Volatile-Rich Magmas Distributed Through the Upper Crust in the Main Ethiopian Rift

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Abstract

Understanding magma storage and differentiation in the East African Rift underpins our understanding of volcanism in continental rift settings. Here, we present the geochemistry of melt inclusions erupted in Main Ethiopian Rift transitional basalts, trachytes, and peralkaline rhyolites, produced by fractional crystallization. Basalts stored on- and off-axis are saturated in an exsolved volatile phase at up to 18 km in the upper crust. Much of the CO2 outgassed from the magmas is likely lost through diffuse degassing. Observed CO2 fluxes require the intrusion of up to 0.14 km3 of basalt beneath the rift each year. On-axis peralkaline rhyolites are stored shallowly, at ~4–8 km depth. In the Daly Gap, magmas saturate in sulfide and an exsolved volatile phase, which promotes magma rise to shallower levels in the crust. Here, magmas undergo further protracted fractional crystallization and degassing, leading to the formation of a substantial exsolved volatile phase, which may accumulate in a gas-rich cap. The exsolved volatile phase is rich in sulfur and halogens: their projected loadings into the atmosphere during explosive peralkaline eruptions in the MER are predicted to be substantially higher than their metaluminous counterparts in other settings. The high fraction of exsolved volatiles in the stored magmas enhances their compressibility and must be considered when interpreting ground displacements thought to be caused by magma intrusion at depth; otherwise, intruding volumes will be underestimated. Pockets of exsolved volatiles may be present at the roof zones of magma reservoirs, which may be resolvable using geophysical techniques.

1. Introduction

An important goal of many studies of volcano-magmatic systems is to extract a record of pre-eruptive melt chemistry and use it to assess magma differentiation and the conditions of magma storage and processing in the crust. Whole-rock compositions in many cases do not represent melt compositions; they encompass not only the carrier liquid but also the crystals the magma carries. There is strong evidence that crystals in volcanic rocks are frequently not in equilibrium with their carrier melts, having been scavenged from different magmas (Davidson & Tepley, 1997; Tepley et al., 2000), crystalline mushes (Bachmann et al., 2002; Cooper & Kent, 2014), or even wall rock (Taylor, 1980). Isolation of pockets of melt trapped inside growing crystals after entrapment in relatively incompressible crystal hosts may allow the preservation of early-stage melts, isolating them from subsequent processing related to storage, ascent, and eruption (Kent, 2008; Lowenstern, 1995). If used carefully, with consideration given to post-entrapment modification (Moore et al., 2015; Steele-Macinnis et al., 2011), primary melt inclusion trace and volatile element concentrations may be used to examine differentiation processes, including mixing and degassing, during the evolution of magmas (Métrich et al., 2001; Sobolev, 1996).

Melt inclusion studies of peralkaline volcanic rocks are scarce in the literature (Barclay et al., 1996; Gioncada & Landi, 2010; Lanzo et al., 2013; Macdonald et al., 2012; Neave et al., 2012), and consequently, we have only a very limited picture of differentiation processes, conditions of pre-eruptive storage, and the volatile budget of peralkaline volcanic systems. Peralkaline melts have an excess of alkalis with respect to aluminum (molar (Na2O + K2O)/Al2O3 > 1) (Shand, 1927). The high alkali contents of the melts enhance solubility of volatiles including CO2, H2O, F, and Cl (Di Matteo et al., 2004; Scaillet & Macdonald, 2006; Shishkina et al., 2014; Webster et al., 2015). Peralkaline eruptions are predicted to release larger masses of sulfur dioxide gas into the atmosphere than their metaluminous and peraluminous counterparts owing to the combination of high sulfur concentrations at sulfide saturation (which minimizes sulfide precipitation) and high fluid/melt partition coefficients (>200) at typical magma reservoir pressures and temperatures (Scaillet & Macdonald, 2006). The systematics of halogen behavior in peralkaline melts is complex (Webster et al., 2015) and may involve saturation of a low-density vapor as well as a brine phase in the shallower...
parts of the crustal storage system, whereby the melt Cl content becomes buffered at a fixed value, which may be used to estimate magma storage depths (Balcone-Boissard et al., 2016).

Understanding the volatile budget of volcanic systems in the Main Ethiopian Rift (MER) is not only important for understanding the liquid line of descent, the outgassing potential for eruptions, and the behavior of the exsolved volatile phase in the crust but also has implications for the interpretation of geophysical monitoring signals captured there in recent years and for estimating magma budgets. Interferometric Synthetic Aperture Radar (InSAR) observations of ground deformation suggest magmatic unrest at a number of MER calderas (Biggs et al., 2011; Hutchison, Fusillo, et al., 2016; Lloyd et al., 2018); however, the compressibility of any exsolved volatile phase is an important control on ground displacements and must be understood to infer magma volumes at depth (Biggs et al., 2014; McCormick Kilbride et al., 2016). Significant diffuse soil CO2 degassing has also been observed along the MER and East African Rift System (EARS) (Hunt et al., 2017; Hutchison et al., 2015; Lee et al., 2016), testifying to the presence of unerupted magma bodies at depth. Understanding the primary melt CO2 contents of the basalts at depth may allow estimates of magma supply rate beneath the rift to be developed.

Here, we present major, trace, and volatile element data for melt inclusions from the eruptive products of five different volcanic sites: Corbetti, Kone, Fentale, and Aluto central volcanoes and the Butajira volcanic field (BVF) (Figure 1). Fractional crystallization models are constructed based on trace element mineral-melt partitioning data, using principal component analysis (PCA) of the liquid line of descent to constrain the crystallizing mineral assemblages. These models are then used, in tandem with volatile saturation models, to track volatile behavior through the evolution of the MER melts. Depths of magma storage and magma fluxes are estimated based on the abundance of H2O and CO2 in the melt inclusions and compared with barometry using clinopyroxene and melt compositions, while estimates of the mass fraction of exsolved volatiles are used to approximate the quantity of sulfur released during past eruptions. Inferences are made about the impact of an exsolved volatile phase on magma compressibility and its potential effects on ground displacements monitored at the surface.

2. Geological Setting

The MER is the northern-most portion of the EARS. Extending for ~1,000 km in a NNE-SSW direction from the Afar to the Turkana depression, it separates the Nubian and Somalian plates (Figure 1) (Mohr, 1983; Woldegabriel et al., 1990). The MER is currently undergoing active east-west extension of ~5 mm/year (Saria et al., 2014), with recent geodetic data showing that 80% of the current strain is accommodated on the Wonji Fault Belt (WFB) (Bilham et al., 1999). The WFB is a group of short N-NE trending en echelon faults that lie within a ~15 km wide axial zone in the MER (Figure 1) (Agostini et al., 2011; Keir et al., 2006). Pleistocene and Holocene volcanism has been focused within tecton-magmatic segments along the rift that are colocated with the WFB (Abebe et al., 2007; Corti, 2009; Fontijn et al., 2018).

Quaternary to recent MER volcanism is typified by peralkaline axis-central caldera systems that are located at the ends of the volcanic segments (Figure 1) (Beutel et al., 2010; Keranen et al., 2004). These areas are under reduced extensional stresses and may involve colder crust (Ebinger et al., 2008). Such conditions might hinder magma ascent and facilitate longer residence times and fractionation (Hutchison et al., 2015; Peccerillo et al., 2003). Pumice samples were selected from four different caldera systems along the length of the MER: Corbetti, Aluto, Kone, and Fentale (Figure 1). Following large (VEI > 5) caldera-forming eruptions at ~300 ka (Hutchison, Fusillo, et al., 2016), the different silicic centers have displayed variable post-caldera eruption styles (Fontijn et al., 2018). Some volcanoes have erupted predominately
rhyolite lava flows (e.g. Fentale), while others have had multiple sub-Plinian eruptions (e.g. Corbetti and Aluto) (Fontijn et al., 2018). Both syn- and post-caldera pumice samples have been investigated. The most recent deposits are the products of basaltic volcanism, with eruptions continuing at sites such as Kone and Fentale into historic times (the last eruption of both volcanoes was in 1820) (Harris, 1844). Basaltic scoria cones and associated lava flows are arranged linearly along faults and extensional fractures (Hunt et al., 2020; Rooney et al., 2011); the stress conditions located at the fault tips are thought to promote magma ascent and cone eruptions.

Recent mafic volcanism has also occurred near the western escarpment of the rift along the Silti-Debre Zeit Fault Zone (SDFZ; Figure 1) (Chernet & Hart, 1999; Rooney et al., 2005; Woldegabriel et al., 1990). Extending from 6.5°N to 9°N (Rooney et al., 2005), the SDFZ is a 2–5 km wide belt dominated by off-axis volcanic fields of basaltic scoria cones and associated lava flows (Woldegabriel et al., 1990). The BVF mafic volcanism in the region has been dated at 0.13 Ma (Woldegabriel et al., 1990) and 0.11 Ma (Chernet et al., 1998), in line with the Wonji Basalts.

3. Methods
The Corbetti pumice samples used in this study were collected by Raffaella Fusillo between 2012 and 2014 (Fusillo, 2018). The Aluto and Kone samples were collected by Karen Fontijn and Keri McNamara in November 2015 and by William Hutchison (Hutchison, 2015) and Michael Rampey (Rampey, 2005). The Aluto samples comprised one post-caldera basaltic scoria sample, one syn-caldera trachyandesite enclave, two syn-caldera welded ignimbrites, three post-caldera rhyolite lavas (glassy selvages), and four post-caldera pumices. Additional Kone samples and Fentale samples were collected by Fiona Iddon, Jonathan Hunt, and Abate Assen in October 2017, which comprised seven post-caldera basaltic scoria samples, seven syn-caldera pumice samples, one syn-caldera welded ignimbrite, and two pre-caldera glassy, silicic lava samples. Tephra samples from six scoria cones in the Butajira volcanic field (hereafter BVF) were collected by Fiona Iddon and Juliane Hubert during a sampling campaign in 2017. Additional detail on the samples and their context is given in Supporting Information S1. Olivines and quartz were handpicked from crushed material and mounted on glass slides. Crystals were manually polished to expose melt inclusions, before the crystals were extracted and mounted into epoxy blocks and polished down to a fine grade using 9, 6, 3, 1, and 0.25 μm grade diamond paste.

Melt inclusions were screened at two stages during their preparation. During initial polishing of the individual host minerals, the inclusions were examined via reflected light microscopy. Those selected for final mounting (those showing no evidence of cracking or daughter crystals) were examined using the Quanta-650F scanning electron microscope at the University of Cambridge. Back-scatter electron (BSE) images and maps of the blocks were taken under low vacuum (to avoid having to carbon coat them and risk contamination prior to secondary ion mass spectrometry analysis of CO₂). Melt inclusions that showed visible evidence of cracks, shrinkage bubbles, or post-entrapment crystallization (PEC) were avoided.

Melt inclusions and adherent matrix glasses were analyzed by secondary ion mass spectrometry using the Cameca ims-4f ion probe at NERC microanalytical facility at the University of Edinburgh for trace and volatile elements. Major elements, Cl and F, were analyzed by electron probe micro-analysis using the Cameca SX-100 Electron Probe Micro-Analyzer at the University of Cambridge. Detailed descriptions of these methods, standards used (Shishkina et al., 2010), and the associated errors are given in the Supporting Information S1.

Corrections for PEC were made for the olivine-hosted melt inclusions. Host olivine compositions were measured using electron probe micro-analysis on spots within 40 μm of the inclusion edge. A combined correction was applied for Fe-loss and PEC (Danyushevsky & Plechov, 2011). The iterative correction scheme requires knowledge of melt inclusion geochemistry, including H₂O content, host olivine Fo content, oxidation state of the melt, and the initial melt inclusion FeO content at the time of entrapment, taken as average matrix glass FeO (Putirka, 2005), resulting in corrections of <5%; for full details see Supporting Information S1. When the major element composition of the quartz-hosted inclusions was recalculated on an anhydrous basis, most do not show any depletion of silica or relative enrichment of other major elements (see Supplementary Material S1) that would reflect PEC of quartz.
4. Results

4.1. Melt Inclusion and Matrix Glass Major Element Compositions

Olivine compositions range from 58 to 77 mol% forsterite (see Data S1). The majority of host olivine cores (compositions provided in Supporting Information S1) are in equilibrium with their host melts (matrix glasses) (Roeder & Emslie, 1970), but there is some variability in olivine forsterite contents for a given melt Mg# (see Figure S4). Melt inclusion and matrix glass compositions are provided in Supporting Information S1 and Figure 2. The melt inclusion compositions are basaltic, trachybasaltic, trachytic, and rhyolitic and display a distinct Daly Gap at between ~52 and 64 wt.% SiO$_2$ (Figure 2a). All of the evolved samples are peralkaline, with most classified as pantellerites based on their high FeO concentrations (Figure 2b) (Macdonald, 1974). The Corbetti inclusions sit on the border with comendite owing to their lower FeO and high Al$_2$O$_3$ contents. The olivine-hosted melt inclusions are basalts and trachybasalts that have a transitional composition (Figure 2a).

With increasing SiO$_2$ content of the glasses, there is a corresponding increase in alkalis and a decrease in ferromagnesian, Ti, Ca, and P oxides (Figure 2). K$_2$O increases smoothly and largely linearly with SiO$_2$ content, while Al$_2$O$_3$ contents rise to ~20 wt.% before falling to <10 wt.% in the pantellerite samples (Figures 2d and 2j). Na$_2$O displays considerable variation (2.0–7.0 wt.%) across the basaltic to pantellerite glasses (Figure 2l).
BVF glasses and inclusions contain up to ~15 wt.% FeO, in contrast to Kone olivine-hosted melt inclusions, which contain between ~5 and 10 wt.% FeO contents (Figure 2e). There appears to be little variation in FeO content between the olivine-hosted and quartz-hosted melt inclusions. BVF glasses have particularly low MgO contents at <4.5 wt.%; additionally, they have low Al₂O₃ contents, at <15 wt.%, and elevated TiO₂ and P₂O₅ contents, ranging to >4 wt.% and >1.5 wt.%, respectively (Figure 2). The quartz-hosted melt inclusions show considerable compositional spread; however, the Corbetti samples are noteworthy for their low FeO and MnO contents, <5 and 0.2 wt.% respectively (Figure 2f).

### 4.2. Melt Inclusion and Matrix Glass Trace Element Compositions

Melt inclusion and matrix glass compositions are provided in Supporting Information S1. The covariation of selected trace elements with Zr, which is highly incompatible in peralkaline melts, is shown in Figure 3. The Kone and BVF mafic melt inclusion Zr contents overlap, while the matrix glasses show a slightly higher Zr content consistent with a greater degree of evolution. The Daly Gap is evident in the trace element compositions: melt inclusions with Zr contents between ~230 and ~600 ppm are sparse (Figure 3). Compatible elements show a negative correlation with Zr: e.g., Sr increases up to ~750 ppm before an inflection point at a Zr content of ~200 ppm, when feldspar begins to crystallize (Figure 3f). Incompatible elements (Rb and the Rare Earth Elements, REE) show approximately linear positive trends (Figures 3a, 3c–3e, 3g, 3h, and 3j–3q). Olivine-hosted melt inclusions from BVF and quartz-hosted melt inclusions from Fentale show a slight enrichment in Y (Figure 3m) and the HREE (Figures 3n, 3o, and 3q) over olivine-hosted melt inclusions from Kone and quartz-hosted melt inclusions from the other silicic centers. Aluto and Fentale melt inclusions show a slight enrichment in the MREE (Figures 3j–3l) relative to the quartz-hosted melt inclusions from the other silicic centers. Quartz-hosted melt inclusions and matrix glasses from Kone show a large spread in Rb contents (Figure 3a). The Rb enrichment observed in the Kone samples, as compared to the other silicic centers, is unlikely to be related to crustal contamination as Rb/Nb ratios are generally lower.
than that of the Precambrian crustal rocks (Peccerillo et al., 1998) (Figure 3r). Ba (Figure 3b) and Eu (Figure 3i) contents show scatter when plotted against Zr, particularly for the quartz-hosted melt inclusions: melt inclusions contain 12–1,200 ppm for Ba and 1.5–15 ppm for Eu. The Fentale samples that show high Ba and Eu concentrations do not show any notable enrichment or depletion in Rb concentrations relative to quartz-hosted melt inclusions from the other silicic centers (Figure 3a).

4.3. Melt Inclusion and Matrix Glass Volatile Concentrations

Melt inclusion and matrix glass volatile compositions are provided in Supporting Information S1. Melt inclusion H2O contents range from ~2 to <0.5 wt.% in the BVF and the Kone olivine-hosted melt inclusions (Figure 4a). There is a large spread in the H2O contents of the quartz-hosted melt inclusions, from <2 to 8 wt.% H2O (Figure 4a). Fentale and Corbetti melt inclusions contain H2O contents up to 4 wt.%. Matrix glasses typically contain <0.05 wt.% H2O.

Olivine-hosted melt inclusion CO2 contents range from <500 to >3,000 ppm over a Zr range of 55–220 ppm in the mafic samples (Figure 4c). BVF melt inclusions show slightly higher CO2 contents of up to 5,000 ppm (Figure 4c). The quartz-hosted melt inclusions contain between ~100 and ~300 ppm CO2 (Figure 4c). Matrix glasses have very low CO2 contents, below detection limits (Figure 4c). Melt halogen contents increase with Zr concentration: Cl and F increase from 130 to ~1,000 ppm and <900 to ~1,500 ppm respectively as Zr increases from 55 to 220 ppm (Figures 4e and 4f). There is a decrease in the gradient on the halogen vs. Zr plots in the quartz-hosted melt inclusions relative to the olivine-hosted melt inclusions. Melt Cl contents reach up to 4,000 ppm in the most evolved samples, while F contents reach up to 7,000 ppm, though the data set shows some spread (Figures 4e and 4f). Corbetti samples show particularly low halogen contents, with Cl <1,900 ppm and F <2,700 ppm; Fentale samples show low F contents (<3,750 ppm) (Figures 4e and 4f).

Olivine-hosted melt inclusions show a positive correlation between melt sulfur contents and Zr, increasing from ~2,000 to ~3,000 ppm S with increasing Zr (Figure 4d). The quartz-hosted melt inclusions contain up to ~600 ppm S, and S does not correlate with Zr (Figure 4d). In contrast to the halogens and sulfur, Li and B increase linearly with melt Zr contents, reaching up to ~50 and ~20 ppm, respectively (Figures 4g and 4h). There is some spread in the Li data set, with the most evolved samples showing values of >50 and up to 200 ppm (Figure 4h). The Corbetti melt inclusions have the lowest Li and B concentrations (Figures 4g and 4h).

5. Discussion

5.1. Characterization of the Liquid Line of Descent for Peralkaline Magmas of the MER

Melt inclusion major and trace element data (Figures 2 and 3) are consistent with pantelleritic magmas being derived via protracted fractional crystallization of a basaltic parental melt, as has been proposed in previous studies (Hutchison et al., 2018; Iddon et al., 2019; Peccerillo et al., 2003). However, there is some variance in the trace element systematics, e.g., changes in slope with increasing Zr, or variability at fixed Zr outside the analytical error (Figure 3).

Fractional crystallization models were constructed to characterize the liquid line of descent to confirm the relationship between the basaltic and pantelleritic samples (Figure 3). The proportion of crystallizing phases required to describe the liquid line of descent observed in the major element data was determined using PCA (Maclennan et al., 2001; Neave et al., 2012) (Supporting Information S1). The Kone sample set was used for PCA as it is most complete. Results for the other sample sets are provided in Supporting Information S1. The results of the analysis suggest that the mafic data array can be explained by the progressive removal of up to 59% clinopyroxene (En32Wo53Fs15), 40% plagioclase feldspar (An85Ab15Or0.4), 0.8% olivine (Fo75), and 0.4% magnetite and accessory apatite. The change in melt composition over the Daly Gap may be explained by the removal of 54% plagioclase (An85Ab15Or0.4), 32% clinopyroxene (En32Wo53Fs15), 8% olivine (Fo90), 5% magnetite, and 1%apatite. The trachytic array may be explained by the removal of 85% alkali feldspar (An32Ab74Or24), 11% fayalite (Fo1.3), 0.3% pyroxene (En3Wo4Fs52), 2% ilmenite, and 1%apatite. The rhyolitic array may be explained by the removal of 78% alkali feldspar (An2Ab74Or24), 3% pyroxene (En3Wo4Fs52), and 19% aenigmatite. PCA root mean square fits are 1.4 × 10−8, 1.1 × 10−10, 1.8 × 10−9, and 0.002, respectively. Lower numbers indicate better fits, values <0.01 are deemed reasonable.
These results are consistent with fractional crystallization models produced for pantellerite magmas in other studies. For example, Peccerillo et al. (2003) modeled a fractionation assemblage made up of 85–90% alkali feldspar, 10% clinopyroxene, 2% fayalite, and 2% Fe-Ti oxides, in the later stages of melt evolution at
Geochemistry, Geophysics, Geosystems

5.2. Modeling Trace Element Behavior

To model trace element behavior during fractional crystallization of MER magmas, the Rayleigh fractional crystallization equation was used:

\[
\frac{C_i}{C_i^0} = F^{D-1},
\]

where \( i \) is the element of interest, \( C_i^0 \) is the original concentration of element \( i \) in the parental liquid, \( C_i \) is the concentration in the liquid, \( D \) is the solid–melt partition coefficient, and \( F \) is the fraction of liquid remaining. Bulk partition coefficients were calculated based on the phase assemblages predicted down the liquid line of descent and observed mineral-melt partitioning data collated from (Bacon & Druitt, 1988; Bindeman & Davis, 2000; Blundy & Wood, 1991; Bougault & Hekinian, 1974; Dawson & Hinton, 2003; Ewart & Griffin, 1994; Fujimaki, 1986; Gaetani & Grove, 1995; Green et al., 1993; Henderson & Pierozynski, 2012; Hill et al., 2000; Klemme & Dalpé, 2003; Larsen, 1979; Lemarchand et al., 1987; Luhr et al., 1984; Mahood & Stimac, 1990; Mathez & Webster, 2005; McCubbin et al., 2015; Nagasawa, 1970; Nagasawa & Schnetzler, 1971; Neave et al., 2012; Nikogosian & Sobolev, 1997; Parat & Holtz, 2004; Paster et al., 1974; Peccerillo et al., 2003; Stix & Gorton, 1990; Villemant, 1988; Villemant et al., 1981; Webster et al., 2009; Webster et al., 2017; White et al., 2009; Wood & Triglia, 2001). See Supporting Information S1 for the full list of partition coefficients used. Feldspar-melt partition coefficients for Sr, Ba, and Rb were additionally calculated using empirically determined equations for plagioclase from (Blundy & Wood, 1991) and (Henderson & Pierozynski, 2012). As Zr is highly incompatible in peralkaline rocks, it was used as a fractionation index. The trachytic samples can be generated by ~85% fractional crystallization of the mafic parental melts. The pantelleritic rhyolites require a further 40% crystallization. The total amount of fractional crystallization required is therefore ~91%. Peccerillo et al. (2003) and (Gleeson et al. (2017) estimated that pantellerites from Gedemsa and Aluto could be generated from a basaltic parent after ~90% fractionation. The pantellerites continue to fractionate, with a total fractionation of 93–94% predicted for some samples (Figure 4).

Incompatible trace element variations are well explained by protracted fractional crystallization of a basaltic parent (Figure 3). The slight deviation from linear patterns can be explained by the crystallization of apatite, which has high partition coefficients for REE of ~7–40 (Mahood & Stimac, 1990). Variations in apatite crystallization cannot account for the enrichment in just the medium and heavy REEs seen in the Aluto, BVF, and Fentale samples (Figure 3). Reduced clinopyroxene fractionation may also occur during this interval. Clinopyroxene-melt partition coefficients for the medium and heavy REEs become larger as the pyroxene Na content increases. The pyroxenes evolve eventually to aegirine augites in peralkaline systems (Fedele et al., 2009; Marks et al., 2004). This is due to an increased preference for these elements in the mineral structure (Marks et al., 2004).

The compatible trace elements are consistent with fractional crystallization. Plagioclase-melt partition coefficients for the Large Ion Lithophile Elements (LILEs) are controlled by feldspar An content and temperature (Blundy & Wood, 1991). Alkali feldspar-melt partition coefficients for Ba and Sr are controlled by melt peralkalinity and temperature; for Rb, they are controlled by mineral Or content (Henderson & Pierozynski, 2012). The spread in Rb, Ba, (Figure 3), and Eu (Supporting Information S1) may be explained by variable amounts of feldspar crystallization, as well as changing partitioning behavior during the evolution between basaltic and trachytic melts. The greater spread in Ba in the most evolved samples is consistent with variability in the partition coefficients in line with observed variations in melt peralkalinity (Figure 3b) (Henderson & Pierozynski, 2012). The observed variation in feldspar Or content cannot, however, account for the spread in Kone Rb data (Figure 3a), suggesting additional sources of enrichment/depletion.
The effect of feldspar resorption was modeled for Ba and Rb, both strongly compatible in feldspar (Figures 3a and 3b). Feldspar Ba compositions from the Afar were used for the modeling (Barberi et al., 1975). While the large spread in Ba for both Kone and Fentale quartz-hosted melt inclusions is consistent with small amounts of feldspar resorption (~10–20%), the model for Rb does not produce such a good fit for the Kone melts (Figures 3a and 3b). Alkali feldspar resorption occurred in the central Kenya peralcaline province, based on anomalous Ba enrichments (Macdonald & Bagiński, 2009). Peccerillo et al. (2003) have linked high Ba concentration in trachytes from Gedemsa to feldspar accumulation.

5.3. Reconstructing Primary Melt Volatile Contents and Degassing Behavior

5.3.1. H2O and CO2 Systematics and Estimates of Magma Storage Depths

Volatile elements will behave like incompatible elements during fractional crystallization if the melts are volatile undersaturated. Mineral-melt volatile partitioning is assumed to be negligible in most phases. Partitioning of water into apatite, as a nominally hydrous mineral with an affinity for halogens, was considered (Mathez & Webster, 2005; Webster et al., 2009). Fractional crystallization models for H2O and CO2 are marked on Figures 4a–4c; the data lie far below the modeled liquid line of descent, suggesting that the melts were saturated with an exsolved volatile phase during fractionation, even for the most primitive melts. The range in CO2 contents is largely due to degassing CO2 into an exsolved volatile phase; there may also, however, be some sequestration of CO2 into a shrinkage bubble (Hartley et al., 2014), perhaps driven by PEC.

The pressure dependence of H2O-CO2 solubility (Papale, 1999) suggests that the on-axis evolved silicic melts, from Figure 5b, are stored at lower pressures in the crust than the mafic parental melts (Figure 5a). The olivine-hosted melt inclusions from the on-axis volcanic center (Kone) record volatile contents consistent with storage pressures of up to ~350 MPa (Figure 5a), equivalent to a depth of ~13 km in the crust assuming an average crustal density of 2,800 kgm m−3 (Wilks et al., 2017), and a temperature of 1170°C, estimated based on clinopyroxene-liquid thermometry (Iddon et al., 2019). The quartz-hosted melt inclusions from the on-axis centers record volatile contents consistent with storage pressures of up to ~300 MPa (Figure 5b), equivalent to a depth of up to ~11 km in the crust, assuming a temperature of ~765°C (Gleeson et al., 2017) (upper bounds). There is significant overlap between both data sets, but this may be due to post-entrapment modification of CO2 contents in the olivine-hosted melt inclusions, H+ loss from the inclusions (Bucholz et al., 2013), or to magmas being stored at a range of depths. Corbetti and Fentale quartz-hosted melt inclusions record slightly lower values for H2O at similar CO2 contents to the Kone and Aluto samples, which might suggest shallower storage pressures of ~170 MPa (Figure 5b), equivalent to a depth of 6 km in the crust.

The olivine-hosted melt inclusions from the off-axis BVF volcanic field record volatile contents consistent with slightly deeper storage pressures of up to ~500 MPa (Figure 5a), equivalent to a depth of 18 km in the crust, assuming a temperature of 1170°C (Iddon et al., 2019). These depth estimates are consistent with the suggestion of deeper fractionation of off-axis melts (Rooney et al., 2007). Using a structural clinopyroxene-only geobarometer (Nimis & Ulmer, 1998) Rooney et al. (2007) estimated storage depths of <10 km for the axis-central WFB basalts but storage depths of up to 35 km for the off-axis melts. Our estimates of storage depths based on H2O-CO2 barometry are minima. Clinopyroxene-liquid geobarometry (Neave & Putirka, 2017) indicates deeper storage of Kone mafic melts, at up to 21 km (Iddon et al., 2019). Basalts appear to be sourced from complex, multileveled storage systems both on and off the rift axis.

The melt inclusions show evidence of extensive degassing. We may use the ratios of volatile to nonvolatile elements that are thought to behave similarly (i.e., during crystallization and melting) to estimate original H2O and CO2 concentrations in primitive basalt melts (Rosenthal et al., 2015). Ratios of CO2 to incompatible elements such as Nb (Saal et al., 2002) or Ba (Hauri et al., 2019; Le Voyer et al., 2017) are typically used to make estimates of primary melt CO2. Ratios of H2O to LREEs (La, Ce, and Nd) are used to make estimates of primary melt H2O (Dixon et al., 2002; Michael, 1995). Rosenthal et al. (2015) suggest a range of CO2/Ba ratios for nonenriched and enriched depleted mantle (DMM) from ~130 to ~150 (Figure 6a). Saal et al. (2002) and Le Voyer et al. (2017) suggest values closer to 100 (Figure 6a). Assuming CO2/Ba ratios of 100 and 140 (Figure 6a) the on-axis WFB basalt primary melt is estimated to have contained 1.8 and 2.5 wt.% CO2, respectively. The off-axis primary melt is estimated to have contained between 0.7 and 1 wt. % CO2. These estimates suggest that between ~1.5 and ~2.2 wt.% CO2 has been lost from the WFB basalts.
prior to eruption and presumably prior to fractionation and between ~0.2 and ~ 0.5 wt.% CO₂ is estimated to have been lost from the off-axis melts prior to eruption.

Estimates of H₂O/Ce for depleted mantle range from 150 ± 10 (Dixon et al., 2002) to 245 ± 12 (Le Voyer et al., 2017) (Figure 6b). If we assume similar primary melt ratios for the MER melts, the WFB basalt primary melt is estimated to have contained 0.8–1.2 wt.% H₂O. The off-axis primary melt is estimated to have contained between 0.6 and 0.8 wt.% H₂O. This suggests that minimal H₂O has been lost from the basalts prior to eruption (which is consistent with the high pressure of storage and high solubility of H₂O) or that the H₂O/Ce ratios presented in the literature are inappropriate for continental rift settings. In all likelihood, this applies to the CO₂/Ba ratios as well. Global variation in H₂O/Ce ratios are apparent, with a much higher H₂O/Ce ratio of 400 reported for HIMU-influenced (high μ, with a particularly radiogenic Pb isotope composition) Mid-Ocean Ridge Basalts (MORB) from the equatorial Atlantic (Kendrick et al., 2017) and for basalts sourced from “plume” mantle sources (Hauri et al., 2019). Ethiopian basalts are thought to be derived from melting induced by the impact of a plume at the base of the subcontinental lithospheric mantle (Rooney et al., 2011).

5.3.2. Sulfur Degassing and Sulfide Saturation

Fractional crystallization models reproduce the sulfur concentrations in the olivine-hosted melt inclusions but significantly overpredict the sulfur contents of the quartz-hosted melt inclusions (Figure 4d). The behavior of sulfur is complex; at sulfide saturation, it partitions between an exsolved volatile phase as well as an immiscible sulfide liquid or mineral phase, depending on temperature, or a sulfate-bearing phase depending

FIGURE 5. Plots of melt CO₂ content versus melt H₂O content (wt.%) for (a) olivine-hosted melt inclusions and (b) quartz-hosted melt inclusions. Melt storage pressure conditions estimated using Papale (1999). Isobars for mafic melt storage were calculated based on a temperature of 1170°C (Iddon et al., 2019) and for evolved melt storage a temperature of ~765°C (upper bounds) (Gleeson et al., 2017) was assumed. (c) Depths of magma storage (assuming a crustal density of 2,800 gm³) (Wilks et al., 2017) plotted against longitude.

FIGURE 6. Ratios of volatile to non-volatile incompatible elements in Main Ethiopian Rift melt inclusions. (a) CO₂/Ba ratios are used to estimate original CO₂ concentrations in primary melts; ratios for enriched (Rosenthal et al., 2015) and non-enriched primary melts (Saal et al., 2002) are shown by dashed lines. (b) H₂O/Ce ratios are used to estimate original H₂O concentrations in primary melts; estimates of primary melts (Dixon et al., 2002; Le Voyer et al., 2017) are shown by dashed lines.
on redox conditions. Under reducing conditions sulfide ($S^{2−}$) is the dominant sulfur species (Carroll & Rutherford, 1987; Mavrogenes & O’Neill, 1999). At higher oxidation states, $S^{6+}$ becomes the dominant species (Fortin et al., 2015; Jugo, 2009; Li et al., 2009). Our data suggest that sulfur behaves incompatibly in the mafic melts (i.e., the melt does not reach saturation in either a solid or liquid immiscible sulfide/sulfate phase nor an exsolved sulfur-bearing volatile phase) before concentrations drop dramatically in the quartz-hosted melt inclusions, down to <0.2 wt.% (Figure 4d).

The sulfur concentration at sulfide saturation (SCSS) was estimated using a number of models (Fortin et al., 2015; Li et al., 2009) (Figure 4d). The oxygen fugacities of MER magmas are thought to be within one log unit of the quartz-magnetite-fayalite (QFM) buffer (QFM to QFM + 1; Gleeson et al., 2017; Iddon et al., 2019; Peccerillo et al., 2003; Rooney et al., 2007; Rooney et al., 2012). Temperatures of 1170°C (Iddon et al., 2019) and 765°C (Gleeson et al., 2017) (upper bounds) and pressures of 300 and 220 MPa were assumed for the mafic and silicic compositions, respectively (Figure 4d). The modified Li et al. (2009) model (Gleeson et al., 2017) shows the SCSS is higher than the sulfur concentration in the olivine-hosted melt inclusions, before dropping to closely follow the concentrations in the quartz-hosted melt inclusions. These trends indicate that melts reach sulfide saturation somewhere in the Daly Gap.

However, for the oxygen fugacity prevalent in MER magmas (~QFM) (Gleeson et al., 2017; Iddon et al., 2019; Peccerillo et al., 2003; Rooney et al., 2007; Rooney et al., 2012), the model by Jugo et al. (2010) is preferred. It links the SCSS with sulfur content at anhydrite saturation, predicting an exponential increase in the SCSS with increasing $fO_2$ from QFM because of the contribution of sulfate (Jugo et al., 2010). Model results for an $fO_2$ of QFM are similar, this time plotting much higher than the sulfur concentration in the olivine-hosted melt inclusions, but again following the sulfur concentration in the quartz-hosted melt inclusions (Figure 4d). The depletion of chalcophile elements such as copper observed in the peralkaline rhyolites (see Supporting Information S1) provides further evidence for the formation of a liquid immiscible or accessory mineral, such as mica (Iddon et al., 2019), which may not be captured. Here, we consider the loss of chlorine to an exsolved volatile phase as the dominant process causing melt depletion in chlorine.

Supporting Information S1 for partition coefficients, but there may be loss to some other chlorine-bearing accessory mineral, such as mica (Iddon et al., 2019), which may not be captured. Here, we consider the loss of chlorine to an exsolved volatile phase as the dominant process causing melt depletion in chlorine.

Once there is a free exsolved volatile phase, sulfur will further partition into it. Scaillet and MacDonald (2006) investigated experimentally the partitioning of sulfur between melt and sulfide/sulfate-bearing phases. For a pantellerite at temperatures of 765°C and an $fO_2$ of QFM, a fluid-melt partition coefficient, $D_f = m$, of ~50 might be expected (Scaillet & Macdonald, 2006). Experiments suggest that after 80% crystallization of a basaltic alkaline melt containing 1,000 ppm S and 1 wt.% H$_2$O, between 60 and 90% of the bulk sulfur partitions into the aqueous fluid. We calculate the mass of sulfur that partitions into the fluid phase using the difference between the fractional crystallization model and the observed melt S concentrations. The bulk sulfur contents in the melt-sulfide-exsolved volatile phase after 94% crystallization would be ~6 wt.%. This sulfur is partitioned between the melt sulfur, solid and liquid immiscible sulfur-bearing phases, and the exsolved volatile phase. For an average melt S content of 340 ppm in the peralkaline rhyolitic melts, an exsolved volatile phase might contain 1.7 wt.%, with the remaining 4.3% sequestered in the solid and/or liquid immiscible sulfur-bearing phases.

### 5.3.3. Behavior of Halogens and Lithium During Differentiation and Degassing

Fractional crystallization models reproduce well the incompatibility of Cl in the mafic melts; however, they fail to predict the lower chlorine concentrations observed in the evolved peralkaline melts (Figure 4e), which suggests that chlorine is being lost to another phase. Cl partitioning into apatite is included in the model (see Supporting Information S1 for partition coefficients), but there may be loss to some other chlorine-bearing accessory mineral, such as mica (Iddon et al., 2019), which may not be captured. Here, we consider the loss of chlorine to an exsolved volatile phase as the dominant process causing melt depletion in chlorine.

The solubility of Cl in silicate melts has a complex pressure dependence. At pressures >200 MPa, it shows a negative dependence, becoming increasingly soluble in silicate melts with decreasing pressure; however, this changes to a positive dependence at pressures <200 MPa (Lukanin, 2015, 2016). In a closed system, where the exsolved volatile phase is not lost, this relationship can reverse again at even shallower pressures (Lukanin, 2015, 2016); this may account for the continued, if slightly subdued, rise in melt Cl contents following the Daly Gap (Figure 4e). However, H$_2$O-CO$_2$ solubility relationships indicate that many of the...
quartz-hosted melt inclusions were trapped at pressures >150 MPa (Figure 5b). Cl solubility shows a strong compositional dependence, becoming increasingly soluble with increasing melt alkali content and decreasing silica activity (Carroll, 2005). The influence of the negative temperature dependence on Cl solubility is also amplified in alkali-rich melt compositions (Carroll & Webster, 1994). The quartz-hosted melt inclusions show a positive correlation between melt Cl concentration and peralkalinity (Figure 7a).

Published experimental data for silicate melts coexisting with low-Cl fluids or with supercritical Cl-bearing fluids show that Cl partitions strongly into aqueous fluids relative to silicate melts by a factor of \( \sim 20-300 \) (Kilinc & Burnham, 1972). For low bulk Cl contents, Cl concentrations decrease in rhyolitic melts coexisting with a single aqueous fluid phase as pressure increases from 200 to 800 MPa and the fluid/melt partition coefficient for Cl increases with increasing pressure. However, with increasing concentration of Cl in the solution at pressures below \( \sim 200 \) MPa, the binary system \( \text{H}_2\text{O}-\text{NaCl} \) is characterized by an immiscibility gap (a subcritical region) where a Cl-poor aqueous fluid coexists with a Cl-rich hydrosaline brine (Carroll, 2005). The compositions of the aqueous fluid and the brine are invariant at constant pressure and temperature, which means that Cl and H\(_2\)O concentrations in the fluids and the coexisting silicate melt will be fixed (Gibbs’ phase rule) (Balcone-Boissard et al., 2016; Signorelli et al., 2001). A constant Cl concentration in the melt as more Cl is added to the system is the typical expression of the melt being saturated with both a hydrosaline liquid and an H\(_2\)O-rich aqueous fluid, and this behavior defines the solubility limit for Cl (Carroll, 2005; Shinohara, 1994; Signorelli & Carroll, 2002).

The MER data show an increase in Cl with melt evolution, with no plateau, suggesting that perhaps, formation of a chlorine-bearing hydrosaline brine does not occur at the pressures of melt inclusion entrapment (Figure 4e). The Cl solubility model by Webster et al. (2015) was established using experiments in which the solubility of Cl was determined for silicate melts saturated in a hydrosaline brine, with or without a coexisting vapor phase. The modeled Cl solubilities, assuming temperatures of 1170°C (Iddon et al., 2019) and

FIGURE 7. Halogen contents against peralkalinity in (a and b) Main Ethiopian Rift melt inclusions, expressed as the agpaitic index (A.I., defined by molar (Na + K)/Al) and (c and d) H\(_2\)O contents.
765°C (Gleeson et al., 2017, upper bounds) and pressures of 300 MPa and 220 MPa for the mafic and silicic compositions respectively, are much higher than the observed data for the MER melt inclusions (Figure 4e). This suggests that hydrosaline brine formation does not occur. Instead, the trends in the data are consistent with the partitioning of chlorine into an exsolved supercritical fluid phase.

The fractional crystallization models accurately reproduce the incompatibility of F in the mafic melts but fail to predict the lower F contents in the evolved peralkaline melts (Figure 4f). As F partitioning into apatite is considered by the crystallization model, and there is no evidence for fluorine-bearing phases such as fluorite; loss to an exsolved volatile phase is considered. F solubility is generally high in silicate melts but could be reduced by the rapid increase in SiO₂ driven by fractional crystallization over the Daly Gap (Figure 2). Increasing melt polymerization has been linked to increased F partitioning into an exsolved volatile phase (Bailey, 1977; Martini, 1984). The low halogen contents of melt inclusions at Corbetti relative to the other data sets may be a consequence of lower melt peralkalinity (Figures 4e and 4f). This cannot account for the situation at Fentale where Cl contents, along with melt peralkalinity, are in line with Kone and Aluto samples (Figure 4e).

The total mass of chlorine and fluorine partitioned into the aqueous fluid phase may be estimated using the difference between the fractional crystallization models and the observed concentrations. This analysis yields apparent fluid-melt partition coefficients (Df⁻m) of 1.75 for F and 3 for Cl, consistent with experimentally determined results (Borodulin et al., 2009; Iveson et al., 2017). Borodulin et al. (2009) carried out experiments on F partitioning between high-silica peralkaline rhyolites and aqueous fluids at 750°C and 100 MPa suggesting a Df⁻m of 1.7 ± 1.6. Iveson et al. (2017) conducted experiments at 810–860°C,150–405 MPa, and fO₂ NNO – 0.5 to NNO + 2 on hydrous rhyodacites showing that Cl strongly partitions into a fluid over a melt phase with a Df⁻m ranging from 3.5 to 22.7. This partitioning of Cl into an exsolved volatile phase is thought to remain >700 MPa at lower pressures, partitioning toward melt has been observed to increase (Kilinc & Burnham, 1972). Figures 7c and 7d show the relationship between the halogens and melt H₂O contents. Constant melt Cl and F above 2 wt.% H₂O demonstrates that melt concentrations are being buffered by a single supercritical fluid phase.

While the fractional crystallization model provides a reasonable fit to the observed Li data, suggesting it behaves relatively incompatibly, the spread in the data might be explained by semivolatile behavior (Figure 4h). Some of the quartz-hosted melt inclusions show Li enrichment over that predicted from fractional crystallization, examples from Fentale show a corresponding slight enrichment in CO₂ and depletion in H₂O in comparison to the other datapoints. Li is complex, as at shallow crustal pressures, it can partition into a number of mineral phases (Bindeman & Davis, 2000; Nikogosian & Sobolev, 1997), but has also been observed to behave as a volatile element in some H₂O-rich magmas. It has been suggested that Li may diffuse into an exsolved volatile phase as rapidly as water (Koga et al., 2008), while other experimental studies have shown that in silica-rich magmas, Li will preferentially partition into a volatile-bearing fluid over the melt (Kent et al., 2007), particularly in the presence of chlorine (Webster et al., 1989). At Mount St Helens, melt inclusion enrichment in Li has been attributed to shallow accumulation of CO₂-rich fluids from deeper degassing magmas and rapid diffusive reequilibration of the melt inclusions (Berlo et al., 2004). At Pantelleria, Neave et al. (2012) explain Li enrichment in melt inclusions by entrapment in the presence of a Cl-rich brine.

5.4. Predicted Volatile Outgassing During Explosive MER Peralkaline Eruptions
If we assume that the system is closed with no passive degassing, the fractional crystallization models for Kone may be used to calculate the volume of pre-eruptive volatiles exsolved during the evolution from a basaltic parent to a pantelleritic rhyolite melt. The proportions of the different volatile species in the exsolved volatile phase can also be estimated. The H₂O contents of the basaltic parental melts is ~1.2 wt.%, which, under conditions of no degassing and complete incompatibility, would increase to 55 wt.% in the residual melt after ~94% crystallization (Figure 4b). The melts actually hold ~7 wt.% H₂O after 94% crystallization at 220 MPa (Figure 5b), which means that the remainder has exsolved for these pressure conditions. In reality, migration of an exsolved volatile phase would likely occur over long timescales during fractionation. For this reason, we predict the mass of the H₂O and CO₂ in the pre-eruptive exsolved volatile phase in the peralkaline rhyolite based on the quartz-hosted melt inclusions alone, assuming that any exsolved volatiles that...
existing prior to the Daly Gap will have been lost to outgassing during decompression of the low viscosity melt on ascent to shallower storage regions and over the long course of evolution (Figures 4a and 4c). The pervasive loss of deep-derived exsolved volatiles from stored magmas is consistent with the diffuse degassing of a CO$_2$-rich magmatic gas observed over much of the MER (Hunt et al., 2017; Hutchison, Fusillo, et al., 2016). We calculate that, after fractionation from trachytic to evolved pantelleritic melt (~60% crystallization) and with no degassing, H$_2$O contents would rise from 7 to 17 wt.%, and CO$_2$ contents would rise from 0.02 to 0.05 wt.%. As the melts hold ~7 wt.% H$_2$O and ~0.025 wt.% CO$_2$ after 94% crystallization at 220 MPa (Figure 5b), this means that ~10 wt.% H$_2$O and ~0.025 wt.% CO$_2$ will have been exsolved from the rhyolite for these pressure conditions.

Using the same method for the halogens, but assuming volatile retention in the mafic melts (Figures 4e and 4f), we find that this exsolved volatile phase will also contain 0.7 wt.% F and 0.6 wt.% Cl. Exsolved S contents of 1.7 wt.% were estimated based on measured values of ~340 ppm in melt inclusions and experimental fluid-melt partition coefficients (Scaillet & Macdonald, 2006). We therefore estimate that a total exsolved volatile phase of ~13 wt.% may develop during late-stage fractionation crystallization, which is equivalent to ~4.5 vol. % (from the Ideal Gas Law) at a pressure of 220 MPa and temperature of 765°C (Gleeson et al., 2017, upper bounds).

The mass of the exsolved volatile phase may be used to make estimates of the potential yield of an explosive peralkaline eruption at one of the MER calderas. Caldera-forming eruptions may have produced >10 km$^3$ eruptive volume (Hutchison, Biggs, et al., 2016). Assuming an average bulk magma density of 2,300 kg/m$^3$, we calculate a volatile yield of 2,300 Mt of H$_2$O (where 1 Mt is equal to 1 × 10$^{12}$ kg), 6 Mt of CO$_2$, 390 Mt of S, 150 Mt of F, and 150 Mt of Cl for an eruption of 10 km$^3$ peralkaline magma. An additional component from syn-eruptive degassing by exsolution can also be estimated, recorded in the difference between the matrix glass and melt inclusion compositions. While F and Cl contents appear similar, matrix glasses show on average a ~50 ppm difference in S. Assuming that melt H$_2$O and CO$_2$ retention at atmospheric pressure is minimal, a melt fraction of 65 vol.% for the erupted magma and a melt density of 2,275 kg/m$^3$, a syn-eruptive degassing (from exsolution) of 365 MT of H$_2$O, 1 Mt of CO$_2$, and 0.5 Mt of S is estimated. This brings the estimated total volatile yield for an explosive peralkaline eruption to 2,665 Mt of H$_2$O, 7 Mt of CO$_2$, 390.5 Mt of S, 150 Mt of F, and 150 Mt of Cl for eruptions of 10 km$^3$. Post-caldara eruptions are much smaller (between 0.01 and 1 km$^3$) (Hutchison, Biggs, et al., 2016) and are typically crystal poor. Making similar assumptions, but with a melt fraction of 90 vol.% for the erupted magma, the estimated total volatile yield for a post-caldara peralkaline eruption would be 3–265 Mt of H$_2$O, <0.01–0.7 Mt of CO$_2$, 0.4–40 Mt of S, 0.2–15 Mt of F, and 0.2–15 Mt of Cl.

The much larger Tambora eruption of 1815 (~50 km$^3$) (Oppenheimer, 2003) is thought to have released ~100 Mt of Cl, 70 Mt of F, and 60 Mt of S (Self et al., 2004), and the S release from Mount Pinatubo (~20 km$^3$) has been estimated at 10 Mt (Gerlach et al., 1996; Wallace & Gerlach, 1994). This suggests that the output of S and halogens may be more significant from peralkaline eruptions, such as those during the formation of the MER calderas, than from their metaluminous and peraluminous counterparts. Neave et al. (2012) highlighted this in their estimates of the S yield from Pantelleria, predicting the release of 80–160 Mt of S during the eruption of the 7 km$^3$ Green Tuff. They interpreted the higher yields of sulfur as relating to high sulfur concentrations at sulfide saturation combined with high fluid/melt partition coefficients, allowing peralkaline melts to retain sulfur for longer during their early differentiation and then release it into aqueous exsolved fluids (Scaillet & Macdonald, 2006). Alkali-related halogen retention and high initial parental melt volatile contents, perhaps due to small fraction melting of enriched subcontinental lithospheric mantle, may also play a role in increasing predicted volatile outputs. Our results further suggest that large, explosive continental rift-related eruptions may be significant sources of HCl into the upper troposphere or stratosphere. Injection of HCl into the stratosphere has also been linked to the ozone destruction and, in the troposphere, to the production of acid rain (Kutterolf et al., 2013).

### 5.5. Implications of Our Results for MER Magma Storage

We interpret the behavior of the volatile species, in particular the timing of volatile saturation and the various controls on melt volatile solubilities, as providing evidence for a vertically extended magmatic storage system beneath the MER (Figure 8). Mafic magma batches, both on- and off-axis, are stored at depths
extending down to 18 km in the crust, and potentially deeper, where they are saturated with an exsolved volatile phase (Figure 5a). Over the course of the Daly Gap, from which melts are not preserved, on-axis magmas saturate in sulfide (which may settle out) and an exsolved volatile phase within the Daly Gap, which may promote magma buoyancy and rapid rise through the crust. Beneath the axis-central calderas melts rise to 6–8 km depth, where they begin to fractionate. Highly evolved residual liquids (peralkaline rhyolites) develop in an extensive mush-rich reservoir and a volatile-rich roof zone may form. Mafic melts are forced to erupt around the shadow zone, external of caldera margins. Mafic recharge may also result in the fluxing of deep CO₂ and Li-rich fluids to shallower levels. The exsolved volatiles are thought to interact with active hydrothermal systems, while intense pre- and syn-rift faulting also likely aids outgassing (white arrows).

Magmatic evolution at multiple storage depths has been proposed for other peralkaline systems in the MER and wider EARS based on petrological evidence. Rooney et al. (2012) suggested a two-step polybaric process at Chefe Donsa, with fractionation of basalts at mid-upper crustal depths occurring prior to extraction and ascent of those liquids to form a second trachytic-rhyolitic fractionating storage region. Rooney et al. (2012) highlight the importance of exsolved volatiles in controlling the eruptibility of intermediate magmas. MacDonald et al. (2008) postulate that a region of several dynamic, interacting, and independent...
reservoirs and conduits, stretching down to depths of 10 km in the crust, feeds the Greater Olkaria volcanic complex. Again, they highlight the influence of an exsolved volatile-rich phase, with negative Ce anomalies linked to an oxidizing, halogen-rich exsolved volatile phase (Macdonald et al., 2008). Direct evidence of volatile loss is also observed, with vesiculation common at the borders between magmatic inclusions and comenditic hosts (Macdonald et al., 2008). Macdonald et al. (2012) suggest that mafic recharge and underplating may be a fundamental source of volatiles for the Greater Olkaria volcanic complex.

5.6. Magma Fluxes in the MER

The mass of a pre-eruptive exsolved volatile phase was calculated based on the assumption that any exsolved volatile phase that existed prior to the Daly Gap will have been lost through outgassing. Lee et al. (2016) examined the diffuse soil degassing in the Magadi-Natron Basin, on the border between Kenya and Tanzania, linking the loss of 4 Mt/year CO₂ to the extensional tectonics of the EARS. Extrapolation of their results provides estimates for a CO₂ flux on the order of tens of Mt per year for the entire Eastern branch of the EARS, comparable to emissions from the global mid-ocean ridge system (53–97 Mt/year; Lee et al., 2016). Numerous authors have highlighted the importance of structural controls on fluid and vapor migration in volcanic areas (Hutchison et al., 2015; Robertson et al., 2016); degassing in the MER is concentrated in discrete areas of volcanic and off-edifice activity (Hunt et al., 2017). Characterization of these areas led (Hunt et al., 2017) to estimate a much lower CO₂ flux of 0.52–4.36 Mt/year for the central and northern portions of the MER and 3.9–32.7 Mt/year for the EARS.

Taking an average CO₂ loss of 1.1 wt.% (see section 5.3.1) and assuming loss is solely via diffuse soil degassing, the CO₂ fluxes presented by Hunt et al. (2017) may be used to estimate the mass of degassing basaltic melt per year of ~45–395 Mt beneath the MER and ~355–2,970 Mt beneath the EARS. Assuming a melt density of 2,750 kg/m³ and crystal densities of 3,320 kg/m³ (clinopyroxene), 3,400 kg/m³ (olivine), and 2,680 kg/m³ (plagioclase), typical phase proportions (40% plagioclase, 35% olivine, and 25% clinopyroxene; Iddon et al., 2019), and a bulk crystallinity of 45%, these estimates of degassing mass of basalt equate to volumes of ~0.02–0.14 and ~0.1–1 km³/year for the MER and EARS, respectively.

If we assume an average crustal thickness of 32 km for the ~1,000 km long MER (Casey et al., 2006), spreading rates of ~5 mm a year (Saria et al., 2014) would require the intrusion of ~0.16 km³ magma a year if extension was predominantly magma assisted (Bastow et al., 2010; Keir et al., 2006; Kendall et al., 2005), comparable with the results of this study based on the upper bounds of CO₂ flux estimates (Hunt et al., 2017). Wadge et al. (2016) have documented 21 historical eruptions along the EARS over the past 200 years. A minimum of 5 km³ of predominantly basalt was erupted on to the surface, with high intrusion/extrusion ratios (4–15; Wadge et al., 2016). Based on these figures, a magma flux for the whole EARS of ~0.13–0.40 km³/year may be estimated, which is within range of the magma degassing rates calculated above.

6. Implications for Geophysical Volcano Monitoring

InSAR observations of volcano deformation are increasingly being used as a monitoring technique as satellite coverage grows. As a remote technique, it is ideal for countries such as Ethiopia, which have a high number of potentially active volcanic sites, many of which are largely inaccessible or too costly to monitor. Magma injection may cause an inflation of a volcanic edifice, while withdrawal might result in a period of deflation (Segall, 2013). Modeling of the spatial and temporal characteristics of the deformation signal can also be used to estimate the source depth and geometry, providing vital information about magma storage (Biggs et al., 2011; Hutchison, Fusillo, et al., 2016; Lloyd et al., 2018). Using InSAR, Biggs et al. (2011) identified four volcanic edifices in the MER (Aluto, Corbetti, Bora, and Haledebi; see Figure 1 for locations) that have undergone significant deformation between 1993 and 2010. However, there are many factors that influence the deformation signal at a volcanic edifice. Magma rheology, edifice type, hydrothermal activity, tectonic setting, and stress fields all play a key role (Biggs et al., 2014). Some volcanoes will show significant pre- and syn-eruptive deformation, while some will not (Biggs et al., 2014), and the volume of erupted material is often much greater than the subsurface volume change implied by the deformation (Anderson & Segall, 2011; McCormick Kilbride et al., 2016; Rivalta & Segall, 2008; Segall, 2013).
Understanding volatile behavior is important for the interpretation of geodetic measurements. Exsolution of magmatic gases can lead to an inflation signal not related to magma injection, and outgassing or resorption into a crystalline mush can equally cause subsidence (Caricchi et al., 2014). In these cases, a coupled geodetic and gravity survey can differentiate between the behavior of melt and exsolved volatiles, as an exsolved volatile phase will lower the bulk magma density (Gottsmann & Battaglia, 2008). The presence of a low-density exsolved volatile phase will increase the compressibility of magma, which can result in muted ground displacements (Biggs et al., 2014; McCormick Kilbride et al., 2016). The difference between the volume erupted ($V_e$) and the subsurface volume change ($\Delta V$) is controlled by the bulk compressibility of the magma (Huppert & Woods, 2002):

$$\beta_m = \frac{1}{\beta_r} + \frac{1}{\rho \delta \rho / \delta P}$$

where $\beta_r$ is the effective bulk modulus of the surrounding wall rock, $\rho$ is the bulk magma density, and $P$ is pressure. The bulk compressibility of the country rock is also vital (Johnson, 1992):

$$\beta_c = \frac{3}{4 \mu}$$

where $\mu$ is the shear modulus of the host rock. Considering the simplest example of a spherical source, $r$, the ratio between $V_e$ and $\Delta V$ (for the “Mogi” source) (Rivalta & Segall, 2008):

$$r = \frac{V_e}{\Delta V} = 1 + \frac{\beta_m}{\beta_c}$$

would be 1 for an incompressible magma. However, a significant exsolved volatile phase will increase $\beta_m$ by an order of magnitude; therefore, a large volume eruption can be accommodated by expansion of the remaining magma, resulting in a minor volume change in the reservoir ($r > 1$) (Johnson, 1992; McCormick Kilbride et al., 2016). Country rock compressibility is different for deep prolate sources, where

$$\beta_c = \frac{1}{\mu}$$

is more appropriate (Anderson & Segall, 2011; McCormick-Kilbride et al., 2016; Rivalta & Segall, 2008). Crustal $\mu$ is not well constrained; it may range from ~0.1 GPa for very compliant rocks to 30 GPa for much stiffer crust (Gudmundsson, 2005). The exact value for $\beta_r$ also varies, depending on the density of microfractures in the rock, but a value of $10^{10}$ Pa is typically used (Tait et al., 1989). Assumptions about geometry and material properties are important; for example, a sill geometry, which is perhaps more appropriate for the MER calderas, would be significantly more compressible than a spherical source (Biggs et al., 2011).

Assuming no outgassing occurred, the $\beta_m$ of MER magmas was calculated to be between $1.98 \times 10^{-8}$ Pa$^{-1}$ and $3.71 \times 10^{-9}$ Pa$^{-1}$ based on the results of the fractional crystallization model and H$_2$O-CO$_2$ solubility pressure estimates. This gives predicted $r$ values of 23–16 for depths of 3–8 km, assuming a spherical source and $\mu$ of 0.3 GPa. Assuming a prolate source, these values change to 17–12. As $r$ is proportional to $\beta_m$, it is predicted to decrease with increasing magma reservoir depth. This analysis suggests that the geodetic displacements observed at MER volcanoes (Biggs et al., 2011; Hutchison, Fusillo, et al., 2016; Lloyd et al., 2018) are likely muted. For a cumulative subsurface volume change of 0.013 km$^3$ at ~5 km depth, as observed by Hutchison, Fusillo, et al. (2016) during rapid inflation events at Aluto, an eruptible volume of ~0.25 km$^3$ would be predicted (Figure 9). For a subsurface volume change of 0.01 km$^3$/year at ~6.5 km depth, as observed by Lloyd et al. (2018) at Corbetti between 2009 and 2017, an eruptible volume of ~1.2 km$^3$ would be predicted (Figure 9).

A number of volcanic monitoring techniques have been deployed across Ethiopia over the past decade. Mickus et al. (2007) presented gravity data that imaged a Bouger anomaly beneath Aluto and Corbetti volcanoes that they interpreted to be high-density bodies (~3,000 kg/m$^3$) in the lower crust (7–17 km). This
could imply that there was no low-density volatile-rich cap at Aluto or Corbetti during the data acquisition period (i.e., outgassing occurred) and that any subsurface volume changes observed from the deformation data would be equivalent to the eruptible volume of magma. However, it may also imply that the features responsible for the Bouger anomaly are denser and/or deeper than modeled (Mickus et al., 2007).

The lower density of an exsolved volatile phase will also dramatically lower seismic velocities (Neuberg & O’Gorman, 2002). Crustal velocities are typically 5–10% higher beneath the rift axis, thought to be the result of mafic intrusions beneath the different volcanic centers (Keranen et al., 2004). However, low-velocity zones are also identified at upper crustal depths beneath these sites, with mid-crustal low-velocity zones also located beneath the WFB and SDFZ (Kim et al., 2012). Wilks et al. (2017) identified seismic b value anomalies in the shallow crust beneath Aluto, thought to correlate with regions of gas accumulation.

As electrical resistivity is sensitive to fluid content, magnetotelluric (MT) surveys can identify the presence of partial melt beneath volcanoes (Johnson et al., 2016). The electrical resistivity of a magmatic reservoir is dependent on the state of the magma itself (Gaillard & Marziano, 2005). Dissolved volatiles can increase melt conductivity (Laumonier et al., 2017); however, exsolved volatile phases have low conductivities $10^{-2} - 10^{1}$ (ohm m)$^{-1}$. This has led to resistive regions beneath volcanoes sometimes being interpreted as gas-rich caps (Aizawa et al., 2009). This would still be consistent with the absence of increased electrical conductivity observed beneath Aluto (Hübert et al., 2018; Samrock et al., 2015). However, if exsolved volatiles escape and mix with groundwater, they can produce highly conductive regions of fluid (Aizawa et al., 2009). This might be observed beneath Aluto, where shallow regions of conductivity have been interpreted as relating to active hydrothermal systems (Hübert et al., 2018; Samrock et al., 2015).

7. Conclusions

Olivine- and quartz-hosted melt inclusions provide the first large-scale study of major, trace, and volatile element concentrations in MER melts. Modeling indicates that the pantelleritic quartz-hosted melt inclusion compositions can be achieved by protracted fractional crystallization (>90%) of an enriched alkali-transitional basaltic parent similar to that of the olivine-hosted melt inclusions. These parental melts are sourced from complex, vertically extended mafic magmatic systems that exist both on- and off-axis.

Mafic melts are saturated in H$_2$O and CO$_2$ at depths of >13 km. Over the course of the Daly Gap, melts saturate in both a sulfide phase and an exsolved volatile phase, into which S and halogens partition. Sulfide
settling and the formation of disseminated low-density bubbles are expected to lower bulk magma density, promoting rise to shallow magma storage regions in the crust, where further fractionation is accompanied by the development of a substantial saline, exsolved volatile phase. There is no evidence of brine formation in the melt inclusion compositions. Possible fluxing of deep-derived fluids is indicated by melt Li concentrations, perhaps suggesting magmatic underplating and/or magmatic recharge by more primitive compositions. Based on our results, an explosive, caldera-forming eruption (VEI > 5) in the MER could outgas up to 2,300 Mt of H₂O, 6 Mt of CO₂, 390 Mt of S, 150 Mt of F, and 150 Mt of Cl into the lower troposphere or stratosphere. The S and halogen yield of such an eruption is significantly larger than would be expected from a metaluminous or peraluminous counterpart. These gas emissions would have severe environmental consequences and pose a risk to the health of humans and livestock in Ethiopia if they were injected into the lower troposphere.

The accumulation of a large fraction (up to 4.5 vol.% or 13 wt.% at 200 MPa) of a pre-eruptive exsolved volatile phase may also cause the underestimation of intruded magma volumes by geodetic monitoring. Subsurface changes in volume of 0.013 and 0.07 km³ at 5–6 km depth inferred from ground displacements at Aluto and Corbetti may well correspond to much larger eruptible melt volumes of 0.25 and 1.19 km³ if a low-density, compressible exsolved volatile phase is present. The characteristics of this exsolved volatile phase will also have an effect on gravity, seismic, and electrical resistivity data, so must be considered as fledgling volcanic monitoring schemes continue to be developed in Ethiopia.

A significant proportion of volatiles are also lost from deep mafic melts through diffuse degassing through the crust. Based on CO₂/Na₂O ratios, we calculate that ~1.1 wt.% CO₂ may be lost from basalts in the MER system. This suggests that recently presented CO₂ fluxes would require ~0.02–0.14 km³ basaltic melt to be intruded every year beneath the MER, consistent with previous magma flux estimates of ~0.16 km³/year for the MER (Saria et al., 2014).

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