

This is a non-peer-reviewed preprint of an article resubmitted to Contributions to Mineralogy and Petrology and uploaded to EarthArXiv in May 2024.

Iron valence systematics in clinopyroxene crystals from ocean island basalts

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Abstract

The valence state of Fe plays a vital role in setting and recording the oxidation state of magmas, commonly expressed in terms of oxygen fugacity (f_{O_2}). However, our knowledge of how and why f_{O_2} varies within and between magmatic systems remains patchy because of diverse challenges associated with estimating the valence state of Fe in glasses and minerals routinely. Here we investigate Fe valence systematics in magmatic clinopyroxene crystals from ocean island basalts (OIBs) erupted in Iceland and the Azores to explore whether they record information about magma Fe^{3+} contents and magmatic f_{O_2} conditions. Although many studies assume that all Fe in augitic clinopyroxene crystals from OIBs occurs as Fe^{2+} , we find that up to half of the total Fe present can occur as Fe^{3+} , with crystals from alkali systems typically containing more Fe^{3+} than those from tholeiitic systems. Thus, Fe^{3+} is a major if under-appreciated constituent of augitic clinopyroxene crystals erupted from ocean island volcanoes. Most Fe^{3+} in these crystals is hosted within esseneite component ($\text{CaFe}^{3+}\text{AlSiO}_6$), though some may be hosted in aegirine component ($\text{NaFe}^{3+}\text{Si}_2\text{O}_6$) in crystals from alkali systems. Observations from samples containing quenched matrix glasses suggest that the incorporation of Fe^{3+} is related to the abundance of tetrahedrally coordinated Al ($^{\text{IV}}\text{Al}$), implying some steric constraints over Fe^{3+} partitioning between clinopyroxene and liquid (i.e., $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values), though this may not be an equilibrium relationship. For example, $^{\text{IV}}\text{Al}$ -rich $\{hk0\}$ prism sectors of sector-zoned crystals contain more Fe^{3+} than $^{\text{IV}}\text{Al}$ -poor $\{\bar{1}\bar{1}1\}$ hourglass sectors. Moreover, $^{\text{IV}}\text{Al}$ -rich compositions formed during disequilibrium crystallisation are also enriched in Fe^{3+} . Apparent clinopyroxene-liquid Fe^{2+} -Mg exchange equilibria (i.e.,

$K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{cpx-lik}}$ values) are similarly affected by disequilibrium crystallisation in our samples. Nonetheless, it is possible to reconcile our observed clinopyroxene compositions with glass Fe valence systematics estimated from olivine-liquid equilibria if we assume that $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{cpx-lik}}$ values lies closer to experimentally reported values of 0.24–0.26 than values of ~ 0.28 returned from a general predictive model. In this case, olivine-liquid and clinopyroxene-liquid equilibria record equivalent narratives, with one of our glassy samples from Iceland recording evolution under f_{O_2} conditions about one log unit above fayalite-magnetite-quartz (FMQ) equilibrium (i.e., $\sim \text{FMQ}+1$) and our glassy Azorean sample recording evolution under significantly more oxidising conditions ($\geq \text{FMQ}+2.5$) before experiencing syn-eruptive reduction, likely as a result of SO_2 degassing; our other glassy sample from Iceland is also affected by reductive SO_2 degassing. Overall, our findings demonstrate that the Fe valence systematics of clinopyroxene crystals can record important information about the conditions under which OIBs evolve, but that further experimental work is required to properly disentangle the effects of magma composition, disequilibrium and f_{O_2} conditions on clinopyroxene-liquid equilibria involving Fe^{2+} and Fe^{3+} .

Keywords: clinopyroxene, ferric iron, ocean island basalt, iron valence, partitioning

Introduction

Magmas erupted in different tectonic settings often record evolution under different oxygen fugacity (f_{O_2}) conditions (Wood et al, 1990; Carmichael, 1991; Cottrell et al, 2022), where f_{O_2} reflects the chemical potential of O in a magma. These different f_{O_2} conditions ultimately reflect differences in the pressure-temperature-composition (PTX) conditions under which magmas evolve in different settings. In particular, the valence state of Fe plays a central role in setting magmatic f_{O_2} because Fe is by far the most abundant multivalent element in terrestrial magmas (Frost, 1991). Specifically, the greater the ratio of ferric-to-total Fe ($\text{Fe}^{3+}/\Sigma\text{Fe}$, where $\Sigma\text{Fe} = \text{Fe}^{2+} + \text{Fe}^{3+}$) in any given magma, the greater its f_{O_2} , as described by various (P) TX -dependent parametrisations (Kress and Carmichael, 1991; Berry et al, 2018; Borisov et al, 2018). Moreover, understanding coupled variations between the f_{O_2} and $\text{Fe}^{3+}/\Sigma\text{Fe}$ content of magmas is important because of the first-order control these variables exert over magmatic phase equilibria (e.g., Toplis and Carroll, 1995; Feig et al, 2010), volatile solubilities (e.g., Jugo, 2009; O’Neill, 2021; Hughes et al, 2023) and equilibrium vapour compositions (e.g., Burgisser and Scaillet, 2007; Oppenheimer et al, 2011). Magma $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents thus determine the trajectories along which magmas evolve, the nature of the minerals they crystallise, and the abundance and speciation of the volatiles they release, which in turn control ore formation processes and mediate long-term planetary habitability (Holland, 2002; Evans and Tomkins, 2011; Gaillard et al, 2011). Generating internally consistent datasets of magma $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents is thus a vital step towards improving our understanding of Earth’s evolution and behaviour through geological time. We aim to further this endeavour by studying the valence state of iron

in clinopyroxene crystals, significant but poorly understood hosts of Fe^{3+} in magmatic systems.

It is generally, though not universally (cf., Lee et al, 2005, 2012), accepted that arc basalts have higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents and evolve under more oxidising conditions (approximately one log unit above fayalite-magnetite-quartz equilibrium; $\sim\text{FMQ}+1$) than mid-ocean ridge basalts (MORBs; $\sim\text{FMQ}$), even if the reasons for this remain contested (Evans, 2006; Kelley and Cottrell, 2009; Gaetani, 2016; Brounce et al, 2019; Cottrell et al, 2022; Evans and Tomkins, 2022). Many ocean island basalts (OIBs) also appear to evolve under more oxidising conditions than MORBs, though global differences between MORBs and OIBs are decidedly more ambiguous than those between MORBs and arc basalts. Observations from Lanzarote and El Hierro in the Canary Islands, Fogo in Cape Verde and Erebus in Antarctica suggest that some OIBs evolve at $\sim\text{FMQ}+2$ or higher depending on the oxybarometer used (Moussallam et al, 2014, 2019; Taracsak et al, 2022; Nicklas et al, 2022b). Observations from Laki in Iceland and Kīlauea and Mauna Kea in Hawaii also imply evolution under somewhat elevated f_{O_2} conditions that extend up to $\sim\text{FMQ}+1$ (Moussallam et al, 2016; Hartley et al, 2017; Helz et al, 2017; Brounce et al, 2017). In contrast, observations from Piton de la Fournaise on Réunion imply evolution at or below FMQ under comparable f_{O_2} conditions to those experienced by MORBs (Brounce et al, 2022; Nicklas et al, 2022a). While Réunion’s divergence from other OIB systems may initially appear confusing, Brounce et al (2022) propose an explanation based on known geochemical differences between ocean island systems. Specifically, they suggest that relatively oxidised OIBs originate from mantle sources rich in recycled components and thus Fe^{3+} (EMI, EMII and HIMU), while relatively reduced OIBs originate from mantle sources poor in recycled components and Fe^{3+} (C/FOZO/PREMA; Zindler and Hart, 1986; Stracke, 2012; Weis et al, 2023). Nevertheless, the internally consistent estimates of magma $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents and magmatic f_{O_2} conditions across different ocean island volcanoes needed to verify or refute this suggestion remain elusive. We aim to address this by investigating the valence state of Fe in volcanic glasses and clinopyroxene crystals from Iceland and the Azores that erupt samples with affinities towards C/FOZO/PREMA and EMII reservoirs, respectively.

Considerable progress has been made in using glass and mineral compositions to estimate magmatic f_{O_2} conditions over recent decades, with two-oxide oxybarometry and Fe-XANES spectroscopy of volcanic glasses being especially fruitful (Cottrell et al, 2022, and references therein). However, the former depends on the presence of equilibrium magnetite and ilmenite pairs (e.g., Bacon and Druitt, 1988; Ghiorso and Evans, 2008), and the latter on the presence of pristine volcanic glass and access to a synchrotron radiation source (e.g., Cottrell et al, 2009; Muth and Cottrell, 2023). Furthermore, the reduction of magmatic liquids by SO_2 degassing during magma ascent and the sensitivity of hydrous glasses to beam damage add further complexity to interpreting results from Fe-XANES spectroscopy (Moussallam et al, 2016; Brounce et al, 2017; Cottrell et al, 2018). Glass and mineral $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents can also be determined by Mössbauer spectroscopy (e.g., McCammon, 2021). However, laboratory-based Mössbauer spectroscopy is ill suited to achieving high sample throughputs and

synchrotron-based Mössbauer spectroscopy can only be performed at a limited number of facilities, limiting the overall utility of the approach. Fortunately, different f_{O_2} -sensitive mineral-liquid or mineral-mineral equilibria can allow us to circumvent these issues and recover better estimates of magmatic f_{O_2} , especially as minerals respond more slowly to syn- or post-eruptive changes in f_{O_2} than magmatic liquids. For example, recent re-evaluations of olivine-liquid equilibria that present high-precision parametrisations of Fe^{2+} -Mg exchange equilibria (i.e., predict $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{ol-liq}}$ values) provide a potential avenue for estimating magmatic f_{O_2} without needing to perform Fe-XANES spectroscopy (Blundy et al, 2020; Davis and Cottrell, 2021; Saper et al, 2022). While developing similar tools based on clinopyroxene-liquid equilibria is complicated by steric constraints associated with the crystal structure of clinopyroxene, we aim to exploit comparatively well understood olivine-liquid equilibria to gain new insights into Fe^{3+} partitioning and Fe^{2+} -Mg exchange equilibria between clinopyroxene crystals and their carrier liquids. A key goal of this work is to start building a better understanding how clinopyroxene compositions reflect magmatic f_{O_2} conditions.

Magmatic clinopyroxene crystals incorporate both Fe^{2+} and Fe^{3+} by virtue of hosting three distinct cation sites: clinopyroxene has the general formula $\text{M2}(\text{R}^{2+})\text{M1}(\text{R}^{2+})\text{T}_2(2\text{R}^{4+})\text{O}_6$, where R is a metal cation, M2 is a distorted octahedral site, M1 is a regular octahedral site and T is a tetrahedral site typically occupied by Si forming the Si_2O_6 chains that define the pyroxene structure (Morimoto et al, 1988). As a consequence, clinopyroxene crystals should be inherently sensitive to magma $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents and magmatic f_{O_2} conditions. However, little is known about Fe valence systematics in magmatic clinopyroxene crystals, which fundamentally limits our ability to explore relationships between f_{O_2} and clinopyroxene compositions. This in turn restricts our capacity to describe phase equilibria relations in natural and experimental systems, as well as calibrate the thermodynamic datasets that underpin algorithms like MELTS, THERMOCALC and MAGEMin that are widely used to model magmatic processes (Sack and Ghiorso, 1994; Ghiorso and Sack, 1995; Holland and Powell, 1998; Powell et al, 1998; Jennings and Holland, 2015; Holland et al, 2018; Riel et al, 2022).

Experiments performed on a Martian (i.e., shergottites-nahklites-chassignites (SNC)-group) meteorite composition under relatively reducing conditions ($\sim\text{FMQ}-4.7$ to $\sim\text{FMQ}+0.3$) suggest that f_{O_2} correlates with clinopyroxene $\text{Fe}^{3+}/\Sigma\text{Fe}$, though this inference is based on highly uncertain determinations of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in clinopyroxene crystals (McCanta et al, 2004). Indeed, the reducing conditions under which these experiments were performed and the poor precision of unoriented Fe-XANES spectroscopy performed on experimentally produced clinopyroxene crystals may have masked the true nature of relationships between f_{O_2} and clinopyroxene $\text{Fe}^{3+}/\Sigma\text{Fe}$. More generally, we speculate that our poor understanding of clinopyroxene $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents in magmatic systems reflects the challenges associated with determining Fe valence in mineral samples, whether by bulk methods or *in situ* microanalysis requiring access to a Mössbauer spectrometer or synchrotron radiation source (Canil and O'Neill, 1996; Dyar et al, 2002; McCammon, 2021; Steven et al, 2022).

Neave et al (2024) recently re-evaluated previously discredited approaches for estimating clinopyroxene Fe^{3+} contents from stoichiometric constraints (cf., McGuire et al, 1989; Canil and O'Neill, 1996). By optimising the electron probe microanalysis (EPMA) technique used to measure clinopyroxene crystals, they demonstrated that clinopyroxene $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents can be determined by stoichiometry using the approach of Droop (1987) with a precision approaching that achievable with Mössbauer spectroscopy. They also demonstrated that more than half of the Fe present in natural augite crystals can occur as Fe^{3+} , in line with the sparse Mössbauer spectroscopic analyses of augite crystals from mafic alkaline rocks that are available in the literature (McGuire et al, 1989; Weis et al, 2015). They also proposed a new scheme for assigning clinopyroxene components that explicitly accounts for the presence of Fe^{3+} . Specifically, they assigned most Fe^{3+} to esseneite component (Es, $\text{CaFe}^{3+}\text{AlSiO}_6$) via a Tschermak-type substitution, with some Fe^{3+} potentially being assigned to aegirine component (Ae, $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$) formed from any Na remaining after forming jadeite component (Jd, $\text{NaAlSi}_2\text{O}_6$). We seek to provide the first systematic survey of Fe valence and Fe^{3+} -sensitive clinopyroxene componentry in OIB samples. Only by developing this deeper understanding of clinopyroxene $\text{Fe}^{3+}/\Sigma\text{Fe}$ systematics will it eventually become possible to investigate how clinopyroxene compositions and phase equilibria involving clinopyroxene reflect magma $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents and ultimately magmatic f_{O_2} conditions.

Here we present high-precision analyses of clinopyroxene crystals in OIB samples from Iceland and the Azores in which clinopyroxene $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents have been estimated by stoichiometry following the approach of Droop (1987). By applying the revised scheme for assigning clinopyroxene components proposed by Neave et al (2024), we show how Fe^{3+} is an important constituent of clinopyroxene crystals from diverse natural magmas that cannot readily be ignored in our treatment of clinopyroxene compositions. Finally, we use our improved understanding of magmatic clinopyroxene $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents to explore Fe^{3+} partitioning and Fe^{2+} -Mg exchange equilibria between clinopyroxene crystals and mafic liquids in OIB samples that evolved under different f_{O_2} conditions.

Samples

We studied six OIB samples erupted from well-characterised but geochemically distinct magmatic systems in the North Atlantic (Figure 1). We investigated samples ranging from tholeiitic and alkali basalts to ankaramites and tephites in order to evaluate major element controls on clinopyroxene compositions and the effects of anticipated variations in magmatic f_{O_2} conditions on clinopyroxene $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents (Moussallam et al, 2019; Cottrell et al, 2022). Lava samples were cut into polished thin sections and tephra samples were mounted in epoxy prior to imaging and microanalysis.

Tholeiitic and moderately primitive (~ 7 wt.% MgO) pillow basalt samples (HOR-11-01 and SKU-11-18) were collected from Skuggafjöll mountain in the Eastern Volcanic Zone (EVZ) of southern Iceland. The petrology of these samples and Skuggafjöll more generally is described by Neave et al (2014). A tholeiitic and moderately primitive (~ 7 wt.% MgO) basaltic tephra sample was collected from 2014–2015

Holuhraun eruption in the Northern Volcanic Zone (NVZ) of central Iceland. Our sample is equivalent to sample H14 described by [Halldórsson et al \(2018\)](#), who also described the petrological evolution of the wider eruption. A tholeiitic and moderately evolved (~ 4.5 wt.% MgO) basaltic lava sample (LAK-04) was collected from the Laki lava flow in the EVZ southern Iceland. The petrology of LAK-04 and the Laki lava flow as a whole is described by [Passmore et al \(2012\)](#) and [Neave et al \(2013\)](#).

Three ankaramite (highly olivine- and clinopyroxene-phyric alkali basalts) lava samples (HVAM13-01, ARN13-01 and HLTS13-01, from Hvammsmúli, Arnarholl and Holtsdalur, respectively) were collected from Eyjafjalljökull in the the EVZ of southern Iceland. The petrology of some of these ankaramite localities is described by [Loughlin \(1995\)](#) and [Nikkola et al \(2019\)](#). An alkali basalt lava sample (PI-011) was collected from the northern flank of Pico volcano in the Azores while a trachybasaltic-to-tephritic tephra sample (PI-041) was collected from a vent on the Panalto da Achada fissure system on the southeastern flank. The petrology of Pico is discussed in detail by [França et al \(2006\)](#), [Zanon et al \(2020\)](#) and [van Gerve et al \(2024\)](#).

Methods

In preparation for EPMA, backscattered electron (BSE) images were collected from epoxy mounts and thin sections using a FEI Quanta 650F scanning electron microscope (SEM) in the Department of Earth and Environmental Sciences at the University of Manchester. Imaging was performed to characterise compositional variability within and between our samples, with a particular focus on clinopyroxene crystals often characterised by complex sector and concentric zoning (e.g., [Leung, 1974](#); [Dowty, 1976](#); [Ubide et al, 2019](#); [Neave et al, 2019](#)).

Quantitative analyses of clinopyroxene, olivine, plagioclase, oxides and glass were performed by EPMA using a JEOL JXA8530F instrument in the School of Earth Sciences at the University of Bristol operated with Probe for EPMA (<https://www.probesoftware.com/>). The following primary standards were used for calibration: Si, albite; Ti, TiO_2 ; Al, sanidine; Cr, Cr_2O_3 ; Fe, hematite; Mn, Mn metal; Mg, St. John's olivine; Ca, wollastonite; Na, albite; K, sanidine; P, Durango apatite; and Ni, Ni metal.

Different analytical conditions were used for different phases, with particular care taken over clinopyroxene analyses to ensure that $\text{Fe}^{3+}/\Sigma\text{Fe}$ could be determined by stoichiometry ([Neave et al, 2024](#)). We used an accelerating voltage of 15 kV and a spot size of 1 μm to analyse clinopyroxene, olivine and oxides. The following elements were analysed with a current of 10 nA (on-peak counting times in seconds are shown in parentheses; background counting times were half on-peak counting times): Si(20), Ti(20), Al(20), Fe(40), Mg(40), Ca(20) and K(40); and the following elements were analysed with a current of 40 nA: Cr(60), Mn(30), Na(60), P(60) and Ni(30). We used this approach to maximise the precision of minor element analyses in clinopyroxene that affect the precision of stoichiometric determinations of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ([Neave et al, 2024](#)). All elements in plagioclase and glass were analysed with an accelerating voltage of 15 kV, a defocused 10 μm spot and a current of 10 nA (on-peak counting

times in seconds are shown in parentheses; background counting times were half on-peak counting times): Si(10), Ti(50), Al(10), Cr(10), Fe(30), Mn(30), Mg(50), Ca(10), Na(10), K(10) and P(40).

Accuracy was monitored by analysing the following secondary standards: in-house diopside, Cr-diopside and labradorite; and international kk1 kaersutite (Reay et al, 1989) and BCR-2G basaltic glass (Jochum et al, 2005). Major element (e.g., SiO₂ and MgO in glass and clinopyroxene) concentrations were typically within 2% of preferred values (based on published values for international standards or longitudinal data for in-house standards), while minor element (e.g., Cr₂O₃ and Na₂O in Cr-diopside and FeO_T in plagioclase) concentrations were typically within 6% of preferred values. Counting statistics from analyses of unknown clinopyroxene crystals indicate that major (SiO₂, Al₂O₃, FeO_T, MgO and CaO) and minor (TiO₂, Cr₂O₃ and Na₂O) elements were determined with 1 σ precisions better than 1% and 5%, respectively; only MnO was measured with a worse 1 σ precision of \sim 8%. Olivine, plagioclase, oxides and glass were measured with comparable 1 σ precisions; better than 2% for major elements and better than 5% for most minor elements. Full details of secondary standard analyses and analytical precision are provided alongside all EPMA data in the Supplementary Material.

Results

Petrography

Tholeiitic pillow basalt samples HOR-11-01 and SKU-11-18 from Skuggafjöll contain macrocrysts of plagioclase, clinopyroxene and olivine in a glassy to microcrystalline and somewhat vesicular groundmass (Neave et al, 2014). Macrocrysts are defined as being >100 μ m in length and texturally distinct from the groundmass (e.g., Thomson and Maclennan, 2013). Clinopyroxene macrocrysts are up to \sim 500 μ m in length and often occur in ophitic arrangement with plagioclase. They typically show weak oscillatory zoning and prominent hourglass sector zoning with low-BSE-intensity {111} hourglass sectors and high-BSE-intensity {hk0} prism sectors (Figure 2A; Neave et al, 2019).

The tholeiitic basalt tephra sample from Holuhraun contains macrocrysts of plagioclase, clinopyroxene and olivine in a glassy and highly vesicular groundmass (Halldórsson et al, 2018). Clinopyroxene macrocrysts are up to \sim 250 μ m in length and often occur in ophitic arrangement with plagioclase, and also sometimes in association with olivine. Most show weak oscillatory and hourglass sector zoning, though this is not well resolved at the resolution of our BSE images given the small size of the crystals examined here (Figure 2B); Halldórsson et al (2018) report larger crystals from other lava and tephra samples.

The tholeiitic basalt lava sample LAK04 from Laki contains macrocrysts of plagioclase, clinopyroxene and olivine in a microcrystalline and vesicular groundmass (Passmore et al, 2012; Neave et al, 2013). Clinopyroxene macrocrysts up to \sim 800 μ m occur in ophitic arrangement with plagioclase, most often in multiphase glomerocrysts that also contain olivine (Figure 2C). Most clinopyroxene crystals also show concentric and hourglass sector zoning like that observed in our samples from Skuggafjöll.

Ankaramitic lava samples HVAM13-01, ARN13-01 and HLTS13-01 from Eyjafjallajökull are dominated by large macrocrysts of olivine and clinopyroxene and smaller oxide macrocrysts in microcrystalline groundmasses, though some plagioclase macrocrysts occur in ARN13-01. Clinopyroxene macrocrysts up to ~ 5 mm in length typically occur as individual, euhedral to subhedral crystals, with some occurring in association with olivine (Figure 2D). Most clinopyroxene crystals are characterised by concentric core-to-rim zoning, though crystals in HVAM13-01 appear to show reaction rims consistent with dissolution prior to final solidification (Neave and MacLennan, 2020).

The alkali basalt lava PI-011 from Pico contains large macrocrysts of clinopyroxene, olivine, plagioclase, magnetite and ilmenite in a microcrystalline and vesicular groundmass that also contains microcrysts (crystals < 100 μm in length that are distinct from the groundmass) of the same phases. Clinopyroxene macrocrysts up to ~ 4 mm in length generally occur as individual, euhedral crystals, though some occur in glomerocrysts with olivine and/or plagioclase. Most crystals show slight core-to-rim zoning imprinted on complex patchy zoning (Figure 2E).

The trachybasaltic-to-tephritic tephra sample PI-041 from Pico contains macrocrysts of clinopyroxene, olivine, plagioclase, magnetite and ilmenite in a glassy and highly vesicular groundmass that also contains microcrysts of the same phases. Clinopyroxene macrocrysts up to ~ 2 mm in length generally occur as individual, euhedral to subhedral crystals, though some occur in association with olivine and ilmenite. Clinopyroxene crystals show evidence for both core-to-rim zoning and complex patchy zoning (Figure 2F).

Major element chemistry

The major element chemistry of clinopyroxene crystals in our OIB samples is summarised in a series of pyroxene quadrilateral diagrams in Figure 3; all crystals plot firmly in the quadrilateral field of a Q–J diagram (Morimoto et al, 1988). In Figure 3A we follow the established convention of Morimoto et al (1988) in calculating the Fe component (ΣFe^*) as the sum of Fe^{2+} , Fe^{3+} and Mn. However, Fe^{3+} is not incorporated into any of the quadrilateral end-member components (diopside, Di, $\text{CaMgSi}_2\text{O}_6$; hedenbergite, Hd, $\text{CaFe}^{2+}\text{Si}_2\text{O}_6$; enstatite, En, MgSiO_3 or ferrosilite, Fs, $\text{Fe}^{2+}\text{SiO}_3$); quadrilateral components only incorporate divalent cations on their M2 and M1 sites. In Figure 3B we therefore show pyroxene quadrilaterals plotted with a modified Fe component (ΣFe^\dagger) calculated from the sum of Fe^{2+} and Mn, with Fe^{2+} determined following Droop (1987). Clinopyroxene crystals from each of our OIB samples define distinct populations in both Figures 3A and 3B.

Clinopyroxene crystals in tholeiitic samples from Laki, Holuhraun and Skuggafjöll define an approximate crystal line of descent (Figure 3A), with those from Skuggafjöll being the most primitive (i.e., having the highest Di contents), those from Holuhraun being slightly more evolved, and those from Laki being the most evolved (i.e., having the lowest Di contents). Although Di and Hd dominate, all clinopyroxene crystals from tholeiitic basalts contain some En and Fs that increase in abundance as Mg and Fe contents decrease and increase, respectively, during magmatic evolution. Clinopyroxene crystals from Skuggafjöll show the greatest variability in DiHd (Di+Hd) and EnFs (En+Fs) contents, consistent with the presence of sector zoning described in greater

detail below (Neave et al, 2019). Clinopyroxene crystals from Laki show the greatest overall spread in compositions, consistent with the protracted magmatic history recorded by these crystals (Neave et al, 2013). Removing Fe^{3+} from the calculation of quadrilateral components has no significant effect beyond moving all data from tholeiitic samples slightly towards the Di vertex.

Despite erupting from two geographically distinct systems, clinopyroxene crystals in alkali samples from Pico and Eyjafjallajökull also define an approximate crystal line of descent (Figure 3A). Although the most primitive clinopyroxene crystals from Eyjafjallajökull and Pico (and PI-011 in particular) lie close to some crystals from the tholeiitic Skuggafjöll eruption in quadrilateral space, evolved clinopyroxene crystals from Eyjafjallajökull and Pico (PI-041 in particular) lie much closer to the Di-Hd tie line than evolved clinopyroxene crystals from the tholeiitic Holuhraun and Laki eruptions. That is, clinopyroxene crystals from alkali samples evolve towards higher DiHd, while those from tholeiitic samples evolve to lower DiHd. This effect is especially pronounced when Fe^{3+} is removed from the calculation of quadrilateral components and clinopyroxene compositions move towards the Di vertex (Fig 3B). In this case, some clinopyroxene crystals from PI-041 fall above the Di-Hd tie line, likely because of the greater contribution of Ca to non-quadrilateral components in clinopyroxene crystals from alkali samples with respect to those from tholeiitic samples (e.g., Robinson, 1980).

Clinopyroxene crystals from alkali samples contain higher Na_2O contents than those from tholeiitic samples ($\sim 0.30\text{--}0.60$ wt.% versus $\sim 0.15\text{--}0.30$ wt.%; Figure 4A). Overall, there is a strong correlation between MgO and Na_2O , though clinopyroxene crystals from different eruptions fall on slightly offset arrays. Although significant (>1 wt.%) concentrations of Cr_2O_3 are only found in relatively primitive clinopyroxene crystals (Figure 4B), analyses from both alkali and tholeiitic samples define the same broad trend; evolved clinopyroxene crystals contain negligible Cr_2O_3 . Clinopyroxene crystals from different eruptions are characterised by different Ti:Al values that are often remarkably constant within the products of any individual eruption. In general, clinopyroxene crystals from alkali samples have higher Ti:Al values than those from tholeiitic samples, with the exception of clinopyroxene crystals from the evolved and tholeiitic Laki eruption that overlap with clinopyroxene crystals in alkali ankaramite samples from Eyjafjallajökull.

Iron valence systematics

The concentration and valence systematics of Fe in clinopyroxene crystals from our OIB samples are summarised in Figure 5. Distinct crystal lines of descent identified on pyroxene quadrilaterals are reproduced on a plot of MgO versus total Fe expressed as FeO (FeO_T ; Figure 5A). Clinopyroxene crystals in tholeiitic samples from Skuggafjöll, Holuhraun and Laki define a relatively steep trend in increasing FeO_T with decreasing MgO (with the highest FeO_T contents found in clinopyroxene rims from Laki), while clinopyroxene crystals in alkali samples from Pico define a shallower trend; crystals from Eyjafjallajökull fall between these two trends. However, relationships are weaker when MgO is plotted against FeO determined by stoichiometry following Droop (1987) (Figure 5B). For example, clinopyroxene crystals in samples from Skuggafjöll and Laki contain ~ 1 and ~ 2 wt.% less FeO than FeO_T , respectively, while FeO and FeO_T are

broadly comparable in the sample from Holuhraun. Conversely, the enrichment in FeO with decreasing MgO is markedly less coherent than the enrichment in FeO_T.

Clinopyroxene Fe₂O₃ contents determined following Droop (1987) are summarised as a function of MgO in Figure 5C. Clinopyroxene Fe₂O₃ contents vary from within uncertainty of 0 wt.%, where 1σ uncertainties of ~0.35 wt.% were obtained using a Monte Carlo approach described by Neave et al (2024), to ~4.5 wt.%, highlighting that Fe₂O₃ is a significant constituent of many clinopyroxene crystals from OIBs. Alongside Al, Fe³⁺ is therefore probably the most abundant cation in magmatic clinopyroxene crystals after those responsible for forming quadrilateral components (i.e., Si, Ca, Mg and Fe²⁺). Overall, Fe₂O₃ contents are much lower in primitive clinopyroxene crystals with high MgO contents (~1 wt.% at 17 wt.% MgO) than evolved clinopyroxene crystals with low MgO contents (~4 wt.% at 13 wt.% MgO). To first order, clinopyroxene crystals from tholeiitic and alkali systems lie on the same MgO-Fe₂O₃ trend. In detail some finer structure arises. For example, clinopyroxene crystals in the Holuhraun sample contain the lowest Fe₂O₃ contents, which rarely exceed 1 wt.% and are often within uncertainty of 0 wt.%; clinopyroxene crystals from Skuggafjöll contain ~1 wt.% more Fe₂O₃ than those from Holuhraun but are notably larger in size and found in lava rather than tephra samples. Many clinopyroxene crystals in alkali samples are relatively evolved and contain high Fe₂O₃ contents that overlap with values from Skuggafjöll and Laki (1–2 wt.%) at their lower limits but extend to much higher values (~4.5 wt.%) at their upper limits. On average, clinopyroxene crystals in samples from Eyjafjallajökull reach any given Fe₂O₃ content at a higher MgO content than those from Pico. Rim and microcryst compositions from sample PI-041 extend from the main trend to low Fe₂O₃ (within uncertainty of 0 wt.%) at a constant MgO (~13 wt.%).

Clinopyroxene Fe³⁺/ΣFe contents estimated following the stoichiometric approach of Droop (1987) are summarised as a function of MgO in Figure 5D. These Fe³⁺/ΣFe contents are typically subject to 1σ uncertainties of ~0.03 according to a Monte Carlo approach described by Neave et al (2024). Clinopyroxene Fe³⁺/ΣFe contents extend from ~0.0–0.3 in primitive crystals in samples from Skuggafjöll and Holuhraun, with the latter having lower values mostly limited to 0.0–0.1, to ~0.4 and ~0.5 in evolved crystals in samples from Eyjafjallajökull and Pico, respectively. Importantly, these high values are consistent with high-precision analyses of clinopyroxene crystals in mafic alkali rocks from the Canary Islands by Mössbauer spectroscopy that yielded Fe³⁺/ΣFe contents of 0.49–0.63 (Weis et al, 2015). Variations in Fe³⁺/ΣFe are nonetheless considerable at any given MgO for any given eruption (≥0.3). However, in contrast with McGuire et al (1989) who ascribed similarly variable clinopyroxene Fe³⁺/ΣFe contents to inadequacies in stoichiometric determinations of Fe³⁺, we believe that much of this variability is geological in origin. Our reasons for this are threefold: firstly, the close correspondence between Fe³⁺/ΣFe contents determined by Mössbauer and stoichiometry in endmember and single-crystal clinopyroxenes suggests that the latter can be reliable when EPMA is performed with sufficient care (Neave et al, 2024); secondly, Monte Carlo-derived estimates of uncertainties in Fe³⁺/ΣFe are smaller than the variability observed (1σ uncertainties of ~0.03 are an order of magnitude smaller than

natural variability of ≥ 0.3 at any given MgO); and finally, our knowledge of clinopyroxene chemistry has grown considerably in recent decades. In particular, we now have a much greater understanding of how kinetics and sector zone development generate compositional variability independently of magmatic evolution and magma storage conditions, especially when considering the abundance and systematics of trivalent Al that may also mediate the incorporation of similarly trivalent Fe^{3+} (Mollo et al, 2010, 2018; Neave et al, 2019; Ubide et al, 2019; Di Fiore et al., 2021; MacDonald et al., 2023; Neave et al, 2024).

Compositional zoning in major elements and iron valence

Magmatic clinopyroxene crystals are often characterised by complex internal zoning (Dowty, 1976; Caricchi et al, 2020; Musu et al, 2023). Compositional variations associated with three types of clinopyroxene zoning observed in our OIB samples are summarised in Figures 6–8. Hourglass sector zoning occurs in diverse magmatic clinopyroxene crystals, and is generally characterised by the differential partitioning of elements between $\{hk0\}$ prism sectors and $\{\bar{1}11\}$ hourglass sectors, though the nature and extent of this differential partitioning depends on bulk composition (i.e., tholeiitic versus alkali), cooling rate and the degree of undercooling, (Leung, 1974; Kouchi et al, 1983; Neave et al, 2019; Ubide et al, 2019; Mollo et al., 2023). Although some recent studies have incorporated Fe^{3+} into discussions of clinopyroxene zoning (Mollo et al, 2018; Di Fiore et al., 2021), the interplay between sector zoning and Fe valence systematics remains to be explored in detail.

Paired compositional profiles through hourglass and prism sectors in clinopyroxene crystals from our Skuggafjöll samples are shown in Figure 6; similar zoning is present in clinopyroxene crystals from the Holuhraun sample but is less intense. Hourglass sectors are characterised by consistently lower Al_2O_3 and $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents than prism sectors, in line with published observations from geochemically similar samples from the Holuhraun eruption (Neave et al, 2019; Caricchi et al, 2020) and considerably more alkaline samples from Mt Etna, Italy (Ubide et al, 2019; MacDonald et al., 2023; Musu et al, 2023).

Compositional profiles through clinopyroxene crystals with concentric (i.e., core-to-rim) zoning in sample PI-041 from Pico are shown in Figure 7. Crystal interiors only show modest variability in Mg# (where $\text{Mg\#} = \text{molar Mg}/(\text{Mg} + \text{Fe}^{2+})$) or $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents that are largely within propagated analytical uncertainties. Core-to-rim zoning in these crystals is most clearly reflected in changes in TiO_2 contents; changes in Mg# and Al_2O_3 are more subtle. Moreover, there are no coherent changes in $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents across core-rim boundaries, suggesting that $\text{Fe}^{3+}/\Sigma\text{Fe}$ zoning can be decoupled from zoning in other components.

Coarse compositional profiles through large clinopyroxene crystals with patchy zoning in sample PI-011 from Pico are shown in Figure 8. Mg#, TiO_2 and Al_2O_3 show coupled variability beyond analytical uncertainty. Variability in $\text{Fe}^{3+}/\Sigma\text{Fe}$ also exceeds analytical uncertainty though there is no clear relationship between Al_2O_3 and $\text{Fe}^{3+}/\Sigma\text{Fe}$ like there is in the crystals with hourglass sector zoning described above and shown in Figure 6. Nonetheless, correlated variability in TiO_2 and Al_2O_3 suggests that the patchy zoning in these crystals may reflect similar crystallographic controls

as hourglass sector zoning (Leung, 1974; Ubide et al, 2019), even if the extent to which this variability is coupled to $\text{Fe}^{3+}/\Sigma\text{Fe}$ differs between samples.

Discussion

Clinopyroxene chemical systematics

Clinopyroxene components calculated following the scheme described by Neave et al (2024) are plotted as functions of clinopyroxene Mg# in Figure 9 (a summary of the scheme is provided in the appendix). There is considerable variability within and between clinopyroxene crystals from different OIB samples. Clinopyroxene crystals from tholeiitic samples contain similar amounts of Jd, while the Jd content of crystals from alkali samples is larger and more variable (Figure 9A). Although it is unsurprising that clinopyroxene crystals from alkali-rich systems contain more Na-bearing Jd than those from tholeiitic systems, differences in Jd contents also reflect differences in magma storage pressures. Both Jd-based clinopyroxene-liquid barometry and clinopyroxene-independent volatile saturation barometry indicate that the tholeiitic magmas erupted at Skuggafjöll, Holuhraun and Laki were stored at lower pressures prior to eruption (~ 200 MPa; Neave and Putirka, 2017; Bali et al, 2018) than the alkali magmas erupted from Pico to produce PI-011 and PI-041 (200–600 MPa; van Gerve et al, 2024). The broadly intermediate Jd content of clinopyroxene crystals from Eyjafjallajökull reflects their intermediate storage depths (~ 300 MPa; Nikkola et al, 2019). As anticipated, relatively few clinopyroxene crystals contain much Ae (Figure 9B), with any Ae present restricted to ^{VI}Al -poor analyses from Na-rich or low-Mg# crystals. Otherwise, there are no clear systematics in the Ae content of clinopyroxene crystals in our OIB samples. In contrast with the inferences of Lindsley (1983), Fe^{3+} does not appear to be hosted by Ae in most magmatic clinopyroxene crystals, aegirine and aegirine-augite crystals from evolved alkali systems notwithstanding (cf., Larsen, 1976; White et al, 2005).

In line with their high Fe^{3+} but low Ae contents, we infer that Es is a major constituent of clinopyroxene crystals in our OIB samples (Figure 9C). With the exception of some very Fe^{3+} -poor analyses in our Holuhraun sample ($X_{\text{Es}} \sim 0$) that are mainly found within $\{111\}$ hourglass sectors (Figure 6), the Es content of clinopyroxene crystals from tholeiitic and alkali samples largely overlap, with the latter extending to slightly higher values (~ 0.10 versus ~ 0.07). Indeed, much of the spread in clinopyroxene Es contents at any given Mg# likely reflects the differential partitioning of Es between sectors as well as propagated uncertainties in clinopyroxene Fe^{3+} contents (Figure 6; Ubide et al, 2019). The tempering of high Es contents in the highest- Fe^{3+} clinopyroxene crystals from alkali samples reflects the formation of minor Ae in some cases (Figure 9B). Overall, it is likely that Es is the most abundant non-quadrilateral component in most clinopyroxene crystals from our OIB samples. Although the Es content of clinopyroxene crystals does not correlate straightforwardly with clinopyroxene Mg# (Figure 9C), Fe_2O_3 correlates negatively with MgO (Figure 5C) on a sample-by-sample basis. While relationships between MgO and Fe_2O_3 are complicated by the details of partitioning behaviour (see below), we note that a broad increase

in clinopyroxene Fe_2O_3 with increasing differentiation may partly reflect the progressive enrichment of magmas in Fe_2O_3 by the crystallisation of Fe^{3+} -poor phases such as olivine and plagioclase. Indeed, such so-called auto-oxidation has been described in experiments on calc-alkaline magmas (Ulmer et al, 2018), and has been invoked to explain the progressive oxidation of evolving MORBs (O'Neill et al, 2018).

The abundance of Ca-Tschermak's component (CaTs, CaAlAlSiO_6) varies considerably between clinopyroxene crystals in different samples (Figure 9D). Clinopyroxene crystals in our samples from Skuggafjöll and alkali systems have large ranges in CaTs contents (0.00–0.05), which reflects the prevalence of hourglass sector zoning and patchy zoning in these samples (Figures 6 and 8). Such zoning is largely defined by the partitioning of quadrilateral and non-quadrilateral components between different sectors (Neave et al, 2019; Ubide et al, 2019). Crystals from our Laki sample are poor in CaTs because their relatively high Fe_2O_3 contents mean that $^{\text{IV}}\text{Al}$ occurs alongside Fe^{3+} in Es rather than alongside $^{\text{VI}}\text{Al}$ in CaTs, consistent with the high FeO_T content of the Laki lava as a whole (Passmore et al, 2012). In contrast, crystals from our Holuhraun sample are relatively rich in CaTs, consistent with their low Fe_2O_3 contents. Although high CaTs contents can reflect disequilibrium crystallisation in some clinopyroxenes, this does not appear to be the case in crystals from Holuhraun (Neave et al, 2019); we return to the high CaTs and low Es contents of Holuhraun clinopyroxene crystals below.

The abundance of titanium pyroxene component (CaTi, $\text{CaTiAl}_2\text{O}_6$) varies significantly between samples (Figure 9E). Clinopyroxene crystals in tholeiitic samples define an approximate differentiation trend at relatively low CaTi for any given Mg# (evolving from ~ 0.01 at Mg# = 0.90 to ~ 0.04 at Mg# = 0.75), while clinopyroxene crystals in alkali samples from Pico evolve towards much higher CaTi (from ~ 0.02 at Mg# = 0.90 to ~ 0.08 at Mg# = 0.75). Clinopyroxene crystals in samples from Eyjafjalljökull define a somewhat intermediate trend that partly overlaps with the trend defined by crystals in samples from Pico. These trends not only reflect the way in which clinopyroxene Ti contents track magmatic evolution, but also the close association between Ti and Al in clinopyroxene crystals from alkali magmas that is generally conserved across sector zones (Leung, 1974; Downes, 1974; Ubide et al, 2019). The incorporation of Ti alongside 2^{IV}Al is consistent with the Ti:Al ratios in excess of 1:2 that are observed in all samples (Figure 4C), where excess Al remaining after CaTi formation can form other components including Jd, Es and CaTs. We also note that calculating CaTi from Ti rather than residual $^{\text{IV}}\text{Al}$ as suggested by Putirka et al (1996) is essential for recovering clinopyroxene Ti systematics accurately; calculating from $^{\text{IV}}\text{Al}$ could overestimate apparent CaTi contents when Es is not accounted for. Although there is no need to form other Ti-bearing components such as Ti-diopside ($\text{CaMgTi}_2\text{O}_6$), neptunite ($\text{NaFe}_{0.5}^{2+}\text{Ti}_{0.5}\text{Si}_2\text{O}_6$), its Mg-bearing equivalent ($\text{NaMg}_{0.5}\text{Ti}_{0.5}\text{Si}_2\text{O}_6$) or the fictive aluminobuffonite ($\text{CaMg}_{0.5}\text{Ti}_{0.5}\text{AlSiO}_6$) of Sack and Ghiorso (1994) to account for the compositions of our clinopyroxene crystals, there is ample scope for further substitutions that are not captured by the componentry scheme of Neave et al (2024). Addressing this complexity would however require a thermodynamic approach that is beyond the scope of this manuscript.

Significant amounts of chromian Ca-Tschermak’s component (CrAlTs, CaCrAlSiO_6) only occur in high-Mg# clinopyroxene crystals (Figure 9F). This is consistent with the relative compatibility of Cr in clinopyroxene and its relatively low abundance in OIB magmas. Thus, CrAlTs contents rapidly decrease from ~ 0.030 to < 0.005 over a Mg# window of ~ 0.90 to 0.75 in clinopyroxene crystals from both tholeiitic and alkali samples. High CrAlTs contents are offset to higher Mg# in clinopyroxene crystals from Pico and Eyjafjallajökull than their tholeiitic equivalents because the higher Fe^{3+} content of these crystals leads to higher Mg# values at any given Mg content.

As anticipated, all clinopyroxene crystals in our OIB samples are dominated by DiHd (Figure 9G). It is notable that the DiHd contents of clinopyroxene crystals from tholeiitic samples are generally lower than those from our alkali samples (0.64 – 0.76 versus 0.70 – 0.80 , respectively). The DiHd content of clinopyroxene crystals from tholeiitic samples also decreases with decreasing Mg# in a manner consistent with the pyroxene solvus between DiHd and EnFs narrowing with decreasing temperature (Lindsley and Andersen, 1983). In contrast, the DiHd content of clinopyroxene crystals from alkali samples remains broadly constant with decreasing Mg#. Importantly, calculating DiHd in this manner accounts for the incorporation of Ca into non-quadrilateral components, meaning we do not observe the excess DiHd implied from pyroxene quadrilaterals shown in Figure 3B that account for Fe^{3+} but not non-quadrilateral Ca; the high and steady DiHd content with decreasing Mg# in clinopyroxene crystals from alkali samples appears to be real. Unsurprisingly, EnFs contents of our clinopyroxene crystals are almost perfectly antithetical to their DiHd contents, with the striking observation that X_{EnFs} does not increase with decreasing Mg# in clinopyroxene crystals from alkali samples.

Ferric iron partitioning

The presence of significant Fe^{3+} in clinopyroxene crystals from diverse OIB samples demonstrates that the valence state of Fe can no longer be ignored in robust descriptions of magmatic evolution that draw on clinopyroxene chemistry. It also implies that clinopyroxene crystals may record widespread but currently under-exploited archives of magmatic f_{O_2} conditions. Indeed, the potential for clinopyroxene oxybarometry has been demonstrated for mantle samples investigated by Mössbauer spectroscopy (Luth and Canil, 1993). However, poorly defined steric constraints on Fe^{3+} incorporation into clinopyroxene mean that it is currently impossible to extend oxybarometric approaches based on olivine-liquid Fe^{2+} –Mg exchange equilibria described by $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{ol-liq}}$ values to clinopyroxene-liquid Fe^{2+} –Mg exchange equilibria (Blundy et al, 2020; Davis and Cottrell, 2021; Saper et al, 2022). Thus, a vital step towards understanding the effects of magmatic f_{O_2} on clinopyroxene compositions involves exploring the systematics of Fe^{3+} partitioning between clinopyroxene crystals and magmatic liquids.

Samples from Holuhraun, Skuggafjöll and Pico (PI-041) contain clinopyroxene crystals in textural equilibrium with their host glasses and are thus suitable for investigating Fe^{3+} partitioning. Clinopyroxene analyses from Skuggafjöll and Holuhraun were filtered to only include high- Al_2O_3 analyses from $\{hk0\}$ prism sectors that Halldórs-son et al (2018) and Neave et al (2019) interpreted as recording equilibrium magma

storage conditions. Specifically, these authors observed that thermobarometric calculations performed on analyses from prism sectors returned pressures in line with estimates from volatile saturation barometers and geophysical observations while analyses from hourglass sectors returned implausibly negative pressures, implying that they do record equilibrium and are thus unsuitable for investigating Fe^{3+} partitioning. Nonetheless, we note that the degree to which different sectors may or may not record equilibrium appears to differ between tholeiitic and alkali systems, as discussed by [Ubide et al \(2019\)](#) and [Neave et al \(2019\)](#). Rim and microcryst analyses feasibly in equilibrium with the matrix glass of PI-041 were identified texturally; compositionally distinct rims in contact with glasses are clear in clinopyroxene crystals from PI-041 (Figures 2F and 7) and appear unaffected by sector zoning. In any case, both prism and hourglass sectors in crystals from alkali systems appear capable of recording equilibrium magma storage conditions ([MacDonald et al., 2023](#)).

The Al_2O_3 and Fe_2O_3 contents of clinopyroxene analyses in textural equilibrium with their host glasses are shown in Figure 10; analyses with $\text{Fe}_2\text{O}_3 < 0.35$ have been removed as they lie below the effective detection limit of stoichiometric determinations. Analyses from our Holuhraun sample show minimal variability, while those from both PI-041 and our Skuggafjöll samples are much more variable. Having eliminated effects from sector zoning, elevated and somewhat correlated Fe_2O_3 and Al_2O_3 contents likely reflect the enhanced incorporation of trivalent cations via Tschermak-type substitutions during disequilibrium crystallisation ([Mollo et al, 2010](#); [Ubide et al, 2019](#); [Di Fiore et al., 2021](#)). That is, while the clinopyroxene analyses we selected appear to be in textural equilibrium with their host glasses, only some of them are likely to have formed at conditions close to chemical equilibrium.

In order to convert our observed clinopyroxene Fe_2O_3 contents into Fe^{3+} partition coefficients (i.e., $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values) we estimated the $\text{Fe}^{3+}/\Sigma\text{Fe}$ content of glasses in our Skuggafjöll, Holuhraun and Pico (PI-041) samples from olivine-liquid equilibria (Figure 11). Specifically, we determined glass $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents from olivine rims and microcrysts, using Equation 10 of [Saper et al \(2022\)](#) to calculate appropriate $K_{\text{D,Fe}^{2+}-\text{Mg}}^{\text{ol-liq}}$ values from which glass Fe^{2+} contents and Mg# values could be estimated (Figure 11A). Glass $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents were then converted into f_{O_2} conditions using the model of [Borisov et al \(2018\)](#), and are reported as log-unit deviations from FMQ in Figure 11B. Best estimates of glass $\text{Fe}^{3+}/\Sigma\text{Fe}$ in our Skuggafjöll and Holuhraun samples of ~ 0.19 are similar to values reported from other Icelandic tholeiites from Fe-XANES spectroscopy (up to 0.20 for Laki; [Hartley et al, 2017](#)). A glass $\text{Fe}^{3+}/\Sigma\text{Fe}$ content of ~ 0.19 corresponds to an f_{O_2} of FMQ+1, which is broadly consistent with S systematics in the products of the Holuhraun eruption that indicate an f_{O_2} of $\sim \text{FMQ}+0.5$ ([Bali et al, 2018](#)). Olivine crystals from PI-041 return higher glass $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents of ~ 0.33 that correspond to an f_{O_2} of $\sim \text{FMQ}+2.5$, in line with glass $\text{Fe}^{3+}/\Sigma\text{Fe}$ maxima observed in OIB samples erupted elsewhere ([Brounce et al, 2017](#); [Moussallam et al, 2019](#)). These values are also comparable to the results of V-in-olivine oxybarometry performed on petrologically similar samples from El Hierro in the Canary Islands ([Taracsak et al, 2022](#)). While subject to analytical uncertainties,

our olivine-based approach nonetheless provides plausible and internally consistent estimates of glass $\text{Fe}^{3+}/\Sigma\text{Fe}$ that facilitate deeper investigations of clinopyroxene-liquid Fe^{3+} partitioning.

Estimated $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values are summarised as a function of clinopyroxene Al_2O_3 contents in Figure 12A. While each of the clinopyroxene populations considered form a distinct cluster on Figure 12A, little overall structure is apparent. Analyses from our Holuhraun sample lie to low Al_2O_3 and low $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$, while those from our Skuggafjöll samples lie to low Al_2O_3 but with a large range in $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ and those from Pico span wide ranges in Al_2O_3 and $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$. However, when $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values are summarised as a function of $^{\text{IV}}\text{Al}$, which forms Es alongside Fe^{3+} via the coupled substitution $(\text{Mg},\text{Fe}^{2+}) + \text{Si} = \text{Fe}^{3+} + ^{\text{IV}}\text{Al}$, some structure can be resolved. Correlated variations in $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ and $^{\text{IV}}\text{Al}$ in our tholeiitic and alkali samples can be fitted with separate linear models of modest quality ($r^2 = 0.35$ and 0.32 , respectively). Nonetheless, our observations suggest that $^{\text{IV}}\text{Al}$ can play a role in mediating Fe^{3+} incorporation into magmatic clinopyroxene crystals (e.g., Di Fiore et al., 2021), and that the nature of this effect may depend on system composition. The shallower slope of the regression through crystals from alkali samples with respect to that through crystals from tholeiitic samples likely reflects the incorporation of greater amounts of Ti as CaTi (i.e., $\text{CaTiAl}_2\text{O}_6$) in the former.

Published estimates of $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ are shown in Figure 12. Mallmann and O’Neill (2009) and Davis and Cottrell (2021) report values of 0.453 ± 0.158 and 0.78 ± 0.30 , respectively, while McCanta et al (2004) report values in the range 0.00–0.77. Iron was only present at trace levels in the (near-)CMAS experiments of Mallmann and O’Neill (2009), casting doubt on the suitability of using their estimated $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ value to describe Fe^{3+} partitioning in OIB samples where Fe_2O_3 is a major constituent (>1 wt.%), despite overlapping with our observations from natural samples. Davis and Cottrell (2021) investigated Fe^{3+} partitioning in ultramafic but nevertheless Fe-poor systems, deriving $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ indirectly through Fe^{2+} –Mg exchange between olivine and clinopyroxene. While Davis and Cottrell (2021) inferred that $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ was not affected by f_{O_2} in their variable f_{O_2} experiments, there is insufficient chemical variability in their experimentally produced clinopyroxene crystals to identify potential chemical controls over Fe^{3+} partitioning. That is, the clinopyroxene crystals they used to estimate $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ have very similar Al_2O_3 and $^{\text{IV}}\text{Al}$ contents, so any potential mediation of Fe^{3+} incorporation by Al_2O_3 or $^{\text{IV}}\text{Al}$ cannot be evaluated. The $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values reported by Davis and Cottrell (2021) are nonetheless consistent with our linear model through clinopyroxene analyses from tholeiitic samples (Figure 12B).

McCanta et al (2004) report values of 0.00–0.77 from their experiments on a SNC meteorite composition, with values of 0.00–0.09 being obtained under reducing conditions when Fe^{3+} was almost absent ($\sim\text{FMQ}-4.7$ to $\text{FMQ}-2.7$) and elevated values of 0.48–0.77 being obtained under conditions approaching those relevant for terrestrial magmatism ($\sim\text{FMQ}-0.7$ to $\sim\text{FMQ}+0.3$). Unfortunately McCanta et al (2004) do not provide the compositional information required to assess whether their reported variations in $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ reflect changes in f_{O_2} alone, or whether clinopyroxene compositions also play a role. Moreover, the Fe^{3+} contents of augite crystals measured by McCanta

et al (2004) were subject to 1σ uncertainties similar in magnitude to the Fe^{3+} contents themselves, and as such their reported $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values should be considered similarly uncertain.

Overall, our observations indicate that $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values in OIB systems likely range between 0.2 and 1.0 depending on the composition of the clinopyroxene and liquid in question. Clinopyroxene $^{\text{IV}}\text{Al}$ contents appear to play a role in mediating their Fe^{3+} contents, but the strength of this effect depends on system alkalinity, with clinopyroxene crystals in alkali systems incorporating less Fe^{3+} for any given increase in $^{\text{IV}}\text{Al}$ than those from tholeiitic systems, likely because of the coupled incorporation of Ti. Importantly, if Fe^{3+} partitioning is linked to the incorporation of $^{\text{IV}}\text{Al}$, then clinopyroxene Fe_2O_3 contents will be equally sensitive to disequilibrium crystallisation as their Al_2O_3 and TiO_2 contents (Mollo et al, 2010, 2013; Ubide et al, 2019). That is, coupled variations in clinopyroxene Fe_2O_3 , Al_2O_3 and TiO_2 contents likely result from disequilibrium processes such that apparent $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values may not always truly reflect equilibrium Fe^{3+} partitioning behaviour. For example, prism sectors may record the best estimates of equilibrium $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values values in our tholeiitic samples (Neave et al, 2019), while either prism or hourglass sectors may record equilibrium $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values in our alkali samples (Ubide et al, 2019; MacDonald et al., 2023). Moreover, our evaluations assume that the clinopyroxene crystals analysed grew from liquids whose $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents were correctly estimated from olivine-liquid equilibria, which may not be the case for our Holuhraun sample for reasons discussed below.

Combining observations from Skuggafjöll prism sectors with observations from Pico samples as a whole suggests that equilibrium $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ may lie close to 0.6, with much of the variability we observe resulting from kinetic effects associated with variable Al_2O_3 incorporation. While our estimated $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values of ~ 0.6 are broadly in line with the sparse experimental observations available, new experiments and analyses are required to develop robust and predictive descriptions of Fe^{3+} partitioning between clinopyroxene and liquid.

Iron-magnesium exchange equilibria

Clinopyroxene crystals primarily record magmatic evolution in a transition from high-Mg# compositions dominated by Di to low-Mg# compositions that are relatively enriched in Hd. As such, clinopyroxene-liquid equilibria are often summarised in terms of Fe^{2+} -Mg exchange (Wood and Blundy, 1997; Putirka, 2008). This convention at least partly reflects similarities between clinopyroxene-liquid equilibria described using $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{cpx-liq}}$ values and olivine-liquid equilibria described using $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{ol-liq}}$ values (Roeder and Emslie, 1970; Blundy et al, 2020; Saper et al, 2022). Equation 35 of Putirka (2008) provides the most recent model capable of predicting $K_{\text{D,Fe-Mg}}^{\text{cpx-liq}}$ values that is feasibly applicable to OIB samples. Although this model incorporates the effect of temperature on $K_{\text{D,Fe-Mg}}^{\text{cpx-liq}}$, and returns a value of ~ 0.28 at temperatures relevant to OIB evolution (~ 1200 °C) that is close to $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{cpx-liq}}$ values from experiments on mafic compositions (0.24–0.26; Sisson and Grove, 1993; Pilet et al., 2010; Salazar-Naranjo and Vlach, 2023), it assumes that all Fe occurs as Fe^{2+} in both clinopyroxene crystals and their host glasses and thus strictly describes Fe-Mg exchange rather than

Fe²⁺–Mg exchange. This assumption is clearly incorrect for basaltic liquids characterised by Fe³⁺/ΣFe contents that range from ~0.1 to ~0.3 across a naturally relevant range of f_{O_2} conditions (FMQ–1 to FMQ+2; Kress and Carmichael, 1991; Borisov et al, 2018; Cottrell et al, 2022). Our findings also demonstrate that this assumption is incorrect from the crystal perspective, with clinopyroxene crystals in diverse OIB samples exhibiting Fe³⁺/ΣFe contents ranging from ~0.0 to ~0.5 (Figure 5D). Given that Fe²⁺ and Fe³⁺ are incorporated into clinopyroxene within quadrilateral and non-quadrilateral components, respectively, Fe³⁺ is unlikely to exchange directly with Mg or Fe²⁺ (e.g., Ubide et al, 2019; Neave et al, 2024), meaning that Fe²⁺–Mg exchange may be only indirectly affected by Fe³⁺. Improving our ability to interpret observations from clinopyroxene crystals in natural and experimental systems thus requires clinopyroxene-liquid Fe²⁺–Mg exchange equilibria and $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{cpx-liq}}$ systematics *sensu stricto* to be investigated in greater depth.

Samples from Skuggafjöll, Holuhraun and Pico (PI-041) contain clinopyroxene crystals in textural equilibrium with their host glasses and are suitable for investigating Fe²⁺–Mg exchange. Combined glass and clinopyroxene Mg# systematics are summarised in Figure 13. Clinopyroxene-liquid Fe–Mg exchange equilibria were first calculated following current recommendations that all Fe should be taken as Fe²⁺ in both clinopyroxene and liquid (Wieser et al, 2023a,b). These calculations return $K_{\text{D,Fe-Mg}}^{\text{cpx-liq}}$ values within uncertainty of (± 0.08 , 1σ), but also consistently lower than, the ~0.28 value calculated with Equation 35 of Putirka (2008) potentially as a result of ignoring of Fe³⁺. Indeed, we speculate that the large uncertainty in $K_{\text{D,Fe-Mg}}^{\text{cpx-liq}}$ values estimated from this equation (± 0.08 , 1σ) compared with uncertainties in $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{ol-liq}}$ values estimated with various recent models (typically ± 0.03 , 1σ , or less; Blundy et al, 2020; Saper et al, 2022) reflects the currently unconstrained influence of Fe³⁺ in clinopyroxene.

Clinopyroxene-liquid Fe²⁺–Mg exchange equilibria were subsequently calculated with clinopyroxene Fe²⁺ contents determined by stoichiometry following Droop (1987) and liquid (i.e., glass) Fe²⁺ contents fixed at a range of relevant f_{O_2} conditions (FMQ to FMQ+3) according to the model of Borisov et al (2018). Accounting for the presence of Fe³⁺ increases both glass and clinopyroxene Mg# values. However, the magnitudes of Mg# increases vary within and between samples because clinopyroxene Fe₂O₃ contents also vary (Figure 5C). Best estimates of clinopyroxene-liquid Fe²⁺–Mg exchange equilibria were estimated by assuming that mean clinopyroxene compositions (from prism sectors for Skuggafjöll and Holuhraun) were in equilibrium with glass Fe³⁺/ΣFe contents estimated from olivine-liquid equilibria (Figure 11), ~0.19 for samples from Skuggafjöll and Holuhraun and ~0.33 for sample PI-041 from Pico.

The best estimate of clinopyroxene-liquid Fe²⁺–Mg equilibrium calculated from the mean clinopyroxene composition in our Skuggafjöll samples is consistent with a $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{cpx-liq}}$ value of ~0.23 (Figure 13A), within model uncertainty of ~0.28, but also much closer to experimentally reported values of ~0.24–0.26 (Sisson and Grove, 1993; Pilet et al., 2010; Salazar-Naranjo and Vlach, 2023). If we assume, for now, that a $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{cpx-liq}}$ value of ~0.28 from Putirka (2008) is correct, our mean Skuggafjöll clinopyroxene composition would indicate f_{O_2} close to ~FMQ+2.5. However, observations from elsewhere in Iceland and the Reykjanes Ridge suggest that such oxidising

conditions are unrealistic for Icelandic tholeiites (Shorttle, 2015; Hartley et al, 2017; Bali et al, 2018; Novella et al., 2020). If we instead assume that a $K_{D,Fe^{2+}-Mg}^{cpx-liq}$ value of ~ 0.23 is more appropriate, as suggested by experimental observations, the mean clinopyroxene composition from Skuggafjöll would be consistent with an f_{O_2} close to $\sim FMQ+1.0$ (Figure 13A), in broad agreement with estimates from the nearby Laki eruption ($\sim FMQ+0.7$; Hartley et al, 2017). If mean compositions were compromised to some degree by disequilibrium crystallisation such that excess Fe_2O_3 had been incorporated alongside excess Al_2O_3 in some analyses (e.g., Mollo et al, 2010; Di Fiore et al., 2021), then true $K_{D,Fe^{2+}-Mg}^{cpx-liq}$ values may be slightly higher and equilibrium f_{O_2} conditions slightly more reducing.

The best estimate of clinopyroxene-liquid $Fe^{2+}-Mg$ equilibrium calculated from the mean clinopyroxene composition in our Holuhraun sample is consistent with a $K_{D,Fe^{2+}-Mg}^{cpx-liq}$ value of ~ 0.28 (Figure 13B). Assuming again that a $K_{D,Fe^{2+}-Mg}^{cpx-liq}$ value of ~ 0.28 is appropriate, the mean clinopyroxene composition from Holuhraun would be consistent with an f_{O_2} close to $\sim FMQ+1.0$. However, if we assume that equilibrium $K_{D,Fe^{2+}-Mg}^{cpx-liq}$ values are closer to experimentally derived values (0.24–0.26), as strongly indicated by observations from Skuggafjöll, then our clinopyroxene crystals would record an f_{O_2} below FMQ (Figure 13B). While such reducing conditions initially seem unlikely (cf., $\sim FMQ+0.5$ for Holuhraun; Bali et al, 2018), it is also possible that the crystals we analysed from Holuhraun formed after reductive SO_2 degassing given their small size (Figure 2B), especially when compared with the larger crystals reported from other eruption products (Halldórsson et al, 2018). Indeed, it is well documented that SO_2 degassing during magma ascent leads to the reduction of magmatic liquids (Moussallam et al, 2016; Helz et al, 2017), with initially high- f_{O_2} OIBs ($\sim FMQ+3$) recording f_{O_2} conditions at or below FMQ at the point of eruption (Taracsak et al, 2022). As such, estimating glass $Fe^{3+}/\Sigma Fe$ contents from olivine-liquid equilibria may have overestimated the true amount of Fe^{3+} present in the Holuhraun carrier liquid during clinopyroxene crystallisation. Indeed, the low $D_{Fe_2O_3}^{cpx-liq}$ values estimated for Holuhraun probably also reflect an incorrect evaluation of liquid $Fe^{3+}/\Sigma Fe$ and should not be considered as reliable equilibrium values.

Interpreting clinopyroxene-liquid $Fe^{2+}-Mg$ equilibria in sample PI-041 from Pico is complex as different crystal populations appear to record growth under different conditions (Figure 13C). If we initially assume a $K_{D,Fe^{2+}-Mg}^{cpx-liq}$ value of ~ 0.28 , the mean microcryst composition would record a plausible f_{O_2} of $\sim FMQ+2.5$ while the mean rim composition would record a seemingly implausible and disequilibrium f_{O_2} conditions well in excess of $FMQ+3$. If we instead assume that equilibrium $K_{D,Fe^{2+}-Mg}^{cpx-liq}$ values are closer to the 0.24–0.25 values observed in the prod cuts of experiments on compositionally analogous systems (Pilet et al., 2010; Salazar-Naranjo and Vlach, 2023), then the mean rim composition returns oxidising but plausible f_{O_2} conditions of $\geq FMQ+2.5$, while mean microcrysts returns relatively reducing conditions of $FMQ+1$ (Figure 13C). However, if rims and microcrysts formed before and after reductive SO_2 degassing, respectively, the seemingly discordant f_{O_2} conditions they record can be reconciled. We hence speculate that the rims of clinopyroxene (and olivine) crystals in sample PI-041 from Pico formed under relatively high f_{O_2} conditions ($\geq FMQ+2.5$)

at depth prior to any significant SO_2 degassing. We suggest that clinopyroxene microcrysts then formed after significant SO_2 degassing occurred during ascent such that they recorded relatively reducing f_{O_2} conditions of $\sim\text{FMQ}+1$.

Overall, our results illustrate that accounting for the presence of Fe^{3+} significantly impacts how clinopyroxene-liquid Fe^{2+} -Mg exchange equilibria in OIB samples are evaluated. Nonetheless, $K_{\text{D,Fe-Mg}}^{\text{cpx-liq}}$ values calculated assuming that all Fe is present as Fe^{2+} are generally within the (large) $\pm 0.08(1\sigma)$ uncertainty of values predicted with Equation 35 of Putirka (2008). Once Fe^{3+} is accounted for, $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{cpx-liq}}$ values estimated from our natural samples generally lie closer to experimentally derived values of 0.24–0.26 than 0.28 (Sisson and Grove, 1993; Pilet et al., 2010; Salazar-Naranjo and Vlach, 2023). Moreover, different clinopyroxene populations within a single sample (PI-041 from Pico) record different Fe^{2+} -Mg systematics, potentially mirroring variations in f_{O_2} conditions reported from other OIB systems that result from SO_2 degassing during ascent (Moussallam et al, 2016; Helz et al, 2017; Taracsak et al, 2022). Considerable uncertainties nevertheless remain in our interpretations. Targeted experiments are thus required to identify and disentangle the effects of composition, disequilibrium and f_{O_2} conditions on clinopyroxene-liquid Fe^{2+} -Mg exchange before we can calibrate a robust predictive model of $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{cpx-liq}}$ for modelling and interpreting OIB samples.

Conclusions

By applying the stoichiometric approach for determining clinopyroxene $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents described by Droop (1987) to compositionally diverse OIB samples from Iceland and the Azores, we demonstrate that Fe^{3+} is an abundant if under-appreciated cation in magmatic clinopyroxene crystals from ocean island volcanoes. On average, clinopyroxene crystals from alkali systems have higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents than those from tholeiitic systems, which translate into higher Es contents and, in some cases, non-negligible Ae contents. The incorporation of Ca and $^{\text{IV}}\text{Al}$ in clinopyroxene crystals alongside Fe^{3+} has important consequences for the relative proportions of other clinopyroxene components such as DiHd and EnFs, and trends in clinopyroxene Jd, CaTi and CrAlTs contents can be variably linked to magma composition (i.e., alkalinity), storage pressure and the degree of magmatic evolution. Clinopyroxene Es contents are somewhat related to the f_{O_2} conditions under which their carrier liquids evolved, with Fe^{3+} -rich crystals from alkali samples that typically evolve under relatively oxidising conditions containing more Es than Fe^{3+} -poor crystals from tholeiitic samples. However, elevated clinopyroxene Es, CaTs and CaTi contents also reflect disequilibrium crystallisation in some cases, including in $\{\bar{1}11\}$ hourglass sectors from crystals in tholeiitic samples. Overall, Fe^{3+} shows similar behaviour to Al and Ti during clinopyroxene crystallisation and its behaviour may thus be interpreted within a growing corpus of knowledge about the textural and chemical evolution of clinopyroxene crystals.

By exploiting the ability to estimate glass $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents from olivine-liquid equilibria, we investigated Fe^{3+} partitioning in a subset of our OIB samples with quenched matrix glasses. Olivine-liquid equilibria in tholeiitic samples from Skuggafjöll and Holuhraun record glass compositions consistent with f_{O_2} conditions of $\sim\text{FMQ}+1$,

while those in the alkali sample PI-041 from Pico record compositions consistent with relatively oxidising f_{O_2} conditions of $\sim\text{FMQ}+2.5$. These values are consistent with observations from a range of ocean island settings, and potentially reinforce suggestions that OIBs with EMII affinities, like those from the Azores, evolve under more oxidising conditions than those with C/FOZO/PREMA affinities, like those from Iceland. Estimated $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values from clinopyroxene analyses in textural equilibrium with their host glasses fall in the range 0.2–1.0, and appear to be mediated by the abundance of $^{\text{IV}}\text{Al}$. This implies that there are steric constraints on the incorporation of Fe^{3+} into clinopyroxene, though the exact nature of $^{\text{IV}}\text{Al}$ - $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ relationships differs between tholeiitic and alkali compositions. Some of the variability in apparent $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values may however reflect disequilibrium, with $^{\text{IV}}\text{Al}$ - and Fe^{3+} -rich analyses in samples from Pico and Skuggafjöll reflecting the enhanced incorporation of non-quadrilateral components during disequilibrium crystallisation; equilibrium $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values during magmatic evolution may thus lie in the middle of the 0.2–1.0 range (i.e., ~ 0.6) given that low values from Holuhraun may also reflect disequilibrium processes. While our findings are consistent with the few experimental determinations of $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ currently available, new experiments are required to disentangle the effects of system composition and disequilibrium crystallisation on clinopyroxene-liquid Fe^{3+} partitioning.

Extending our evaluation to clinopyroxene-liquid Fe^{2+} -Mg exchange equilibria suggests that $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{cpx-liq}}$ values (as opposed to $K_{\text{D,Fe-Mg}}^{\text{cpx-liq}}$ values) lie close to experimental estimates (0.24–0.26) when f_{O_2} conditions are similar to those recorded by olivine-liquid equilibria in samples unaffected by SO_2 degassing (i.e., $\sim\text{FMQ}+1$ for Skuggafjöll and $\sim\text{FMQ}+2.5$ for Pico). Differences in apparent $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{cpx-liq}}$ values within and between different populations of clinopyroxene crystals we analysed reflect the same disequilibrium processes recorded in $^{\text{IV}}\text{Al}$ - Fe^{3+} systematics, and highlight the importance of evaluating whether phases are in chemical as well as textural equilibrium before interpreting the meaning of Fe^{2+} -Mg exchange equilibria. Overall, our findings demonstrate that the non-negligible abundance of Fe^{3+} in clinopyroxene crystals from OIB settings has a significant effect on clinopyroxene-liquid Fe^{2+} -Mg exchange equilibria. While our investigation suggests that $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ and $K_{\text{D,Fe}^{2+}\text{-Mg}}^{\text{cpx-liq}}$ values offer potential routes for estimating glass $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents and magmatic f_{O_2} conditions, further experiments are required to robustly define clinopyroxene-liquid equilibria involving both Fe^{2+} and Fe^{3+} . These experiments will also pave the way towards understanding equilibria between clinopyroxene and other minerals that will open new opportunities for determining and modelling the behaviour of Fe^{2+} and Fe^{3+} and thence f_{O_2} in glass-free systems.

Acknowledgements

We thank Lee Paul, David Oliver and Lewis Hughes at the University of Manchester for their help with sample preparation, thin section production and scanning electron microscopy, respectively. We also thank Stuart Kearns and Ben Buse for their help with electron probe microanalysis at the University of Bristol. We thank Luca Caricchi, Elizabeth Cottrell, Alice MacDonald and one anonymous reviewer for their

constructive comments on an earlier version of this manuscript, and Othmar Müntener for his editorial handling. We note that [Rudra et al \(2021\)](#) and [Rudra and Hirschmann \(2022\)](#) recently presented highly relevant clinopyroxene $\text{Fe}^{3+}/\Sigma\text{Fe}$ determinations by Fe-XANES. However, these articles have been retracted and can no longer form part of our discussion. This work was supported by a NERC Independent Research Fellowship (NE/T011106/1) and a Royal Society Research Grant (RGS\R1\201344) to DAN.

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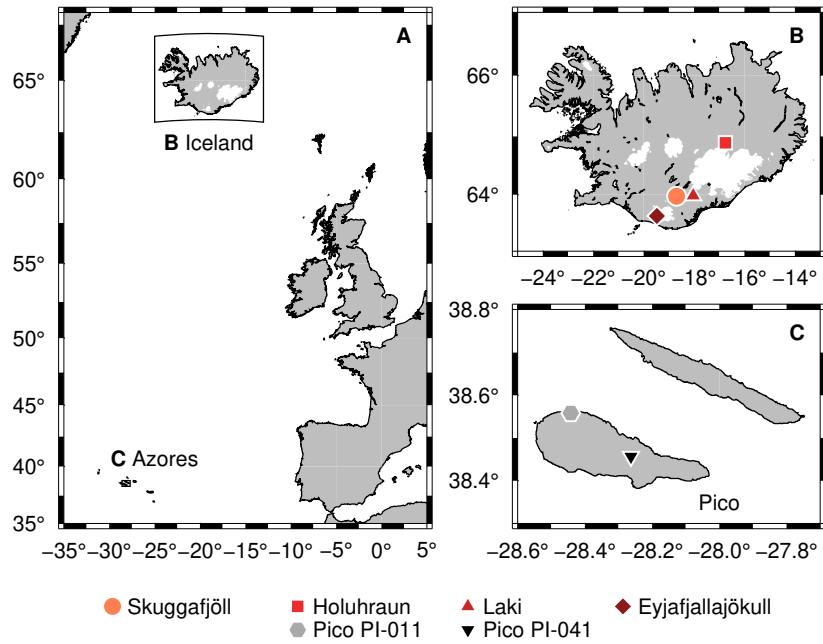


Figure 1: (A) Map of the North Atlantic showing sample locations in Iceland and the Azores. (B) Map of Iceland showing the location of samples from Skuggafjöll, Holuhraun, Laki and Eyjafjallajökull. (C) Map of part of the Azores archipelago showing the location of samples on Pico Island.

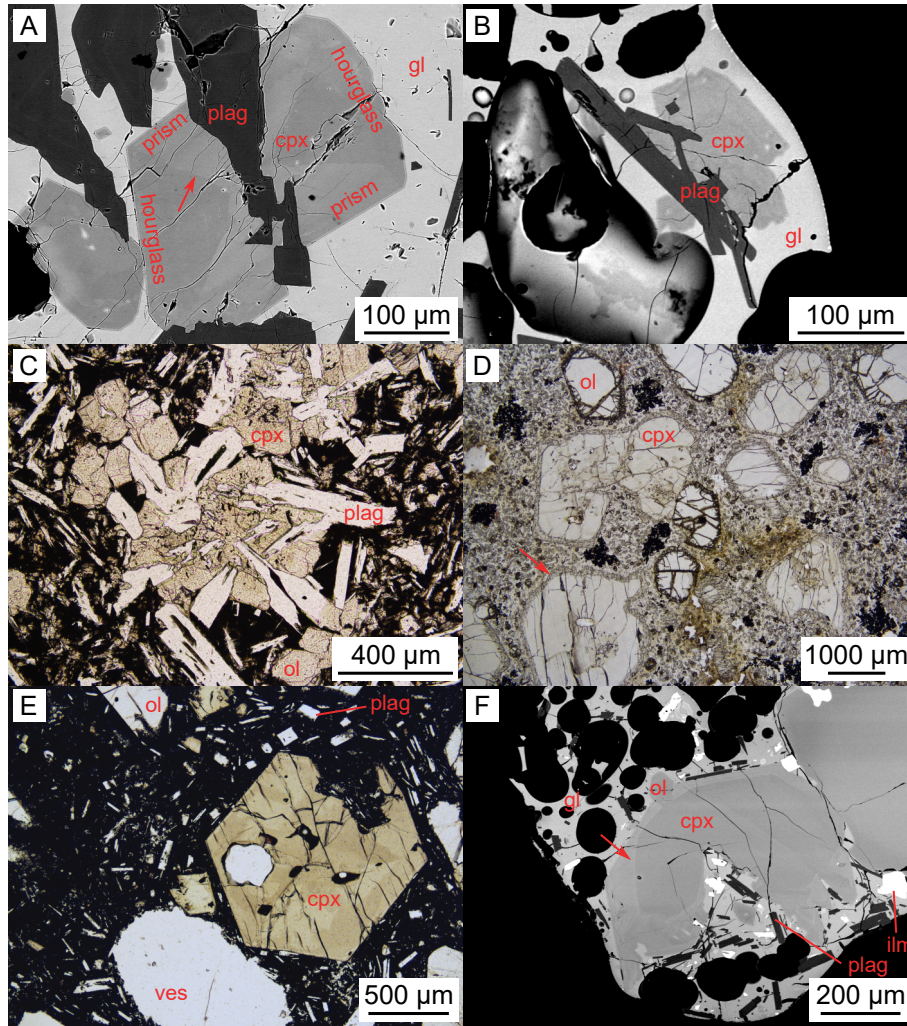


Figure 2: Clinopyroxene textures in ocean island basalt samples from Iceland and the Azores. Labels are as follows: cpx, clinopyroxene; ol, olivine; plag, plagioclase; gl, glass; ilm, ilmenite; and ves, vesicle. (A) Backscattered electron (BSE) image of clinopyroxene in pillow basalt HOR-11-01 from Skuggafjöll. An interface between high-BSE-intensity $\{hk0\}$ prism sectors and low-BSE-intensity $\{111\}$ hourglass sectors is highlighted with an arrow. (B) BSE image of ophitic clinopyroxene in a basaltic tephra sample from Holuhraun. (C) Photomicrograph of clinopyroxene in ophitic arrangement in basaltic lava sample LAK-04 from Laki. (D) Photomicrograph of large clinopyroxene macrocrysts in ankaramitic lava sample HVAM13-01 from Eyjafjallajökull. The arrow shows rims undergoing dissolution (Neave and MacLennan, 2020). (E) Photomicrograph of a large clinopyroxene macrocrysts in basaltic lava sample PI-011 from Pico, Azores. Patchy zoning is reflected in the variable colour of the clinopyroxene macrocryst. (F) BSE image of large clinopyroxene macrocrysts in basaltic tephra sample PI-041 from Pico, Azores. A prominent concentric zoning boundary is highlighted with the arrow.

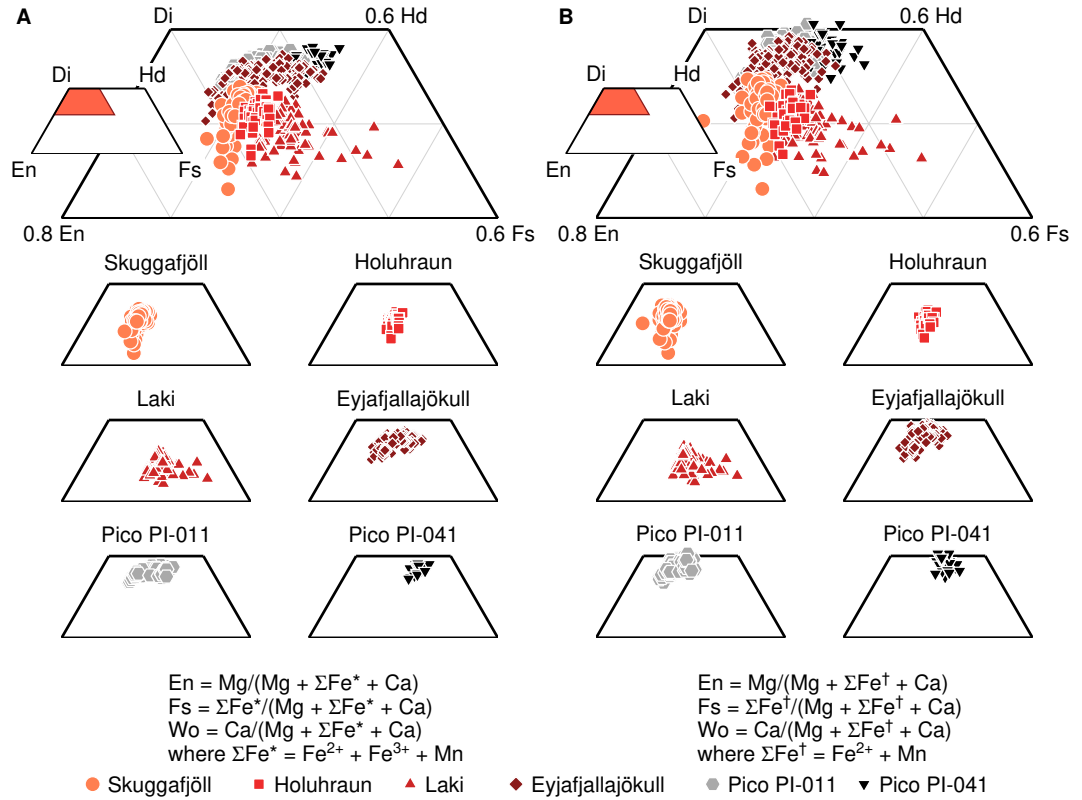


Figure 3: Summary of clinopyroxene compositions in ocean island basalt samples from Iceland and the Azores. (A) Pyroxene quadrilateral showing clinopyroxene quadrilateral components (diopside, Di; hedenbergite, Hd; enstatite, En; and ferrosilite, Fs) calculated following Morimoto et al (1988) where the Fe component (ΣFe^*) is equal to the sum of Fe^{2+} , Fe^{3+} and Mn. (B) Pyroxene quadrilateral showing adjusted clinopyroxene quadrilateral components (diopside, Di^\dagger ; hedenbergite, Hd^\dagger ; enstatite, En^\dagger ; and ferrosilite, Fs^\dagger) calculated following Morimoto et al (1988) where the Fe component (ΣFe^\dagger) is equal to the sum of Fe^{2+} and Mn, with Fe^{2+} determined by stoichiometry following Droop (1987).

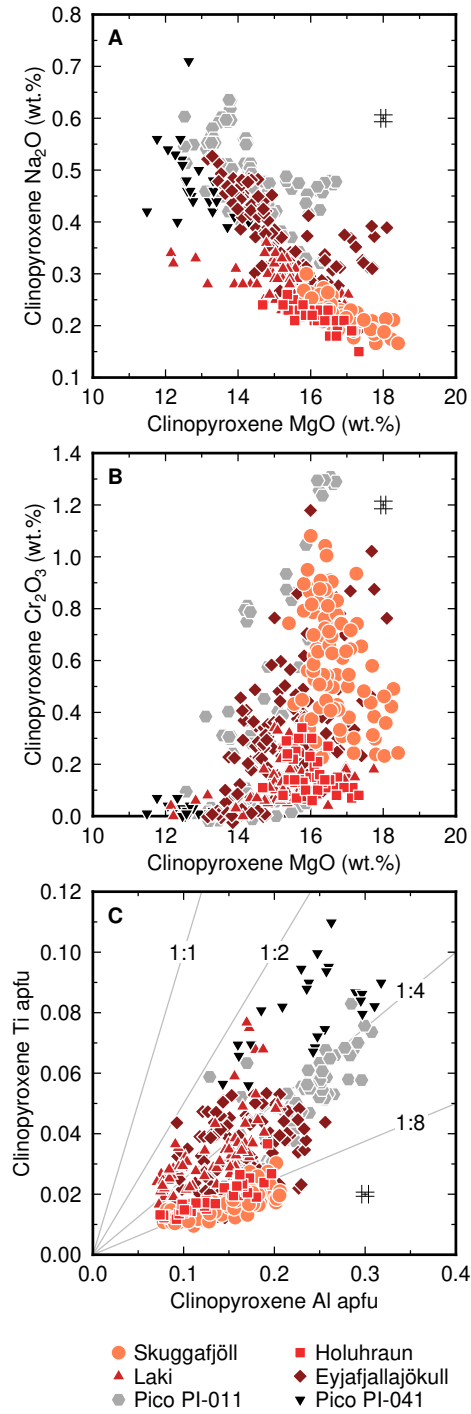


Figure 4: Systematics of major elements hosted in non-quadrilateral clinopyroxene components in ocean island samples from Iceland and the Azores; 1σ analytical uncertainties are shown. (A) Variation in Na₂O as a function of MgO. (B) Variation in Cr₂O₃ as a function of MgO. (C) Covariation of Ti and Al atoms per formula unit (apfu) calculated on a six-oxygen basis.

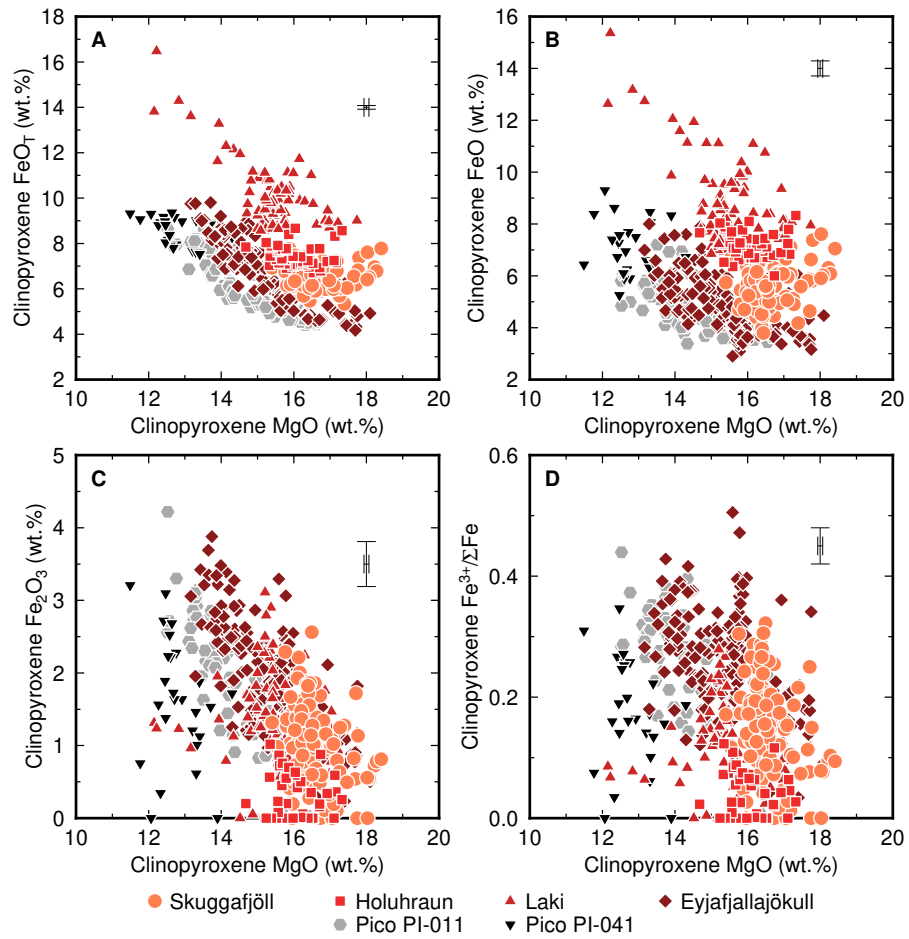


Figure 5: Iron concentration and valence systematics in clinopyroxene crystals from Iceland and the Azores; 1σ analytical uncertainties are shown. (A) MgO versus total Fe expressed as FeO (FeO_T). (B) MgO versus FeO determined by stoichiometry following Droop (1987). (C) MgO versus Fe_2O_3 determined by stoichiometry following Droop (1987). (D) MgO versus $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined by stoichiometry following Droop (1987).

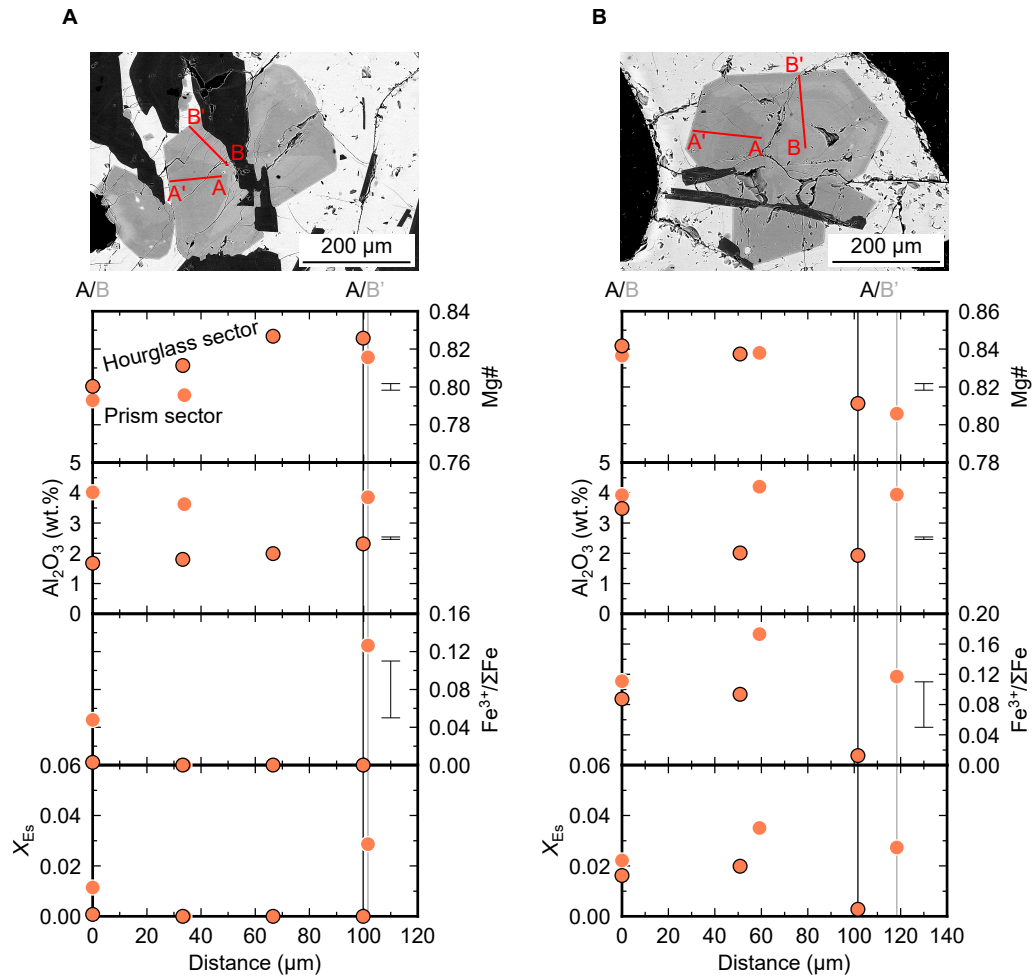


Figure 6: Chemical systematics of clinopyroxene crystals with hourglass sector zoning in samples from Skuggafjöll, Iceland. Light- and dark-rimmed symbols show core-to-rim profiles from high- and low-backscattered electron (BSE)-intensity zones associated with prism and hourglass sectors, respectively; 1σ analytical uncertainties are shown. Vertical lines show the positions of crystal rims. Hourglass sectors (A-A' profiles and dark-rimmed symbols) are poorer in Al₂O₃, Fe³⁺ and esseneite (Es, CaFe³⁺AlSiO₆) component than prism sectors (B-B' profiles and light-rimmed symbols).

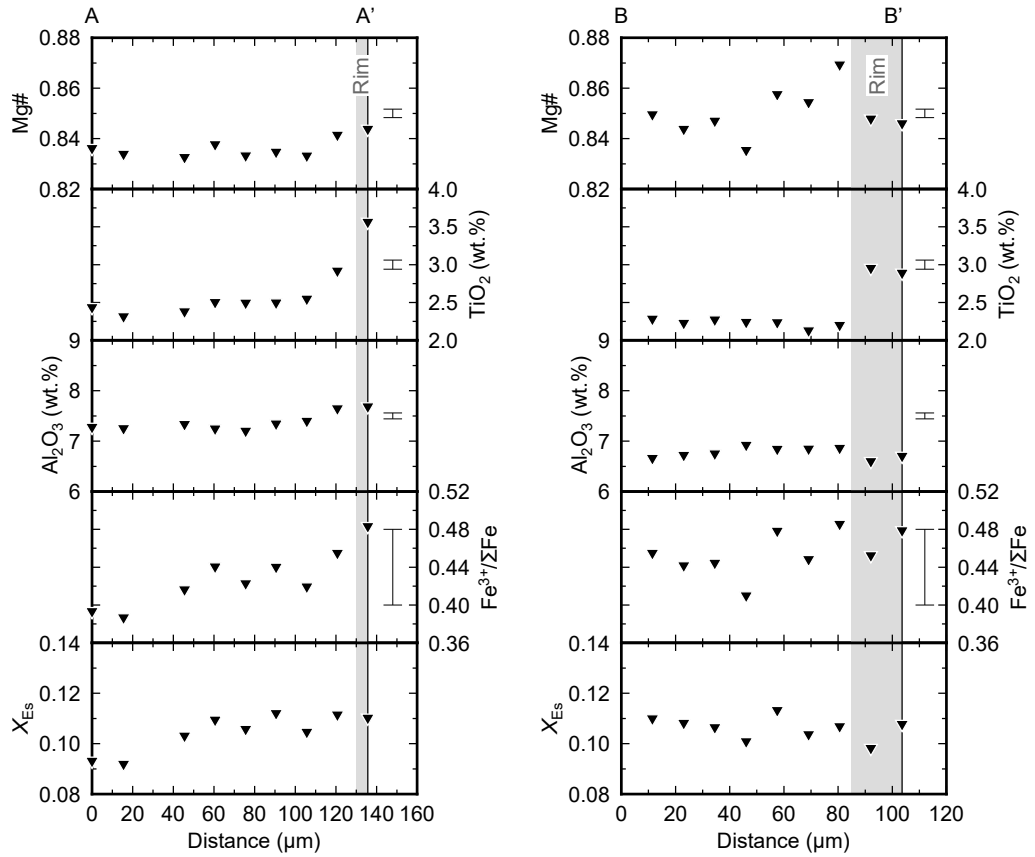
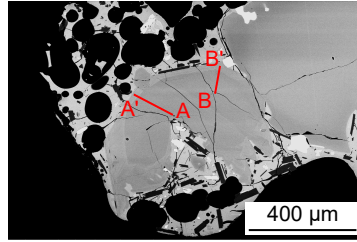


Figure 7: Chemical systematics of clinopyroxene crystals with concentric core-to-rim zoning in samples from Pico (PI-041), Azores. Vertical lines show the positions of crystal rims and grey shading shows the extent of rim zones identified from backscattered electron (BSE) images; 1σ analytical uncertainties are shown. Rims are primarily reflected in changes in Mg# and TiO₂ content rather than systematic changes in Fe³⁺/ΣFe and esseneite (Es, CaFe³⁺AlSiO₆) component.

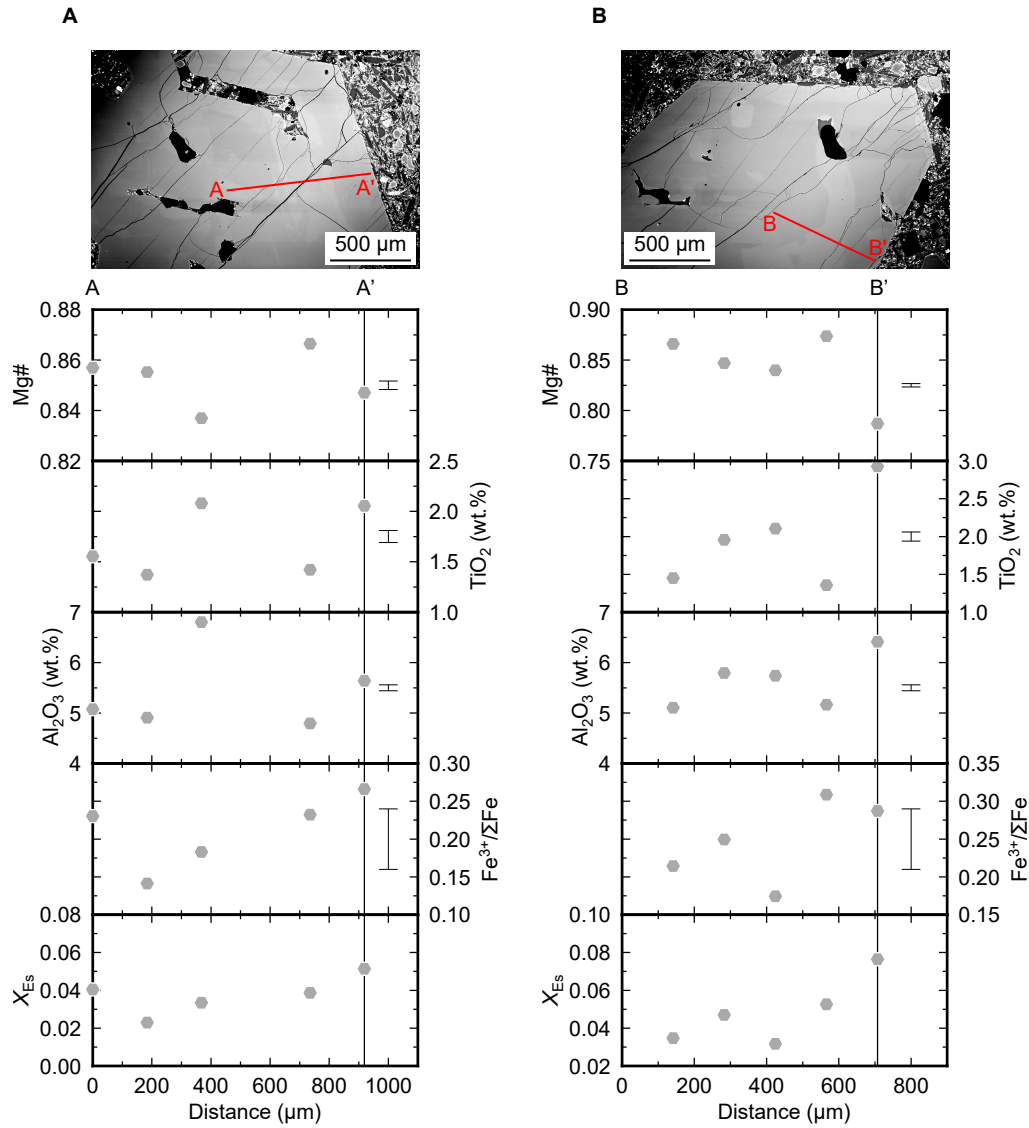


Figure 8: Chemical systematics of clinopyroxene crystals with patchy zoning reflected by variations in BSE intensity in samples from Pico (PI-011), Azores. Vertical lines show the positions of crystal rims; 1σ analytical uncertainties are shown. There is considerable variability in Mg#, TiO₂, Fe³⁺/ΣFe and esseneite (Es, CaFe³⁺AlSiO₆) component contents in crystals with patchy zoning but this variability is less systematic than that observed in crystals with hourglass sector zoning or concentric core-to-rim zoning (Figures 6 and 7).

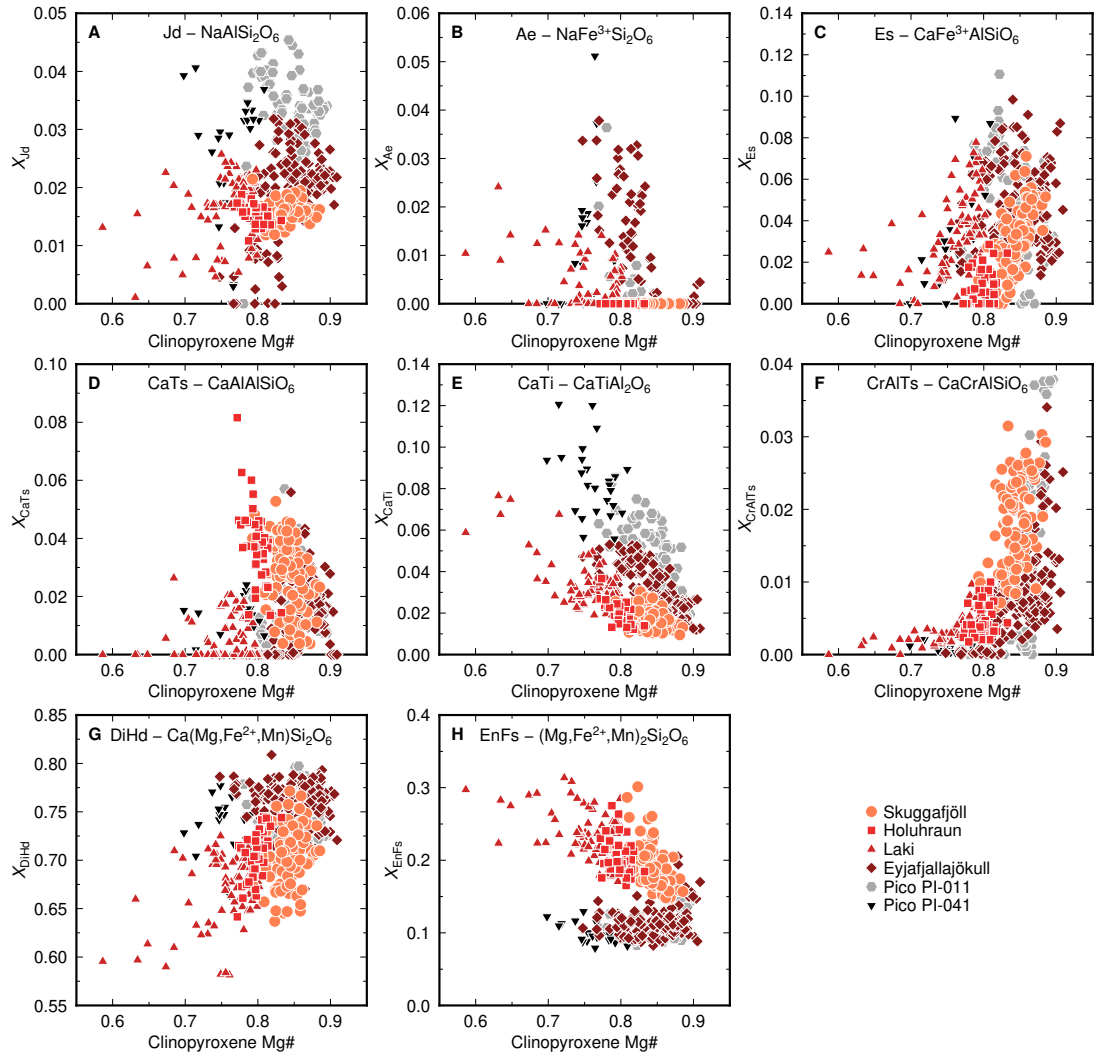


Figure 9: Clinopyroxene components in ocean island samples from Iceland and the Azores summarised as functions of clinopyroxene Mg#, where Mg# = molar Mg/(Mg+Fe²⁺). The scheme for calculating the following components was described by Neave et al (2024) and is summarised in the appendix. (A) jadeite, Jd; (B) aegirine, Ae; (C) esseneite, Es; (D) Ca-Tschermak's component, CaTs; (E) titanian Ca-Tschermak's component, CaTi; (F) chromian Ca-Tschermak's component, CrCaTs; (G) diopside and hedenbergite, DiHd; and (H) enstatite and ferrosilite, EnFs.

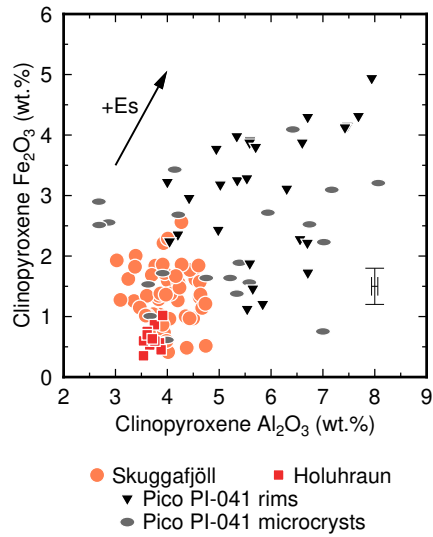


Figure 10: Variations in clinopyroxene Al_2O_3 and Fe_2O_3 contents in samples from Skuggafjöll, Holuhraun and Pico (PI-041) that are textural in equilibrium with their host glasses. Although analyses in PI-041 and our samples from Skuggafjöll are more variable than those in our Holuhraun sample, much of the coupled variability across these samples can be explained by incorporating variable amounts of esseneite (Es, $\text{CaFe}^{3+}\text{AlSiO}_6$) component, as illustrated by the vector labelled +Es.

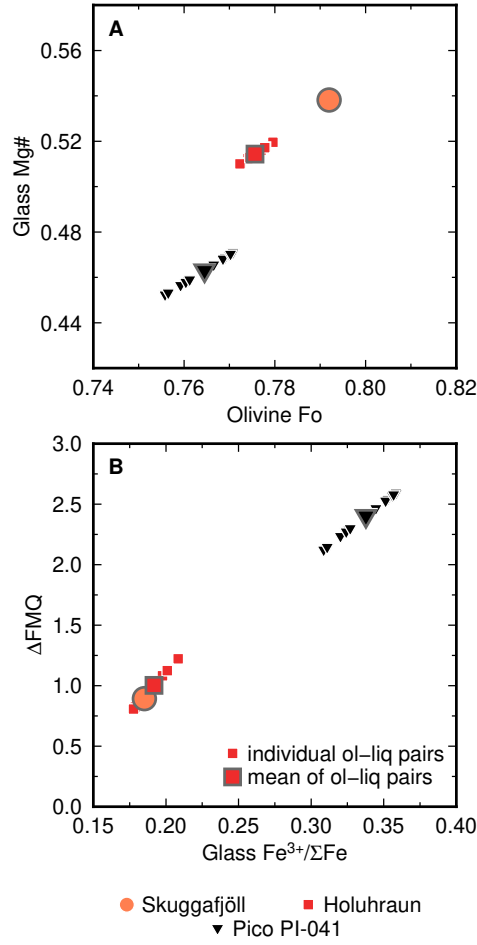


Figure 11: Estimating pre-eruptive magmatic oxygen fugacity (f_{O_2}) conditions recorded by olivine-liquid equilibria in samples from Skuggafjöll, Holuhraun and Pico (PI-041). (A) Estimation of glass Mg# contents, where $\text{Mg\#} = \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$. Glass Fe^{2+} contents were estimated using the $K_{\text{D,Fe}^{2+}-\text{Mg}}^{\text{ol-liq}}$ model of Saper et al (2022) that assumes all Fe occurs as Fe^{2+} . Equilibrium olivine-liquid pairs were identified texturally from BSE images. (B) Conversion of estimated glass $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents into f_{O_2} conditions (expressed as log units relative to fayalite-magnetite-quartz equilibrium; ΔFMQ) according to the model of Borisov et al (2018). Large symbols show mean values that reflect our best estimates of magmatic f_{O_2} conditions.

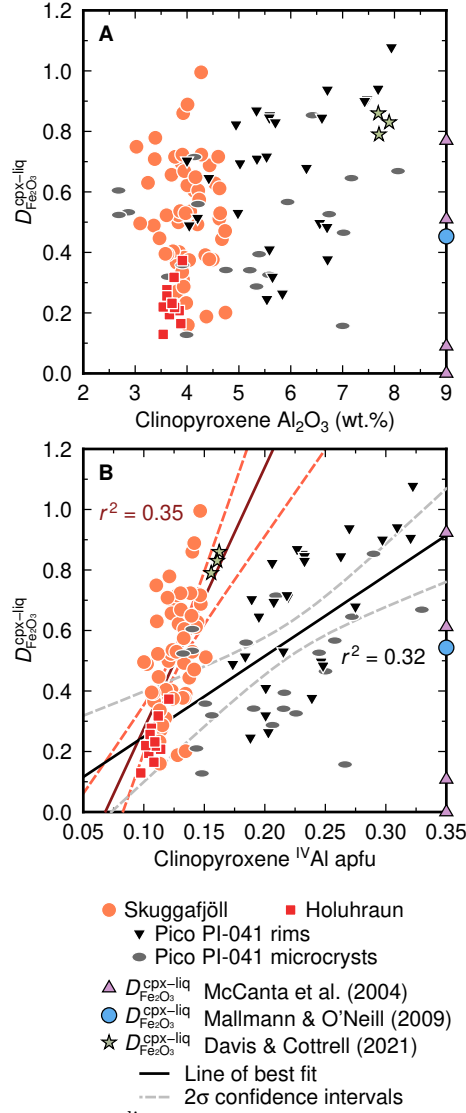


Figure 12: Estimates of $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ from clinopyroxene-liquid pairs in samples from Skuggafjöll, Holuhraun and Pico (PI-041) that are textural equilibrium. Clinopyroxene Fe^{3+} contents were determined by stoichiometry following Droop (1987) and liquid (i.e., glass) Fe^{3+} contents were estimated via olivine-liquid equilibria (Figure 11). Published $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ estimates from McCanta et al (2004), Mallmann and O'Neill (2009) and Davis and Cottrell (2021) are shown; compositional information is not available for McCanta et al (2004) or Mallmann and O'Neill (2009). (A) Clinopyroxene Al_2O_3 contents correlate weakly and positively with $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ in our samples, and our estimated $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$ values span the same range as published estimates. (B) Clinopyroxene $^{\text{IV}}\text{Al}$ contents correlate positively and modestly with $D_{\text{Fe}_2\text{O}_3}^{\text{cpx-liq}}$, consistent with clinopyroxene Fe^{3+} contents being mediated by the abundance of esseneite (Es , $\text{CaFe}^{3+}\text{AlSiO}_6$) component and implying steric constraints on Fe^{3+} partitioning.

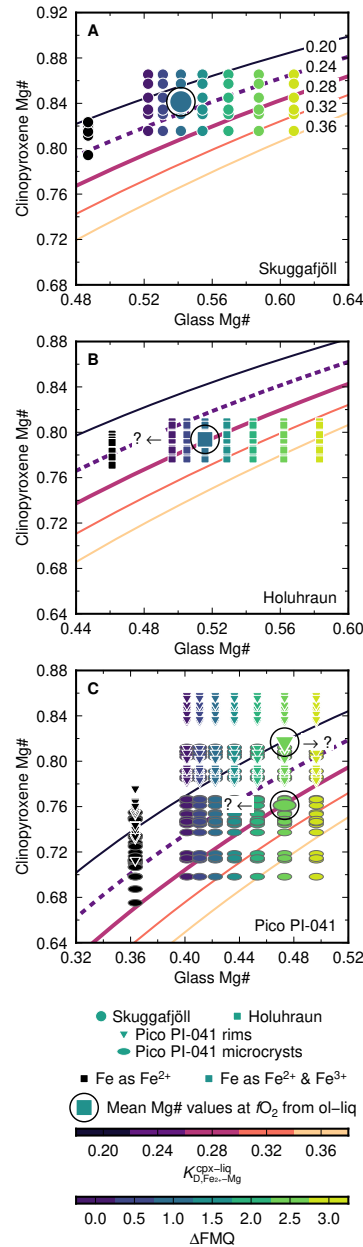


Figure 13: The effect of Fe³⁺ on Fe²⁺-Mg exchange equilibria between clinopyroxene crystals and their host glasses in samples from: (A) Skuggafjöll, Iceland (B) Holuhraun, Iceland, and (C) Pico (PI-041), Azores. Coloured lines show $K_{D,Fe^{2+}-Mg}^{cpx-liq}$ values. A nominally equilibrium value of 0.28 determined with Equation 35 of Putirka (2008) at 1200°C is shown as a thick, solid liune line; this equation assumes that all Fe is present as Fe²⁺ and thus returns $K_{D,Fe^{2+}-Mg}^{cpx-liq}$ values. A arguably more appropriate $K_{D,Fe^{2+}-Mg}^{cpx-liq}$ value of 0.24 suggested by experiments on mafic alkaline magmas is shown as a thick, dashed line (Pilet et al., 2010; Salazar-Naranjo and Vlach, 2023). Black symbols show clinopyroxene-liquid equilibria calculated assuming that all Fe occurs as Fe²⁺, as recommended by Wieser et al (2023b). Coloured symbols show values calculated with clinopyroxene Fe²⁺ contents determined by stoichiometry following Droop (1987) and liquid (i.e., glass) Fe²⁺ contents fixed at a range of different oxygen fugacity (f_{O_2}) conditions according to the model of Borisov et al (2018). Large symbols show mean clinopyroxene compositions at f_{O_2} conditions estimated via olivine-liquid equilibria (Figure 11). Arrows and question marks indicate where clinopyroxene records of f_{O_2} may deviate from olivine records, likely as a result of reductive SO₂ degassing in the cases of Holuhraun and PI-041 microcrysts.

Appendix A Scheme for assigning clinopyroxene components

The following scheme for assigning clinopyroxene components is described in Part I and repeated here for reference:

1. Calculate clinopyroxene cation fractions (X_{cation}) from oxide concentrations on a six oxygen basis
2. Determine clinopyroxene $X_{\text{Fe}^{2+}}$ and $X_{\text{Fe}^{3+}}$ contents following [Droop \(1987\)](#) encompassing the renormalisation of cations (including total Fe) by multiplying each cation by T/S as outlined in his point (iv); the total number of all original cations will now equal four and values of $X_{\text{Fe}^{2+}}$ and $X_{\text{Fe}^{3+}}$ can be used to convert FeO_T into FeO and Fe_2O_3
3. Determine the relative proportions of tetrahedral and octahedral Al ($^{\text{IV}}\text{Al}$ and $^{\text{VI}}\text{Al}$, respectively) such that $X_{^{\text{IV}}\text{Al}} = 2 - X_{\text{Si}}$ and $X_{^{\text{VI}}\text{Al}} = X_{\text{Al}} - X_{^{\text{IV}}\text{Al}}$; if X_{Si} exceeds 2 there is no $X_{^{\text{IV}}\text{Al}}$
4. Form Jd ($\text{NaAlSi}_2\text{O}_6$) from whichever is less between Na and $^{\text{VI}}\text{Al}$ such that $X_{\text{Jd}} = X_{\text{Na}}$ or $X_{\text{Jd}} = X_{^{\text{VI}}\text{Al}}$
5. Form Ae ($\text{NaFe}^{3+}\text{Si}_2\text{O}_6$) from whichever is less between Na remaining after Jd formation and Fe^{3+} such that $X_{\text{Ae}} = X_{\text{Na}} - X_{\text{Jd}}$ or $X_{\text{Ae}} = X_{\text{Fe}^{3+}}$
6. Form Np ($\text{NaFe}_{0.5}^{2+}\text{Ti}_{0.5}\text{Si}_2\text{O}_6$) from any Na remaining after Ae formation such that $X_{\text{Np}} = X_{\text{Na}} - X_{\text{Jd}} - X_{\text{Ae}}$; only relevant for alkali clinopyroxenes
7. Form Es ($\text{CaFe}^{3+}\text{AlSiO}_6$) from any Fe^{3+} remaining after Ae formation such that $X_{\text{Es}} = X_{\text{Fe}^{3+}} - X_{\text{Ae}}$
8. Form CaTs (CaAlAlSiO_6) from any $X_{^{\text{VI}}\text{Al}}$ remaining after Jd formation such that $X_{\text{CaTs}} = X_{^{\text{VI}}\text{Al}} - X_{\text{Jd}}$
9. Form CaTi ($\text{CaTiAl}_2\text{O}_6$) from any Ti remaining after Np formation such that $X_{\text{CaTi}} = X_{\text{Ti}} - X_{\text{Np}}/2$; Np is only present in alkali clinopyroxenes
10. Form CrAlTs (CaCrAlSiO_6) from Cr such that $X_{\text{CrAlTs}} = X_{\text{Cr}}$
11. Form DiHd ($\text{Ca}(\text{Mg}, \text{Fe}^{2+}, \text{Mn})\text{Si}_2\text{O}_6$) from any Ca remaining after Es, CaTs, CaTi and CrAlTs formation such that $X_{\text{DiHd}} = X_{\text{Ca}} - X_{\text{Es}} - X_{\text{CaTs}} - X_{\text{CaTi}} - X_{\text{CrAlTs}}$
12. Form EnFs ($(\text{Mg}, \text{Fe}^{2+}, \text{Mn})_2\text{Si}_2\text{O}_6$) from any Mg, Fe^{2+} and Mn remaining after DiHd formation such that $X_{\text{EnFs}} = (X_{\text{Mg}} + X_{\text{Fe}^{2+}} + X_{\text{Mn}}) - X_{\text{DiHd}}/2$