Melting the Lithosphere: metasomes as a source for mantle-derived magmas

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ABSTRACT

Peridotite constitutes most of the Earth's upper mantle, and it is therefore unsurprising that most mantle-derived magmas exhibit evidence of past equilibrium with an olivine-dominated source. Although there is mounting evidence for the role of pyroxenite in magma generation within upwelling mantle plumes, a less documented non-peridotite source of melts are metasomatic veins (metasomes) within the lithospheric mantle. Here we present major and trace element analyses of 66 lavas erupted from a small Miocene shield volcano located within the Ethiopian flood basalt province. Erupted lavas are intercalated with lahars and pyroclastic horizons that are

overlain by a later stage of activity manifested in small cinder cones and flows. The lavas form two distinctive petrographic and geochemical groups: (A) an olivine-phyric, low Ti group (1.7-2.7 wt. % TiO_2 ; 4.0-13.6 wt. % MgO), which geochemically resembles most of the basalts in the region. These low Ti lavas are the only geochemical unit identified in the later cinder cones and associated lava flows. (B) a clinopyroxene-phyric high Ti group (3.1 - 6.5 wt. % TiO_2 ; 2.8-9.2 wt. % MgO), which resembles the Oligocene HT-2 flood basalts. This unit is found intercalated with low Ti lavas within the Miocene shield. In comparison to the low Ti group, the high Ti lavas exhibit a profound depletion in Ni, Cr, Al, and Si, and significant enrichment in Ca, Fe, V, and the most incompatible trace elements. A characteristic negative K anomaly in primitive-mantle normalized diagrams, and $\text{Na}_2\text{O} > \text{K}_2\text{O}$, suggest a source rich in amphibole, devoid of olivine, and perhaps containing some carbonate and magnetite. While melt generation during rift development in Ethiopia is strongly correlated with the thermo-chemical anomalies associated with the African Superplume, thermobaric destabilization and melting of mantle metasomes may also contribute to lithospheric thinning. In regions impacted by mantle plumes, such melts may be critical to weakening of the continental lithosphere and the development of rifts.

1. Introduction

The process of mantle melting is foundational to studies of igneous rock, yet the composition of the melt source within the mantle can be difficult to discern from erupted lava compositions. Evidence from seismic, experimental petrology studies, and detailed examination of mantle xenoliths and ophiolites has resulted in a broad consensus where peridotite constitutes the bulk of the Earth's upper mantle. On the basis of this paradigm, it has been assumed that mantle-derived magmas will exhibit evidence of past equilibrium with a peridotite source, and detailed models outlining the melting modes and intensive parameters of melt generation from peridotite have

47 been constructed. However, inconsistencies have been recognized when such models are applied
48 to broad datasets due to the subtle differences imposed upon primary melt compositions by mass
49 contribution from mantle lithologies other than peridotite.

50 The acknowledgement that pyroxenite may play a critical role in magma production
51 within upwelling mantle plumes, either through direct melting (Sobolev et al., 2007) or
52 hybridization with surrounding peridotite (Herzberg, 2011), has challenged the conventional
53 assumptions of peridotite-dominated mantle melting mechanisms and has resulted in an
54 increased focus on distinguishing the potential source lithologies of mantle melts. Pyroxenite
55 that is located within upwelling mantle plumes or as rafts within the asthenosphere may
56 dominate the mass contribution to magma production from non-peridotitic source lithologies;
57 however, a less well-documented source of non-peridotite derived magmas lies within the
58 lithospheric mantle. Mantle metasomes are regions of the lithospheric mantle that have been
59 modally or geochemically (cryptically) enriched as a result of chromatographic interaction
60 between upper mantle-derived melts/fluids percolating through pre-existing peridotitic
61 lithospheric mantle. As a result of this interaction, peridotite may become enriched in
62 metasomatic phases such as amphibole or phlogopite, or veins/domains dominated by these
63 metasomatic phases. Initial models developed to account for melting of these enriched
64 metasomatic domains considered modal melting equations which incorporated the surrounding
65 peridotitic matrix (e.g., Späth et al., 2001), however experimental evidence suggests that
66 thermobaric perturbation of mantle metasomes will generate melt that is dominated by the
67 metasomatic phases, with little if any contribution from the surrounding peridotite (Pilet et al.,
68 2008). Mantle metasomes therefore represent another non-peridotite source lithology for melt
69 generation.

70 Studies of primary magmas derived from mantle metasomes have some particular
71 challenges in comparison to the more abundant peridotite- and pyroxenite-derived magmas.
72 Firstly, magmas derived from mantle metasomes are more geographically restricted and are
73 typically better represented in regions with thicker lithospheric mantle - such as on the
74 continents. Secondly, melt transport processes may lead to equilibration between metasome-
75 derived melts and the peridotite which constitutes the bulk of the lithospheric mantle (Pilet et al.,
76 2008). Finally, dilution of melts derived from these relatively small-volume domains by
77 asthenospheric-derived lavas may prevent their effective identification in the first instance.
78 Despite such challenges, constraining the fingerprint of magmas derived from mantle metasomes
79 is necessary in order to effectively unravel their potentially important role in lavas formed from
80 the homogenization of contributions from multiple source domains. While small in volume,
81 melts derived from mantle metasomes can exhibit potentially extreme isotopic heterogeneity and
82 have significant concentrations of many incompatible trace elements (Rosenthal et al., 2009),
83 therefore potentially playing an outsized role in the isotopic budget of mixed source lavas
84 (Rogers et al., 1998). Furthermore, the presence of melt with the lithosphere can have an impact
85 on lithospheric stability by focusing strain and facilitating rifting of the lithosphere with
86 significantly less stress (Buck, 2006). Given the low melting point of lithospheric metasomes
87 (Niida and Green, 1999), relatively minor thermobaric perturbation of the lithosphere may
88 facilitate melt generation (Rogers et al., 1998), with a consequential impact on rift development.

89 Here we present a study of the geochemical characteristics of a large suite of lavas which
90 we interpret to be derived from the asthenosphere and an amphibole-dominated mantle
91 metasome located in the lithospheric mantle. Through petrographic, major element and trace
92 element analysis we show distinctive differences between metasome-derived lavas and

contemporaneous asthenosphere-derived lavas in the region. The metasome-derived lavas exhibit little evidence of equilibration with peridotite and therefore represent an unusually pure endmember of a metasomatically-derived magma. We leverage our whole-rock data with high-precision olivine analysis to show that the unusual compositions of these lavas are imparted onto their olivine phenocrysts. We suggest that the thermal perturbation imparted by the Afar plume upon the East African lithosphere destabilized easily-fusible metasomatic veins which had resided at mid-lithospheric depths since the Pan-African subduction event. We conclude that thermobaric perturbation of the continental lithospheric mantle might facilitate rift development through strain focusing associated with the presence of magma within the lithospheric mantle.

2. Samples

The samples of the Gerba Guracha series were collected from flows emanating from a distinct edifice near the towns of Fiche and Gerba Guracha to the northwest of Addis Ababa on the western Ethiopian plateau (Fig. 1). In hand specimen, Gerba Guracha series rocks appear fresh, an observation confirmed by petrographic examination revealing broadly unaltered crystals and matrix. One of the most notable petrographic characteristics of the Gerba Guracha lavas are the large (cm-scale) zoned clinopyroxene crystals. Zoning in these crystals may manifest as both sector and fine-scale (possibly oscillatory) zoning (Fig. S1). Crystals are typically set in dark, almost glassy matrix. Glomeroporphyritic textures of mm-scale clinopyroxene and olivine are also observed. There are abundant opaque minerals present which can range up to 1 mm-scale. Zeolite- or carbonate-filled vesicles are evident in hand specimen but were largely avoided during sample collection and billet preparation. Some samples where these vesicles were unavoidable produced values with exceedingly elevated concentrations of Sr (e.g. sample

3222ves). A less common variety of strongly olivine-phyric flows were identified on the floor of the volcanic edifice and appear to post-date the rest of the volcanic activity on the basis of morphology.

3. Methods

Whole rock geochemical results were derived from hand samples by preparing ~30g billets, which were polished to remove saw marks. These billets were then crushed in a steel jaw crusher before being powdered in a BICO flat plate pulverizer that has been fitted with ceramic plates. The resulting powders were fused with lithium tetraborate at a ratio of 1:3 following procedures detailed elsewhere (Rooney et al., 2015). The resulting disks were analyzed for major elements by a Bruker S4 Pioneer XRF at Michigan State University. The glass disks were then analyzed for trace element contents by laser ablation inductively coupled plasma mass spectrometry using a Photon Machine Excimer G2 coupled with a Thermo iCAP-Q at Michigan State University following procedures detailed elsewhere (Rooney et al., 2015). Analytical results and values for standards are provided in Tables S2 and S3.

Samples with visible olivine were selected for high precision electron microprobe analysis of minor elements in olivine (Table S4; S5), which was undertaken at Rutgers University using the methods described by Sobolev et al. (2007).

Samples of fresh matrix were hand-picked from a single sample and sent for Ar-Ar dating to the Geochronology Laboratory at the University of Michigan under the supervision of Dr. Chris Hall. Analytical details of procedures followed are outlined elsewhere (Rooney et al., 2012a). Ar release spectra for the duplicate analysis are presented in Fig. S3.

4. Results

4.1 Major and Trace elements

To a first order, lava series at Gerba Guracha can be divided on the basis of their geochemical characteristics into a high- and low-Ti group (Table S2). The low-Ti group may be further divided into a silica-undersaturated basanitic group and a sub-alkaline basalt group. The high-Ti group is found dominantly within the elevated portions of the existing edifice (Fig. 1), while the low-Ti group is typically restricted to small flows and cinder cones along the flat floor of the edifice, though there is some evidence of intercalation between low- and high-Ti groups within lahars along the walls (e.g. samples 3267, 3268). This geochemical division is mirrored in a petrographic variation where olivine is more abundant in the low-Ti group, while clinopyroxene is more abundant within the high-Ti group.

4.1.1 High-Ti Group

While the initial division between groups at Gerba Guracha is based upon Ti concentrations, virtually every element exhibits significant differences between the two groups. The high-Ti group has a relatively high value for calculated loss on ignition (~4-5%; Table S1), though the samples do not have the appearance of significant alteration. The high-Ti group is particularly deficient in silica, ranging from 0 to 10% normative nepheline for the more mafic samples, extending to 30% for more evolved samples (CIPW normalization). High-Ti samples are not particularly alkali-rich; however, the somewhat average alkali contents combined with their low SiO₂ contents places them within the foidite, basanite/tephrite, phonotephrite, and tephriphonolite fields (Figure S2).

The major element variations of the high-Ti Gerba Guracha group are distinct from virtually all other groups in the region. In particular, the low values of SiO₂, Al₂O₃ and the

elevated values of CaO, TiO₂, Fe₂O_{3T}, and P₂O₅ extend beyond the trends typical of all other groups (Fig. 2). There are some similarities between the high-Ti Gerba Guracha group and the Oligocene HT-2 flood basalt group from the northeastern Ethiopian plateau (e.g. low Al₂O₃, elevated Fe₂O_{3T}, TiO₂); however, the Gerba Guracha high-Ti suite extends to significantly lower concentration of SiO₂, and higher values of Fe₂O₃, P₂O₅ and CaO.

Gerba Guracha high-Ti lavas are profoundly depleted in some compatible trace elements (Ni, Cr; Fig. 3), and enriched in V, Zr, and light to medium REE in comparison to many other regional suites at similar MgO content. Incompatible trace element variation within the Gerba Guracha high-Ti group show a marked variation in incompatible element concentrations at common values for MgO and extend to some of the most enriched values reported in the region. Primitive mantle normalized trace element patterns (Fig. 4) for the Gerba Guracha high-Ti group exhibit a distinctive enrichment in the most incompatible elements, with the exception of Rb and K. The characteristic negative K anomaly and trace element pattern is similar to the Oligocene Ma HT-2 basalts, though the Gerba Guracha series has a greater degree of enrichment in the more incompatible trace elements.

4.1.2 Low-Ti group

The low-Ti group exhibits a range in silica saturation: while the majority of samples have no normative nepheline, a subset parallels the high normative nepheline found within the high-Ti group. This reveals a clear basanite and basalt subdivision within the low-Ti group as evident in the total alkali-silica diagram (Fig. S2). Major element variation within the low-Ti group parallel most of the other regional suites (with the exception of the Oligocene HT-2 basalts noted above) and are therefore significantly different in comparison to the high-Ti suite.

The Gerba Guracha low-Ti suite has compatible and incompatible element variations that are strongly correlated with MgO and parallel other regional suites (Fig. 2). In particular there are marked similarities with the Pliocene Akaki basalt group from the margin of the Ethiopian Rift (Rooney et al., 2014a). Rocks from the basanite sub-group typically plot at elevated values of the more incompatible elements. The basalt sub-group of the low-Ti suite exhibits remarkable correlation in primitive-mantle normalized values when compared to the Akaki basalts as noted above and also overlaps the few Miocene shield volcano samples with sufficiently primitive MgO contents (Fig. 4). The basanite sub-group extends to higher values of more incompatible elements (notably Nb-Ta), and has a steeper slope in the less incompatible trace elements in comparison to the basalt sub-group. In many ways, the basanite sub-group of the low-Ti group shares more similarities with the high-Ti group.

4.2 Olivine geochemistry

We measured olivine major and minor element abundances in two high-Ti lavas (3187T; 3225), four basanites (3267; 3268; 3242C), one low-Ti lava (3761), and one of the underlying Oligocene flood basalts for comparison. Olivine within the high-Ti group is rare, and the results from the two samples presented followed detailed examination of many of the higher MgO high-Ti samples. The olivine grains in these high-Ti samples exhibit a wide range of Ni (71-830 ppm), Ca (1770-3913 ppm), and Mn (1594-3265 ppm) over a small compositional range (Fo = 79-81). Olivine from the other samples records a wider range in compositions (Fo₆₆₋₉₀). Olivine from these other Gerba Guracha units follow Ni and Ca evolutionary trends similar to other regions (e.g., Afar and Hawaii; Fig 5A; B), though for olivine <Fo₈₀ (with the exception of the flood basalts) Mn values extend above simple olivine-clinopyroxene fractionation models (Fig. 5D). The critical results from these data are the broad correlations between the whole-rock values and

the olivine chemistry: (1) The elevated values of CaO in the whole-rock and olivine datasets are evident in the high-Ti group ; (2) the profoundly low concentrations of Ni recorded in the whole rock data from the high-Ti group is also reflected in the olivine data, effectively discriminating between the basanites and high-Ti olivine (Fig. 5B). These data also reveal evidence of xenocrystic and antecrystic olivine. A subset of the olivine data collected from the basanites form a distinct trend toward the San Carlos standard (Fig. 5E), which may thus reflect some xenocrystic olivine in these samples. Similarly, the high-Ti olivine data are anchored within the basanite trends, suggestive of potentially antecrystic crystals derived from the basanite lavas – a conclusion strengthened by the discovery of an olivine crystal in sample 3187T that appears to exhibit characteristics of both the high-Ti olivines and the basanite olivines (phenocryst 2; Table S4).

4.3 Argon Geochronology

The $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra and replicate analysis are presented in Fig. S3. The age data (~24-25 Ma) are consistent with the shield-building phase on the western Ethiopian plateau. In particular, this period coincides with activity at the Choke and Gugufu shield volcanoes (Kieffer et al., 2004) and a subset of related dikes along the Afar margin (Rooney et al., 2013). The activity at Gerba Guracha therefore post-dates the main flood basalt phase at ~30 Ma (Kieffer et al., 2004), but predates the primary period of extension in the region that commences ca. 20 Ma (Wolfenden et al., 2005)

5. Discussion

5.1 AFC and magma mixing processes

The low-Ti lavas erupted at Gerba Guracha exhibit major and trace element characteristics consistent with magmatic evolution following a path similar to other lavas from the Ethiopian Cenozoic magmatic province (Fig. 2, 3). We thus assume a dominantly fractional crystallization origin for these evolutionary trends with subordinate contributions from magma mixing and assimilation (e.g., Kieffer et al., 2004; Rooney et al., 2014a). In contrast, the high-Ti magma series occupies an unusual compositional space within the regional dataset, in part overlapping the Oligocene HT-2 lavas of the Ethiopian flood basalts. Previous studies have shown that the evolutionary trends of the HT-2 flood basalts are dominated by deep fractionation of clinopyroxene and olivine, consistent with the phenocryst phases observed in those lavas (Pik et al., 1998). Petrographic evidence of cumulate textures and finely-zoned clinopyroxene crystals in the Gerba Guracha high-Ti group is evidence that these magmas have spent some time residing in the crust while undergoing differentiation. Significant clinopyroxene fractionation is supported by a strong correlation between decreasing MgO, increasing values of Al_2O_3 , and decreasing CaO (Fig. 2), and supported by a significant decrease in Sc concentrations at lower MgO values (Table S1). Unlike the HT-2 flood basalts, olivine is a rare phenocryst phase in the Gerba Guracha high-Ti group. Instead, Fe-Ti oxide removal appears to be a more dominant process contributing to magma evolution – supported by strongly positive correlations between V and Fe_2O_3 with MgO, and negative correlations with SiO_2 (Fig. 3). Vanadium partitions preferential into ilmenite ($K_D = 11$) and magnetite ($K_D = 0.11\text{-}190$) over clinopyroxene ($K_D = 0.05\text{-}5$), resulting in the preferential removal of V during fractionation of Fe-Ti oxides (Shervais, 1982; Zack and Brumm, 1998). The importance of Fe-Ti oxides in controlling trace element partitioning is further support by the ubiquitous presence of Fe-Ti oxides as large crystal phases (Figure S1). Evidence of magma mixing is preserved within the olivine data from the Gerba

Guracha high-Ti magma group (Fig. 5). In particular, these data form arrays that are consistent with mixing of basanite and high-Ti magmas (Fig. 5).

5.2 Mantle Origin of the Low-Ti Groups

The major and trace element characteristics of the low-Ti lavas from Gerba Guracha match closely the Pliocene Akaki lavas from the western rift margin (Fig. 2, 3). Indeed, the trace element patterns evident in the Gerba Guracha low-Ti and Akaki lavas (Fig. 4) are common in Quaternary lavas found throughout the Main Ethiopian Rift (Rooney et al., 2012b; 2014a). The Fe/Mn values of the low-Ti alkaline lavas are elevated above MORB and instead match Fe/Mn values from Akaki and other oceanic islands (Qin and Humayun, 2008), consistent with a plume-influenced mantle source (Fig. 6).

Detailed isotopic studies have shown that lavas from the Main Ethiopian Rift are the result of contributions from a plume source, the depleted upper mantle, and the African lithosphere (e.g., Furman et al., 2006), consistent with estimates of elevated mantle potential temperature (Rooney et al., 2012c). These Ethiopian Rift lavas are considered to be derived from the mixing of melts from the Afar plume and an ambient upper mantle that has been variably contaminated with lithospheric materials (Rooney et al., 2012b). Previous high-precision olivine data from Afar, show that the magmas are likely derived from a dominantly peridotitic source (Fig. 5) (Sobolev et al., 2007). On the basis of their remarkable similarity to lavas from throughout the Main Ethiopian Rift, the low-Ti Gerba Guracha lavas are therefore interpreted to be derived from partial melting of the same largely peridotitic plume-influenced variably contaminated upper mantle source. Similar to other asthenosphere-derived magmatism erupted in

this region over the past 30 Ma, we propose that the low-Ti Gerba Guracha magmas are generated by sub-lithospheric melts caused by excess mantle potential temperature and decompression as a result of lithospheric thinning (e.g., Furman et al., 2006; Rooney et al., 2012a,b,c, 2014).

5.3 Potential Asthenospheric Origins of the Gerba Guracha High-Ti Group

5.3.1 Possible Peridotite Source?

Gerba Guracha high-Ti magmas are distinguished from other African-Arabian volcanic suites by their high CaO and $\text{Fe}_2\text{O}_{3\text{T}}$ values as well as their low Al_2O_3 and SiO_2 abundances. These features have been recognized previously as key major element signatures of HIMU magmas globally (e.g., Dasgupta et al., 2010), and consistent with the HIMU-like isotopic characteristics of these lavas (Rooney et al., 2014b). While low silica and elevated iron concentrations have been associated with greater depth of melting in a peridotite source, it is difficult to generate the broad range of major element characteristics of HIMU by partial melting of a volatile-free peridotite (Dasgupta et al., 2010). Melting a water-fluxed peridotite will result broadly in magmas with lower iron and elevated silica contents (Gaetani and Grove, 1998), while silica-deficient magmas may be generated by CO_2 -fluxed partial melting of peridotite due in part to the enhanced stability of orthopyroxene under these conditions (e.g., Brey et al., 2008). While melting of a carbonated peridotite is a plausible mechanism to explain most of the geochemical characteristics of the Gerba Guracha high-Ti lavas, the elevated values of TiO_2 (Fig. 7), relatively modest alkali concentrations, and position within the Ne-Di-Ol ternary (Fig. 8) precludes this origin (e.g., Pilet et al., 2008).

5.3.2 Possible Pyroxenite Source?

Pyroxenites (including eclogites) have been identified as a subordinate yet pervasive component within the mantle (~10%: Gerbode and Dasgupta, 2010). The origin of these components has been linked to subducted oceanic crust (basalts and gabbros) and delaminated continental lithosphere that is converted into garnet, clinopyroxene, a free SiO₂ phase, and variable amounts of orthopyroxene (e.g., Herzberg, 2011). However, experimental melting results of nominally volatile-free pyroxenites show that the experimental melts are too enriched in alkalis and insufficiently enriched in titanium to explain the origin of the high-Ti Gerba Guracha lavas (Fig. 7).

Partial melting of carbonated MORB-like pyroxenites (protoliths that are relatively high in silica) can produce some of the major element features of HIMU-like primary magmas: specifically where deep melting initially occurs at ~6 GPa (Gerbode and Dasgupta, 2010) and is followed by a complex series of processes that involve solid-state interaction and reaction of pyroxenite (or derived melts) with surrounding peridotite to form a hybrid lithology that subsequently melts to produce HIMU-like magmas (e.g., Herzberg, 2011). Pyroxenite melts that have reacted with peridotite may also have similarities to HIMU-like magmas (Mallik and Dasgupta, 2012). Similarly, melting of carbonated, silica-deficient pyroxenites at moderate depths (~3 GPa) create major element compositions similar to the high-Ti Gerba Guracha suite (Dasgupta et al., 2006) (Fig. 7, 8).

Given the array of potential lithologies from which mantle-derived magmas may originate, minor elements in olivine phenocrysts have increasingly been used to probe the composition of primary magmas from which the olivine crystallized and, by extension, the

lithology that melted to form the primary melt (Sobolev et al., 2007; Herzberg, 2011; Herzberg et al., 2014). Initially, Ni content of olivine was used to probe the contributions of peridotite and pyroxenite to derivative mantle melts: high Ni values in magmatic olivine were theorized to represent pyroxenite-derived melts, while lower values were attributed to peridotite melts (Sobolev et al., 2007). Further evidence for pyroxenite contribution was evident where low Ca and Mn abundances in olivine were cited as evidence of pyroxenite melting (Sobolev et al., 2007). With the growing realization that pyroxenite, peridotite, and their respective derivative melts may interact to form a complex array of hybrid sources and magmas (e.g., Herzberg, 2011; Mallik and Dasgupta, 2012), olivine source determinations have evolved from a binary peridotite/pyroxenite predictive model to one where substantial ranges in lithological variation are possible (Herzberg, 2011).

The high precision analysis of Gerba Guracha olivine shows significant heterogeneity in the minor elements over a limited Fo range (Fig. 5). However, the most significant division is evident between the low-Ti and high-Ti groups: (A) The low-Ti group olivine crystals plot in a region such that they could be derived from a melt of a peridotite source that experienced dominantly clinopyroxene fractionation, or a hybrid pyroxenite-peridotite source partially depleted in olivine and clinopyroxene removal (Fig. 5). The compositional trends of these crystals are consistent with data from the underlying flood basalt olivine and from other plume environments. (B) Heterogeneities within the composition of olivine from the high-Ti group are noted above to be derived from a mix of low-Ti crystals and an endmember unique to the high-Ti group. This endmember is defined by profoundly low Ni and very high Ca concentrations, and is unlike any other olivine in the database. These results mirror the whole rock data of the high-Ti group, which shows enrichment in CaO and depletion in Ni (Fig. 2, 3).

The low Ni contents of the primitive Gerba Guracha high-Ti magmas may have implications for the interpretation of their origin. Previous studies have suggested that *high* Ni contents in olivine phenocrysts were indicators of melt derived from melting of pyroxenites, as the lack of olivine in the mantle source (and its high K_D for Ni) resulted in melts and olivine phenocrysts with Ni concentrations that are elevated above peridotite melts and derivative olivine (Sobolev et al., 2007). However, olivine in the somewhat alkaline Gerba Guracha lavas is *depleted* in Ni. It also notable that clinopyroxene and not olivine is the dominant mafic phase in Gerba Guracha high-Ti lavas. The preferential removal of clinopyroxene would only serve to deplete the Ni concentration in the remaining magma to an even lesser degree, making the mismatch between Gerba Guracha and other regional lava suites even more pronounced. Low Ni contents in olivine have been previously attributed to potential sequestration in a sulfide phase (Herzberg, 2011). However, the observed depletion in the high-Ti Gerba Guracha lavas of both a chalcophile (Ni) and lithophile (Cr) element (Fig. 3) is inconsistent with the sequestration of Ni by sulfide formation in a regular mantle-derived magma. We therefore conclude that the hybrid pyroxenite-peridotite processes described above are entirely inappropriate to describe the origin of high-Ti Gerba Guracha lavas.

5.4 Lithospheric mantle origins of the High-Ti Group

5.4.1 Generation and destruction of lithospheric metasomes

Previous isotopic studies of the Gerba Guracha high-Ti group suggested a source within the lithospheric mantle which has been isolated since the Pan-African assembly of the lithosphere in this region (Rooney et al., 2014b). The formation of this source is considered the result of the

interaction between the lithospheric mantle and asthenospheric melts/liquids derived from both peridotite and pyroxenite sources (e.g., Pilet et al., 2008). Within the deeper lithosphere (>100km), migrating metasomatic fluids/melts may generate anhydrous cumulate veins; surrounding these veins, enrichment of the existing peridotite may take the form of modal metasomatism (i.e. phlogopite) or cryptic enrichment (e.g., Bedini et al., 1997). At shallower depths, hydrous cumulate suites dominated by amphibole will form (Stein et al., 1997). Experimental evidence suggests that the major element composition of amphibole within hydrous metasomatic veins does not exhibit significant melt composition-dependent variance (except Ti) (e.g., Pilet et al., 2008). Thus, despite the wide range in possible compositions of the initial metasomatic agent, the ultimate result is a metasomatized mantle characterized by a stratified assemblages of hydrous and anhydrous metasomatic minerals (e.g., Pilet et al., 2008).

The solidi of hydrous veins are substantially depressed compared to that of anhydrous peridotite (e.g., Pilet et al., 2008), making the veins a potentially important source of melt. Experimental and modeled partial melts of metasomatic veins hosted within the lithospheric mantle have been shown to closely resemble OIB magmas, despite the wide variety of phases present within these enriched lithospheric zones (Pilet et al., 2008; Pilet et al., 2011). These experimental studies have shown that incongruent melting of amphibole dominates the melt reactions in such systems, such that similar melt compositions are derived from a wide variety of hydrous metasomatic assemblages (Pilet et al., 2008). Importantly, the melting of amphibole-rich lithologies produces nepheline-normative magmas (Médard et al., 2006) such as observed in the high-Ti Gerba Guracha lavas. The Gerba Guracha high-Ti lavas follow similar trends (Fig. 7) to the experimental melts of natural hornblendite and clinopyroxene-hornblendite at 1.5 GPa over a range of temperatures (Pilet et al., 2008), with some discrepancies: (i) at common values of SiO₂,

iron in the experimental melts is lower than observed which may be due to melting of small amounts of magnetite (Médard et al., 2006); and (ii) Al_2O_3 and CaO discrepancies may indicate a role for some residual garnet. Importantly, hornblende experimental melts yield appropriate titanium and alkali contents to be a potential source of the Gerba Guracha high-Ti lavas (Fig. 7). Thus, experimental melts of carbonated amphibole-rich lithologies broadly correlate with the major and trace element characteristics of the Gerba Guracha magmas and support an origin for these magmas as a melt of a mantle metasome containing phases such as amphibole, sphene, Fe-Ti oxides, and minor carbonate (Pilet et al., 2008).

The strong enrichment in incompatible trace elements of the high-Ti lavas in comparison to other regional magma suites may further support a metasomatic origin for these lavas. Hydrous cumulate veins, which form subsequent to the anhydrous assemblages, contain significant enrichment in incompatible elements (e.g., Pilet et al., 2008), typically concentrated in accessory phases (e.g., apatite, ilmenite, allanite, zircon, and titanite). The trace element characteristics of the hydrous metasomatic veins are largely controlled by the partition coefficients and mass of minor metasomatic phases within a vein, and are not particularly sensitive to the composition of the original melt/liquid which formed such veins (Pilet et al., 2011). The relatively large degree of melting within the hydrous veins (in comparison with a peridotite) results in magmas that have trace element characteristics broadly similar to their source vein, though slightly more enriched (Pilet et al., 2008; Pilet et al., 2011). Ultimately, magmas derivative of hydrous metasomatic veins may exhibit similar major element characteristics controlled by incongruent melting of amphibole, but considerable variation in trace element concentrations that are dependent on the type and mass of accessory phases within a particular source vein. Trace element patterns similar to that observed for the Gerba Guracha

suite (Fig. 9) can be produced through models simulating melting of hydrous cumulates with 0-2% rutile, ilmenite, titanite, allanite, apatite, sulfide, and zircon (Pilet et al., 2011).

5.5 Constraints on the mineralogy of the metasome: Oxygen fugacity, garnet, and the role of Fe-Ti oxides.

The high-Ti group exhibits elevated concentrations of first-row transition elements (FRTE), and unusual fractionation of these elements during magma differentiation (Fig. 6). These characteristics can provide insight into the mineralogy of the metasomatic veins and the intensive parameters imposed upon the derivative melt (i.e. oxygen fugacity). The whole-rock Fe/Mn (~40-110) of the high-Ti group extends to values that are significantly above and below the typical range of MORB and OIB (Fe/Mn ~50-75) (Qin and Humayun, 2008; Davis et al., 2013), and is significantly more scattered than other magma suites in the region (Fig. 6). The Fe/Mn range in the high-Ti group is not imposed by unusually high or low values of Fe or Mn; indeed the concentrations of both these elements exceeds that of other regional suites (Fig. 3). Instead, Fe/Mn is positively correlated with MgO, suggesting control of iron oxide fractionation, which is ubiquitous in the high-Ti group even at higher MgO values. This assertion is consistent with the observation of a parallel depletion in V concentrations (Fig. 3). Thus, unlike most magmatism in Ethiopia, the Gerba Guracha high-Ti lava suite follows a fraction path more typical of magmas characterized by significantly higher fO_2 . Given the evidence for the early stabilization of magnetite, the fO_2 is likely on the order of arc magmas (QFM+1 to 2). Such observations are consistent with highly alkaline rocks (e.g., carbonatites) from elsewhere in the East African rift

where magnetite is an early, and volumetrically important, fractionating phase (e.g., Guzmics et al., 2015).

The initially high concentration of Fe, Mn and Fe/Mn in the high-Ti lavas is not typical of peridotite melts (Fig. 6). Hydrous melting of garnet peridotite can elevate Fe/Mn values (Balta et al., 2011), however, the whole-rock and olivine Fe/Mn values observed extend beyond that likely to be derived from peridotite melt (Herzberg, 2011). Higher values of Fe/Mn in melts are possible in source lithologies with more garnet and less olivine, such as a pyroxenite (Balta et al., 2011) or garnet-bearing amphibolite. While the influence of garnet in the high-Ti group source is seemingly supported by elevated V/Sc (Davis et al., 2013), V/Yb (Laubier et al., 2014), and apparent fractionation of $(\text{Tb/Yb})_{\text{CN}}$ (Fig. 6), on close inspection we see that $(\text{Tb/Yb})_{\text{CN}}$ is uncorrelated with V/Sc and Fe/Mn. Furthermore, the REE values for the more primitive high-Ti lavas ($>7\%$ MgO) show substantially parallel MREE and HREE patterns (Tb -0.97-1.85; Yb -1.36-2.89), contrasting with the compression of the more incompatible REEs evident in magmas derived from variable degrees of melting of a garnet-bearing hornblendite on primitive mantle normalized diagrams (e.g., Ma et al., 2011). We instead suggest a two-step mechanism to explain the fractionated REEs: (A) a metasomatic melt/fluid is generated by partial melting of a lithology containing garnet. This melt/fluid percolates up through the lithospheric mantle and creates a metasomatic vein with depleted HREE. (B) Subsequent melting of the garnet-free metasomatic vein will yield magmas with fractionated HREE. This mechanism is supported by experimental results from melting of garnet-free HREE depleted hornblendite lithologies, which have produced melts with fractionated $(\text{Tb/Yb})_{\text{CN}}$ 2-3 and parallel REE patterns (Pilet et al., 2008), similar to that observed in our high-Ti group. Magmas derived from metasomatic veins may thus have fractionated HREE without the direct influence of garnet in their source, with resulting

implications for the use of apparent 'garnet signatures' in establishing the intensive parameters of magmagenesis in such magmas.

On the basis that garnet is not a controlling phase in the source of the high-Ti group, the unusual concentrations of FRTes (e.g., Ti, Sc, Fe, V, Mn) in these lavas remains unexplained. We have previously noted that these elements are strongly controlled by the early appearance and fractionation of iron oxides during magma evolution, suggesting a higher fO_2 in these lavas and raising the question: was the mantle source of the high-Ti group unusually oxidized? Over the past decade significant attention to mantle oxidation states has highlighted a substantial degree of uncertainty as to the possible cause (or indeed existence) of oxidized domains within the mantle (e.g., Brounce et al., 2015). Regardless of the precise mechanism for driving high fO_2 in subduction-related magmas, the interaction of such high fO_2 magmas with the overlying lithospheric mantle results in the formation of amphibole-rich metasomes where spinel has been converted to Ti-rich magnetite (Blatter and Carmichael, 1998), resulting in elevated values of fO_2 in the sub-arc mantle (FMQ up to +4: Evans et al., 2012). We therefore suggest that the high apparent fO_2 in the high-Ti lavas is inherited from its metasomatic source - a Pan-African subduction-influenced lithospheric mantle (Rooney et al., 2014b).

5.6 Tectonic Implications

Prior investigation of the Gerba Guracha high-Ti group has revealed an unusual isotopic signature that approaches the HIMU reservoir (Rooney et al., 2014b). This signature is quite distinctive from other lavas erupted during the Oligocene flood basalt event and subsequent rift-related volcanism, which are dominated by the "C", depleted mantle, and lithospheric reservoirs (Rooney et al., 2012b). In contrast, the HIMU-like signature evident in the high-Ti group

resembles lavas erupted in northeast Africa and Arabia, distant from the locus of the Afar plume (Fig. 1). Prior studies have shown that this HIMU-like signature likely results from in-situ evolution of a metasomatically enriched lithospheric mantle metasome emplaced during the Pan-African subduction event (Rooney et al., 2014b). The potentially widespread presence of an easily-fusible metasome within the Pan-African lithosphere, has implications for lithospheric stability and rift development throughout the region.

Amphibole-bearing metasomes, which have the potential to melt at significantly lower temperatures in comparison to peridotite (Pilet et al., 2008), may become destabilized by thinning or thermo-mechanical erosion of the continental lithospheric mantle. The presence of magma within the continental lithospheric mantle can facilitate weakening and lead to further destabilization of the lithosphere (Buck, 2006). The initial interaction of a mantle plume with the lithospheric mantle may provide the impetus needed to melt lithospheric metasomes, however, the eruption of the Gerba Guracha lavas ~5 Ma *after* the flood basalt episode had terminated presents difficulties for this model. While large volumes of flood basalt passed through the continental lithosphere during the Oligocene, studies of lithospheric mantle xenoliths beneath the northwestern Ethiopian plateau suggest that the transit of flood basalts was likely focused into distinct channels (Roger et al., 1999), allowing for the preservation of metasomes away from such channels.

The 24 Ma eruption of the Gerba Guracha series occurred during an unusually quiescent period, immediately preceding the development of rifting at this latitude (Wolfenden et al., 2005), thus raising the question of how the Gerba Guracha magmas might have been generated? Given the lack of evidence for lithospheric stretching at this time (e.g., Wolfenden et al., 2005), and the improbability of thermo-mechanical erosion of the lithosphere during this period due to

low magma flux (Rooney et al., 2013), we consider thermal perturbation of the continental lithospheric mantle as a mechanism to destabilize lithospheric metasomes (Fig. 10). Studies from the western branch of the EAR suggest that some early silica-undersaturated alkaline magmas erupted there also lack a clear extensional causation and were instead generated by thermal destabilization of lithospheric metasomes (Rogers et al., 1998). Over a ca. 10 Ma period, plume-resultant conductive heating of the lithospheric mantle melted the metasomatized lithosphere and generated magmas observed in the Virunga province (Rogers et al., 1998). For the Gerba Guracha area, eruption occurs ca. 7-9 Ma after the initial manifestations of Cenozoic magmatism in this region and we explore the potential for heating of the lithosphere in this region. We presume an initial lithospheric thickness of ~120 km (Dugda et al., 2007), and the maximum pressure limits for pargasitic amphibole (in a peridotite matrix - we are unaware of equivalent high pressure amphibolite experiments) of ~90km (Niida and Green, 1999). On the basis of a continental geotherm of 50mW/m^2 , the continental lithosphere at 90 km would be ~920°C, significantly below the 1075°C stability limit for pargasitic amphibole (Niida and Green, 1999). Using the formulation of Turner et al., (1996), where a 300°C increase in mantle potential temperature was imposed upon the base of the lithosphere, the region of the lithosphere 30km from the lithospheric base increased ~140°C over 9 Ma, approaching the 1075°C amphibole stability limit. This model of progressive lithospheric thermal destabilization is supported by xenolith-based geotherms for the Ethiopian plateau that suggest that at 5 Ma, the lithosphere at 90 km depth was ~1166°C (Conticelli et al., 1999).

6. Conclusions

The thermal perturbation of the East African lithosphere by the Afar plume destabilized easily-fusible metasomes at mid-lithospheric depths. These metasomes, which had resided in the lithospheric mantle since the Pan-African subduction event, were likely carbonated and dominated by amphibole and Fe-Ti oxides. Melts derived from these metasomes erupted at ~24 Ma on the Ethiopian plateau and had distinctive geochemical characteristics in comparison to contemporaneously erupted low-Ti lavas that resemble others lavas in the region. Gerba Guracha high-Ti magmas are distinguished by being silica-undersaturated, rich in incompatible trace elements and most first-row transition elements, but profoundly depleted in Ni and Cr. The high oxygen fugacity imparted by the mineralogy of the source metasome resulted in the early appearance of Fe-Ti oxides in the derivative melts. The presence of metasomes that may generate melt upon thermobaric perturbation of the continental lithosphere has implications for our understanding of long-term lithospheric stability, given the potential for such melts to focus strain and facilitate rift development. The conceptual model we present herein opens opportunities for further studies to constrain the volume of melt generated by this process, and in assessing its role in modifying the lithospheric strain profile during the initiation of rifting.

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541

542 **FIGURES**

543 Figure 1.

544 Location of study within the East African Rift system. (A) Regional Cenozoic volcanism divided
545 into small-volume intra-plate activity (blue) and flood basalts/rift basalts (red). (B) Topography
546 and the outline of the border faults of the Main Ethiopian Rift (MER) in addition to the
547 quaternary volcanic centers along the Wonji Fault Belt. Also shown is the quaternary Silti-Debre
548 Zeyit Fault Zone (SDFZ), and Pliocene Akaki chain. The Miocene shield volcanoes of Choke
549 and Gugufu are also shown (Kieffer et al., 2004). (C) Digital elevation model of the Gerba
550 Guracha edifice derived from Shuttle Radar Topography Mission data. This perspective image
551 has 4x vertical exaggeration and shows sampling localities. Red squares are high-Ti lavas, blue
552 squares are low-Ti lavas localities.

553

554 Figure 2.

555 Variance of major element oxides for Gerba Guracha lavas shown against mafic lavas from other
556 regional suites:

557 Oligocene LT flood basalts (Pik et al., 1998; Pik et al., 1999; Kieffer et al., 2004)

558 Oligocene HT-2 flood basalts (Pik et al., 1998; Pik et al., 1999; Beccaluva et al., 2009)

559 Pliocene Akaki (adjacent to MER) (Rooney et al., 2014a)

Miocene Shield volcanoes (Kieffer et al., 2004) and temporally synchronous dikes
(Rooney et al., 2013).

All data presented as weight percent and normalized to 100%.

Figure 3.

Variance of selected trace element for Gerba Guracha lavas shown against the same lava suites
referenced in Figure 2.

Figure 4.

Primitive mantle normalized (Sun and McDonough, 1989) trace element diagram showing the
Gerba Guracha lavas in comparison to the Oligocene HT-2 flood basalts, Pliocene Akaki, and
Miocene shield volcano lavas (see Figure 2 for data sources). All samples are greater than 7wt.
% MgO.

Figure 5.

Olivine from the Gerba Guracha lavas shown plotted against OIB and MORB suites from the
high precision database of Sobolev et al. (2007). Fields shown are calculated for olivine from
primary and derivative peridotite melts (Herzberg, 2011). Note that 'flood basalt' here refers to a
sample of the Ethiopian Flood basalts collected below the Gerba Guracha units.

A. Ni versus forsterite (Fo) content of Gerba Guracha magmas and other suites. Grey field
are for olivine crystals derived from hybridized pyroxenite sources.

- B. Ni versus Fo, same suites as in A but scale is adjusted to log to show the degree of Ni depletion at Gerba Guracha
- C. Mn values versus Fo content of Gerba Guracha olivine compared to other suites. Shown are a series of models simulating the impact of clinopyroxene and olivine fractionation on the path of an evolving primitive magma.
- D. Ca versus Fo content of Gerba Guracha magmas and other suites. Clinopyroxene fractionation strongly leverages the Ca content of olivine to lower concentrations.
- E. Ca versus Ni content of Gerba Guracha magmas and Ethiopian Flood basalt.

Figure 6.

Variations of the first row transition elements (FRTE) in the Gerba Guracha lavas.

A) Previous studies have noted the inaccuracy of MnO measurements by XRF (Qin and Humayun, 2008), we therefore present data collected on the same sample disks by XRF and LA-ICPMS. The agreement between the XRF and LA-ICPMS results is good and, given the large range in Fe/Mn ratios, we thus assert that the XRF data is sufficient.

B) The variation of V/Sc against Co/Fe for primitive lavas (>7 wt. % MgO) show that the Gerba Guracha lavas are likely not derived from a peridotite melt (Davis et al., 2013). Furthermore, their elevation in V/Sc may in part be the result of increased fO_2 in their mantle source. Fields for modeled melts of eclogite (grey = altered oceanic crust, dotted = MORB), melt of peridotite (dark grey), and primitive OIB (dashed line) are from Davis et al., (2013).

C&D) There is strong control of MgO on the Fe/Mn and V/Sc values in the High-Ti suite. This contrasts with the high precision MORB and OIB suites (Qin and Humayun, 2008), and the well-constrained Pliocene Akaki suite (Rooney et al., 2014a) for Fe/Mn. For more primitive lavas (8-12 wt. % MgO), V/Sc has been used to infer fO_2 values in the mantle source (Lee et al., 2005). For a 10% partial melt of a spinel lherzolite, the V/Sc values in the low-Ti group plot approximately within the QFM domain (Lee et al., 2005). The high-Ti V/Sc values could be produced by increasing fO_2 values of the same mantle source (QFM+2), or a 5% partial melt of a garnet-bearing source with similar fO_2 to the low-Ti group. Lee et al., (2005) specifically caution against using such models to make determinations of fO_2 in cases where metasomatic veins may have contributed to melt (such as Gerba Guracha). In such cases, smaller degrees of melting, residual garnet, differing initial V and Sc concentrations and exotic phases obscure the role of fO_2 . However, the plots illustrate the potential influence of both fO_2 and garnet on the geochemical systematics of the Gerba Guracha lavas.

E&F) Plot of V/Sc and Fe/Mn versus an index of garnet in the source (Tb/Yb – chondrite normalized) for primitive lavas (>7wt. % MgO) from Gerba Guracha. No strong correlation between V/Sc, Fe/Mn, and Tb/Yb is observed, making a clear determination of the presence of garnet in the source of these lavas equivocal (Lee et al., 2005; Davis et al., 2013). Enhanced fO_2 may also have also contributed to the observed variability in first row transition elements.

Figure 7.

Major element data from primitive Gerba Guracha samples plotted with experimentally derived melts from a variety of mantle materials. All data is presented as weight percent and normalized on a volatile free basis to 100%. We have not plotted experimental data where the volatile-free total is lower than 75%, or the data point is a significant outlier. Citations to the data sources used may be found in the supplemental material. We have selected 7 wt. % MgO as a lower filter for our data on the basis of experimental work by Pilet et al., (2008). These authors have shown that primary melts derived from the melting of hornblendite have ca. 6.9 wt. % to 11.9 wt. % MgO. Gerba Guracha samples with >7 wt. % MgO may represent primary melts and it is thus appropriate to compare them with experimentally derived primary melts. The final panel depicts TiO₂ vs total alkalis and has been previously used to separate melts derived from carbonated peridotites and eclogites/hornblendites (Zeng et al., 2010).

Figure 8

CIPW normalization plotted on the Ne+Lc (nepheline + leucitite), Ol (olivine), Di (diopside), Hy (hypersphene), Q (quartz). CIPW normalization was completed using the assumption that 90% of the total iron was in the form FeO for consistency with previous datasets. Fields for experimental melting data as outlined in Figure 7. We have selected 7 wt. % MgO as a lower filter for our data as in Figure 7.

Figure 9

Primitive mantle normalized McDonough & Sun (1995) trace element diagram showing the Gerba Guracha lavas in comparison to a model range of melts produced from metasomatized hydrous lithosphere composed of hydrous veins plus 0-5% trapped liquid (Pilet et al., 2011). The

643 red line is the high-Ti Gerba Guracha median value for samples are greater than 7 wt. % MgO;
644 the two yellow lines are 1 standard deviation from this median.

645 Figure 10

646 Conceptual model where metasomatism during the Pan-African event enriched the continental
647 lithospheric mantle forming amphibole rich veins within the lithospheric mantle. During the late
648 Oligocene and Miocene, thermal destabilization of the continental lithospheric mantle by
649 interaction with the Afar plume created melts from these metasomes. Contemporaneous with
650 this, low-Ti magmas were generated from broadly the same asthenospheric reservoirs as modern
651 day lavas in the Main Ethiopian Rift. The basanites may be a mixture of the lithospheric and
652 asthenospheric reservoirs.

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Pan-African Subduction event

Miocene