tr>
<tr>
<td>Kistufell</td>
<td>GL</td>
<td>9.6</td>
<td>10.7</td>
<td>88.4</td>
<td>89.7</td>
<td>4–8</td>
<td>&lt;1</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>Þjóðubreiðartögl</td>
<td>GL</td>
<td>9.9</td>
<td>11.5</td>
<td>86.4</td>
<td>88.1</td>
<td>5–10</td>
<td>&lt;1</td>
<td>-</td>
<td>7, 8</td>
</tr>
<tr>
<td>Stapafell</td>
<td>GL</td>
<td>8.1</td>
<td>11</td>
<td>85.8</td>
<td>88.1</td>
<td>10</td>
<td>&lt;1</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Einstaðingur</td>
<td>GL</td>
<td>7</td>
<td>7.3</td>
<td>81.8</td>
<td>88.1</td>
<td>&lt;5</td>
<td>15–20</td>
<td>-</td>
<td>8, 9</td>
</tr>
<tr>
<td>Lágafell</td>
<td>PG</td>
<td>9.8</td>
<td>10.4–28.0</td>
<td>90.2</td>
<td>91.2</td>
<td>&lt;5–50</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Möðfell</td>
<td>GL</td>
<td>9.1</td>
<td>9.6–22.6</td>
<td>88.6</td>
<td>91</td>
<td>&lt;1–30</td>
<td>&lt;1–5</td>
<td>0–8</td>
<td>5, 10</td>
</tr>
<tr>
<td>Mæifell</td>
<td>PG</td>
<td>9.4</td>
<td>9.2–25.6</td>
<td>87.7</td>
<td>90.9</td>
<td>&lt;1–30</td>
<td>&lt;1–5</td>
<td>0–8</td>
<td>5, 10</td>
</tr>
<tr>
<td>Laki</td>
<td>PG</td>
<td>5.4</td>
<td>5.78</td>
<td>78.1</td>
<td>85.8</td>
<td>1</td>
<td>7</td>
<td>4</td>
<td>11</td>
</tr>
</tbody>
</table>

Eruption types are given as PG (post-glacial) or GL (sub-glacial). For postglacial samples, glass compositions were obtained from clean tephra glasses and for GL they were from clean pillow rim glasses. In both types olivine macrocryst compositions were measured in the glassy samples and in lava samples with crystalline groundmass. The glass compositions are shown as MgO and the whole-rock compositions as MgOav. When substantial variation is present in whole-rock compositions, the range of observed values is given. The average and maximum forsterite contents of olivine macrocrysts in each unit are indicated. Estimates of the modal proportions of olivine, plagioclase and clinopyroxene macrocrysts are provided. Those in bold are well-constrained estimates of average mineralogy based on extensive point counting data. Data are from the following sources: 1, Sigurðsson et al. (2000); 2, Maclennan et al. (2003a); 3, Maclennan (2008a); 4, Gee et al. (1998); 5, Gurenko & Chaussidon (1995); 6, Breddam (2002); 7, Maclellan et al. (2001b); 8, this paper; 9, Shorttle et al. (in preparation); 10, Hansteen (1991); 11, Passmore et al. (2012).

Larsen & Pedersen (2000) for the West Greenland picrites, are absent from these Icelandic samples. In more slowly cooled parts of pillow or tephra, however, microlites of plagioclase are present. Although it is believed that the glass analyses are taken from parts of the sample that were unaffected by quench crystallization, it is important to note that plagioclase microlite crystallization will have negligible influence on the Mg# of the analysed glass. The investigation of olivine–liquid relationships described in this study is based on Mg# and it is likely that the estimates of carrier liquid Mg# from the measured basaltic glass compositions are robust to the effects of quench crystallization. These glass compositions are therefore interpreted as the composition of the basaltic liquid that carried the olivine macrocrysts to the surface for eruption.

Olivine macrocrysts in Icelandic basalts and picrites display a range of textural features. Euhedral olivines are common, sometimes with skeletal overgrowths, and blocky olivines are also an important component of the more MgO-rich basalts and picrites (Maclennan et al., 2003a, 2003b). Blocky olivine macrocrysts regularly display kink-bands bounded by planar extinction discontinuities, like that in Fig. 2a from a Peistareykir picrite (Maclennan et al., 2003b; Holness et al., 2007a). This feature is commonly associated with crystals found in cumulate deposits, such as the Rum peridotite shown in Fig. 2b (Holness et al., 2007b). The interpretation of workers who have previously described kink-bands in olivine macrocrysts (Francis, 1985; Helz, 1987) is interpreted to suggest that the macrocrysts have been derived from cumulate rocks or mush prior to eruption. Polycrystalline nodules containing aggregated, and deformed, olivine crystals erupted in Icelandic lavas further witness the involvement of crystalline mush in the generation of Icelandic macrocrysts (Francis, 1985; Helz, 1987). Furthermore, the overlap of textural types and compositions observed between olivines found in gabbroic and wehrlitic nodules and as isolated macrocrysts in the Borgarhraun flow indicates that many macrocrystic olivines may be derived by disaggregation of cumulates or such material (Maclennan, 2003a).

Another important feature of olivines in Icelandic basalts and picrites is the dominance of crystals with compositionally uniform interiors and thin normally zoned rims. Element intensity maps and backscatter electron intensity (e.g. Fig. 3a–c) reveal strong compositional gradients exist within 50–100 μm of the outermost edges of crystals. Similar observations (Costa & Dungan, 2005; Maclennan, 2008a; Costa et al., 2010) have been interpreted as late
Fig. 2. Photomicrographs of thin sections, all in cross-polarized light except (d), which is in plane-polarized light. The white scale bar in each figure represents 500 μm. (a) A large olivine crystal from a Þeistareykir picrite set in a fine-grained groundmass. (b) A sample taken from a peridotitic cumulate layer on the ancient volcanic island of Rum. Olivine crystals in both (a) and (b) have internal dislocation alignment features and undulating extinction position, potentially formed by the same cumulate processes. (c) A Borgarhraun sample with two fused olivine crystals that both demonstrate dislocation alignment. It is interpreted they were once part of a mush layer. (d) A mush nodule from the Brandur tuff-cone. The sample has a cumulate texture, with brown interstitial basaltic glass between mostly plagioclase and some interstitial clinopyroxene crystals. This provides direct evidence of mushes being erupted on Iceland. (e) Section of an olivine mush xenolith from the Hofuhreidarnúpur picrite in Þeistareykir, composed of a cluster of small olivine crystals, set in a plagioclase and glassy matrix. (f) A wehrlitic nodule from Borgarhraun; another example of the eruption of olivine-rich cumulates from Iceland.
re-equilibration of crystals with their carrier liquid after re-entrainment from a cumulate. Alongside other textural evidence this diffusional overprint strongly indicates that Icelandic olivine macrocrysts are often incorporated in mushes prior to eruption.

New sample collection and analysis

New sampling for this study took place in the summer of 2010 in the Northern Volcanic Zone of Iceland. Hand-specimens were collected from pillow lavas, including glassy rims, of the Herðubreiðartögl and Einstaðingur mountains, both products of subglacial eruptions (see location in Fig. 1). Pillow rim samples of these units are composed of a black glassy matrix containing olivine macrocrysts, up to ~2 mm in diameter. Whereas the dominant macrocryst phase in Herðubreiðartögl is olivine, Einstaðingur is more plagioclase rich (Table 1).

These samples were prepared for chemical analysis using the Cameca SX100 electron microprobe at the University of Cambridge by mounting handpicked macrocrysts and glass chips from crushed hand-specimen samples in epoxy. Macrocrysts from Herðubreiðartögl were picked from glassy pillow rim samples, whereas the Einstaðingur samples came from pillow interiors. Polished samples were analysed using an accelerating voltage of 15 keV and beam current of 10 nA (Si, Fe and Mg) or 100 nA (Ca, Ni, Mn, Cr, Ti and Al) for olivine and 4 nA (Na, Si, K, Ca, Ti, Fe, Al and Mg) or 60 nA (F, S, P, Mn, Cr and Ni) for glass. A spot size of 1 µm was used for olivine analyses and 10 µm for glasses, with calibration achieved using a variety of silicate, metal and oxide standards. Alongside errors provided by counting statistics, the precision of analyses was evaluated using repeated measurement of mineral standards. This technique estimates the precision and accuracy of Mg# to be ±0.2% 1σ relative.

Olivine core compositions were analysed to avoid any diffusional overprint, and glass analyses were made on homogeneous spots, free of microlites. Closely spaced linear profiles across several olivines were also measured, confirming the presence and shape of diffusional rim overprints. Rim gradients were found to be both normal and reverse in character, with the reverse zoned rims in

Fig. 3. (a) An iron concentration map, obtained by electron microprobe at Edinburgh University, of a sample collected from Stapafell (colour image available online). The crystals are forsteritic olivines with uniform core compositions and narrow rims of Fe-rich (lower Mg#) material. They sit in a very uniform, less magnesian basaltic glass. (b) An iron concentration map of an olivine grain from Hóleyjabunga that has a thin layer of different composition on its rim. The variation of Mg# along the profile marked A–A’ is plotted in (c), demonstrating a uniform core and narrow rim, <50 µm, of more evolved material.
Herðubreiðartógl being unusual amongst Icelandic olivines. Different species (Mg–Fe, Ni, Ca) have different rim widths, indicating that they are produced as diffusional overprints from re-equilibration with a disequilibrium carrier liquid [as described by Costa & Morgan (2010)] and are not the result of crystallization upon cooling during eruption. In total, the core compositions of 131 olivine macrocrysts were obtained from Einstaðingur and Hl from Herðubreiðartógl.

**Data compilation**
The data collected as described above were then collated with a large quantity of other analyses from Icelandic samples taken from the published literature (Gurenko et al., 1990; Nicholson, 1990; Gurenko & Chausiodon, 1995, 1997; Slater, 1996; Sigurdsson et al., 2000; Bredsdam, 2002; Maclennan et al., 2003a, 2003b; Gurenko & Sobolev, 2006; Sobolev et al., 2007; Guilbaud et al., 2007; Maclennan, 2008a, 2008b; Passmore et al., 2012) and unpublished work. The dataset includes over 13 000 unique electron microprobe analyses of glasses, crystals, nodules, melt inclusions and mineral inclusions from Icelandic eruptions. It is assumed that all data have similar uncertainties to the newly measured data, which, judging from the reported accuracy and precision of some of the older data in the compilation, is likely to be a fair assumption for Mg#. Unfortunately, the larger relative uncertainty for Ni and particularly Ca in some of the older analyses precludes their use for robust statistical investigation of olivine compositional distributions.

Data were ordered by lava flow, and reduced to two separate files containing only olivine crystal and glass analyses respectively (see Supplementary Data, available for downloading at http://www.petrology.oxfordjournals.org). There were found to be 11 flows for which both glass and more than 60 olivine analyses were present, allowing investigation of the melt–olivine relationship. The olivine macrocryst distribution for another 12 flows could also be defined without any relation to host melt composition.

The dataset was further filtered, removing duplicates (by averaging) from single crystals and crystal rim analyses, such that only a single olivine core analysis per crystal (avoiding sampling bias on certain crystals) remained. The effects of rim composition will be considered further below. By retaining a single analysis for each olivine crystal it is effectively assumed that each crystal is homogeneous, consistent with the interpretation of rim zoning as a diffusional overprint (Costa & Dungan, 2005; Costa et al., 2010). It is also indirectly assumed that each crystal in the dataset was originally of uniform size, as insufficient crystal size distribution information exists for database samples to relax this assumption. In the cases of Borgarhraun, Gásafjöll, Haleÿjabunga, Herðubreiðartógl, Stapafell, Einstaðingur and Laki, where one of the co-authors carried out the analysis, it is known that macrocrysts across the full available size range were measured, with the number of crystal analyses roughly correlating with the size of the crystals.

**DATA ANALYSIS AND MELT–CRYSTAL RELATIONSHIPS**
As should be clear from the introduction to this paper, it is well established that olivine macrocrysts are seldom in equilibrium with their host glasses. In previous studies evaluation of olivine–liquid compositional relationships has been achieved using a single value for the equilibrium constant between solid and melt phases, alongside the use of histograms to define crystal distributions (e.g. Maclennan, 2008a). We aim to provide a statistical analysis of geochemical data from Icelandic lavas; therefore a statistically rigorous method of analysing the olivine distributions has to be employed.

Following the work of Rudge (2008), the use of histograms to define distribution shapes has been replaced by two preferred methods. Kernel density estimation (KDE) (Silverman, 1986), a non-parametric method for estimation of the probability density function of a random variable, provides a method with more statistical and physical meaning than a simple histogram. Where the form of a distribution plotted using a histogram essentially depends on the definition of the physically meaningless bin-size parameter, a KDE is smooth and defined by a parameter known as the bandwidth. The KDE is generated by summation of Gaussian functions, with standard deviation equal to the bandwidth, placed at every point in the data set. The bandwidth used and uncertainty in compositional analysis are closely linked, as the physical significance of the bandwidth in this context is the analytical error. It is intuitive that altering the bandwidth choice will change the shape of the distribution produced, leading to possible over- or under-sampling of the data (Fig. 4). For this reason an automated bandwidth picking method (e.g. Sheather & Jones, 1991) was preferred over a manual choice, which can create erroneous results. In cases where the calculated bandwidth was smaller than the analytical error, the bandwidth was fixed at 0.002 units of the mole fraction of forsterite. To ensure that features in the resulting distribution have physical significance the SiZer method (Significant Zero crossings of the derivative) of Chaudhuri & Marron (1999) was employed as suggested by Rudge (2008). This technique identifies significant features by looking at how the KDE changes with varying bandwidth, highlighting peaks and troughs by detecting regions of significant gradient (the significant level used throughout this work is 5%). This approach highlights all significant features in a distribution in a SiZer plot [see
Mg(Olivine) + Fe$^{2+}$ (Liquid) = Mg(Liquid) + Fe$^{2+}$(Olivine)

$$K_d = \frac{Fe^{Oliq}}{Fe^{Liq}} \cdot \frac{Mg^{Oliq}}{Mg^{Liq}}$$

The original work defining $K_d$ for an olivine–melt system conducted by Roeder & Emslie (1970) concluded that $K_d$ is 0.3 ± 0.03. However, the last 40 years have led to the identification of a great deal of complexity in the definition of $K_d$, which is now understood to vary with changes in pressure, temperature, melt composition, melt polymerization and oxygen fugacity. Some studies evaluate $K_d$ by fitting a parameterization to all available experimental data (e.g. Ford et al., 1983; Beattie, 1993; Herzberg & O’Hara, 2002) without trying to separate the effects of single variables. Other studies approach the problem by attempting to isolate the effect of each variable (e.g. Toplis, 2005). A recent review by Putirka (2008) has provided a comprehensive examination of all work on $K_d$. Here $K_d$ is employed to calculate the forsterite content of an olivine that would be in equilibrium with the analysed glass compositions from the dataset.

For all sub-glacial eruptions considered in this study, the mean of all glass data was used to calculate equilibrium olivine compositions with a $K_d$ calculated based on the parameterization of Herzberg & O’Hara (2002). These are plotted as an Mg# value with an error of ±0.2 wt %. Also plotted are values calculated using $K_d$ values from Roeder & Emslie (1970) and an estimate of $K_d$ from Toplis (2005) for comparison. Our Tothlis (2005) estimates were calculated assuming crystallization occurred at a temperature of 1300°C and pressure of 7 kbar with Fe$^{3+}$/Fe$^{2+}$ of 0.1. All plots were initially created using an oxygen fugacity of FMQ = 1 (where FMQ is fayalite–magnetite–quartz), which corresponds to Fe$^{3+}$/Fe$^{2+}$ of 0.1 (Macleman, 2008a). To observe the effect of changes in fO$_2$, the Borgarhraun data were re-plotted using Fe ratios representing the extremes measured in Icelandic samples from the literature, Fe$^{3+}$/Fe$^{2+}$ of 0.08 and 0.132 from Breddam (2002) and Óskarsson et al. (1994) respectively. The position of melt equilibrium values is also plotted on cumulative density distributions of the olivine data, allowing the fraction of macrocrysts more or less primitive than the melt equilibrium composition to be easily determined (Fig. 5).

Olivine population distributions

It can be seen from the analysis of data from single eruptions plotted in Fig. 5a–k that, in all eruptions except Laki, the olivine population falls within a narrow range of Mg# and is approximately described as unimodal (a single large peak) or bimodal (combination of two significant peaks). It is noted that the Borgarhraun olivine
Fig. 5. (a)–(k) Plots of data from 11 Icelandic eruptions. Olivine populations plotted as probability density against composition [Mg# as molar Mg/(Mg + Fe)]. The kernel density estimate (KDE), calculated as described in the text, is plotted as a continuous line, and the mixture model as a dashed line. The equilibrium olivine composition calculated from analysed melt composition using the $K_d$ of Herzberg & O’Hara (2002) is shown as an annotated grey bar. The width of this grey bar corresponds to an Mg# of ±0.002, the estimated analytical error. Equilibrium olivine values calculated using the $K_d$ values of Toplis (2005) and Roeder & Emslie (1970) (R&E) are plotted as labelled vertical lines. The values of $K_d$ for each method are reported in Table 2. bw, bandwidth used in production of the KDE; N, number of olivine crystals from each lava flow. (l) The cumulative density distribution of data from Borgarhraun (black line) and the remaining 10 eruptions combined (grey line), are plotted as cumulative probability. $\Delta$Mg# is calculated as the difference between the single olivine composition and calculated equilibrium olivine composition using the Herzberg & O’Hara $K_d$ [as in (a)–(k)]. $\Delta$Mg# is positive for an olivine more primitive (higher Mg#) than the equilibrium olivine and negative if more evolved. Positive values of $\Delta$Mg# are taken to represent crystals not in equilibrium with the host lava, thus it is concluded that less than 10% of crystals are in equilibrium with host lava flows.
Fig. 5. Continued.
distribution contains more detail and four Mg# peaks are identified by both KDE and mixture model techniques, which is most probably due to the sample size \((n = 1653)\) being a factor of \(\sim 5 \sim 20\) times larger than for all other eruptions. By examining the SiZer plot for Borgarhraun (Supplementary Data) it can be seen that the four peaks reduce back into a single dominant peak, leading to the population being classified as unimodal, which can be confirmed by randomly resampling the data to 300 data points. Therefore, eight of the 11 eruptions investigated in detail are unimodal and two are bimodal (Múlafell and Mælifell). Laki is the only flow that does not comfortably fit in either category, with 3–4 identified significant peaks, and is also spread over a much larger Mg# range.

**Melt equilibrium olivine composition**

In all plots the olivine in equilibrium with the measured glass composition, using the \(K_d\) from Herzberg & O’Hara (2002) with an error of \(\pm 0.2\) wt % (corresponding to the analytical error), is plotted as a vertical grey region. \(K_d\) values calculated for each eruption are shown in Fig. 5 and in Table 2. In general it can be seen from the table and figures that the \(K_d\) calculated from Toplis (2005) is larger than that of Herzberg & O’Hara (2002), and all \(K_d\) values are within Roeder & Emslie’s (1970) original value of 0.3 ± 0.03. The value of Herzberg & O’Hara (2002) is taken as the primary value as it does not require, like the value of Toplis (2005), estimation of crystallization conditions for its calculation. If the true value was slightly larger, as the Toplis (2005) estimates suggest, then this shifts the equilibrium olivine compositions to more evolved (lower Mg#) compositions. The eruptions where the use of Toplis (2005) might be preferred are those with more evolved melt compositions, particularly Einstaðingur and Laki (MgO < 7.5 wt %), owing to the larger dataset used for parameterization.

**Relationship between melt and crystals**

It is observed that in 10 of the 11 localities sampled the equilibrium olivine composition is offset to more evolved Mg# than the majority of crystals in the distribution. The inset cumulative probability distributions reveal that less than 15% (see Table 2) of crystals are in equilibrium with, or more evolved than, the calculated equilibrium composition using Herzberg & O’Hara (2002). This percentage would further decrease if the \(K_d\) of Toplis (2005) were used to calculate the equilibrium olivine compositions. It is therefore justified to conclude that very few of the olivine crystals are in equilibrium with the eruptive melt.

**Effect of oxygen fugacity and rim gradients**

To ensure that results are not simply an artefact of incorrect oxygen fugacity choice, the Borgarhraun data are re-plotted using a range of glass ferric iron ratios. This range corresponds to the measured range in Icelandic samples and Fig. 6 shows that such changes in \(\phi_{O2}\) makes very little difference to the equilibrium olivine composition. The effect of changes in \(R_{Fe3+}^{tot}/R_{tot}\) are of the same order as the analytical errors, and so are not significant.

Throughout this analysis it has so far been assumed that each crystal is perfectly uniform in composition. As discussed above, there are compositional gradients within crystals towards the rims. Although it is likely that they represent diffusional overprinting, and arguably should be ignored, they are investigated here, as it is instructive to determine their influence on the overall distributions.

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**Table 2: Summary of observations and parameters calculated for each Icelandic eruption studied**

<table>
<thead>
<tr>
<th>Eruption</th>
<th>Olivine population</th>
<th>Sample size ((n))</th>
<th>(K_d) Herzberg &amp; O’Hara (2002)</th>
<th>(K_d) Toplis (2005)</th>
<th>(K_d) Roeder &amp; Emslie (1970)</th>
<th>KDE bandwidth</th>
<th>Melt wt % MgO</th>
<th>Approx. % Ol in eq’m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borgarhraun</td>
<td>Unimodal</td>
<td>1653</td>
<td>0.308</td>
<td>0.323</td>
<td>0.3</td>
<td>0.0025</td>
<td>9.065</td>
<td>8</td>
</tr>
<tr>
<td>Gæsafjöll</td>
<td>Unimodal</td>
<td>251</td>
<td>0.298</td>
<td>0.324</td>
<td>0.3</td>
<td>0.002</td>
<td>7.735</td>
<td>4</td>
</tr>
<tr>
<td>Háleyjabunga</td>
<td>Unimodal</td>
<td>281</td>
<td>0.314</td>
<td>0.321</td>
<td>0.3</td>
<td>0.002</td>
<td>10.19</td>
<td>2</td>
</tr>
<tr>
<td>Kistufell</td>
<td>Unimodal</td>
<td>218</td>
<td>0.311</td>
<td>0.317</td>
<td>0.3</td>
<td>0.002</td>
<td>9.623</td>
<td>5</td>
</tr>
<tr>
<td>Herðubreiðantögl</td>
<td>Unimodal</td>
<td>141</td>
<td>0.312</td>
<td>0.323</td>
<td>0.3</td>
<td>0.00206</td>
<td>9.749</td>
<td>49</td>
</tr>
<tr>
<td>Stapafell</td>
<td>Unimodal</td>
<td>123</td>
<td>0.301</td>
<td>0.321</td>
<td>0.3</td>
<td>0.00456</td>
<td>8.132</td>
<td>3</td>
</tr>
<tr>
<td>Einstaðingur</td>
<td>Unimodal</td>
<td>131</td>
<td>0.291</td>
<td>0.326</td>
<td>0.3</td>
<td>0.002</td>
<td>7.039</td>
<td>6</td>
</tr>
<tr>
<td>Lágafell</td>
<td>Unimodal</td>
<td>63</td>
<td>0.312</td>
<td>0.32</td>
<td>0.3</td>
<td>0.00244</td>
<td>9.795</td>
<td>2</td>
</tr>
<tr>
<td>Múlafell</td>
<td>Bimodal</td>
<td>130</td>
<td>0.311</td>
<td>0.318</td>
<td>0.3</td>
<td>0.00204</td>
<td>9.562</td>
<td>5</td>
</tr>
<tr>
<td>Mælifell</td>
<td>Bimodal</td>
<td>81</td>
<td>0.308</td>
<td>0.323</td>
<td>0.3</td>
<td>0.00351</td>
<td>9.105</td>
<td>9</td>
</tr>
<tr>
<td>Laki</td>
<td>Other</td>
<td>285</td>
<td>0.273</td>
<td>0.335</td>
<td>0.3</td>
<td>0.00388</td>
<td>5.435</td>
<td>15</td>
</tr>
</tbody>
</table>
If the rim on each crystal is volumetrically significant, the offset between olivine and melt could be removed.

To test this idea each core composition in the dataset was transformed into a volumetric crystal function as illustrated in Fig. 7b. In this case it was assumed that every crystal in the flow is of equal radius (1), spherical and with equal rim thickness. Each crystal rim was modelled as a series of thin shells, across which Mg# varied linearly, on the outside of a uniform core. This geometry leads to the following relationship between volume and composition in the rim:

$$\frac{\partial V_f}{\partial \text{Mg#}} = \frac{3r^2(R-r)}{R^3(\text{Mg#}_c - \text{Mg#}_r)}$$

where $V_f$ is the fractional volume of each spherical shell, $R$ is the crystal radius, $r$ is the rim width, Mg#$_c$ is magnesium number in the core, and Mg#$_r$ is magnesium number at the very edge of the crystal. The effect of this conversion into crystal functions for two crystal sizes with variable rims can be seen in Fig. 7a for the Borgarhraun distribution. This plot shows that if all crystals had a radius of 1mm then a rim width in excess of at least 200 $\mu$m is required to create equilibrium. As this width is larger than any single observed rim thickness, and most rim widths are <50 $\mu$m (Fig. 3), it can be concluded that the inclusion of rim volumes does not remove the requirement of disequilibrium between the distribution of olivine compositions and their carrier liquids.

**Significance of results**

From the introduction and analysis above it is apparent that within Icelandic lava flows, and probably basaltic flows in general, macrocrysts and melt are very rarely in equilibrium, with the macrocrysts almost always too forsteritic to be in equilibrium with their carrier liquids. These conclusions have been tested for variable $K_d$ and $f_{O_2}$ values as well as inclusion of zoned rims to ensure
confidence in the results. The key new observation that can be obtained from the statistical analysis is that the olivine macrocryst compositional distributions consistently display strong unimodal peaks or bimodal distributions, with one of the peaks being 2–3 mol % too high in forsterite for equilibrium with the carrier liquid.

**A MODEL OF OLIVINE–MELT RELATIONSHIPS IN A MAGMATIC MUSH**

**Model premise**

Any model proposed to account for the general observations of the relationship between olivine compositional distributions and the carrier liquid from Icelandic olivine-bearing lavas must have the following attributes.

1. It must produce single crystals that have homogeneous core compositions and are zoned in a thin layer around their rim, of varying widths for different species.
2. It must involve a process, such as mush or cumulate processes, capable of producing olivines with kink-bands.
3. It must produce both unimodal and bimodal olivine crystal populations that can be approximated by a mixture of Gaussian functions.
4. It must have an output where the majority of olivine crystals in the lava flow are more primitive than the carrier melt, creating the observed disequilibrium system.

A conceptual model of the output of various magma chamber processes, as represented by the schematic illustration in Fig. 8, can account for the key observations listed above. It can be surmised that if batch crystallization were occurring in the magma chambers under Iceland then all crystals would remain in magma suspension until

![Fig. 8. Schematic illustration showing how various magma chamber processes would be expected to affect the olivine population. Equilibrium crystallization of an initial basaltic melt would be predicted to result in uniform macrocrysts that remain in equilibrium with the basalt throughout evolution (a, b). Fractional crystallization leads to the generation of a cumulate pile, in which olivines too high in Mg# for the carrier liquid can be stored until eruption (c). However, compositional distribution of the macrocrysts will not be unimodal or polymodal in shape (d). If crystals are allowed to reside in a cumulate pile after fractional crystallization then diffusion will begin to homogenize the mush (e). Throughout this process only crystals at the melt–mush interface will remain in equilibrium with the melt, all others are able to freely evolve. It is assumed that local diffusion is able to remove local heterogeneities within single crystals, whereas entire mush diffusion alters the erupted distribution. Given enough time the olivine distribution will become unimodal, with a peak offset to higher Mg# than the chamber melt (f). The longer this process continues the fewer crystals are able to remain in equilibrium with the carrier melt.](https://academic.oup.com/petrology/article-abstract/54/4/745/1548250)
they were erupted. It is also understood that this process would result in all crystals being of the same composition and would provide no mechanism to account for kink-banded olivines. Equilibrium crystallization provides no explanation for the range of observed crystal compositions, thus fractional crystallization is indicated.

In the scenario presented in Fig. 8c dense olivine crystals are expected to descend from their point of creation towards the chamber floor and form a mush pile at the base or walls of the chamber. If the Icelandic olivine macrocrysts do indeed represent disaggregated mush piles, then it is likely that these piles formed dominantly by crystal settling rather than in situ growth at the chamber margins. The simplest argument against significant in situ crystallization is that none of the olivines have the distinctive crescumulate textures that have been interpreted to result from growth on intrusion margins (Wager et al., 1960). Furthermore, investigation of the textures of cumulate and mushy nodules from Iceland supports the origin of such cumulates through an initial stage of accumulation of crystals by settling (Holness et al., 2005, 2007a). Loading in the mush pile provides a mechanism for creating internal macrocryst deformation. In the simple case of evolution of a closed chamber by fractional crystallization, the composition of the crystals accumulating in the pile will vary as the liquid composition in the chamber evolves, producing a mush pile with more forsteritic olivines at its base than at its top. The olivines at the base of the pile will have been in equilibrium with the primitive melt injected into the chamber, and the olivines at the top of the mush will be in equilibrium with the more evolved melt generated after an interval of cooling and crystallization.

The unimodal distribution of olivine macrocryst compositions observed for most of the studied Icelandic units indicates, however, that an additional process must be involved, because the distribution of olivine compositions generated by simple fractional crystallization does not have strong peaks (see Fig. 8d). If after cumulate formation the crystals are allowed to rest as a mush for enough time, diffusion may occur. In this situation it can be envisaged that chemical diffusion will occur to remove heterogeneity within the mush. During diffusion there will be two different length-scales that will be significant for understanding the evolution of the system (illustrated in Fig. 9). Locally, single olivines will undergo diffusion within their crystal lattice to produce uniform crystals. The compositional homogeneity of single olivine macrocryst cores in Icelandic porphyritic rocks may be generated by such crystal-scale diffusion within a mush pile. At the same time the chemical gradient across the entire mush pile will evolve, reducing the variance in the olivine macrocryst population. The timescale for entire mush pile homogenization is longer, as it is still incomplete when eruption occurs. If diffusion across the mush pile goes to completion before disaggregation of the mush into the carrier liquid, then there would be no variation present in the population of olivine macrocryst core compositions and the distribution would have a unimodal peak at fixed forsterite content. The fact that unimodal peaks are observed, but have finite width, may indicate that diffusion across the mush pile has occurred, but not gone to completion. As a final step, the mush must be disaggregated into the relatively evolved liquid in the open chamber, which carries the crystals to the surface for eruption. Narrow normally zoned rims on the macrocrysts can be generated by short-lived diffusive exchange between the disaggregated mush crystals and the evolved carrier liquid. This conceptual framework appears to provide a potentially satisfactory explanation for the first-order observations (Fig. 8f).

This sequence of events can account for not only the presence of macrocrysts with homogeneous cores and narrow rims, but also the presence of unimodal peaks in the observed olivine macrocryst compositions offset to higher Mg# than the olivines in equilibrium with the carrier liquid. To test this conceptual framework, a simple
numerical model of crystallization and diffusion in a mush pile following the above outline was developed. The model parameters were chosen to reproduce the principal features of the olivine macrocryst compositional distribution observed in the Borgarhraun flow, because this flow has undergone the most detailed study of its geochemistry, petrology and petrography (Sigurdsson et al., 2000; Maclellan, 2003a, 2003b; Holness et al., 2005). However, the general features of the model, which produces a unimodal distribution of olivine compositions offset to higher forsterite contents that those in equilibrium with the carrier liquid, can be applied to all of the studied units. It is important to note that the aim of the models is not to exactly reproduce the details of each observed distribution, nor to uniquely constrain the physical characteristics of the mushes in Icelandic magma chambers. Instead, the simple model presented is used to establish if diffusion in mushes can reproduce the first-order observations described above and to investigate whether such distributions can place any constraints upon mush properties.

Model details—fractional crystallization

For simplicity we assumed that all crystals in a lava flow form by fractional crystallization of a single parental melt. In reality, there are likely to be multiple injections of initial melts into a magma chamber that is envisaged as an open system (Holness et al., 2007b, 2007c; Holness & Wimpenny, 2009). The parental melt composition used for the modelling corresponds to an Icelandic whole-rock sample that will initially crystallize the most forsteritic olivine observed in the Borgarhraun flow (Fo92). To calculate the phases forming as the liquid evolves we used vectors fitted to major element trends from Icelandic whole-rock and glass samples (Maclellan et al., 2001a). It was assumed that ol and cpx would crystallize in a 70:30 ratio above a melt MgO of 9.5 wt % and ol, cpx and plag would crystalize in a 10:40:50 ratio below 9.5 wt % MgO (Maclellan et al., 2001a). Macrocrystal and evolving melt compositions were evaluated at increments throughout the crystallization process by using the Herzberg & O'Hara (2002) parameterization for $K_d$ between olivine and melt and $K_d = 0.28$ for Mg/Fe in clinopyroxene. Clinopyroxene compositions were also corrected using an empirical function linking Mg# and FeO contents of the Borgarhraun crystals. As crystallization continues the parental melt progressively shifts to lower Mg#, as does the olivine crystallizing at each modelling increment. Crystallization ceased when the olivine composition forming was Fo96, in equilibrium with the observed Borgarhraun glass composition, which is likely to correspond to that of the carrier liquid.

The output is converted from mass to volume and into a virtual mush pile by assuming that crystal settling occurs rapidly after crystal formation. Thus, the most Mg-rich crystals, the first to form, make up the base of the mush pile. The initial distribution of olivine compositions generated by fractional crystallization from Fo92 to Fo96, in equilibrium with Borgarhraun liquids, is shown in Fig. 10b, as the distribution at $t = 0$.

Model details—mush diffusion

It is supposed that after mush pile formation the chemical gradient across the pile causes diffusion to occur. The effect of diffusion on the mush's composition can be evaluated by employing Fick's second law, which describes the change in composition with time over a one-dimensional system:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}.$$

The above expression of Fick's law assumes a constant diffusion coefficient, $D$, which for most natural systems is a strong approximation. A relevant example of a system with non-uniform diffusion coefficient is that of Mg/Fe diffusivity in natural olivine, which varies with temperature, pressure, oxygen fugacity and composition (Dohmen & Chakraborthy, 2007). In our modelling it is assumed that the appropriate diffusion coefficients are constant to aid solution of the problem.

The focus of the modelling is to track how the compositional distribution of olivine crystals within the mush evolves over time. In this problem it is necessary to assess two pairs of diffusion lengths and timescales. The single macrocrysts within the cumulate are assumed to be spheres of constant radii that undergo diffusion, defined using $D_{\text{ol}}$ for Mg/Fe, to homogenize the single crystals. The diffusion problem is illustrated and annotated in Fig. 9. It is known that single crystals have entirely homogenized, as the cores are uniform upon eruption, providing a minimum diffusion time. The outer layer of each macrocryst is assumed to be constantly in equilibrium with the adjacent interstitial melt.

On larger length-scales the composition of the entire mush pile will also evolve, dominated by the fastest diffusion path, which is through the interstitial melt, using the diffusion coefficient $D_{\text{melt}}$. In reality, there will also be slower diffusion mechanisms occurring across the whole mush by diffusion through touching solid phases, but this pathway is ignored, as solid-state diffusion of Mg–Fe is many orders of magnitude slower than melt diffusion. The mush is assumed to have a porosity of 40%, and is approximated as an infinite slab of material bounded by two parallel planes, thus allowing analytical solution of Fick's second law for specified boundary and initial conditions. The porosity is fixed at 40%, slightly larger than that expected from perfect spherical close packing (36%), but similar to the estimated porosity during the initial formation of olivine-rich cumulate layers (Jerram et al., 1996).
This may be compared with an estimated initial porosity of 60% in plagioclase-rich cumulates such as the Sept Iles Layered Series (Namur & Charlier, 2012) or Skaergaard (Tegner et al., 2009), meaning that our model underestimates the bulk diffusivity across the mush pile by up to 50% relative for the generation of gabbroic cumulates. As Borgarhraun contains both olivine-rich wehrlite and gabbroic nodules (Maclean et al., 2003b) there is uncertainty in choosing the most appropriate value for the initial porosity. However, the uncertainty associated with initial porosity is far smaller than that associated with our lack of knowledge of the dimensions of the mush pile, as discussed below, and has no control on the ability of diffusion to match the form of the unimodal peaks in the observed olivine compositional distribution.

The diffusion coefficient for Mg/Fe exchange in the solid olivine macrocrysts is assumed to be $7 \times 10^{-7}$ m s$^{-2}$, taken from Dohmen & Chakraborty (2007). To calculate the coefficient for the Mg–Fe interdiffusion in the melt phase, $D_{\text{Mg/Fe}}$, experimental values for the self diffusion of Mg and Fe$^{2+}$ in basaltic melts were used from Kress & Ghiorso (1995) at 1300°C. These were combined to calculate the interdiffusivity of Mg/Fe in a basaltic melt for both ionic interdiffusion (Hellerich & Plesset, 1959) and neutral species diffusion (Darken, 1948), as it is uncertain which mechanism will be occurring (Zhang, 2010). The two results, assuming the Mg–Fe in the melt is approximately 1:1 and the thermodynamic factor equates to unity, are $D_{\text{Mg/Fe}}$ of $2.08 \times 10^{-10}$ m s$^{-2}$ and $2.10 \times 10^{-10}$ m s$^{-2}$ respectively. As these values are effectively equivalent, the latter value is used. However, as the mush is not purely composed of a melt phase the influence of crystals increasing the path length and the porosity of the mush must be accounted for. The diffusion coefficient is multiplied by $\pi/2$ and 0.4 to take account of these factors, producing a final diffusion coefficient $D_{\text{Mg/Fe}}$ of $1.92 \times 10^{-9}$ m s$^{-2}$.

We can now consider the timescales over which each system, the single crystals and the entire mush pile, become homogeneous. If the single crystals homogenize much faster than the entire mush then they will effectively always remain in equilibrium with the liquid at the same level in the evolving mush pile. In this scenario we need to consider only diffusion within the interstitial liquid, as over timescales of evolution of the interstitial mush liquid, single crystals will be homogeneous. For crystals of 0.5 mm radius, the time for homogenization estimated using the method of Larsson & Karlsson (1975) for a single crystal is $1.07 \times 10^9$ s (34 years). A simple evaluation of a one-dimensional timescale for the entire mush (using $\sqrt{Dt} = L/2$) shows that as long as the mush is at least 0.75 m thick then the assumption that single macrocrysts homogenize more quickly than the mush holds. It is therefore assumed that only diffusion throughout the mush pile must be considered in this model to predict the composition of evolving macrocryst cores.
Although this is clearly a simplification, it appears to be justified and is certainly sufficient for this simple modelling approach.

Boundary conditions appropriate for the mush pile system concerned are not well constrained, owing to the lack of a priori information regarding the geometry of the system. Two types of condition for each boundary have been investigated, combined in all possible combinations. First, a fixed boundary, where composition cannot change; perhaps appropriate if the boundary is in contact with an infinite or buffered magma reservoir. Second, boundaries with zero mass transfer, corresponding to a physically isolated boundary. The most satisfactory results are achieved by defining both boundaries using a zero mass-transfer condition, where the analytical solution, derived with reference to Carslaw & Jaeger (1959), is as follows:

\[
C = \frac{1}{l} \int_0^l f(x) \, dx + 2 \sum_{n=1}^{\infty} \exp \left( \frac{-D_n \pi^2 t}{l} \right) \cos \left( \frac{n \pi x}{l} \right) \int_0^l f(x) \cos \left( \frac{n \pi x}{l} \right) \, dx.
\]

The solution was plotted in Mathematica 7, compared with numerical solutions of Fick's second law using the method of Skeel & Berzins (1990), and shown to be equal to them. Although these boundary conditions are certainly simplified when compared with the natural system, they demonstrate that a combination of crystallization and diffusion can fit the observations, in this case where the mush is partly closed to any melt sitting above it. The closure of the upper boundary in models that successfully fit the unimodal peak in olivine compositions may be understood in terms of continued growth of the mush pile during diffusion.

The resulting distribution was then randomly sampled using a bootstrap algorithm to recreate field and laboratory sampling and converted into a kernel density estimate with 95% confidence intervals for comparison with observations.

**Model results**

The output from the modelling is shown in Fig. 10, demonstrating that as fractional crystallization and diffusion continue in the system the olivine composition distribution evolves, from an initially sloped shape \((t = 0)\) into a sharp unimodal peak. Importantly, during evolution the distribution also passes through a period of time where the olivine population is bimodal. In the case of a 1 m thick mush pile, the distribution becomes unimodal within \(1.5 \times 10^9\) s (\(\sim 42\) years) after the beginning of diffusion. If instead the mush was 5 m thick or 10 m thick it takes less than \(3.5 \times 10^9\) s (\(\sim 115\) years) or \(2.5 \times 10^9\) s (\(\sim 7950\) years) respectively for the distribution to become unimodal in our model. The relevance of these timescales is discussed in the following section.

Figure 10 shows that a simple model of fractional crystallization followed by crystal residence in a mush pile and re-entrainment prior to eruption is capable of accounting for several of the key features of the olivine macrocrysts in Icelandic basalts including: (1) the presence of peaks in the macrocryst Mg# distribution; (2) disequilibrium between macrocrysts and their carrier liquid such that the macrocrysts have higher Mg# than olivines in equilibrium with the liquid; (3) the homogeneous cores but narrow crystal rim zoning of the macrocrysts; (4) the occasional presence of kink-banding. This model does not account for the distribution of olivine compositions observed in the Laki basalt, which display at least three resolved peaks in macrocryst olivine composition. However, if mush-pile formation and entrainment happens in a series of chambers during ascent of the magma it may be possible to match such polymodal distributions. Late primitive magma injection is the probable explanation for the reverse zoned rims observed from Herðubreiðartögl.

**DISCUSSION**

This investigation of the melt–olivine relationship in Icelandic basalts has provided a conceptual framework through which many previously unrelated observations can be understood and eventually quantified. However, it is necessary critically to assess the assumptions that have been used during the study to consider how they might alter our conclusions, and reflect on how this work may be improved upon in the future.

The most notable assumption made throughout this work is that all crystals observed and modelled are of uniform size. Most macrocrysts have a size within a single order of magnitude, between 0.5 and 2 mm diameter; however, this range corresponds to a large volume range between samples. The introduction of crystal size distributions (CSDs) into modelling and observation plots would be a significant development of this work. Marsh (1988, 1998) and Vernon (2004) have studied CSDs for multiple systems in detail but until now there are still no studies known to us that provide a quantitative investigation of the relationship between crystal sizes and composition in basaltic lavas. In the absence of such data it could be argued that the largest crystals are likely to be the most primitive, as they probably formed first and have had longer growth times. In this situation it is possible that considering size distributions would bias the olivine populations to higher Mg# values, thus making the disequilibrium even stronger than it currently appears. Thus, none of the significant conclusions of this work are likely to be affected. Looking at the data that are currently available it is observed that the basaltic picrites of West Greenland display no such size-composition
relationship (Larsen & Pedersen, 2000), and therefore the assumption of uniform crystal size may be appropriate anyway.

It was also assumed that the extent of sampling in the geological dataset is sufficient to entirely define the crystal population from each flow. It is clear that in flows with greater sampling, such as Borgarhraun, the olivine population is defined in more detail. This extra sampling does not appear to alter the underlying basic shape of the population, a unimodal distribution, and therefore we conclude that increased sampling will only reveal details, and not change population classification or overall form.

As already stressed, the model developed is designed to be illustrative, and not to re-create the full complexities of the natural system. In reality, multiple source melts are probably injected into a complex magma chamber system over a period of time during which crystallization and mush evolution are constantly occurring. Evidence for such behaviour can be seen in the cumulates of exposed ancient magma chambers, such as that of Rum. Here layered cumulate piles of peridotite and troctolite show evidence of multiple episodes of magma influx and eruption in a complex open system (e.g. Holness et al., 2007b, 2007c; Holness & Winpenny, 2009) recorded by cumulate composition and varying petrological textures. Furthermore, the composition of olivine-hosted melt inclusions and clinopyroxene macrocrysts from primitive Icelandic eruptions indicates that diverse parental melts may be supplied to near-Moho magma chambers, perhaps concurrently (Maclean, 2008a, 2008b; Winpenny & Maclean, 2011). Nevertheless, the observation that the characteristic unimodal distribution of olivine macrocryst compositions is found not only in primitive flows but also in more evolved eruptions such as Einshøjindur indicates that these distributions are controlled by mush processes rather than mantle-derived magma compositional diversity.

The simple model presented involves diffusion within a static, isolated mush layer and successfully demonstrates the role that such diffusion may play in controlling the compositional distribution observed in the olivine macrocrysts. A number of modifications, may, however, be made to this simple model to allow for future comparisons of the model results with the plutonic record of mush zone processes preserved in layered intrusions or the lower crust and Moho transition zone of ophiolites. Growth of the mush pile by crystal settling may be incorporated into the model by changing the nature of the upper boundary condition.

Within the mush pile the interstitial melt was assumed to be static. However, if cumulate compaction (McKenzie, 1984, 1987) or interstitial melt convection (Tait & Jaupart, 1992) occurs, then the homogenization of liquid and crystal compositions will occur more rapidly than predicted from diffusion alone. The importance of fluid migration as a result of compaction or compositional convection is strongly controlled by the thickness of the mush pile. The role of compaction can be assessed by calculating the characteristic compaction length of McKenzie (1984). The permeability, \( k_0 \), is evaluated using the Koseny–Carman formula

\[
k_0 = \frac{\phi^3 a^2}{K(1 - \phi)^3}
\]

with \( K=1000, \) porosity, \( \phi, \) of 0.4 and a grain size, \( a, \) of 1 mm, giving a value for \( k_0 \) of \( 1.78 \times 10^{-10} \).

If the fluid viscosity, \( \mu, \) is 15 Pa s (Tegner et al., 2009), and the matrix bulk and shear viscosities are \( \eta = 10^{15} \) Pa s (Tegner et al., 2009), then the compaction length, \( \delta_c, \) is calculated as \( \sim 166 \) m using the expression from McKenzie (1984):

\[
\delta_c = \left[ \frac{\zeta + \frac{2\eta}{\mu} k_0}{\mu} \right]^{1/2}
\]

The more complete calculations of Tharp et al. (1998) and McKenzie (2011) also indicate that reduction of porosity and fluid migration becomes important once the mush pile is over \( \sim 100 \) m in thicknesses. Similarly, the calculations of Tait & Jaupart (1992) indicate that compositional convection may occur in mush piles that are \( \sim 200 \) m thick or more. The mush piles for which models are presented in this contribution are relatively thin, all less than 10 m, and in such thin mushes the importance of fluid migration is likely to be minimal. Evidence in favour of such thin mushes comes from the study of the layered gabbros of the lower crust and Moho Transition Zone of ophiolites, which were interpreted by Korenaga & Kelemen (1997) and others to have formed in a series of discrete, thin sills. Although the determination of mush thicknesses that were present during the assembly of large layered intrusions is a topic of vigorous discussion at present, it is worth noting that a series of textural observations indicate that mush thicknesses may not have been sufficiently high for substantial compaction of compositional convection to occur (Holness et al., 2007c; Holness & Winpenny, 2009).

Although the simplification of the mush pile model by neglecting fluid advection may be justified for Iceland, it is worth examining what role such advection would play in homogenizing the mush. The effect of interstitial melt convection would be to allow more chemical communication between the overlying chamber melt and the mush. This effect could be evaluated by adding an advective transport term to Fick’s second law, resulting in the peak of the olivine distribution shifting to lower Mg\# values, closer to equilibrium with the melt composition. Diffusion is still required to produce the distribution shapes and as...
In this model timescales of diffusion are produced; however, in the current form their absolute values have little significance. They are based on a 1 m, 5 m or 10 m thick mush pile formed before diffusion commences, and using only a single diffusion coefficient. Further work could lead to realistic timescales of diffusion between crystallization and eruption being calculated, but here it has been sufficient to prove that given a certain time, of the order of 42–8000 years, it is possible to reproduce all the observations made from natural systems.

CONCLUSIONS
The compositional relationship between olivine macrocrysts and the liquid that carried them to the surface for eruption has been investigated for a number of Icelandic lava flows. Analysis of a large dataset of olivine compositions indicates that the liquid in the overlying chamber is reproduced. If this mush pile were to evolve in a closed system, it would eventually produce a single peak in olivine compositions determined by the mean Mg/Fe of the contents of the mush pile, rather than by the composition of the overlying melt. In our model, the diffusion does not go to completion across the mush pile, so some spread in compositions is retained, and the unimodal peak in olivine compositions offset to higher Mg# than the olivine in equilibrium with the overlying liquid is reproduced. If this mush pile is partially re-entrained before eruption, then narrow diffusional rims will develop on the edges of the olivine macrocrysts as observed.

The effectiveness of this conceptual model was tested by the development of a simple analytical solution to Mg–Fe diffusion in a mush pile. The predicted distribution of olivine compositions and the relationship of these compositions to the liquid in the open chamber share many common features with the observed macrocryst and basalt glass compositions. The compositional evidence for the importance of mush re-entrainment in Icelandic lava flows is consistent with textural evidence from rare cumulate nodules and the presence of kink-banded olivines.

The textural and compositional characteristics of the Icelandic olivine macrocrysts are similar to those described globally from basaltic magmatism at mid-ocean ridges, ocean islands and in large igneous provinces. Application of the statistical and analytical methods described here may provide information about the properties of magmatic mushes in diverse settings.

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

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