Title
Volatiles and Redox Along the East African Rift

Journal
Geochemistry Geophysics Geosystems, 25(8)

ISSN
1525-2027

Authors
Brounce, Maryjo
Scoggins, Sara
Fischer, Tobias P
et al.

Publication Date
2024-08-01

DOI
10.1029/2024gc011657

Volatiles and Redox along the East African Rift

Maryjo Brounce[1*], Sara Scoggins[1,2], Tobias P. Fischer[3], Heather Ford[1], and Joseph Byrnes[4]

[1]Department of Earth and Planetary Sciences, University of California Riverside, Riverside CA USA 92592
[2]City of Fort Worth Environmental Sciences, Fort Worth TX USA 76102
[3]Earth and Planetary Sciences, University of New Mexico, Albuquerque NM USA 87131
[4]School of Earth and Sustainability, Northern Arizona University, Flagstaff AZ USA 86011

*corresponding author

Abstract

The upper mantle under the Afar Depression in the East African Rift displays some of the slowest seismic wave speeds observed globally. Despite the extreme nature of the geophysical anomaly, lavas erupted along the East African Rift record modest thermal anomalies. We present measurements of major elements, H_2O, S, and CO_2, and $Fe^{3+}/\Sigma Fe$ and $S^{6+}/\Sigma S$ in submarine glasses from the Gulf of Aden seafloor spreading center and olivine-, plagioclase-, and pyroxene-hosted melt inclusions from Erta Ale volcano in the Afar Depression. We combine these measurements with literature data to place constraints on the temperature, H_2O, and fO_2 of the mantle sources of these lavas, as well as initial and final pressures of melting. The Afar mantle plume is C/FOZO/PHEM in isotopic composition, and we suggest that this mantle component is damp, with 852 ± 167 ppm H_2O, not elevated in fO_2 compared to the depleted MORB mantle, and has temperatures of ~1401-1458°C. This is similar in fO_2 and H_2O to estimates of C/FOZO/PHEM in

other locations. Using the moderate H_2O contents of the mantle together with the moderate thermal anomaly, we find that melting begins around 93 km depth and ceases around 63 km depth under the Afar Depression and around 37 km depth under the Gulf of Aden, and that ~1-29% partial melts of the mantle can be generated in these conditions. We speculate that the presence of melt, and not elevated temperatures or high H_2O contents, are the cause for the prominent geophysical anomaly observed in this region.

Plain Language Summary

The mantle under the Afar Depression and Gulf of Aden, in Northeastern Africa is geophysically distinct from the mantle elsewhere on Earth. Typically, these geophysical distinctions are thought to arise from elevated temperatures, but the composition of lavas erupted in this region demonstrate that the mantle is only moderately warm and cannot fully explain the geophysical nature of the mantle in this region. We produce new measurements of submarine pillow glasses erupted from Erta Ale volcano and find that in addition to being somewhat warm, the mantle in this region is also somewhat hydrated compared to the mantle that feeds mid-ocean ridge volcanoes, but is not substantially different in bulk oxidation state from the mantle. These conditions together produce a region of partial melt that exists between 93 km and 63-36 km depth under the surface. We speculate that this lens of melt can explain the geophysical observations of the mantle in this region.

1. Introduction

Continental rifting is a primary component of the plate tectonic cycle. It records the onset on continental fragmentation and the progression to the production of new oceanic crust and ocean basins. The East African Rift is one modern example that includes incipient continental extension in the southern termini of the Eastern and Western branches, well-developed continental rifting in the Main Ethiopian rift and Afar Depression, and full oceanic spreading and the production of new oceanic crust in the Gulf of Aden (Figure 1). Despite the importance of continental rifting to plate tectonic cycles, the physical mechanisms that drive the initiation and development of continental rifts remain uncertain. The expected magnitudes of the major tectonic forces such as slab pull, asthenospheric drag, and ridge push (Forsyth & Uyeda, 1975) may be insufficient to overcome the expected strength of continental lithosphere, suggesting that continental lithosphere is weakened prior to rifting. One way this could be accomplished is through the injection of magma or other fluids into the continental lithosphere, and indeed, some continental rifts are associated with significant magmatism at the time of initiation of the rift (e.g., East African Rift and the Ethiopian Flood Basalt Province; Hofmann et al., 1997). However, the production of this magmatism through mantle melting presents new challenges - continental lithosphere ranges from 40 km to 280 km in thickness (Pasyanos, 2010) and there is significantly lower heat flow beneath continents (a mean value of 64.7 mW m^{-2}) than beneath oceans (a mean value of ~95.9 mW m^{-2}; Davies, 2013; Jaupart and Mareschal, 2007). Thus, one would expect limited extents of melting in a mantle at high pressures and cool ambient temperatures as predicted to exist beneath pre-rifted continental lithosphere. This suggests that if continental rifting is magma assisted from the onset, it requires elevated mantle temperatures and/or hydrous and/or carbonated mantle lithologies that melt at lower temperatures than nominally dry, carbon-free peridotite.

The challenge of understanding the role of magmatism in continental rifting is displayed in the East African Rift. Tomographic models of P- and S-wave speeds along the rift present one of the most prominent geophysical anomalies in Earth's upper mantle, with seismic wave speeds of δVp~ -6%, δVs~ -4% relative to standard Earth models (Bastow et al., 2008; Emry et al., 2018). Elevated mantle potential temperatures are expected to slow seismic wave velocities by reducing the sheer and bulk moduli of peridotite (Karato & Jung, 2003). If the observed slowness is due to increased mantle temperatures alone, it requires lavas that record mantle potential temperatures near 1700 °C (Gallacher et al., 2016). However, the major element compositions of relatively unevolved lavas erupted throughout the Ethiopian/Afar triangle (where seismic wave speeds are slowest) in the last 10 my suggest moderate thermal anomalies of 1490°C (Ferguson et al., 2013; Rooney et al., 2012). This is not only low compared to mantle potential temperature estimates for the mantle sources of other flood basalts and ocean island basalts which range from nominal ambient mantle temperatures near 1350°C for some Azores lavas to in excess of 1600°C for some Hawaiian lavas (Rooney et al., 2012), but also at odds with a thermal-only explanation for present day geophysical observations of the upper mantle in this region. As suggested by Rooney et al. (2012) the combination of very slow seismic wave speeds and moderate thermal anomaly for the mantle along the East African Rift may require the influence of other factors hypothesized to change the bulk and shear moduli of peridotite, such as melt (Hammond & Humphreys, 2000), H_2O (Karato & Jung, 1998), or high fO_2 (Cline II et al., 2018) in the mantle under the East African Rift.

The H_2O and CO_2 contents and fO_2 of the mantle beneath the ridge axis are largely unconstrained, all properties which influence the extent of melting of peridotite (Dasgupta et al., 2013; Stagno et al., 2013; Till et al., 2012). This uncertainty exists in part because the sources of lavas along the rift are complicated by the potential presence of the depleted upper mantle, material from the Afar plume/African superplume that may extend from the base of the continental lithosphere in this region to the core-mantle boundary (Mulibo & Nyblade, 2013), and contamination by some degree of the assimilation of a wide variety of materials contained within the continental lithosphere that record long histories of plate tectonic cycles (Hutchison et al., 2018). Each of these materials may vary in their H_2O, CO_2 contents and fO_2, making reasonable predictions of their importance to the observed geophysical characteristics of the upper mantle and the role of each in rifting difficult. Additionally, the volatile elements CO_2 and H_2O are typically quantitatively degassed from subaerially erupted lavas (such as those erupted in the Afar Depression and along the Main Ethiopian Rift, where the geophysical anomaly is most pronounced), and to constrain the CO_2 and H_2O contents of the undegassed magmas requires either (1) submarine erupted glasses where the confining pressure of the water column limits/prohibits degassing or (2) in the case of subaerially erupted lavas, analysis of naturally glassy phenocryst-hosted melt inclusions. Submarine erupted glasses are rare in continental settings by definition, and melt inclusions are complex, integrated records of (1) the magma from which the phenocryst crystallized and thus the mantle sources of those magmas (e.g., Kelley et al., 2010), (2) crystallization and diffusion processes within the melt inclusion after entrapment in the phenocryst host (Newcombe et al., 2014; Saper & Stolper, 2020), and (3) the evolving host magma composition, which can be communicated through the phenocryst to the melt inclusions by rapid diffusion (Brounce et al., 2021; Bucholz et al., 2013; Humphreys et al., 2022). Further, preservation of naturally glassy melt inclusions is not guaranteed, as many phenocrysts erupt and cool relatively slowly in large volcaniclastic blocks/bombs and/or lava flows, causing the melt pocket contained in the phenocryst to crystallize (Lloyd et al., 2013), at which point spectroscopic measurements of H_2O and CO_2 and $Fe^{3+}/\Sigma Fe$ and $S^{6+}/\Sigma S$ are not feasible. The result is that there are relatively few datasets available to assess parental and primary melt H_2O, CO_2 and fO_2.

The East African Rift is comprised of the Main Ethiopian Rift and Eastern and Western branches. The Main Ethiopian Rift forms a triple junction along with spreading centers in the Red Sea and Gulf of Aden, the latter of which continues eastward and forms the Central Indian Ridge of the Indian Ocean mid-ocean ridge spreading center (Figure 1). The radiogenic isotopic (Sr-Nd-Hf-Pb) compositions of Quaternary-aged Gulf of Aden submarine pillow glasses (dredged by the R/V Vema cruise 33-07; Schilling et al., 1992) and subaerial lavas of the Main Ethiopian Rift have been used to elucidate the complex contributions from three distinct sources to the magmas that erupt along the Gulf of Aden and into the Main Ethiopian Rift: the depleted upper mantle, the Afar mantle plume, and the Pan-African lithosphere (Rooney et al., 2012; Schilling et al., 1992). Gulf of Aden submarine glasses can be described as predominantly (i.e., >88% contribution) melts of the depleted upper mantle (sample V3307-64D-3g; Schilling et al., 1992) or predominantly (i.e, >98% contribution) melts of the Afar mantle plume (sample V3307-50D-1g; Schilling et al., 1992), all with some small contributions (<5%) of melts of the Pan-African lithosphere. This framework was extended to include the lavas of the Main Ethiopian Rift, where contributions from the Pan-African lithosphere increase, and the influence of the Afar mantle plume appears to have a toroidal surface expression (Rooney, et al., 2012). These glassy pillow basalt samples are critical to constraining the composition, including H_2O, CO_2, and fO_2, each of the main mantle sources for lavas along the East African Rift, and thus in improving our understanding of the geophysical anomaly present in the upper mantle under the rift.

Here we present new measurements of H_2O, CO_2, $Fe^{3+}/\Sigma Fe$, and $S^{6+}/\Sigma S$ of the same submarine Gulf of Aden glasses studied by Schilling et al. (1992) shown in Supplementary Data Table 1, and together with published major and trace element and radiogenic isotopic compositions, place constraints on the H_2O content and fO_2 of the Afar mantle plume (Table 1, Supplementary Data Table 2), depleted upper mantle, and Pan-African lithosphere. We also calculate the temperatures and pressures of melting along the Gulf of Aden, and melt fractions represented by the erupted submarine lavas (Supplementary Data Table 2). We combine these new data on the pillow basalts with new measurements of the major and trace element compositions of naturally glassy, olivine- and plagioclase-hosted melt inclusions and their hosts, along with dissolved S and H_2O, $Fe^{3+}/\Sigma Fe$, and $S^{6+}/\Sigma S$ ratios in the glassy melt inclusions from Erta Ale volcano (Supplementary Data Table 3). We integrate previously collected melt inclusion datasets from the same volcano (de Moor et al., 2013; Field, et al., 2012), and nearby Dabbahu (Field et al., 2012) and Nabro volcanoes (Donovan et al., 2018) to assess the relative importance of various differentiation processes active prior to and during eruption of the host tephra, and to constrain pre-erupted water concentrations of magmas erupted subaerially in the Afar Depression. As for Gulf of Aden submarine glasses, we place constraints on the H_2O and fO_2 of the mantle sources of these magmas, temperatures and pressures of melting, and melt fractions represented by the erupted lavas (Table 1; Supplementary Data Table 4). From this combined data set, we assess the importance for the range of the observed slowness and attenuated nature of seismic waves in the region.

2. Geologic Background and prior work

The northern terminus of the East African Rift is where the Main Ethiopian Rift meets the Afar Depression, a broad low-lying land region that includes northern Ethiopia, Djibouti, Eritrea, and northwestern Somalia (Figure 1). The Red Sea spreading center continues away from Afar to the northwest and the Gulf of Aden spreading center continues to the east, where new oceanic lithosphere is actively produced. Though in detail there are complex micro-tectonic processes and structures in this area, the region encompassing the Afar Depression and Red Sea and Gulf of Aden spreading centers is thought to broadly be the final transition away from continental rifting to the development of true oceanic spreading in the eastern Gulf of Aden and the Red Sea. The lavas erupted here have clear trace element and radiogenic isotopic influences from melts of the depleted upper mantle, the Afar plume, and the Pan-African lithosphere (Hutchison et al., 2018; Rooney et al., 2012); the proportions of each component present have been calculated using three component mixing models and Sr-Nd-Pb isotopic compositions (see Supplementary Data Table 5 for calculation reproduction), and these proportions have been shown to vary spatially in recent magmatism and through time as the rift matured in this region (Rooney, 2020).

Gulf of Aden submarine pillow lavas dredged to the east of 47.1°E have negatively sloped rare earth element patterns (i.e., La/Sm < 1) and Sr-Nd-Pb isotopic compositions that indicate that these lavas are predominantly melts of the depleted mid-ocean ridge mantle (DMM; Schilling et al., 1992). Submarine pillow lavas dredged to the west, between 43.9-46.7°E, have more steeply positively sloped rare earth patterns (i.e., La/Sm = 2.5 - 4), and trace element patterns and Sr-Nd-Pb isotopic compositions that indicate that these lavas are mixtures of melts of the DMM and the mantle endmember C/FOZO/PREMA, thought to be transported into the melting region by the Afar plume (Rooney et al., 2012; Schilling et al., 1992). The lithological identity of the C/FOZO/PREMA mantle endmember is debated, possibly representing portions of the transition zone or lowermost mantle (Hanan & Graham, 1996; Hart et al., 1992; Hauri et al., 1994). It may sample the long-lived residue of the extraction of continental crust from a chondritic mantle (Giuliani et al., 2021), or may contain recycled oceanic lithosphere of a composition that is not currently present at Earth's surface (Castillo, 2015). Whatever the origin of this isotopic endmember, the radiogenic isotopic composition of Gulf of Aden submarine lavas between 43.9-46.7°E, and along the West Sheba Ridge in particular, can be explained as being 25-99% comprised of melts of C/FOZO/PREMA (Schilling et al., 1992). Submarine lavas further west from 43.9°E require greater contributions from melts of the African lithosphere to explain their flat to gently positively sloped rare earth element patterns and radiogenic Sr and Nd but unradiogenic Pb isotopic compositions (Schilling et al., 1992).

There are three locations in the Afar Depression where melt inclusion studies place constraints on the volatile contents of magmas prior to eruption: Erta Ale, Dabahhu, and Nabro volcanoes (Figure 1). Erta Ale is associated with the Red Sea spreading center that extends to the north, though it is offset to the west relative to the Red Sea spreading center by the Danakil Block, which is being rifted from Afar. It is one in a series of aligned stratovolcanoes that mark the edge of the Danakil Block and have trace element and radiogenic isotopic compositions that indicate that the lavas erupted here are predominantly melts of material from the Afar plume, with minimal crustal assimilation and contributions from melts of DMM (Barrat et al., 1998; Rooney, 2020). Two melt inclusion studies from Erta Ale reveal that pre-eruptive magmas have low H_2O and CO_2 contents (<0.13 wt% H_2O, <200 ppm CO_2; de Moor et al., 2013; Field et al., 2012), and suggest shallow crystallization of the host phenocrysts from relatively dry (<0.15 wt% H_2O) magmas near 1150°C and fO_2 of ΔQFM ≈ 0.

The lineament of volcanoes in which Erta Ale resides is connected to the Main Ethiopian Rift by a series of rift sectors, one of which includes Dabbahu volcano. Dabbahu lavas range widely in composition from basalt to rhyolite, and the only melt inclusion study available is on the 2011 eruption of evolved magmas with melt inclusion glass compositions containing 68-75 wt% SiO_2 (Field et al., 2012). These glass inclusions contain between 3-5 wt% H_2O and 0-400 ppm CO_2 (Field et al., 2012) and the parental basaltic magma to these evolved compositions is thought to contain <1 wt% H_2O (Field et al., 2012). Magnetite-ilmenite pairs in the basaltic trachy-andesite lavas from Dabbahu indicate crystallization at ΔQFM = 0 to +0.7 (Field et al., 2012).

To the northeast of Dabbahu is Nabro volcano, which sits atop the Precambrian-aged Danakil metamorphic rocks and whose magmas undergo substantial magma mixing in a large crystal mush zone in the crust (Donovan et al., 2018). Basaltic trachyandesitic tephra containg olivine- and plagioclase-hosted melt inclusions are basaltic to trachy-basaltic, with as high as ~7 wt% MgO, and record pre-eruptive magmas with between 0.25-

2.0 wt% H_2O and 0-3,000 ppm CO_2 (Donovan et al., 2018). The parental magma to these melt inclusion compositions is thought to have major element compositions like those of lavas from the Edd Volcanic Field, that contain approximately 1.3 wt% H_2O, 2000 ppm CO_2, and fO_2 between ΔQFM = 0 to +0.7 (Donovan et al., 2018).

3. Samples and Methods

3.1 Sample Descriptions

3.1.1 Erta Ale

The tephra sampled in this study was collected from a cinder/spatter cone during the November 2010 overflow and is the same tephra studied by de Moor et al. (2013). The tephra consists of vesicular, glassy scoria clasts that are < 2 cm in the longest dimension. Olivine, plagioclase, and pyroxene are found throughout the tephra; however, the pyroxene is somewhat less abundant than olivine and plagioclase with ~10% of the crystal load consisting of pyroxene, ~40% olivine, and ~50% plagioclase. Olivine (~1-2mm) in this tephra are subhedral to anhedral and are encrusted with matrix glass. These olivine contain several spherical to oblate, pale-brown naturally glassy silicate melt inclusions that are ~150-250 μm in diameter. The pyroxene (~1-2mm) are deep green in color, are subhedral to anhedral and are encrusted in matrix glass. Typically, one to two naturally glassy spherical to oblate silicate melt inclusions are found towards the center of each pyroxene grain; these melt inclusions are ~90-250 μm in diameter. The plagioclase (~1-2mm) are milky white in color, and anhedral. These plagioclase grains contain several spherical to oblate pale brown naturally glassy silicate melt inclusions that are ~60-300 μm in diameter.

3.1.2 Gulf of Aden

The samples in this study were dredged in 1976 during R/V Vema cruise 33-07, where sampling of the ridge axis took place along with physiographic, structural, and magnetic anomaly mapping (Schilling et al., 1992). Most of the basalts collected in the Gulf of Aden were from fresh pillows and sheet flows, with fresh glass present on many of the basalts (Schilling et al., 1992). The samples provided consist of naturally glassy, pale brown, submarine glass chips (~2-4mm). Some samples contain small olivine and plagioclase phenocrysts (~60-100 μm), that are anhedral to subhedral.

3.2 Electron probe micro-analysis

Olivine-, plagioclase-, and pyroxene-hosted melt inclusions from Erta Ale and matrix glasses adhered to the outside of these mineral grains were exposed on a single side and polished for electron probe micro-analysis (EPMA) using a JEOL-JXA 8200 Superprobe at the University of California Los Angeles for major element analyses of glass inclusions and their phenocryst hosts. During major element analyses of both the glass and the phenocrysts, the beam was focused and operated at a current of 15 nA, an accelerating voltage of 15 keV. For measurements of the phenocryst hosts, sodium and potassium were measured first with 10 second peak and 5 second background counting times to minimize alkali loss. Calcium, silicon, and total iron were also measured in the first round with 20 second peak and 5 second background counting times. Titanium, aluminum, manganese, magnesium, and phosphorus were measured in a second round with 20 second peak and 5 second background counting times. For measurements of the glass inclusions and matrix glasses, sodium and potassium were measured first with 20 second peak and 10 second background counting times to minimize alkali loss (i.e., no corrections were made). Calcium, silicon, and total iron were also measured in the first round, with 20 second peak and 5 second background counting times for silicon and 30 second peak and 15 second background counting times for calcium and total iron. Titanium, aluminum, manganese, magnesium, and phosphorus were measured in a second round with 40 second peak and 20 second background counting times.

All data were subject to ZAF correction procedures. Primary calibration standards include forsterite, magnetite, anorthite, Ti-albite, K -feldspar, sphene, manganese, and Durango apatite. The VG-A99 glass was monitored as secondary standard during each run. Sulfur and chlorine were measured separately on Erta Ale glass inclusions and matrix glasses, as well as on chips of Gulf of Aden submarine glasses using a 10 μm beam operated at 80 nA and an accelerating voltage of 15 kV. Both sulfur and chlorine were measured with 100 second peak and 25 second background counting times. The peak position for sulfur was searched for on unknown samples because the position of the k-alpha peak for sulfur is known to vary as the oxidation state of sulfur changes from S^{2-} to S^{6+} (Carroll and Rutherford, 1988). Pyrite, barite, Ba-Cl apatite, and synthetic BAAP were used as the primary calibration standards. The VG-A99 glass was monitored as a secondary standard during each run. The major element compositions of the olivine, plagioclase, and pyroxene hosts were measured adjacent to the glass inclusions.

3.3 FTIR analysis

After EPMA of melt inclusions and their phenocryst hosts, all sample surfaces were polished to remove possible beam damage within the activation volume of each EPMA spot. Melt inclusions were then polished from the opposite side until doubly exposed, and Gulf of Aden glasses were wafered to thicknesses of 17-125 μm to create wafers with analyzable pools of optically clear glass. All wafered samples were washed gently with acetone to remove epoxy residues. Dissolved H_2O and CO_2 concentrations in glass inclusions and Gulf of Aden submarine glasses were analyzed by Fourier-transform infrared (FTIR) spectroscopy at the University of California, Riverside using a Thermo Scientific Nicolet iS50 Fourier-transform infrared spectrometer with a Nicolet Continuum microscope attachment. Spectra for all samples were collected between 1000 and 6000 cm^{-1} using a tungsten-halogen source, KBr beamsplitter and a liquid nitrogen cooled MCT-A detector. The bench, microscope, and samples were continuously purged by air free of water and carbon dioxide using a Whatman purge-gas generator.

Aperture dimensions were selected for each sample depending on the geometry of free glass pathway, ranging in size from 11x14 μm to as large as 100x145 μm. The thicknesses of each sample were measured using a piezometric digimatic indicator with a precision of ± 1 μm.

3.4 XANES analysis

The $S^{6+}/\Sigma S$ ratios of melt inclusions and Gulf of Aden submarine glasses, and $Fe^{3+}/\Sigma Fe$ ratios of Gulf of Aden submarine glasses, were determined by micro-X-ray absorption near-edge structure (μ-XANES) spectroscopy at beamline 13-IDE, Advanced Photon Source, Argonne National Laboratory. For S measurements, spectra were collected in fluorescence mode from 2447 eV to 2547 eV, with a dwell time of two seconds on each point, using a Si [111] monochromator and a defocused beam, with effective diameter of 15 μm. Counts were recorded on a multi-element silicon drift detector X-ray spectrometer, equipped with two Si drift diode detectors. All analyses were done in a helium atmosphere to avoid interaction between the incident photon beam and atmosphere. Incident beam intensity was on the order of 10^7 photons per second per μm^2, reflecting a balance between the intensity required to produce interpretable S-XANES spectra from materials with low S-abundances (i.e., <2000 ppm) and the mounting evidence that very high photon density fluxes electronically damage Fe and S in silicate materials (e.g., S^{6+}, when present, is reduced to S^{4+}: Brounce et al., 2017; Fe^{3+} is reduced to Fe^{2+}: Cottrell et al., 2018). Each analysis was performed using a stationary beam. Spectral merging, background subtraction, and normalization for these spectra was done using the X-ray absorption spectroscopy data software package ATHENA (Ravel and Newville, 2005), applied uniformly to all spectra so that the region from 2447-2462 eV varies around a value of 0 and region from 2485-2457 varies about a value of 1. These normalized spectra were then subject to spectral fitting routines using the Peak ANalysis (PAN) software package. Each normalized spectrum was fit between 2462-2487 eV with four Gaussian curves – one for the background (peak center fixed at 2485 eV) and one each for sulfate (peak center fixed at 2481 eV), the broad sulfide feature (peak center fixed at 2477 eV), and the narrow sulfide feature (peak center fixed at 2470 eV). The integrated $S^{6+}/\Sigma S$ ratios were calculated using the area under the curve of the 2485 eV peak divided by the sum of the areas under the curves of the 2477 and 2485 eV peaks (after Brounce et al., 2022). Alternative methods for calculating $S^{6+}/\Sigma S$ ratios from these spectra (i.e., Nash et al., 2019; Brounce et al., 2017) are provided in the supplement.

For Fe measurements, spectra were collected in fluorescence mode from 7012 eV to 7485 eV using a Si [111] monochromator and a defocused beam diameter of ~10 μm. Counts were recorded on a multi-element silicon drift detector x-ray spectrometer, equipped with two Si drift diode detectors. 100 μm of aluminum foil was placed in the path of the incident photon beam to decrease the intensity of the photon beam prior to interaction with the sample surface, which could lead to auto-oxidation of Fe species dissolved in the glass. The incident photon beam intensity resulted in on the order of 2 x 10^7 photons/second/μm^2. The Fe-XANES spectra were normalized, and the pre-edge features were fit following the techniques of Brounce et al. (2017), using two background functions and two Gaussian curves to fit the Fe^{2+} and Fe^{3+} peaks. The calibration glasses of Cottrell et al. (2009) recalibrated according to Zhang et al. (2018) were used to calculate $Fe^{3+}/\Sigma Fe$ ratios from the ratio of the areas of the two Gaussian features fit to the pre-edge peaks.

4. Results

4.1 Gulf of Aden

The new Gulf of Aden data presented in this manuscript are available in EarthChem Library (Brounce et al., 2025b) and are available as supplementary data tables in this publication. The major element compositions of Gulf of Aden submarine dredged glasses are reported by Kelley et al. (2013) and summarized here. They are basaltic in composition and range in composition from 6.7-11.7 wt% MgO, 8.6-13.4 wt% FeO*, 10.2-12.8 wt% CaO, 0.04-0.7 wt% K_2O, and 0.9-3.4 wt% TiO_2 (Figure 2a-d). The FeO*, K_2O, and TiO_2 contents are loosely negatively correlated with MgO, as expected for magmas with variable extents of crystallization of variable proportions of olivine, plagioclase, and/or pyroxene (Figure 2a, c, d). There is no correlation between CaO with MgO. The K_2O contents of Gulf of Aden glasses vary from values < 0.1 wt % to as high as 0.7 wt% K_2O, forming three distinct groups. “Low K_2O” glasses contain less than 0.2 wt % K_2O (light gray box, Figure 2d), “Medium K_2O” glasses contain between 0.2 and 0.5 wt

% K_2O (medium gray box, Figure 2d), and a single “High K_2O” glass contains 0.7 wt% (dark gray box, Figure 2d). The “Low K_2O”, “Medium K_2O”, and “High K_2O” glasses are each found in specific geographic regions - “Low K_2O” glasses are mostly found east of 49°E, “Medium K_2O” glasses are found between 43°E and 48°E, and the single “High K_2O” glass is found at 46°E. One sample, V60 (indicated by italic font on Figure 2), a glassy fragment recovered by a core aboard R/V Valdivia (originally called sample VA3-302P by Bäcker et al. 1973) and renamed V60 by Schilling et al. (1992) has anomalously high FeO* and TiO_2 compared to the rest of the sample suite and has K_2O contents that put it in the “Medium K_2O” group. The high FeO* and TiO_2 suggest higher pressure and lower extent of melting of a mantle source with much lower K_2O contents for this glassy fragment compared to the rest of the suite, and the overall lack of correspondence between K_2O and TiO_2 in the sample suites taken together suggests that the variation in K_2O is not driven by variably extents of melting of a mantle source of constant composition.

Our FTIR measurements of these same Gulf of Aden submarine glasses have 0.2-0.8 wt% H_2O, CO_2 from below detection limits via FTIR (i.e., < 30 ppm CO_2 for thinned wafers <75 µm thick, such as used in this study) to 158 ppm CO_2, 800-1300 ppm S, and 20-415 ppm Cl (Figure 3a-d; Supplementary Data Table 1). The sulfur and FeO* contents of these glasses cluster around the sulfide saturation curve, consistent with saturation with a free sulfide phase (Figure 3d). The sulfur contents of these glasses are uncorrelated with

H_2O contents (Figure 3c). The H_2O contents of Gulf of Aden glasses are also uncorrelated with MgO but are positively correlated with K_2O within the “Low K_2O” and “Medium K_2O” groups (Figure 3b).

Measured $Fe^{3+}/\Sigma Fe$ values range between 0.136-0.189, and $S^{6+}/\Sigma S$ values range from 0.06-0.27. There are negative correlations between both $Fe^{3+}/\Sigma Fe$ and $S^{6+}/\Sigma S$ and MgO contents (Figure 4a), consistent with the observed slight increase in fO_2 in silicate magmas during low pressure crystallization of olivine +/- plagioclase (Cottrell and Kelley, 2011; Brounce et al., 2014; Brounce et al., 2021; Birner et al., 2018; Shorttle et al., 2015; Le Voyer et al., 2014; O’Neill et al., 2018). There are two glasses with anomalously high $Fe^{3+}/\Sigma Fe$ compared to the rest of the sample suite – one is sample V60 and the other is sample V3307-51D-1g (labelled on Figure 4a for clarity). Sample V60 also has the highest FeO* and TiO_2 contents of all the Gulf of Aden glasses and has “Medium K_2O”. Sample V3307-51D-1g is indistinguishable in FeO* and TiO_2 from the other Gulf of Aden glasses, and like V60, has “Medium K_2O”. Measured $Fe^{3+}/\Sigma Fe$ ratios are positively correlated with $S^{6+}/\Sigma S$ (Figure 4b). Both $Fe^{3+}/\Sigma Fe$ and $S^{6+}/\Sigma S$ are uncorrelated with their radial distance from Lake Abhe – in particular, most samples have $Fe^{3+}/\Sigma Fe$ ~0.147 and $S^{6+}/\Sigma S$ ~0.11 (Figure 5). However, samples V60 and V3307-51D-1g have anomalously high $S^{6+}/\Sigma S$ and are higher by ~5 times the standard deviation of the rest of the measurements (standard deviation = +/- 0.03) (Figure 4a).

4.2 Erta Ale

The new Erta Ale data presented in this manuscript are available in EarthChem Library (Brounce et al., 2025a) and are available as supplementary data tables in this publication. Erta Ale melt inclusions are trapped in 2 olivine grains with compositions of Fo_{79} and Fo_{80}, 10 plagioclase grains that range in composition from An_{71} to An_{82}, and 5 pyroxene grains that range in composition from Di_{89} to Di_{92}. The major element compositions of these inclusions were assessed for the effects of post-entrapment crystallization of the host mineral on the edges of the melt inclusions as follows. For olivine grains, we predicted the composition of olivine in equilibrium with our measured melt inclusions assuming $Fe^{3+}/\sum Fe$ = 0.16 (de Moor et al., 2013) and $Fe^{2+}/Mg\ K_D^{ol/liq}$ as calculated according to Toplis et al. (2005). This yielded and $Fe^{2+}/Mg\ K_D^{ol/liq}$ of 0. 298 and predicted equilibrium forsterite number of 81.0 for Erta Ale-10, compared to measured forsterite number of 80.1 from measurements of the olivine host, and $Fe^{2+}/Mg\ K_D^{ol/liq}$ of 0. 300 and predicted equilibrium forsterite number of 79.2 and 79.5 for Erta Ale-14A and B respectively, compared to measured forsterite number of 79.8 from measurements of the olivine host. We consider these within the range of uncertainties of the value of $Fe^{3+}/\sum Fe$ for these specific melt inclusions and we opted to apply no correction for post-entrapment crystallization for these inclusions. For pyroxene grains, the Diopside-Hedenbergite component of a modeled pyroxene that is in equilibrium with the measured melt inclusion composition was calculated according to the model of Putirka (1999). This predicted equilibrium composition was then compared to the measured composition of the pyroxene host. Any melt inclusion-host pair that was >4 units apart was disregarded from further consideration. For plagioclase grains, the anorthite component of a modeled plagioclase that is in equilibrium with the measured melt inclusion composition was calculated using the Post-Entrapment Crystallization MELTS calculator of Kress & Ghiorso (2004). This predicted equilibrium composition was then compared to the measured composition of the plagioclase host. Any melt inclusion-host pair that was >4 units apart was disregarded from further consideration. In this way, we limit the effects of post-entrapment crystallization in our data consideration and narrow our dataset from 51 discrete melt inclusion measurements in 17 grains to 16 discrete melt inclusion measurements in 7 grains.

The major element compositions of the accepted inclusions are basaltic with 4.9-6.8 wt% MgO, 10.5-12.9 wt% FeO*, 9.0-11.3 wt% CaO, 0.6-0.9 wt% K_2O, and 2.1-2.7 wt% TiO_2 (Figure 3a-d; Supplementary Data Table 3). The K_2O, FeO*, and TiO_2 contents of Erta Ale inclusions are negatively correlated with MgO (Figure 3a, b, d), while CaO/Al_2O_3 is positively correlated with MgO (Figure 3c). Matrix glass adhered to the outside of olivine, plagioclase, and pyroxene grains that contain the melt inclusions measured here was also analyzed, and these matrix glass compositions range from 6.2-6.5 wt% MgO, 11.0-12.9 wt% FeO*, 10.6-11.1 wt% CaO, 0.59-0.66 wt% K_2O, and 2.4-2.5 wt % TiO_2 (light green circles Figure 3a-d; Supplementary Data Table 3). There is no distinction in major element compositions of melt inclusions according to the identity of the mineral host (plagioclase, pyroxene, and olivine).

Erta Ale melt inclusions range from 0.05 to 0.4 wt% H_2O and 30 to 1220 ppm S, and CO_2 below detection via FTIR. The S contents of Erta Ale inclusions are uncorrelated, or perhaps loosely negatively correlated, with FeO* as FeO* concentrations range between 10.6 and 12.9 wt% FeO* while S concentrations change by ~25x (Figure 4d). Olivine hosted melt inclusions extend to higher sulfur concentrations (~1218 ppm) than plagioclase or pyroxene hosted inclusions, and pyroxene hosted inclusions have the lowest sulfur concentrations (~136 ppm), overlapping with those of the matrix glass.

The measured $S^{6+}/\Sigma S$ ratios for these melt inclusions range between 0.06 and 0.14, and one measurement of the matrix glass adhered to the outside of an olivine phenocryst containing one of the melt inclusions discussed above has $S^{6+}/\Sigma S$ of 0.17 (Figure 4a; Supplementary Data Table 3). The $Fe^{3+}/\Sigma Fe$ ratios of these inclusions were not measured.

5. Discussion

5.1 Parental magmas for Gulf of Aden and Erta Ale from new measurements

To estimate the effects of fractional crystallization on major element chemistry of Gulf of Aden glasses, we used Rhyolite-MELTS v.1.2.1 (Gualda et al., 2012) at a pressure equal to 300 bar (i.e., the pressure indicated by volatile saturation and their eruption pressure on the seafloor, see next paragraph), a starting fO_2 of $\Delta QFM = 0$ and $H_2O = 0.5$ wt%. At this pressure and starting fO_2, a modelled melt that begins with a composition equal to that of sample V3307-66D-1g crystallizes olivine, then olivine and plagioclase, then olivine, plagioclase and clinopyroxene, as well as small amounts of spinel and apatite as it cools from a calculated liquidus temperature of 1278 °C to 900 °C. This model (solid curve, Figure 2) is broadly consistent with the measured major element compositions of Gulf of Aden glasses (except for K_2O, see below) and indicates that samples with MgO > 8.5 wt% are separated from their parental and primary melt compositions only by crystallization of olivine.

We calculated the pressure of volatile saturation of Gulf of Aden glasses using VolatileCalc2 (Newman & Lowenstern, 2002). For the five glasses where CO_2 contents could be resolved using FTIR (V3307-64D, -66D, -69D, -42D, and -46D), the saturation pressure of the volatile contents (92-357 bars) correspond closely to the pressure of collection on the seafloor (130-355 bars; supplementary data table 1). In the remaining glasses, there were no resolvable CO_2 peaks in the FTIR spectra, and these H_2O-only volatile saturation pressures are much lower than the pressure of collection on the seafloor. This, and positive correlations between H_2O and K_2O in these samples, lead us to assume that, while CO_2 was lost during degassing, significant loss of H_2O from these magmas during volcanic degassing did not occur, following in the style of Dixon and Stolper (1995) on other mid-ocean ridge basaltic magmas. We therefore use the measured values of H_2O and

fO_2 as parental magma values from which we calculate primary melt compositions.

We also estimated the effects of fractional crystallization on major element chemistry of Erta Ale glass inclusions using Rhyolite-MELTS v.1.2.1 (Gualda et al., 2012), this time at a pressure equal to 770 bar (see paragraph below), a starting fO_2 of ΔQFM = -0.5 and H_2O = 0.2 wt%. At this pressure and starting fO_2, a modelled melt that begins with a composition equal to sample BS-h2-MI1 (de Moor et al., 2013) crystallizes as it cools from its liquidus temperature of 1180°C and decompresses to 10 bar, beginning with clinopyroxene and plagioclase, then also olivine at 6 wt% MgO. This model is broadly consistent with the measured compositions of Erta Ale melt inclusions in this study and previous works and indicates that the melts trapped by the inclusions studied here can be produced by 5-41% crystallization from a parental magma similar in composition to sample BS-h2-MI1. We also model the effects of fractional crystallization on major element chemistry, beginning with a composition equal to sample G-111 (Castillo et al., 2020) which has higher MgO contents than any melt inclusion measured. This model was run under the identical parameters described above except with a starting fO_2 of ΔQFM=-0.15, H_2O = 0.2 wt%, and a liquidus temperature of 1198°C. This melt cools to 900°C and decompresses to 10 bar, beginning with the crystallization of olivine. Plagioclase begins to crystallize along with olivine when the melt reaches 7.56 wt% MgO, and clinopyroxene joins the crystallizing assemblage when the melt reaches 7.26

wt% MgO. This model (dashed curve, Figure 2) is consistent with the major element composition of whole rock and melt inclusions from Erta Ale and demonstrates that olivine is the only phase crystallizing from magmas with MgO > 8.0 wt% (Figure 2).

To assess the possible variation in magma composition (including fO_2) that would result from degassing, we calculated a degassing trajectory for the same parent magma (BS-h2-MI1; the highest MgO sample measured for Erta Ale; de Moor et al., 2013) one starting with 0.20 wt% H_2O (informed from H_2O measurements of Erta Ale melt inclusions in this study, see supplementary data tables) and one starting with 0.1 wt% H_2O (the highest H_2O measurements from Field et al., 2012), 200 ppm CO_2, and 1200 ppm S. We chose this volatile composition as most representative of the highest volatile contents measured in melt inclusions at Erta Ale from a combination of studies (this study; de Moor et al., 2013; Field et al., 2012), though it remains unclear whether magmas at depth may have been more volatile rich. We ran the model at a starting fO_2 of ΔQFM = -0.5 (the same fO_2 as used in the crystallization model, corresponding to $Fe^{3+}/\Sigma Fe$ = 0.135 and $S^{6+}/\Sigma S$ = 0.098) and 1180°C, neglecting the effect of crystallization on H_2O. Because we have measured $Fe^{3+}/\Sigma Fe$ and $S^{6+}/\Sigma S$ directly in our Gulf of Aden glasses, following Muth & Wallace (2021) we choose a value for B in log K = A/T + B for which Sulfur_X (Ding et al., 2023) returned the measured $Fe^{3+}/\Sigma Fe$ and $S^{6+}/\Sigma S$ of our Gulf of Aden glasses. This results in an expression for the reaction $8Fe^{3+} + S^{2-} = S^{6+} + 8Fe^{2+}$ of log K = -2863/T + 7.5. This modelled magma composition is vapor saturated at 770 bars, and proceeds to degas CO_2 immediately, then also S beginning substantially near 250 bars total pressure, and H_2O does not much change to 2 bars total pressure at these temperatures and compositions. The fO_2 of this modelled melt decreases slightly from its starting value of ΔQFM = -0.5 to ΔQFM = -0.65 (corresponding to $Fe^{3+}/\Sigma Fe = 0.127$ and $S^{6+}/\Sigma S = 0.05$) by 2 bars total pressure, and degasses S from the residual melt down to 830 ppm S. Our melt inclusion analyses and those of previous studies are consistent with this degassing trajectory with respect to H_2O and CO_2 measurements, but we find that S remains more soluble in the model than measurements suggest. Nonetheless, degassing in these conditions (namely starting at relatively low fO_2, low volatile contents, and low pressures), and like previous studies of Erta Ale magmas (de Moor et al., 2013; Field et al., 2012), we will use the most volatile rich compositions and highest measured fO_2s as parental melt compositions from which to calculate primary melt compositions and the mantle source.

We note that it is highly likely that all samples measured in this study and prior studies reflect some amount of CO_2 lost from a parental magma to a gas phase. Estimates for the CO_2 content of an undegassed magma in the Afar region are 1000-1200 ppm CO_2 (Gerlach, 1989). The degassing of CO_2 is slightly oxidizing to residual magmas – loss of ~1000 ppm CO_2 has been shown to result in an increase in the residual magma fO_2 by ~0.1 log unit (Brounce et al., 2017). This is small, and we do not correct for it here.

5.2 Fe-S redox

The $Fe^{3+}/\Sigma Fe$ and $S^{6+}/\Sigma S$ were both measured via XANES in the Gulf of Aden submarine glasses (Figure 4b). The two are positively correlated, however the $S^{6+}/\Sigma S$ ratios reported for these Gulf of Aden submarine glasses are higher than recent models predict for a given major element composition, S content, temperature, and $Fe^{3+}/\Sigma Fe$ (Boulliung & Wood, 2022; O'Neill & Mavrogenes, 2022; Supplementary Data Table 1). The difference between measured and modeled $S^{6+}/\Sigma S$ ratios is large – on average the measured values are 11% (absolute) higher than models predict. However, if one assumes that major element composition, S content, and $Fe^{3+}/\Sigma Fe$ are known and temperature is varied, we find that relatively modest changes in assumed temperature away from the MgO magmatic temperature (calculated using Helz and Thornber, 1987) is required to reproduce the measured $S^{6+}/\Sigma S$ ratios. All but one sample required a decrease of between 5-49°C relative to the MgO magmatic temperature and the one sample required a 16°C increase. The average change in temperature required across all samples with both $Fe^{3+}/\Sigma Fe$ and $S^{6+}/\Sigma S$ measurements is a 32°C decrease in the temperature recorded by $Fe^{3+}/\Sigma Fe$ and $S^{6+}/\Sigma S$ ratios compared to the MgO thermometer magmatic temperature (Supplementary Data Table 1; Fig. 4b). This uncertainty in temperature is small.

5.3 Primary magmas and mantle sources under the northern terminus of the East African Rift

We estimated primary melt compositions, defined as compositions immediately before their segregation from their mantle residues, prior to crystallization-differentiation and degassing, for the Gulf of Aden lavas, Erta Ale, Nabro, and Dabbahu. We used two approaches: (1) by adding equilibrium olivine back to measured compositions until we obtained melt compositions in equilibrium with olivine of various compositions typically assumed to be representative of mantle peridotite olivine – Fo_{89}, Fo_{90}, and Fo_{91}, and (2) using the PRIMELT-3P software, which combines the inverse model of olivine addition approach with forward models of batch and fractional peridotite partial melting to inform at what extent of olivine addition should the inverse model stop (Herzberg et al., 2023). We describe the results of these calculations and compare them below.

5.3.1 Primary melts from olivine addition

For Gulf of Aden glasses, we incrementally added equilibrium olivine back to the compositions of Gulf of Aden glasses with MgO > 8 wt%. For Fo_{90} compositions, this required between 2-15% olivine addition and produces model melt compositions with 11.4-13.5 wt% MgO, 8.8-10.4 wt% FeO*, 0.13-0.73 wt% H_2O, and $Fe^{3+}/\Sigma Fe$ ratios of 0.136-0.185 (see supplement for full report of these calculations results, and Table 1 for a summary).

Because models of fractional crystallization for Erta Ale magma conditions recorded by melt inclusion and whole rock studies indicate that these magmas are multiply saturated with olivine, plagioclase and/or clinopyroxene below 8.0 wt% MgO (see above, section 5.1), we use the major element composition of whole rock lavas from the GeoROC database for Erta Ale volcano, combined with parental magma H_2O=0.2 wt% and $Fe^{3+}/\Sigma Fe$ = 0.145 (constraints from melt inclusions in this study and de Moor et al. 2013; Field et al. 2012) to calculate primary melt compositions, only for GeoROC compositions with >8.0 wt% MgO (Barberi et al., 1971; Barrat et al., 1998). As above, we incrementally added equilibrium olivine back to these compositions until we obtained melt compositions in equilibrium with Fo_{89}, Fo_{90}, and Fo_{91} olivine (see supplement for full report of these calculation results). For Fo_{90} compositions, this required between 5-23% olivine addition and produces model melt compositions with 12.5-15.5 wt% MgO, 9.6-11.6 wt % FeO*, 0.16-0.19 wt% H_2O, and $Fe^{3+}/\Sigma Fe$ ratios of 0.117-0.137 (Table 1).

Similarly, we use literature whole rock data for Nabro (De Fino et al., 1978) and Dabbahu (Barberi et al., 1975) for lavas that have compositions that are plausible parental melts for those volcanoes. These samples have greater than 8.0 wt% MgO, and we use the recommendations of melt inclusion studies at each location for parental melt H_2O equal to 1.3 wt% (Nabro; Donovan et al., 2018) and 1 wt% (Dabbahu; Field et al., 2012). Both studies estimate that magmas at each volcanic center crystallized at fO_2 between ΔQFM = 0 and = 0.7, so we calculate primary melts assuming Fe^{3+}/

ΣFe = 0.145, and Fe^{3+}/ΣFe = 0.190. Again, we incrementally added equilibrium olivine back to these compositions until we obtained melt compositions in equilibrium with Fo_{89}, Fo_{90}, and Fo_{91} olivine (see supplement for full report of these calculation results). For Fo90 compositions at Nabro volcano, in the oxidized scenario (parental melt Fe^{3+}/ΣFe = 0.190) this required between 0-16% olivine addition and produces model melt compositions with 10.4-13.9 wt% MgO, 8.2-10.7 wt% FeO*, 1.1-1.3 wt% H_2O, and Fe^{3+}/ΣFe ratios of 0.167-0.190 (Table 1). In the reduced scenario (parental melt Fe^{3+}/ΣFe = 0.145) this required between 2-18% olivine addition and produces model melt compositions with 11.0-14.6 wt% MgO, 8.2-10.6 wt% FeO*, 1.1-1.3 wt% H_2O, and Fe^{3+}/ΣFe ratios of 0.121-0.143 (Table 1). For Fo90 compositions at Dabbahu volcano, in the oxidized scenario (parental melt Fe^{3+}/ΣFe = 0.190) this requires 12% olivine addition and produces a model melt composition with 13.7 wt% MgO, 10.9 wt% FeO*, 0.9 wt% H_2O, and Fe^{3+}/ΣFe ratios of 0.170 (Table 1). In the reduced scenario (parental melt Fe^{3+}/ΣFe = 0.145) this required 14% olivine addition and produces a model melt composition with 14.5 wt% MgO, 11.0 wt% FeO*, 0.9 wt% H_2O, and Fe^{3+}/ΣFe ratios of 0.126 (Table 1).

We use these primary melt compositions to calculate the fraction of melt required to produce those compositions and the H_2O content of the mantle source following methods described by Kelley et al. (2006). The following describes primary melts in equilibrium with Fo_{90} olivine (see Table 1 for summary); the full details for modeled primary melts in equilibrium with

Fo_{89}, Fo_{90}, and Fo_{91} olivine can be found in the supplemental materials (Supplementary Data Tables 2 and 4). We calculate mantle source TiO_2 for our samples by comparing the TiO_2/Y ratios of our samples to that of MORB, bulk partition coefficient during mantle melting for TiO_2 of 0.04, and an assumed TiO_2 content for DMM of 0.133, following equation 11 from Kelley et al. (2006). Using this approach, the primary melt compositions described in the previous paragraphs correspond to melt fractions of 8-16% for the Gulf of Aden glasses. In the absence of trace element compositions for samples used to constrain primary melt compositions at Erta Ale, Nabro, and Dabbahu volcanoes, we calculated melt fractions H_2O contents of the mantle sources three ways – one assuming the mantle source has a value equal to the lowest calculated mantle source TiO_2 from the Gulf of Aden (0.128 wt%, from sample 64D; supplementary data table 2), one assuming the mantle source has a value equal to DMM (0.133 wt%; Kelley et al., 2006), and one assuming the mantle source has a value equal to the average calculated mantle source TiO_2 of the most Afar mantle plume influenced Gulf of Aden samples (0.191 wt%, from samples 51D, 48D, and 50D; supplementary data table 2). For Fo90 magmas, this resulted in calculated melt fractions of 2-11% for Erta Ale magmas, 1-4% for Nabro magmas, and 1-4% for Dabbahu magmas (Table 1). Using these melt fractions and assuming a bulk partition coefficient during mantle melting for H_2O of 0.012 (Kelley et al., 2006), these calculations suggest that the mantle sources of Gulf of Aden glasses have H_2O contents from 304 ± 105 ppm H_2O to the east of 49°E (i.e., in normal mid-ocean ridge spreading scenario and approaching the Central Indian Ridge), 852 ppm ± 167 ppm H_2O between 45°E and 49°E (i.e., along the West Sheba Ridge), and ~330 ppm H_2O in the Gulf of Tadjoura (i.e., approaching the subaerial Afar Depression; Table 1). For the subaerial volcanic centers, these parameters suggest that the mantle sources of: (1) Erta Ale have H_2O contents of 113 ppm H_2O ± 46 ppm H_2O, (2) Nabro have H_2O contents of 397 ppm ± 152 ppm H_2O, and (3) Dabbahu have H_2O contents of 288 ± 114 ppm H_2O (Table 1).

We also calculate the temperatures of these modeled primary melts from MgO contents according to the olivine liquidus relations (Herzberg et al., 2023), as well as the fO_2 indicated by the calculated $Fe^{3+}/\Sigma Fe$ ratios at these temperatures and 1 atm pressure (Borisov et al., 2018; Jayasuriya et al., 2004; O'Neill et al., 2018) as well as at 1.5 GPa pressure (Kress & Carmichael, 1991; other oxybarometer results can be found in the supplemental materials). East of 49°E along the Gulf of Aden, modeled primary melts have temperatures of 1378°C ± 24° and record fO_2s of ΔQFM = -0.02 ± 0.12 at 1.5 GPa (Kress & Carmichael, 1991), or ΔQFM = -0.17 ± 0.11 at 1 atm (Borisov et al., 2018; Table 1). Between 45°E and 49°E, temperatures and fO_2s of modeled primary melts increase somewhat, to 1401°C ± 33° and ΔQFM = +0.20 ± 0.43 at 1.5 GPa (Kress & Carmichael, 1991), or ΔQFM = -0.03 ± 0.51 at 1 atm (Borisov et al., 2018), driven strongly by sample V3307-51D-1g (Table 1). In the Gulf of Tadjoura, the temperature and fO_2 of the one modeled primary melt in this study in this location drops to 1387°C and ΔQFM = +0.08 ± 0.43 at 1.5 GPa (Kress & Carmichael, 1991), or ΔQFM = -0.11 at 1 atm (Borisov et al., 2018). For the subaerial volcanic centers, modeled primary melts record temperatures and fO_2s of 1412°C ± 25° and ΔQFM = -0.08 ± 0.08 at 1.5 GPa (Kress & Carmichael, 1991), or ΔQFM = -0.39 ± 0.16 at 1 atm (Borisov et al., 2018) at Erta Ale, and 1375°C ± 43° and ΔQFM = +0.30 ± 0.41 at 1.5 GPa (Kress & Carmichael, 1991), or ΔQFM = +0.04 ± 0.47 at 1 atm (Borisov et al., 2018) at Nabro (Table 1). For Dabbahu, we calculated primary melts assuming a parental melt at ΔQFM = 0 and =0.7. Accordingly, the temperatures calculated for primary melt from the one sample available for this calculation with MgO > 8.0 wt% are 1402°C (ΔQFM = 0) or 1422°C (ΔQFM = +0.7), and the primary melt fO_2 is either ΔQFM = 0.09 at 1.5 GPa (for parental melt ΔQFM = 0) (Kress & Carmichael, 1991), or ΔQFM = 0.85 at 1.5 GPa (for parental melt ΔQFM = +0.7; Table 1). Using the Borisov calibration, the primary melt fO_2 at 1 atm would be ΔQFM = -0.37 (for parental melt ΔQFM = 0) or ΔQFM = 0.39 (for parental melt ΔQFM = +0.7; Table 1).

5.3.2 Primary melts from PriMELT3

We use the same samples as described in the previous section in the excel calculator to constrain the composition of primary melts using PriMELT-3P (Herzberg et al., 2023). Importantly, though we have tried to identify and avoid compositions that are multiply saturated with olivine +/- pyroxene +/- plagioclase, the PriMELT3 calculator identifies several samples from which there is evidence of pyroxene fractionation at high pressures as indicated by inappropriately low CaO at a given MgO concentration. This warning eliminates the single sample constraint for Dabbahu, but constraints for the Gulf of Aden submarine pillows, Erta Ale, and Nabro remain.

The PriMELT-3P calculations proceeded in general with greater extents of olivine addition to olivine compositions of higher fosterite content, yielding primary melt compositions with higher MgO. For example, for Gulf of Aden glasses, in the calculation combined with batch melting forward model, PriMELT-3P proceeded with 16-24% olivine addition until equilibrium with Fo_{91}-Fo_{92} olivine was reached. This produced primary melts with 14-18 wt% MgO, 8.9-10 wt% FeO*, and $Fe^{3+}/\Sigma Fe$ ratios of 0.107-0.150 (compare to 2-15% olivine addition to obtain a melt with 11.6-13.8 wt% MgO, 8.8-10.4 wt% FeO*, and $Fe^{3+}/\Sigma Fe$ ratios of 0.136-0.185 for the same parental/initial melt compositions when stopping at Fo90 as described in the previous section; Table 1). The batch melting approach by PriMELT-3P predicts substantially higher degrees of melting – 20-29% melting of harzburgitic mantle source – than calculated using primary TiO_2 as described in the previous section (8-15% melting; Table 1). When combined with a fractional melting forward model, PriMELT-3P proceeded with somewhat less olivine addition – 13-19% - and returns primary melt compositions with 13-16 wt% MgO, 8.9-10 wt% FeO*, and $Fe^{3+}/\Sigma Fe$ ratios of 0.111-0.156. Whether combined with batch or fractional melting forward models, because PriMELT-3P predicts primary melts with higher MgO contents than olivine addition to assumed olivine compositions, it also calculates higher temperatures for primary melts along the Gulf of Aden of 1469 ± 43°C (batch melting) or 1431 ± 32°C (fractional melting). At these conditions, PriMELT-3P predicts that melting under the spreading ridge of the Gulf of Aden begins at 2.8 ± 0.3 GPa (~85 ± 9 km depth) and stops at 1.3 ± 0.3 GPa (~40 ± 9 km depth; Figure 6, Table 1). These pressures for the start of melting are very close to the spinel-garnet transition (Figure 6), though most Gulf of Aden samples do not display obvious signs of garnet as a residual phase during melting (Figure 7), e.g., they have flat sloped heavy rare earth element patterns. The exception to this is sample V60, which has a Dy/Yb_N value of 1.5. This sample however does not pass our filtering methods for calculating primary melt compositions, and thus is not involved in calculating the initial pressures of melting described in this paragraph.

The PriMELT-3P calculation similarly proceeded with greater extents of olivine addition to higher forsterite number olivines for Erta Ale. In the case of combining olivine addition with the forward batch melting model, 8-30% olivine addition was done, yielding primary melts with 13.4-18.9 wt% MgO, 9.8-10 wt% FeO*, and $Fe^{3+}/\Sigma Fe$ ratios of 0.108-0.133 (compare to 5-23% olivine addition and model melt compositions with 12.5-15.5 wt% MgO, 9.6-11.6 wt% FeO*, and $Fe^{3+}/\Sigma Fe$ ratios of 0.117-0.137 for the same parental/initial melt compositions when stopping at Fo_{90} as described in the previous section; Table 1). These compositions are obtained through 21-28% melting of harzburgitic mantle source. When combined with a fractional melting forward model, PriMELT3 added 8-24% olivine to the parental/initial compositions, yielding primary melt compositions with 13-17 wt% MgO, 9.8-10 wt% FeO*, and $Fe^{3+}/\Sigma Fe$ ratios of 0.112-0.132, obtained through 19-26% melting of a harzburgitic mantle source (Table 1). These primary melts yield higher temperatures than the method described in the previous section of 1458 ± 35°C (Table 1). At these conditions, PriMELT-3P predicts that melting under Erta Ale begins at 3.1 ± 0.3 GPa (93 ± 10 km depth) and stops at 2.1 ± 0.2 GPa (63 ± 7 km depth; Figure 6; Table 1).

For Nabro, the two styles of calculation are more similar in part because there are fewer samples to constrain the parental melt composition, and as is the case with the olivine addition method described in the previous section, the result of the PriMELT-3P calculations depends on the $Fe^{3+}/\Sigma Fe$ of the parent/initial magma composition, which changes depending on the fO_2 of the parent magma within the reported range of ΔQFM = 0 to +0.7. In the case that the parent magma has fO_2 of ΔQFM = 0, PriMELT3 proceeds with 0-17% olivine addition to reach olivine compositions of Fo90.2-90.7. This results in primary melts with 10.5-14.7 wt% MgO, 8.6-10.8 wt% FeO*, and $Fe^{3+}/\Sigma Fe$ ratios of 0.158-0.190 (compare to 2-18% olivine addition and melt compositions with 11.0-14.6 wt% MgO, 8.2-10.6 wt% FeO*, and $Fe^{3+}/\Sigma Fe$ ratios of 0.121-0.143 for the same parental/initial melt compositions when stopping at Fo90 as described in the previous section, Table 1). In the case that the parent magma has fO_2 of ΔQFM = +0.7, PriMELT-3P adds somewhat more olivine (0-21%) to reach somewhat more forsteritic mantle olivine compositions (Fo90.4-90.9), resulting in primary melts with somewhat higher MgO (11.3-15.7 wt% MgO) and lower $Fe^{3+}/\Sigma Fe$ ratios (0.116-0.145; Table 1). These primary melts can be obtained by 7-13% melting of a harzburgitic mantle source at 1384 ± 66°C (Table 1). PriMELT-3P predicts a narrow range for melting, beginning at 2.3 ± 0.6 GPa (71 ± 18 km depth) and stopping within the uncertainty of 18 km (Figure 6), for both the lower and higher estimates parent magma starting fO_2s (assuming the parent/initial magma has fO_2 of ΔQFM = +0.7 yields estimates of the pressure of the start of melting of 2.5 ± 0.6 GPa).

5.4 The H_2O and fO_2 of the Afar plume

To summarize, the Gulf of Aden samples collected east of 49°E have Sr-Nd-Pb-Hf isotopic compositions that are characteristic of the depleted upper mantle (Schilling et al., 1992). Our new measurements of H_2O, $Fe^{3+}/\Sigma Fe$, and $S^{6+}/\Sigma S$ indicate that these samples, specifically their modeled primary melts, have low water contents (calculated via method 1 described above 0.27 ± 0.09 wt% H_2O), and $Fe^{3+}/\Sigma Fe$ characteristic of MORB primary melts (0.126 ± 0.01 using method 1, or 0.112 ± 0.01 using method 2). The Gulf of Aden samples collected between 45°E and 49°E have Sr-Nd-Pb-Hf isotopic compositions along with enriched trace element patterns that have been interpreted as arising due to major contributions in their mantle sources from the Afar mantle plume and minor contributions from the Pan African lithosphere and the depleted upper mantle (Schilling et al., 1992). The modeled primary melts for these samples have elevated concentrations of H_2O (0.6 ± 0.11 wt% H_2O calculated via method 1 described above), but $Fe^{3+}/\Sigma Fe$ still characteristic of MORB primary melts (0.140 ± 0.02 using method 1, or 0.132 ± 0.02 using method 2), corresponding to fO_2s near the QFM oxygen buffer. These redox measurements indicate that the Afar mantle plume is not substantially different in fO_2 from that of DMM (Zhang et al., 2018; O'Neill et al., 2018).

Using the radiogenic isotopic studies of Schilling et al. (1992) and Rooney et al. (2012) as templates and using constraints on primary melt compositions from our new measurements of H_2O and $Fe^{3+}/\Sigma Fe$ of Gulf of Aden glasses, we can calculate H_2O contents and $Fe^{3+}/\Sigma Fe$ ratios of the depleted upper mantle, the Afar mantle plume, and the Pan-African lithosphere. We use the same endmember compositions as Rooney et al. (2012), which differ from those of Schilling et al. (1992) in the composition of the isotopic endmember of the Afar plume, which is now thought of as a C/FOZO/PHEM plume (Figure 8). We calculate that the isotopic compositions of Gulf of Aden glasses east of 49°E require 79-88% contribution from melts of the depleted upper mantle, 10-17% contribution from melts of the Afar plume, and 2-4% contribution from melts of the Pan African lithosphere (Supplementary Data Table 5). The contributions from the Afar plume increase and contributions from the depleted upper mantle decrease in some samples collected between 45°E and 49°E, requiring 0-70% contribution from melts of the depleted upper mantle, 26-100% contribution from melts of the

Afar plume, and 0-5% contribution from melts of the Pan African lithosphere. Importantly, the isotopic composition of sample V3307-50D-1g can be entirely described as a melt of the Afar plume with a composition indicated by Rooney et al. (2012) and from this we assign the H_2O and $Fe^{3+}/\Sigma Fe$ of the modeled primary melt from this sample as representative of primary melts of the Afar plume (Table 1). These values are 0.7 wt% H_2O and $Fe^{3+}/\Sigma Fe = 0.123$ (Table 1), both calculated using method 1, corresponding to an fO_2 of ΔQFM = -0.27 using Borisov et al. (2018). Combined with the estimates of ~13% melting of the mantle to produce this primary melt composition, estimated from primary melt TiO_2 contents as described above (see above, *5.3.1 Primary magmas and mantle sources*) and the simple batch melting equation, this suggests that the Afar plume contains ~1082 ppm H_2O.

Because PriMELT-3P requires greater extents of olivine addition to reach equilibrium with higher forsterite number olivine to satisfy both the inverse olivine addition and forward mantle melting models simultaneously, it is likely that the primary melt H_2O contents calculated using method 1 are higher compared to the PRiMELT-3P approach. If we take sample V3307-51D-1g, which passes PriMELT3 calculation requirements, and continue adding olivine as in method 1 to the PriMELT-3P suggested olivine composition of Fo_{92}, we obtain a primary melt composition with 0.91 wt% TiO_2 and 0.45 wt% H_2O (compare to the Fo_{90} composition stopping point from method 1 of 1.00 wt% TiO_2 and 0.50 wt% H_2O). Following the same approach to calculate degree of melting and mantle source water contents described above, this yields a mantle source with 924 ppm H_2O (Table 1). This is lower but not substantially different (i.e., does not lead to large differences in interpretation of the tectonic setting) than the estimate of 1082 ppm H_2O, obtained using sample V3307-50D-1g, for which PriMELT-3P indicates the CaO content of the primary melt is too low to be both derived from peridotite and experienced only olivine fractionation prior to eruption, and method 1 for primary melt calculations. This illustrates well the level of uncertainty in various approaches to the “primary melt problem” and using erupted basaltic liquids to place constraints on mantle rock compositions.

We can also compare H_2O/Ce ratios of samples in this study (133-537; Figure 5d) to those from other locations. The H_2O/Ce of MORB range between 150-500 (Dixon et al., 2002, 2017; Michael, 1995; Wang et al., 2021), with the highest of these values occurring in the Southwest Indian Ridge (Wang et al., 2021). The highest H_2O/Ce ratios in Gulf of Aden samples in this study occur to the east of 49°E, in samples that are far from the influence of the Afar mantle plume. These high H_2O/Ce ratios are driven by low Ce concentrations that are not accompanied by depletions in H_2O. The reason for these high H_2O/Ce ratios in MORB has been proposed to be related to ancient subduction zone mantle wedge material in the melting region of mid-ocean ridge spreading centers (Wang et al., 2021), and warrant further study in the context of mid-ocean ridge source mantle. Here, we focus on the H_2O/Ce ratios of the samples most influenced by the Afar mantle plume (i.e., from radiogenic isotopes require 47-99% of the Afar plume; 48D-2, 50D-1, and

51D-1; Figure 5), which have H_2O/Ce ratios of 234-244. These H_2O/Ce ratios are similar to values for the isolated component FOZO at Hawaii (~200; Shimizu et al., 2019), the Azores mantle plume (210-279; Dixon et al., 2002, 2017; Asimow et al., 2004), and the Easter Salas y Gomez mantle plume (223; Simons et al., 2002). Using the batch melting equation, bulk DCe = 0.01 (following from Wang et al., 2021), and melt fractions calculated in this study (from Fo90 olivine addition calculations), these H_2O/Ce values predict mantle source H_2O contents of 904 ppm (51D-1), 851 ppm (48D-2) and 1182 ppm (50D-1), and an average of 979 ppm H_2O. In summary, our full range of constraints on the H_2O content of the Afar mantle plume is 697-1182 ppm H_2O, or 951 ± 169.

5.5 Geophysical and Geochemical models of the mantle

As described in the introduction, the mantle under the East African Rift presents one of the most prominent geophysical anomalies present in the upper mantle and it has been challenging to understand the (1) the primary reasons for these anomalous seismic wave behaviors and (2) the importance of the characteristics of the anomaly to rifting strong continental lithosphere more broadly.

We present constraints on the mantle potential temperature, water content, fO_2, degrees of melting and initial and final pressures of melting for the Afar Depression, where the anomaly is the most prominent, in the preceding sections. The average of all constraints (Gulf of Aden, Erta Ale, Nabro, and Dabbahu) yield potential temperatures of 1458 ± 68°C, in good agreement with previous studies in this area (Figure 6). This is warmer than ambient mantle that feeds the typical, global mid-ocean ridge spreading center system (1280-1400°C using the model presented here, Herzberg et al., 2023, Figure 6), but not remarkably hot in the context of global mantle plume potential temperatures (e.g., the Hawaiian mantle plume is estimated to be 1510 to nearly 1600°C; Rooney et al., 2012; Figure 6). Using the Gulf of Aden submarine glasses and three component mixing models to match radiogenic isotopic compositions, we suggest that the Afar plume has ~852 ± 167 ppm H_2O – higher than estimates for the combined mantle sources of Hawaiian lavas, which vary from 350-450 ppm H_2O (Wallace, 1998, Dixon et al., 2008) and substantially lower than e.g., the mantle wedge in subduction zones, which have 2000-8000 ppm H_2O (Kelley et al., 2010). The estimate of ~852 ± 167 ppm H_2O for the Afar mantle plume is broadly consistent with estimates for the isolated FOZO/C/PHEM mantle component in other FOZO-dominant plume or plume component of 620-920 ppm, including Jan Mayen, Iceland, Azores, Easter Salas y Gomez, and the FOZO component in the Hawaiian plume (Asimow et al., 2004; Dixon et al., 2017; Nichols et al., 2002; Shimizu et al., 2019; Simons et al., 2002). We show that existing melt inclusion constraints on the pre-eruptive water contents of subaerially erupted lavas in the Afar Depression suggest that the combined mantle sources of recently erupted Erta Ale, Nabro, and Dabbahu lavas (mixtures of the depleted upper mantle, the Afar plume, and the Pan-African lithosphere) have 100-300 ppm H_2O, intermediate between values for DMM (50-100 ppm H_2O; Shimizu et al., 2019; Dixon et al., 2008) and the Afar plume (this study). Additionally, we show that the mantle sources of all samples studied here have fO_2 at or ~0.25 orders of magnitude within ΔQFM = 0. PRiMELT-3P predicts that melting begins as deep as ~93 km depth and proceeds as shallow as ~63 km depth under Afar and ~37 km depth under the Gulf of Aden (Figure 6). We emphasize that the mantle temperatures for melt generation, mantle source H_2O contents, and mantle source fO_2 constraints presented here are not extreme examples of these values in the upper mantle in any tectonic setting, and thus can be eliminated as the sole explanation for the extremely slow seismic wave speeds. Of variables otherwise suggested to impact the bulk and shear moduli of the Earth's mantle and thus impact seismic wave behaviors, we are left to evaluate the role of the presence of partial melt.

These results are broadly consistent with other geochemical models of melting in the region, based on major and trace element compositions of lavas erupted to the surface in the East African Rift (Rooney et al., 2012; Ferguson et al., 2013; Beccaluva et al., 2009; Furman et al., 2016.). We highlight key points from Figure 6: 1) The initial pressures of melting at Erta Ale and the most heavily plume-influences Gulf of Aden spreading center ridge segment occur slightly deeper and cooler than the dry peridotite solidus. This requires that melt generation is fundamentally driven by the presence of fusible mantle components, in this case, the Afar plume transporting some material that contains higher-than-tpyical H_2O contents; 2) Under the Gulf of Aden spreading center, melting under the most heavily plume-influenced ridge segment proceeds to shallower depths (~27 km depth, pink cirlce, Figure 6) than under the ridge segments not influenced by the Afar plume (~42 km depth, black circle, Figure 6). The Afar plume has a clear role in enabling melt generation to lower pressures within the oceanic spreading regime; 3) At Erta Ale, where the Afar plume is present like it is under the heavily plume-influenced segment of the Gulf of Aden spreading center, but melt generation occurs under the continental lithosphere, melting stops at deeper depths (~63 km, green circle, Figure 6) than any location under the Gulf of Aden spreading ridge. The lithosphere, or some other thermomechanical boundary, stops melting at rather high pressures. These observations outline a clear role of the Afar plume in enabling melt generation. These results also support hypotheses that there is a thick and diffuse thermomechanical boundary layer between the asthenosphere and lithosphere and that this may explain for instance observed differences in the position of the lithosphere-asthenosphere boundary as placed by seismic tomography (60 km depth; Emry et al., 2018) and receiver functions (30 km depth; Rychert et al., 2012). Our results suggest that a ~30 km thick melt-rich (~10-20% melt fraction) layer exists under the Afar Depression beginning ~93 km depth (the predicted depth of the start of melting under Erta Ale, Table 1) and extending up the final depth of melting of ~63 km at Erta Ale, and about ~27 km in the Gulf of Aden where the Afar mantle plume has the strongest influence, and ~42 km in the Gulf of Aden far from influence from the Afar mantle plume today (Table 1). This final depth of melting in each region may correspond to the lithosphere-asthenosphere boundary in the region or may reside below that boundary.

Because the presence of melt has a first order impact on the speed of seismic wave speeds, we hypothesize that this melt layer plays a primary role in defining the nature of the geophysical anomaly under the Afar Depression and may reconcile geophysical and geochemical models of the mantle in this region, as proposed by previous seismological studies in the region (e.g., Bastow et al., 2005; Kendell et al., 2005). The thermal anomaly is modest, water contents are elevated but not remarkable, fO_2 values are like those of the upper mantle that feeds the mid-ocean ridge spreading system – these variables independently cannot drive the remarkable nature of the geophysical anomaly under the Afar rift. The modest thermal anomaly and somewhat elevated H_2O contents are characteristics of the Afar mantle plume and in combination, do however provide a mechanism for generating and sustaining the presence of partial melts in the mantle in this region. While there are several competing models for both the shear-wave velocity of melt-free peridotite and the effect of melt on shear-wave velocity, no current model can explain shear-wave velocities at the temperatures inferred in this study below ~4.1 km/s without recourse to some effect of melt (Byrnes et al., 2023). Our PriMELT-3P calculations report that the mantle residue for samples in this study is peridotitic to harzburgitic in composition (see supplement), and at 2 GPa and 1400°C this rock is expected to have V_S~4.3 km/s (Hacker and Abers, 2004) for typical grain sizes of ~1 cm. Observed V_S at this depth in Afar are ~4.0 km/s or lower, representing a 7% or greater decrease in V_S (Emry et al., 2018). This can be achieved by the persistent presence of ~1% or slightly less of partial melt (1% melt produces a decrease in V_S of 7.9%; Hammond and Humphreys, 2000). In a broad sense, this is supported by our PriMELT-3P calculations that suggest for instance, that Erta Ale lavas are 21-28% partial melts of a harzburgitic mantle source produced over a range of ~30 km in the mantle from 93 km to 63 km depth. This is a simplification, but if this melt were distributed evenly within that range of melting, it would correspond to ~0.7-0.9% melt per km of mantle rock below the edifice. Our work supports recent similar calculations from seismological perspectives (e.g., Chambers et al., 2019); chemical and physical models for the crust and the mantle in the East African Rift converge. Importantly, the persistent presence of broadly distributed melt is likely supported by the presence of the Afar plume and argues for the importance of the plume and magmatism more broadly in the initiation and continued development of the rift.

6.0 Conclusions

Gulf of Aden submarine glasses range in H_2O contents from 0.14 to 0.84 wt% and have 0.06 to 0.30 $S^{6+}/\Sigma S$ and 0.135 to 0.189 $Fe^{3+}/\Sigma Fe$ ratios. The glasses recovered east of 49°E have radiogenic isotopic compositions most like melts of the depleted MORB mantle and have the lowest $S^{6+}/\Sigma S$, $Fe^{3+}/\Sigma Fe$ and H_2O contents. Glasses erupted between 45°E and 49°E have radiogenic isotopic compositions most like melts of the Afar mantle plume and have higher H_2O contents (average = 0.61 wt%) but low $Fe^{3+}/\Sigma Fe$ (average = 0.158) and moderate $S^{6+}/\Sigma S$ (average = 0.18). Erta Ale melt inclusions in plagioclase, pyroxene, and olivine all have H_2O < 0.67 wt% and $S^{6+}/\Sigma S$ ~ 0.12, consistent with two previous melt inclusion studies of the same eruption. Combined with previous studies, we model the primary melt and mantle source characteristics of the mantle along the Gulf of Aden and into the Afar Depression and find that the Afar mantle plume has moderate H_2O contents of ~852 ± 167 ppm H_2O and fO_2 of ΔQFM ~ -0.2, similar to that of the depleted MORB mantle. This is consistent with its radiogenic isotopic character as a C/FOZO/PHEM plume which has been shown to not produce lavas substantially elevated in fO_2 at Reunion Island (Brounce et al., 2022; Nicklas et al., 2022). The mantle sources of Afar Depression volcanoes Erta Ale, Dabbahu, and Nabro have 113-397 ppm H_2O and fO_2 of ΔQFM ~0 to +0.8. Melting is estimated to begin under the Afar Depression and the Gulf of Aden around 93 km and end at 37 km under the Gulf of Aden and at 63 km under the Afar Depression. This occurs in a mantle with average region wide potential temperature of 1458°C, producing melt fractions of 11-16% (simple olivine addition) or 27-29% (PriMELT3P) along the Gulf of Aden most influenced by the Afar plume, to melt fractions of ~1-11% (simple olivine addition) or 7-28% (PriMELT3P) under the Afar Depression. We find our results are consistent with recent geophysical models of seismic wave speeds that suggest a melt rich lens in the asthenosphere under the Afar Depression to explain the extreme nature of the present-day geophysical anomaly. Taken together, these works reconcile seemingly disparate views of the mantle under the East African Rift – moderate geochemical anomalies (i.e., slightly elevated mantle potential temperatures and a damp mantle plume) generate melt, which has a pronounced impact on seismic wave behaviors. It emphasizes the continued importance of the role of the Afar mantle plume in the East African Rift through to the present day.

Acknowledgements

We are grateful for two constructive reviews from Bruno Scaillet and Tanya Furman, and the comments and editorial handling of Jackie Dixon. This work was supported by NSF GeoPRISMS Award 1849700 to MjB and HF, and NSF EAR 1049891 to TF. Portions of this work was performed at GeoSoilEnviroCARS (The University of Chicago Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS was supported by the National Science Foundation – Earth Sciences (EAR – 1634415). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. We thank the UCLA EPMA laboratory for access, including during the COVID-19 pandemic. TF thanks J. Maarten de Moor and

Bernard Marty who participated in the expedition to Erta Ale for sample collection and research in 2011.

OPEN RESEARCH: Data availability Statement

The major and volatile element, and Fe and S redox data used in the study are available as EarthChem libraries (Brounce et al., 2025a; 2025b).

Figure Captions

Figure 1. Map of the East African Rift with major segment names indicated. The location of samples for which new data are presented here are marked as stars, the location of samples for which we rely on literature data are marked as circles. Important geographical features are labeled, including the position of Lake Abhe, the suggested center of the Afar mantle plume. The basemap was created using GeoMapApp (http://geomapapp.org; Ryan et al., 2009)

Figure 2. Major element variations for phenocryst-hosted melt inclusions and matrix glasses from Erta Ale (large dark and light green circles with black outlines) and submarine pillow glasses from the Gulf of Aden (large black circles), as well as phenocryst-hosted melt inclusions from Erta Ale and Nabro volcano from the literature (Field et al., 2012; de Moor et al., 2013; Donovan et al., 2018) and submarine pillow glasses from the Central Indian Ridge mid-ocean ridge spreading system (Gale et al., 2013). Black curves

show the trajectory of a cooling basaltic liquid during crystallization produced using MELTs (see main text for details).

Figure 3. Volatile element variations for phenocryst-hosted melt inclusions from Erta Ale and submarine pillow glasses from the Gulf of Aden, as well as phenocryst-hosted melt inclusions from Erta Ale and Nabro volcano. Symbols are as in figure 2. The black curve in panel (d) shows the calculated sulfur content at sulfide saturation for a selected Gulf of Aden glass, calculated using the model of O’Neill & Mavrogenes (2022), using measured $Fe^{3+}/\Sigma Fe$, major element composition, Ni and Cu abundances, and pressure of seafloor at the point of sampling for that sample.

Figure 4. (a) S oxidation states for phenocryst-hosted melt inclusions and matrix glass from Erta Ale (large dark and light green circles with black outlines), Fe oxidation states for phenocryst-hosted melt inclusions from Erta Ale from de Moor et al. (2013; small tan circles) and paired Fe oxidation states (large black circles) and S oxidation states (large gray circles with black outlines) on Gulf of Aden submarine glasses. Note that values for S oxidation states are shown on the right hand y-axis, and values for Fe oxidation states are shown on the left hand y-axis. (b) Fe and S oxidation states measured in the same glass chips for submarine pillow glasses from the Gulf of Aden. The black curve shows the line of best fit through model calculations of the S oxidation states of these glasses, given their major

element composition, temperature, and measured Fe oxidation states, using the model of O’Neill & Mavrogenes (2022; note that the model of Boulliund & Wood, 2023 produces a very similar curve). Gray arrow indicates the expected shift in S oxidation state of a basaltic silicate glass as a function of temperature at a fixed Fe oxidation state.

Figure 5. Geochemical compositions of Gulf of Aden submarine glasses as a function of their distance from Lake Abhe, used by Rooney et al. (2012) as a marker of the presumed center of the Afar Mantle plume under the Afar Depression. The shaded gray region in panel (a) indicates the composition of the “C” mantle component by Hanan & Graham (1996), in which the Afar Mantle Plume is thought to be abundant. Panel (d) plots H_2O contents (left y-axis, black circles) and H_2O/Ce ratios (right y-axis, gray circles). The dark gray, light gray, and pink rectangles demarcate the H_2O/Ce ratios measured in MORB (light gray; Dixon et al. 2002, Michael, 1995), proposed value for FOZO based on measurements in Hawaii (dark gray; Shimizu), and measured in SWIR (pink; Wang et al., 2021). Panel (e) plots $Fe^{3+}/\Sigma Fe$ (left y axis, black circles) and $S^{6+}/\Sigma S$ (right y axis, gray circles). The fO_2 shown in panel (f) is calculated using the calibration of Kress & Carmichael (1991) at 1 atmosphere and the magmatic temperature calculated using MgO glass compositions according to Helz and Thornber (1987; see supplement).

Figure 6. Summary of proposed pressures and temperatures of melting for lavas erupted in the Afar Depression. New constraints from this study are the fractional melting models from PriMELT3, with initial pressures (P_i) and final pressures (P_f) of melting indicated by two circles (large white, green, black, and pink circles). Results from other studies are shown in gray circles (Ferguson et al., 2013; Furman et al., 2016), gray rectangles with black outlines (Rooney et al., 2012); black crosses (Beccaluva et al., 2009), and black vertical lines, also with initial and final pressure of melting indicated by the length of the line (Beccaluva et al., 2009). Also shown are equilibration pressures and temperatures of lithospheric xenoliths (light gray shapes with no outline; Beccaluva et al., 2009; Conticelli et al., 1999). We include temperature estimates for melting along the mid-ocean ridge spreading system, at the Azores, and at Hawaii, calculated using an earlier version of PriMELT (black horizontal lines, Rooney et al., 2012). The spinel to garnet transition is marked by the thick dashed gray curve (Roobinson and Wood, 1998). Two dry peridotite solidi are shown (Hirschmann, 2000, thin black curve; Sarafian et al., 2017, thin dashed black curve), as well as the damp peridotite solidus (Sarafian et al., 2017) and the dry pyroxenite solidus (Pertermann and Hirschmann, 2003).

Figure 7. Rare earth element diagrams for Gulf of Aden glasses (normalized to chondrite from, Sun and McDonough, 1995). Bold curves in the top panel mark two samples with exceptionally high H_2O/Ce ratios. Bold curves in the

middle panel mark three samples with exceptionally high contributions from the Afar plume (as calculated from radiogenic isotopic mixing calculations, see main text and supplement). Bold curves in the bottom panel mark a fourth sample with exceptionally high contributions from the Afar plume (red curve) and the only sample with high Dy/Yb_N (green curve).

Figure 8. Plot of $^{87}Sr/^{86}Sr$ and $^{206}Pb/^{204}Pb$ isotopic compositions of oceanic basalts. Small gray circles are global MORB and OIB from Stracke (2012). Gulf of Aden samples from this study are large black circles, isotopic compositions reported by Schilling et al. (1992). Colored circles are isotopic compositions at OIB locations where some samples have Fe-XANES constraints for fO_2 at the time of writing (Brounce et al., 2021 and references therein).

References

Asimow, P., Dixon, J.E., & Langmuir, C.H. (2004) A hydrous melting and fractionation model for mid-ocean ridge basalts: Application to the Mid-Atlantic Ridge near the Azores. *Geochemistry, Geophysics, Geosystems,* 5. https://doi.org/10.1029/2003GC000568.

Bäcker, H., Clin, M., & Lange, K. (1973). Tectonics in the Gulf of Tadjura. *Marine Geology*, *15*(5), 309–327. https://doi.org/10.1016/0025-3227(73)90048-0

Barberi, F., Bizouard, H., & Varet, J. (1971). Nature of the clinopyroxene and iron enrichment in alkalic and transitional basaltic magmas.

Contributions to Mineralogy and Petrology, *33*(2), 93–107. https://doi.org/10.1007/BF00386108

Barberi, F., Ferrara, G., Santacroce, R., Treuil, M., & Varet, J. (1975). A Transitional Basalt-Pantellerite Sequence of Fractional Crystallization, the Boina Centre (Afar Rift, Ethiopia). *Journal of Petrology*, *16*(1), 22–56. https://doi.org/10.1093/petrology/16.1.22

Barrat, J. A., Fourcade, S., Jahn, B. M., Cheminée, J. L., & Capdevila, R. (1998). Isotope (Sr, Nd, Pb, O) and trace-element geochemistry of volcanics from the Erta'Ale range (Ethiopia). *Journal of Volcanology and Geothermal Research*, *80*(1), 85–100. https://doi.org/10.1016/S0377-0273(97)00016-4

Bastow, I. D., Nyblade, A. A., Stuart, G. W., Rooney, T. O., & Benoit, M. H. (2008). Upper mantle seismic structure beneath the Ethiopian hot spot: Rifting at the edge of the African low-velocity anomaly. *Geochemistry, Geophysics, Geosystems*, *9*(12). https://doi.org/10.1029/2008GC002107

Bastow, I. D., Stuart, G. W., Kendall, J. M., & Ebinger, C. J. (2005). Upper-mantle seismic structure in a region of incipient continental breakup: northern Ethiopian rift. Geophysical Journal International, 162(2), 479-493. https://doi.org/10.1111/j.1365-246X.2005.02666.x

Beccaluva, L., Bianchini, G., Natali, C., & Siena, F. (2009) Continental flood basalts and mantle plumes: a case study of the northern Ethiopian Plateau. *Journal of Petrology, 50(7),* 1377-1403.

Birner, S.K., Cottrell, #., Warren, J.M., Kelley, K.A., & Davis, F.A. (2018). Peridotites and basalts reveal broad congruence between two independent records of mantle fO_2 despite local redox heterogeneity. *Earth and Planetary Science Letters, 494*, 172-189.

Borisov, A., Behrens, H., & Holtz, F. (2018). Ferric/ferrous ratio in silicate melts: A new model for 1 atm data with special emphasis on the effects of melt composition. *Contributions to Mineralogy and Petrology*, *173*(12), 98. https://doi.org/10.1007/s00410-018-1524-8

Boulliung, J., & Wood, B. J. (2022). SO2 solubility and degassing behavior in silicate melts. *Geochimica et Cosmochimica Acta*, *336*, 150–164. https://doi.org/10.1016/j.gca.2022.08.032

Boulliung, J., & Wood, B. J. (2023). Sulfur oxidation state and solubility in silicate melts. *Contributions to Mineralogy and Petrology*, *178*(8), 56. https://doi.org/10.1007/s00410-023-02033-9

Brounce, M., Boyce, J.W., & McCubbin, F.M. (2022). Sulfur in apatite from the Nakhla meteorite record a late-stage oxidation event. *Earth and Planetary Science Letters, v. 595, 117784.*

Brounce, M.N., Kelley, K.A., & Cottrell, E. (2014). Variations in $Fe^{3+}/\Sigma Fe$ of Mariana Arc Basalts and Mantle Wedge fO_2. *Journal of Petrology, 55(12),* 2513-2536. https://doi.org/10.1093/petrology/egu065.

Brounce, M., Reagan, M.K., Kelley, K.A., Cottrell, E., Shimizu, K., & Almeev R. (2021). Covariation of Slab Tracers, Volatiles, and Oxidation during Subduction Initiation. *Geochemistry, Geophysics, Geosystems,* https://doi.org/10.1029/2021GC009823.

Brounce, M. N., Scoggins, S., Fischer, T. P., Ford, H., Byrnes, J., 2025a. Erta Ale phenocryst hosted melt inclusion major elements, $S^{6+}/\Sigma S$, and volatile element compositions, Version 1.0. Interdisciplinary Earth Data Alliance (IEDA). https://doi.org/10.60520/IEDA/113243.

Brounce, M. N., Scoggins, S., Fischer, T. P., Ford, H., Byrnes, J., 2025b. Gulf of Aden submarine glass $Fe^{3+}/\Sigma Fe$, $S^{6+}/\Sigma S$, and volatile element compositions, Version 1.0. Interdisciplinary Earth Data Alliance (IEDA). https://doi.org/10.60520/IEDA/113242.

Brounce, M., Stolper, E., & Eiler, J. (2017). Redox variations in Mauna Kea lavas, the oxygen fugacity of the Hawaiian plume, and the role of volcanic gases in Earth’s oxygenation. *Proceedings of the National Academy of Sciences*, *114*(34), 8997. https://doi.org/10.1073/pnas.1619527114

Brounce, M., Stolper, E., & Eiler, J. (2021). The mantle source of basalts from Reunion Island is not more oxidized than the MORB source mantle.

Contributions to Mineralogy and Petrology, *177*(1), 7. https://doi.org/10.1007/s00410-021-01870-w

Bucholz, C. E., Gaetani, G. A., Behn, M. D., & Shimizu, N. (2013). Post-entrapment modification of volatiles and oxygen fugacity in olivine-hosted melt inclusions. *Earth and Planetary Science Letters*, *374*, 145–155. https://doi.org/10.1016/j.epsl.2013.05.033

Byrnes, J. S., Gaherty, J. B., and Hopper, E. (2023) Seismic Architecture of the Lithosphere-Asthenosphere System in the Western United States from a Joint Inversion of Body- and Surface-wave Observations: Distribution of Partial Melt in the Upper Mantle. *Seismica*, *2(2)*, https://doi.org/10.26443/seismica.v2i2.272

Carroll, M.R. & Rutherford, M.J. (1988). Sulfur speciation in hydrous experimental glasses of varying oxidation state; results from measured wavelength shifts of sulfur X-rays. *American Mineralogist, 73(7-8),* 845-849.

Castillo, P. R. (2015). The recycling of marine carbonates and sources of HIMU and FOZO ocean island basalts. *Lithos*, *216–217*, 254–263. https://doi.org/10.1016/j.lithos.2014.12.005

Castillo, P.R., Liu, X., & Scarsi, P. (2020) The geochemistry and Sr-Nd-Pb isotopic ratios of high $^3He/^4He$ Afar and MER basalts indicate a significant role of the African Superplume in EARS magmatism. *Lithos, 376-377, 105791.*

Chambers, E.L., Harmon, N., Keir, D., Rychert, C.A. (2019). Using ambient noise to image the Northern East African Rift. Geochemistry, Geophysics, Geosystems. https://doi.org/10.1029/2018/GC008129.

Cline II, C. J., Faul, U. H., David, E. C., Berry, A. J., & Jackson, I. (2018). Redox-influenced seismic properties of upper-mantle olivine. *Nature*, *555*(7696), 355–358. https://doi.org/10.1038/nature25764

Conticelli, S., Sintoni, M.F., Abebe, T., Mazzarini, F., & Manetti, P. (1999) Petrology and geochemistry of ultramafic xenoliths and host lavas from the Ethiopian Volcanic Province: an insight into the upper mantle under Eastern Africa. *Acta Vulcanologica, 11(1)* p. 143-159.

Cottrell, E., and Kelley, K.A. (2011). The oxidation state of Fe in MORB glasses and the oxygen fugacity of the upper mantle. *Earth and Planetary Science Letters, 305(3-4),* 270-282. https://doi.org/10.1016/j.epsl.2011.03.014.

Cottrell, E., Kelley, K. A., Lanzirotti, A., & Fischer, R. A. (2009). High-precision determination of iron oxidation state in silicate glasses using XANES. *Chemical Geology*, *268*(3), 167–179. https://doi.org/10.1016/j.chemgeo.2009.08.008

Cottrell, E., Lanzirotti, A., Mysen, B., Birner, S., Kelley, K. A., Botcharnikov, R., Davis, F. A., & Newville, M. (2018). A Mössbauer-based XANES calibration for hydrous basalt glasses reveals radiation-induced oxidation of Fe. *American Mineralogist*, *103*(4), 489–501. https://doi.org/10.2138/am-2018-6268

Dasgupta, R., Mallik, A., Tsuno, K., Withers, A. C., Hirth, G., & Hirschmann, M. M. (2013). Carbon-dioxide-rich silicate melt in the Earth's upper mantle. *Nature*, *493*(7431), 211–215. https://doi.org/10.1038/nature11731

Davies, J. H. (2013). Global map of solid Earth surface heat flow. *Geochemistry, Geophysics, Geosystems*, *14*(10), 4608–4622. https://doi.org/10.1002/ggge.20271

De Fino, M., La Volpe, L., & Lirer, L. (1978). Geology and volcanology of the Edd-Bahar Assoli area (Ethiopia). *Bulletin Volcanologique*, *41*(1), 32–42. https://doi.org/10.1007/BF02597681

de Moor, J. M., Fischer, T. P., Sharp, Z. D., King, P. L., Wilke, M., Botcharnikov, R. E., Cottrell, E., Zelenski, M., Marty, B., Klimm, K., Rivard, C., Ayalew, D., Ramirez, C., & Kelley, K. A. (2013). Sulfur degassing at Erta Ale (Ethiopia) and Masaya (Nicaragua) volcanoes: Implications for degassing processes and oxygen fugacities of basaltic systems. *Geochemistry, Geophysics, Geosystems*, *14*(10), 4076–4108. https://doi.org/10.1002/ggge.20255

Ding, S., Plank, T., Wallace, P. J., & Rasmussen, D. J. (2023). Sulfur_X: A Model of Sulfur Degassing During Magma Ascent. *Geochemistry, Geophysics, Geosystems*, *24*(4), e2022GC010552. https://doi.org/10.1029/2022GC010552

Dixon, J.E., Bindeman, I.N., Kingsley, R.H., Simons, K.K., Le Roux, P.J., Hajewski, T.R., Swart, P., Langmuir, C.H., Ryan, J.G., Walowski, K.J., Wada, I., & Wallace, P.J. (2017). Light stable isotopic compositions of enriched mantle sources: resolving the dehydration paradox. *Geochemistry, Geosystems, Geophysics*, 18, p. 3801-3839.

Dixon, J.E., & Stolper, E.M. (1995) An experimental study of water and carbon dioxide in basaltic liquids. Part II: applications to degassing. Journal of Petrology, 36(6), 1633-1646. https://doi.org/10.1093/oxfordjournals.petrology.a037268.

Dixon, J.E., Clague, D.A., Cousens, B., Monsalve, M.L., & Uhl, J. (2008) Carbonatite and silicate melt metasomatism of the mantle surrounding the Hawaiian plume: Evidence from volatiles, trace elements, and radiogenic isotopes in rejuvenated-stage lavas from Niihau, Hawaii. *Geochemistry, Geophysics, Geosystems.* https://doi.org/10.1029/2008GC002076.

Dixon, J.E., Leist, L., Langmuir, C.H. & Schilling, J. (2002). Recycled dehydrated lithosphere observed in plume-influenced mid-ocean ridge basalt*. Nature 420(6914*), 385-389. https://doi.org/10.1038/nature01215.

Donovan, A., Blundy, J., Oppenheimer, C., & Buisman, I. (2018). The 2011 eruption of Nabro volcano, Eritrea: Perspectives on magmatic processes from melt inclusions. *Contributions to Mineralogy and Petrology*, *173*(1), 1. https://doi.org/10.1007/s00410-017-1425-2

Emry, E. L., Shen, Y., Nyblade, A. A., Flinders, A., & Bao, X. (2018). Upper Mantle Earth Structure in Africa From Full-Wave Ambient Noise Tomography. *Geochemistry, Geophysics, Geosystems*, *20*(1), 120–147. https://doi.org/10.1029/2018GC007804

Ferguson, D. J., Maclennan, J., Bastow, I. D., Pyle, D. M., Jones, S. M., Keir, D., Blundy, J. D., Plank, T., & Yirgu, G. (2013). Melting during late-stage rifting in Afar is hot and deep. *Nature*, *499*(7456), 70–73. https://doi.org/10.1038/nature12292

Field, L., Barnie, T., Blundy, J., Brooker, R. A., Keir, D., Lewi, E., & Saunders, K. (2012). Integrated field, satellite and petrological observations of the November 2010 eruption of Erta Ale. *Bulletin of Volcanology*, *74*(10), 2251–2271. https://doi.org/10.1007/s00445-012-0660-7

Field, L., Blundy, J., Brooker, R. A., Wright, T., & Yirgu, G. (2012). Magma storage conditions beneath Dabbahu Volcano (Ethiopia) constrained by petrology, seismicity and satellite geodesy. *Bulletin of Volcanology*, *74*(5), 981–1004. https://doi.org/10.1007/s00445-012-0580-6

Forsyth, D., & Uyeda, S. (1975). On the Relative Importance of the Driving Forces of Plate Motion*. *Geophysical Journal International*, *43*(1), 163–200. https://doi.org/10.1111/j.1365-246X.1975.tb00631.x

Furman ,T., Nelson, W.R., & Elkins-Tanton, L.T. (2016) Evolution of the East African Rift: drip magmatism, lithospheric thinning, and mafic volcanism. Geochimica et Cosmochimica Acta, 185, 418-434.

Gale, A., Dalton, C. A., Langmuir, C. H., Su, Y. & Schilling, J.G. (2013) The mean composition of ocean ridge basalts. Geochemistry, Geophysics, Geosystems, 14. 489-518. https://doi.org/10.1029/2012GC004334.

Gallacher, R. J., Keir, D., Harmon, N., Stuart, G., Leroy, S., Hammond, J. O. S., Kendall, J.-M., Ayele, A., Goitom, B., Ogubazghi, G., & Ahmed, A. (2016). The initiation of segmented buoyancy-driven melting during continental breakup. *Nature Communications*, *7*(1), 13110. https://doi.org/10.1038/ncomms13110

Gerlach, T. (1989). Degassing of carbon dioxide from basaltic magma at spread centers: I. Afar transitional basalts. *Journal of Volcanology and Geothermal Research, 39,* p. 211-219.

Giuliani, A., Jackson, M. G., Fitzpayne, A., & Dalton, H. (2021). Remnants of early Earth differentiation in the deepest mantle-derived lavas. *Proceedings of the National Academy of Sciences*, *118*(1), e2015211118. https://doi.org/10.1073/pnas.2015211118

Gualda, G. A. R., Ghiorso, M. S., Lemons, R. V., & Carley, T. L. (2012). Rhyolite-MELTS: a Modified Calibration of MELTS Optimized for Silica-rich, Fluid-bearing Magmatic Systems. *Journal of Petrology*, *53*(5), 875–890. https://doi.org/10.1093/petrology/egr080

Hacker, B.R., & Abers, G.A. (2004) Subduction Factory 3: An Excel worksheet and macro for calculating the densities, seismic wave speeds, and H_2O contents of minerals and rocks at pressure and temperature. Geochemistry, Geophysics, Geosystems. https://doi.org/10.1029/2003GC000614.

Hammond, W. C., & Humphreys, E. D. (2000). Upper mantle seismic wave velocity: Effects of realistic partial melt geometries. *Journal of Geophysical Research: Solid Earth*, *105*(B5), 10975–10986. https://doi.org/10.1029/2000JB900041

Hanan, B. B., & Graham, D. W. (1996). Lead and Helium Isotope Evidence from Oceanic Basalts for a Common Deep Source of Mantle Plumes. *Science*, *272*(5264), 991–995. https://doi.org/10.1126/science.272.5264.991

Hart, S. R., Hauri, E. H., Oschmann, L. A., & Whitehead, J. A. (1992). Mantle Plumes and Entrainment: Isotopic Evidence. *Science*, *256*(5056), 517. https://doi.org/10.1126/science.256.5056.517

Hauri, E. H., Whitehead, J. A., & Hart, S. R. (1994). Fluid dynamic and geochemical aspects of entrainment in mantle plumes. *Journal of Geophysical Research: Solid Earth*, *99*(B12), 24275–24300. https://doi.org/10.1029/94JB01257

Helz, R. T. & Thornber, C. R. (1987) Geothermometry of Kilauea Iki lava lake, Hawaii. *Bulletin of Volcanology*. 49, 651-668. https://doi.org/10.1007/BF01080357.

Herzberg, C. T., Asimow, P. D., & Hernández-Montenegro, J. D. (2023). The Meaning of Pressure for Primary Magmas: New Insights From PRIMELT3-P. *Geochemistry, Geophysics, Geosystems*, *24*(1), e2022GC010657. https://doi.org/10.1029/2022GC010657

Hirschmann, M. (2000) Mantle solidus: experimental constraints and the effects of peridotite composition. Geochemistry, Geophysics, Geosystems. https://doi.org/10.1029/2000GC000070.

Hofmann, C., Courtillot, V., Féraud, G., Rochette, P., Yirgu, G., Ketefo, E., & Pik, R. (1997). Timing of the Ethiopian flood basalt event and implications for plume birth and global change. *Nature*, *389*(6653), 838–841. https://doi.org/10.1038/39853

Humphreys, J., Brounce, M., & Walowski, K. (2022). Diffusive equilibration of H2O and oxygen fugacity in natural olivine-hosted melt inclusions. *Earth and Planetary Science Letters*, *584*, 117409. https://doi.org/10.1016/j.epsl.2022.117409

Hutchison, W., Mather, T. A., Pyle, D. M., Boyce, A. J., Gleeson, M. L. M., Yirgu, G., Blundy, J. D., Ferguson, D. J., Vye-Brown, C., Millar, I. L., Sims, K. W. W., & Finch, A. A. (2018). The evolution of magma during continental rifting: New constraints from the isotopic and trace element signatures of silicic magmas from Ethiopian volcanoes. *Earth and Planetary Science Letters*, *489*, 203–218. https://doi.org/10.1016/j.epsl.2018.02.027

Jaupart, C. & Mareschal, J.-C. (2007). Heat flow and thermal structure of the lithosphere. *Treatise on Geophysics*, *1*(6), 218–246.

Jayasuriya, K. D., O'Neill, H. St. C., Berry, A. J., & Campbell, S. J. (2004). A Mössbauer study of the oxidation state of Fe in silicate melts. *American Mineralogist*, *89*(11–12), 1597–1609. https://doi.org/10.2138/am-2004-11-1203

Karato, S., & Jung, H. (1998). Water, partial melting and the origin of the seismic low velocity and high attenuation zone in the upper mantle. *Earth and Planetary Science Letters*, *157*(3), 193–207. https://doi.org/10.1016/S0012-821X(98)00034-X

Karato, S.-I., & Jung, H. (2003). Effects of pressure on high-temperature dislocation creep in olivine. *Philosophical Magazine*, *83*(3), 401–414. https://doi.org/10.1080/0141861021000025829

Kelley, K. A., Kingsley, R., & Schilling, J.-G. (2013). Composition of plume-influenced mid-ocean ridge lavas and glasses from the Mid-Atlantic Ridge, East Pacific Rise, Galápagos Spreading Center, and Gulf of Aden. *Geochemistry, Geophysics, Geosystems*, *14*(1), 223–242. https://doi.org/10.1002/ggge.20049

Kelley, K. A., Plank, T., Grove, T. L., Stolper, E. M., Newman, S., & Hauri, E. (2006). Mantle melting as a function of water content beneath back-arc basins. *Journal of Geophysical Research: Solid Earth*, *111*(B9). https://doi.org/10.1029/2005JB003732

Kelley, K. A., Plank, T., Newman, S., Stolper, E. M., Grove, T. L., Parman, S., & Hauri, E. H. (2010). Mantle Melting as a Function of Water Content beneath the Mariana Arc. *Journal of Petrology*, *51*(8), 1711–1738. https://doi.org/10.1093/petrology/egq036

Kendall, JM., Stuart, G., Ebinger, C, Bastow, I., & Keir, D. (2005), Magma-assisted rifting in Ethiopia. *Nature, 433*, 146–148. https://doi.org/10.1038/nature03161

Kress, V. C., & Carmichael, I. S. E. (1991). The compressibility of silicate liquids containing Fe2O3 and the effect of composition, temperature, oxygen fugacity and pressure on their redox states. *Contributions to Mineralogy and Petrology*, *108*(1), 82–92. https://doi.org/10.1007/BF00307328

Kress, V. C., & Ghiorso, M. S. (2004). Thermodynamic modeling of post-entrapment crystallization in igneous phases. *Journal of Volcanology and Geothermal Research*, *137*(4), 247–260. https://doi.org/10.1016/j.jvolgeores.2004.05.012

Le Voyer, M., Cottrell, E., Kelley, K.A., Brounce, M., & Hauri, E.H. (2014) The effect of primary versus secondary processes on the volatile content of MORB glasses: An example from the equatorial Mid-Atlantic Ridge (5°N-3°S). JGR: Solid Earth, https://doi.org/10.1002/2014JB011160.

Lloyd, A. S., Plank, T., Ruprecht, P., Hauri, E. H., & Rose, W. (2013). Volatile loss from melt inclusions in pyroclasts of differing sizes. *Contributions* *to Mineralogy and Petrology*, *165*(1), 129–153. https://doi.org/10.1007/s00410-012-0800-2

Michael, P.J. (1995) Regionally distinctive sources of depleted MORB: Evidence from trace elements and H_2O. *Earth and Planetary Science Letters, 131(3),* 301-320. https://doi.org/10.1016/0012-821X(95)00023-6.

Mulibo, G. D., & Nyblade, A. A. (2013). The P and S wave velocity structure of the mantle beneath eastern Africa and the African superplume anomaly. *Geochemistry, Geophysics, Geosystems*, *14*(8), 2696–2715. https://doi.org/10.1002/ggge.20150

Muth, M. J., & Wallace, P. J. (2021). Slab-derived sulfate generates oxidized basaltic magmas in the southern Cascade arc (California, USA). *Geology*, *49*(10), 1177–1181. https://doi.org/10.1130/G48759.1

Nash, W.M., Smythe, D.J., Wood, B.J. (2019). Compositional and temperature effects on sulfur speciation and solubility in silicate melts. *Earth and Planetary Science Letters, v. 507, 187-198.*

Newcombe, M. E., Fabbrizio, A., Zhang, Y., Ma, C., Le Voyer, M., Guan, Y., Eiler, J. M., Saal, A. E., & Stolper, E. M. (2014). Chemical zonation in olivine-hosted melt inclusions. *Contributions to Mineralogy and Petrology*, *168*(1), 1030. https://doi.org/10.1007/s00410-014-1030-6

Newman, S., & Lowenstern, J. B. (2002). VolatileCalc: A silicate melt–H2O–CO2 solution model written in Visual Basic for excel. *Computers &*

Geosciences, *28*(5), 597–604. https://doi.org/10.1016/S0098-3004(01)00081-4

Nichols, A.R.L., Carroll, M.R., & Höskuldsson, Á. (2002). Is the Iceland hot spot also wet? Evidence from the water contents of undegassed submarine and subglacial pillow basalts. *Earth and Planetary Science Letters, v. 202, 77-87.*

Nicklas, R.W., Hahn, R.K.M., & Day, J.MD. (2022). Oxidation of Réunion Island lavas with MORB-like fO_2 by crustal assimilation. *Geochemical Perspective Letters, 20, 32-36.*

O'Neill, H. St. C., Berry, A. J., & Mallmann, G. (2018). The oxidation state of iron in Mid-Ocean Ridge Basaltic (MORB) glasses: Implications for their petrogenesis and oxygen fugacities. *Earth and Planetary Science Letters*, *504*, 152–162. https://doi.org/10.1016/j.epsl.2018.10.002

O'Neill, H. St. C., & Mavrogenes, J. A. (2022). The sulfate capacities of silicate melts. *Geochimica et Cosmochimica Acta*, *334*, 368–382. https://doi.org/10.1016/j.gca.2022.06.020

Pasyanos, M. E. (2010). Lithospheric thickness modeled from long-period surface wave dispersion. *Insights into the Earth's Deep Lithosphere*, *481*(1), 38–50. https://doi.org/10.1016/j.tecto.2009.02.023

Pertermann, M. & Hirschmann, M.M. (2003) Partial melting experiments on a MORB-like pyroxenite between 2 and 3 GPa: constraints on the presence of pyroxenite in basalt source regions from solidus location and melting rate. Journal of Geophysical Research: Solid Earth. https://doi.org/10.1029/2000JB000118.

Putirka, K. (1999). Clinopyroxene + liquid equilibria to 100 kbar and 2450 K. *Contributions to Mineralogy and Petrology*, *135*(2), 151–163. https://doi.org/10.1007/s004100050503

Ravel, B., & Newville, M. (2005) ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using EFEFFIT, *Journal of Synchrotron Radiaiton 12, 537-541*.

Robinson, J.A.C. & Wood, B. (1998) The depth of the spinel to garnet transition at the peridotite solidus. Earth and Planetary Science Letters, 164(1-2), p. 277-284.

Rooney, T. O. (2020). The Cenozoic magmatism of East Africa: Part V – Magma sources and processes in the East African Rift. *Lithos*, *360–361*, 105296. https://doi.org/10.1016/j.lithos.2019.105296

Rooney, T. O., Hanan, B. B., Graham, D. W., Furman, T., Blichert-Toft, J., & Schilling, J.-G. (2012). Upper Mantle Pollution during Afar Plume–Continental Rift Interaction. *Journal of Petrology*, *53*(2), 365–389. https://doi.org/10.1093/petrology/egr065

Rooney, T. O., Herzberg, C., & Bastow, I. D. (2012). Elevated mantle temperature beneath East Africa. *Geology*, *40*(1), 27–30. https://doi.org/10.1130/G32382.1

Ryan W. B. F, Carbonette S. M., Coplan J. O., O'Hara, S., Melkonian, A., Arko, R., Weissel R. A., Ferrini V., Goodwillie A., Nitsche F., Bonczkowski J., & Zemsky R. (2009) Global multi-resolution topography synthesis. Geochemistry, Geophysics, Geosystems. 10. https://doi.org/10.1029/2008gc002332

Rychert, C. A., Hammond, J. O. S., Harmon, N., Michael Kendall, J., Keir, D., Ebinger, C., Bastow, I. D., Ayele, A., Belachew, M., & Stuart, G. (2012). Volcanism in the Afar Rift sustained by decompression melting with minimal plume influence. *Nature Geoscience*, *5*(6), 406–409. https://doi.org/10.1038/ngeo1455

Saper, L. M., & Stolper, E. M. (2020). Controlled Cooling-Rate Experiments on Olivine-Hosted Melt Inclusions: Chemical Diffusion and Quantification of Eruptive Cooling Rates on Hawaii and Mars. *Geochemistry, Geophysics, Geosystems*, *21*(2), e2019GC008772. https://doi.org/10.1029/2019GC008772

Sarafian, E., Gaetani, G.A., Hauri, E.H., & Sarafian, A. (2017). Experimental constraints on the damp peridotite solidus and oceanic mantle potential temperature. Science, 355(6328), p. 942-945.

Schilling, J.-G., Kingsley, R. H., Hanan, B. B., & McCully, B. L. (1992). Nd-Sr-Pb isotopic variations along the Gulf of Aden: Evidence for Afar Mantle Plume-Continental Lithosphere Interaction. *Journal of Geophysical Research: Solid Earth*, *97*(B7), 10927–10966. https://doi.org/10.1029/92JB00415

Shimizu, K., Ito, M., Chang, Q., Miyazaki, T., Ueki, K., Toyama, C., Senda, R., Vaglarov, B.S., Ishikawa, T., Kimura, J.I. (2019) Identifying volatile mantle trend with the water-fluorine-cerium systematics of basaltic glass. Chemical Geology, 522, 283-294.

Shorttle, O., Moussallam, Y., Hartley, M.E., Maclennan, J., Edmonds, M., & Murton, B.J. (2015) Fe-XANES analyses of Reykjanes Ridge basalts: Implications for oceanic crust's role in the solid Earth oxygen cycle. *Earth and Planetary Science Letters, 427*, 272-285. https://doi.org/10.1016/j.epsl.2015.07.017.

Simons, K., Dixon, J., Schilling, J.G., Kinglsey, R., Poreda, R. (2002) Volatiles in basaltic glasses from the Easter-Salas y Gomez Seamount chain and Easter microplate: Implications for geochemical cycling of volatile elements. Geochemistry, Geophysics, Geosystems. https://doi.org/10.1029/2001GC000173.

Stagno, V., Ojwang, D. O., McCammon, C. A., & Frost, D. J. (2013). The oxidation state of the mantle and the extraction of carbon from Earth's interior. *Nature*, *493*(7430), 84–88. https://doi.org/10.1038/nature11679

Stracke, A. (2012). Earth's heterogeneous mantle: A product of convection-driven interaction between crust and mantle. *Chemical Geology, v. 330-331, 274-299.*

McDonough, W.F., & Sun S.-s (1995). The composition of the Earth. *Chemical Geology, 120(3-4),* p. 223-253.

Till, C. B., Grove, T. L., & Withers, A. C. (2012). The beginnings of hydrous mantle wedge melting. *Contributions to Mineralogy and Petrology*, *163*(4), 669–688. https://doi.org/10.1007/s00410-011-0692-6

Toplis, M.J. (2005) The thermodynamics of iron and magnesium partitioning between olivine and liquid: criteria for assessing and predicting equilibrium in natural and experimental systems. Contributions to Mineralogy and Petrology, 149, 22-39. https://doi.org/100.1007/s00410-004-0629-4.

Wallace, P.J. (1998) Water and partial melting in mantle plumes: Inferences from the dissolved H_2O concentrations of Hawaiian basaltic magmas. *Geophysical Research Letters, 25(19),* 3639-3642.

Wang, W., Kelley, K.A., Li, Z., Chu, F., Dong, Y., Chen, L., Dong, Y., & Li, J. (2021) Volatile element evidence of local MORB mantle heterogeneity beneath the Southwest Indian Ridge, 48°-51° E. Geochemistry, Geophysics, Geosystems, https://doi.org/10.1029/2021/GC009647.

Zhang, H. L., Cottrell, E., Solheid, P. A., Kelley, K. A., & Hirschmann, M. M. (2018). Determination of Fe3+/ΣFe of XANES basaltic glass standards by Mössbauer spectroscopy and its application to the oxidation state of iron in MORB. *Chemical Geology*, *479*, 166–175. https://doi.org/10.1016/j.chemgeo.2018.01.006