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Geochemistry, Geophysics, Geosystems®

RESEARCH ARTICLE

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Key Points:

- Discovery and characterization of a new suite of CO₂-undersaturated melt inclusions
- High CO₂/CITE ratio suggests a CO₂-rich mantle domain
- No relation between degree of partial melting and Fe³⁺/ΣFe indicates efficient buffering or decreasing Fe₂O₃ partition coefficient with T

Supporting Information:

Supporting Information may be found in the online version of this article.

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CO₂-Undersaturated Melt Inclusions From the South West Indian Ridge Record Surprisingly Uniform Redox Conditions

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Abstract The behavior of Fe³⁺ during mantle partial melting strongly influences the oxidation state of the resulting magmas, with implications for the evolution of the atmosphere's oxidation state. Here, we challenge a prevailing view that low-degree partial melts are more oxidized due to the incompatible behavior of Fe³⁺. Our study is based on measurements of Fe³⁺/ΣFe along with major, minor, trace and volatile elements in olivine- and plagioclase-hosted melt inclusions of CO₂ undersaturated mantle melts in South West Indian Ridge lava. These inclusions record minimum entrapment pressures equivalent to depths up to 10 km below the seafloor, record magma ascent rates of 0.03–0.19 m/s, and display exceptionally high CO₂/Ba, CO₂/Rb, and CO₂/Nb ratios, indicative of a CO₂-rich mantle source. Accounting for fractional crystallization, we find a uniform melt oxidation state (with an Fe³⁺/ΣFe at 0.140 ± 0.005 at MgO = 10 wt.%) that displays no systematic variation with major, minor, volatile or trace element contents, thus providing no evidence for a relationship between the degree of partial melting and Fe³⁺/ΣFe. This can be explained by efficient buffering of Fe³⁺/ΣFe and *f*O₂ of mid-ocean ridge basalt melts by their surrounding mantle and/or a decrease in the bulk peridotite-melt Fe₂O₃ partition coefficient with increasing partial melting. We conclude that changes in the Earth's upper mantle temperature over geological time need not have affected the oxidation state of volcanic products or of the atmosphere.

1. Introduction

Nearly all mid-ocean ridge basalts (MORBs) are believed to be saturated with a CO₂ fluid phase during ascent and emplacement, as the CO₂ contents of MORB glasses typically yield volatile saturation pressures consistent with or slightly higher than their collection/eruption pressure (e.g., Aubaud, 2022; Dixon et al., 1988; Le Voyer et al., 2019; Michael & Graham, 2015; Shimizu et al., 2016, 2019). Yet, once thought to be extremely rare, occurrences of undegassed MORBs have now been documented at several locations, including:

1. The mid-Atlantic ridge, 14°N, the so-called “popping rock” (e.g., Cartigny et al., 2008; Javoy & Pineau, 1991),
2. The East Pacific Rise, 8°N, in olivine-hosted melt inclusions (MI) from the Siqueiros transform fault (Saal et al., 2002),
3. The equatorial Mid-Atlantic Ridge, 5°S, in olivine-hosted MIs (Le Voyer et al., 2017),
4. In MORB glasses with ultra-low volatile contents from the Atlantic, Pacific, Indian Ocean and Gakkel Ridge (Michael & Graham, 2015).

Here we report a new occurrence of CO₂-undersaturated MORBs in a suite of olivine- and plagioclase-hosted MIs and embayments collected from the South West Indian Ridge (SWIR). We present Fe³⁺/ΣFe measurements obtained by means of X-ray absorption near-edge structure (XANES) spectroscopy at the iron K-edge, together with volatile, major, minor and trace element concentrations and water diffusion profiles in embayments. We show that the oxidation state of these melts, at least some of which must have been entrapped at mantle depth (minimum volatile saturation pressures of 316 MPa), is uniform, and is uncorrelated with trace element enrichment.

2. Samples and Methods

2.1. Geological Setting, Sample Description and Processing

The sample investigated for this study, EDUL_DR75_1_04 (CNRS 000 000 2592), was collected from the South West Indian Ridge (SWIR) by dredging during the EDUL (Echantillonnage d'une Dorsal Ultra Lente) campaign under the auspices of IGP in 1997. The South West Indian Ridge (SWIR) is one of the slowest-spreading mid-ocean ridges (spreading rate ≤ 18 mm/year; Dick et al., 2003). It is characterized by a high isotopic heterogeneity (e.g., Hamelin & Allègre, 1985; Janney et al., 2005; Mahoney et al., 1992) and low magma supply (e.g., Cannat et al., 1999). The pillow basalt sample was collected at a depth of 2,650–2,900 m at $37^{\circ}51'48''\text{S}$, $49^{\circ}20'12''\text{E}$ (<https://lithotheque.ipgp.fr/edul.html>), corresponding to ridge segment 28 to 29 (numbering from Cannat et al., 1999). This ridge segment has been studied by Wang et al. (2021) who suggested that the mantle source in this region is a refractory mantle residue that previously melted within a subduction zone, and is more depleted in highly incompatible trace elements relative to other regions of the SWIR. Samples from the same dredge (at 49°E ; EDUL_DR75) were previously studied by Font et al. (2007). They analyzed plagioclase- and olivine-hosted MIs and concluded that they represented batches of melt generated by higher degrees of melting at greater mean depths in the mantle melting column compared with MIs from the NE end of the ridge (64°E). Font et al. (2007) also found systematic differences between plagioclase- and olivine-hosted MIs in EDUL_DR75, which they attributed to a two-step formation (see their Figure 10), with plagioclase-hosted MIs representing final batches of melt generated at the top of the mantle melting column, and olivine-hosted MIs corresponding to melts generated from less depleted, more fertile mantle at greater depths.

Sample EDUL_DR75_1_04 is porphyritic with centimeter-scale plagioclase and millimetric to sub-millimetric clinopyroxene and olivine phenocrysts within an aphyric matrix. Pillow rims are vitreous with a phenocryst proportion close to 50%. The outer 3 cm of pillow basalt samples (i.e., the rim that quenched the fastest) were sliced using a diamond saw, then ground and sieved, and crystals and glass separated magnetically. MI-bearing olivine macrocrystals in the 0.5–2 mm size fraction were hand-picked under a binocular microscope. MIs were first exposed by polishing single crystals to $0.25\text{ }\mu\text{m}$ using silicon carbide paper followed by corundum mats. We avoided using diamond polishing pastes to avoid contaminating MI surfaces with carbon. Polished crystals were subsequently mounted in indium for analysis by secondary ion mass spectrometry (SIMS) followed by electron probe microanalysis (EPMA). MIs are entirely glassy, and 25% of them contain a bubble occupying 0.3%–2% of the MI by volume (calculated from 2D observations and assuming spherical MIs and bubbles). The MIs are $58\text{--}442\text{ }\mu\text{m}$ along their long axis (average of $151 \pm 67\text{ }\mu\text{m}$). After SIMS and EPMA analyses, host olivine crystals were removed from the indium mount and polished on the reverse side, parallel to the first polish, to obtain double-polished wafers. Double-polished MIs were then mounted on a glass slide using CrystalBond for XANES analysis such that the newly exposed MI surface faced outwards. Finally, MIs were analyzed for trace elements by LA-ICP-MS.

2.2. Electron Probe Microanalyses (EPMA)

The major element compositions of matrix glasses, MIs and their host crystals were measured with a Cameca SX100 electron microprobe at the Laboratoire Magmas et Volcans in Clermont-Ferrand. For crystalline phases (olivine and plagioclase), beam conditions of 15 kV and 20 nA were employed, with 20 s counting times (and 20 s off peak counting times). Errors (two standard deviations) are ± 0.5 for SiO_2 , ± 0.06 for TiO_2 , ± 0.04 for Al_2O_3 , ± 0.4 for FeO , ± 0.07 for MnO , ± 0.06 for CaO , ± 0.5 for MgO , and ± 0.07 for NiO . For glass analyses, the beam current was decreased to 8 nA and the beam defocused to $10\text{ }\mu\text{m}$. Sodium was analyzed first to limit the effects of Na loss. Counting times of 10 s minimum were used (with off peak counting times similar to on peak ones). Errors (two standard deviation) are ± 0.1 for SiO_2 , ± 0.07 for Na_2O , ± 0.07 for K_2O , ± 0.05 for Al_2O_3 , ± 0.1 for CaO , ± 0.2 for FeO , ± 0.1 for MgO , ± 0.04 for TiO_2 , ± 0.04 for MnO , and ± 0.03 for P_2O_5 . The instrument was calibrated on natural and synthetic mineral standards and glasses: wollastonite (Si, Ca), MnTiO_3 (Ti, Mn), orthoclase (K and Al in minerals), standard glass VG2 (Al in glasses, see Óladóttir et al., 2008), Cr_2O_3 (Cr), fayalite (Fe), forsterite (Mg), NiO (Ni), albite (Na) and apatite (P).

2.3. Assessment of Post-Entrapment Crystallization

The amount of post-entrapment crystallization (PEC) for olivine-hosted inclusions was calculated using Petrolog3 (Danyushevsky & Plechov, 2011). Calculations were performed using the olivine-melt model

of Danyushevsky (2001), the density model of Lange and Carmichael (1987), the model for melting oxidation of Kress and Carmichael (1988) and the model of Toplis (2005) for the compositional dependence of the olivine-liquid Fe-Mg exchange coefficient (Kd). Calculations were performed assuming an oxygen-buffered system at quartz-fayalite-magnetite (QFM). The resulting PEC estimates ranged from -11% to 0.3% , with an average of -3% and standard deviation of $\pm 2\%$. Performing the same calculations assuming a closed system to fO_2 yields similar results with a range from -8 to 1% , an average of -1% and standard deviation of $\pm 2\%$. Given these results and the fact that calculations in Petrolog3 are performed assuming anhydrous conditions at 1 atm (i.e., conditions that are far from natural ones), we did not modify the MI compositions from their measured values.

2.4. Secondary Ion Mass Spectrometry (SIMS)

Volatile (H_2O , CO_2 , Cl, F, S) contents in MIs, embayments and matrix glasses were determined using a Cameca IMS 1280 multi-collection ion microprobe at CRPG-CNRS-Nancy during the same analytical session and hence the same analytical conditions as reported in Moussallam et al. (2021). We used a Cs^+ primary beam with a current of 1 nA and an electron gun to compensate for the charge build-up at the sample surface. A 3-min pre-sputter with a $30\ \mu m \times 30\ \mu m$ square raster was applied, and then analyses were performed on the $15\text{--}20\ \mu m$ spot in the center of the clean rastered area using a mechanical aperture placed at the secondary ion image plane. We collected signals for ^{12}C (8 s), ^{17}O (3 s), $^{16}O^1H$ (6 s), ^{18}O (3 s), ^{19}F (4 s), ^{27}Al (3 s), ^{30}Si (3 s), ^{32}S (4 s) and ^{35}Cl (6 s; counting times in parentheses), with 2 s waiting time after each switch of the magnet. This cycle was repeated 10 times during one analysis for a total analysis duration of 12 min. The mass resolution of ~ 7000 (with the contrast aperture at $400\ \mu m$, the energy aperture at 40 eV, the entrance slit at $52\ \mu m$ and the exit slit at $173\ \mu m$) meant that complete discrimination of the following mass interferences was achieved: $^{34}S^1H$ on ^{35}Cl ; ^{17}O on $^{16}O^1H$; $^{29}Si^1H$ on ^{30}Si ; $^{31}P^1H$ on ^{32}S . Element concentrations were determined using calibration curves obtained by measuring a set of natural and experimental basaltic glasses (KL2G, Jochum et al., 2006; KE12, Mosbah et al., 1991; VG2, Jarosewich et al., 1980; experimental glasses N72, M35, M40 and M48, Shishkina et al., 2010; Macquarie glasses 47,963 and 25,603, Kamenetsky et al., 2000) under the same analytical conditions at the beginning, middle, and end of the session. These standards span a large range of volatile element concentrations that bracket the volatile contents of the unknowns. Maximum relative errors, based on reproducibility over 10 cycles of analyses, were less than 15% for CO_2 , 3% for Cl, 4% for S, and 5% for F and H_2O .

2.5. XANES Analyses

We carried out Fe K-edge XANES (X-ray absorption near-edge structure spectroscopy) on beamline I18 at the Diamond Light Source (DLS), UK. The X-rays were focused with Kirkpatrick-Baez mirrors down to $7\ \mu m$ (horizontal) $\times 2\ \mu m$ (vertical) beam size. The beamline uses a liquid nitrogen-cooled double-crystal monochromator with silicon crystals, and the Si (333) reflection was used to increase the energy resolution. Measurements were performed in fluorescence mode. We used two energy-dispersive Vortex ME-4 silicon drift detectors positioned at 45° to the incident beam: one located directly above the other, and both pointing toward the sample. The sample was positioned so that the normal to the sample surface was at 45° to the incident X-ray beam. Default analytical conditions for XANES at I18 yield a primary beam with photon flux of 10^{12} ph/s upstream of the ion chamber; we used a combination of aluminum foils and slit geometries to attenuate the beam to 10^{10} ph/s at the sample surface. For MI analyses, the incident X-ray beam was further attenuated with 0.1 mm-thick Al foil to ensure there was no beam damage to the sample (see section below). The energy step sizes and dwell times used are given in Table S1 in Supporting Information S2 (Moussallam, 2023b). All MI XANES spectra were examined for contamination from the olivine host (Figure 1a). Spectra showing any structure in the edge or post-edge region were rejected (see Figure S6 in Moussallam et al., 2014 for an example of a contaminated XANES spectrum).

The effect of sample exposure to focused X-ray beams on iron speciation has been investigated in several studies for a range of sample compositions under a range of beam conditions (e.g., Cottrell et al., 2009, 2018; Moussallam et al., 2014, 2016, 2019; Shorttle et al., 2015). Accordingly, we selected beam attenuation conditions to eliminate beam damage. To test our analysis conditions, we performed a beam damage test on a SWIR glass containing 0.45 wt.% H_2O (the highest water content in the samples investigated in this study). We positioned the monochromator at a fixed energy of 7114.3 eV corresponding to the oxidized peak of the pre-edge doublet. We then opened the shutter and counted the fluoresced X-rays every second for 700 s (Figure 1c). Under our analytical conditions,

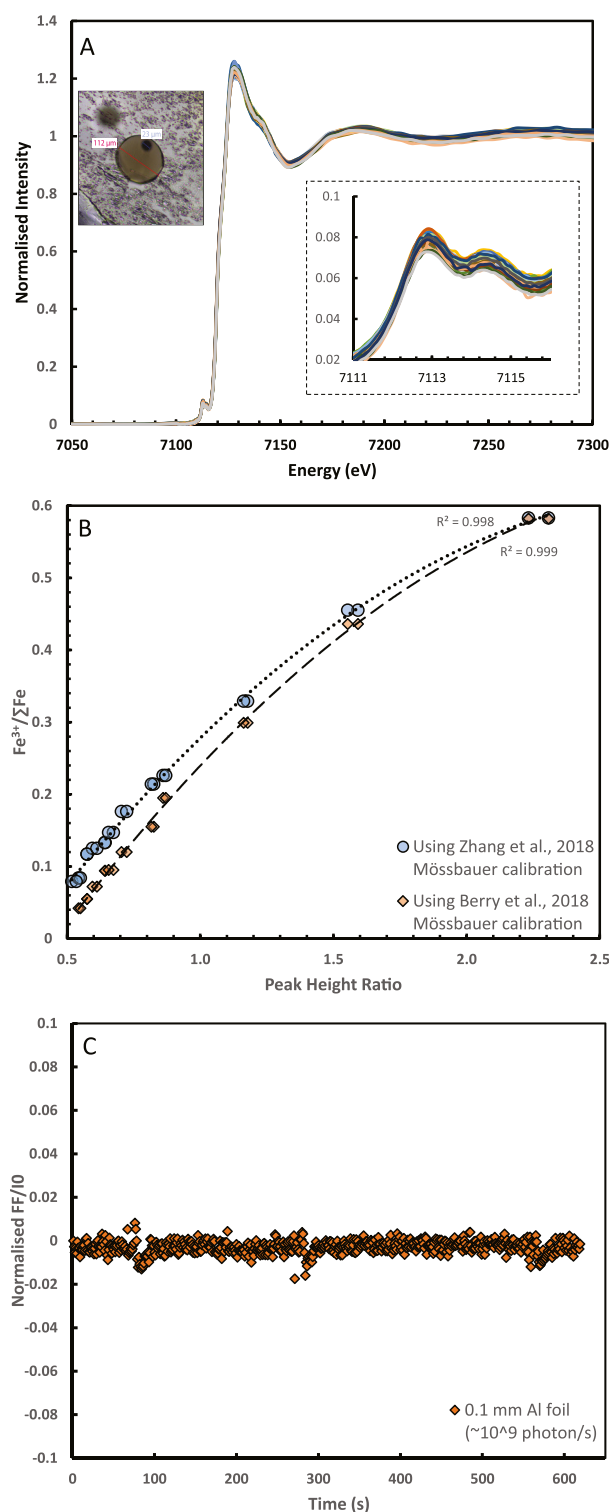


Figure 1. (a) Edge step-normalized XANES spectra of SWIR MIs ($n = 38$) and glasses ($n = 5$). The lower right inset shows spectra over the pre-edge region energy range. Upper left inset shows a transmitted light photomicrograph of a typical olivine-hosted MI. (b) Calibration line of the peak height ratio determined by XANES compared with $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios determined by Mössbauer spectroscopy in basaltic standard glasses from the Smithsonian NMNH (Mössbauer $\text{Fe}^{3+}/\Sigma\text{Fe}$ values from Zhang et al. (2018) and Berry et al. (2018) are shown). (c) Time series of normalized fluoresced intensity (FF) over I0 at 7114.3 eV integrated over 1 s intervals for a SWIR glass containing 0.45 wt.% H_2O .

0.1 mm-thick Al foil was used to attenuate the beam to $\sim 16\%$ of its original flux (calculated based on theoretical absorption, equivalent to $\sim 10^9$ photon/s or $\sim 10^8$ photon/s/ μm^2), and we detected no change in fluoresced intensity under beam exposure indicating that Fe in our natural samples was not oxidized during XANES analyses.

The pre-edge region (7110–7118 eV) was fitted using a combination of a linear function and a damped harmonic oscillator function (DHO) to fit the baseline. The relative intensity at the ~ 7112.5 eV and ~ 7114.3 eV peaks was then used to calibrate the spectra to the published $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of the NMNH 117393 basalt reference glasses (Cottrell et al., 2009) loaned by the Smithsonian Institution National Museum of Natural History and using the $\text{Fe}^{3+}/\Sigma\text{Fe}$ values reported in Zhang et al. (2018) and in Berry et al. (2018) (Figure 1b). Repeat measurements of standards ($n = 12$) gave a standard deviation of ± 0.004 on the measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios (relative error). Absolute error is estimated at ± 0.005 , based on absolute deviation between theoretical (i.e., Mössbauer values) and measured standard values.

2.6. LA-ICP-MS Analyses

Trace element measurements on MIs, embayments (partially entrapped melt that remained opened to the outside melt in one direction; also called re-entrants), and glasses were carried out using a laser ablation system (193 nm Excimer RESolution SE) associated with an inductively coupled plasma mass spectrometer (Agilent 8900 QQQ ICP–MS) at the Institut des Sciences de la Terre d'Orléans (ISTO), France. Analyses were performed following conventional procedures (e.g., Le Voyer et al., 2010; Moussallam et al., 2019b; Rose-Koga et al., 2012). We used a pulse energy of about 5 mJ, a spot diameter between 32 and 100 μm , depending on the inclusion size and a laser pulse frequency of 2–3 Hz to keep a fluence at the sample surface of 2.8 J/cm^2 . The background was measured for 30–40 s before ablation, and the analysis time was approximately 100 s. Data reduction was performed using GLITTER software (www.es.mq.edu.au/GEMOC). This technique uses calcium (CaO measured by EPMA) as an internal standard. Reproducibility was constrained by systematic analyses of two external standards, BCR2-G ($<4\%$ on all elements except Be, Sn and Ta $<7\%$, 1σ relative) and NIST-SRM-610 ($<3\%$ on all elements except Li $<4\%$, 1σ relative), measured at the beginning, middle and end of the session.

3. Results

The major element compositions (by EMPA) and volatile contents (by SIMS) of 80 MIs, 2 embayments and 13 matrix glasses were obtained; the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio was measured (by XANES) in 38 of these MIs and five of these matrix glasses; and trace element concentrations (by LA-ICP-MS) were measured in 31 of these MIs and four of these matrix glasses.

3.1. Major Elements

The major element compositions of MIs, embayments, and matrix glasses are given in Table S2 in Supporting Information S2 (Moussallam, 2023b) together with MI and bubble dimensions. The major element compositions of the host crystals (olivine and plagioclase) are given in Table S3 in Supporting Information S2 (Moussallam, 2023b).

The SWIR matrix glass composition appears to be very different from that of the MIs. The glass is much richer in FeO and TiO_2 , and has lower CaO, Al_2O_3 and SiO_2 (Figure 2). The olivine forsterite content at equilibrium with the matrix glasses ($\text{Fo}_{80\pm 1}$) was calculated following Toplis (2005) at a temperature of 1200°C , at 50 MPa, $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.15 and the measured water content of $0.44 \pm 0.06 \text{ wt.}\%$ (see next section). According to these calculations the matrix glass is far from equilibrium with the olivine (Figures 2j and 2k). Interestingly, the embayments are also different from the matrix glasses, with one embayment having a composition very similar to that of the MIs and one having a composition midway between the MIs and the matrix glass, suggesting mixing of two magmas.

In order to determine if a crystallization relationship existed between the matrix glass and the MIs, we performed a series of fractional crystallization calculations using MELTS v1.2.0 (Ghiorso & Sack, 1995). About 20 MI were randomly picked as starting compositions for the calculation, and four scenarios were tested:

1. Sea floor crystallization: isobaric (15 MPa), cooling from MELTS liquidus to 1050°C —equilibrium crystallization.
2. Sea floor crystallization: isobaric (15 MPa), cooling from MELTS liquidus to 1050°C —fractional crystallization.

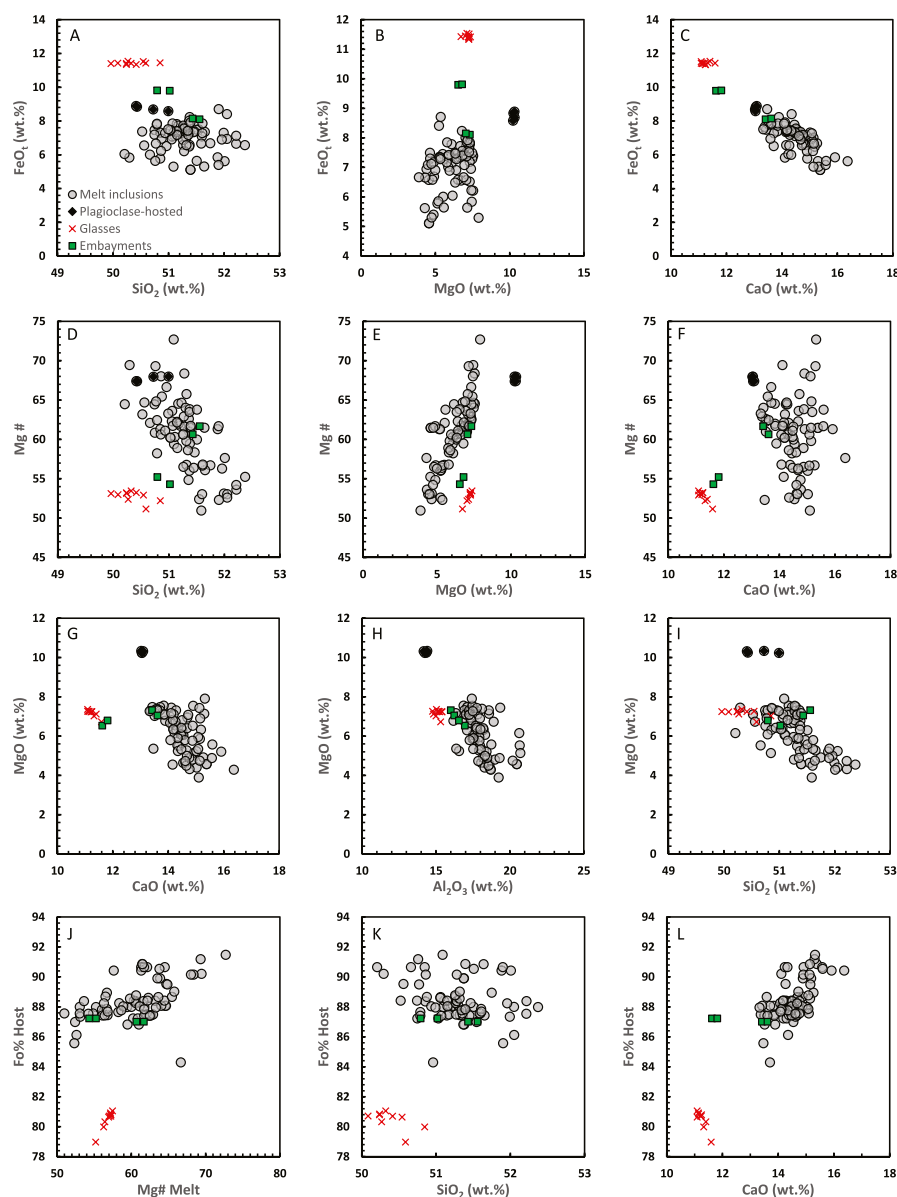


Figure 2. Comparison between major element oxides in MIs and matrix glasses from SWIR. The corresponding Fo% for matrix glasses was calculated using the model of Toplis (2005) at a temperature of 1200°C, 50 MPa, $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of 0.15 and their measured water content. The two embayment compositions were measured at both of their extremities (i.e., the furthest inside and at the mouth).

3. Deep crystallization: isobaric (at MI volatile saturation pressure), cooling from MELTS liquidus to 1050°C—equilibrium crystallization.
4. Deep crystallization: isobaric (at MI volatile saturation pressure), cooling from MELTS liquidus to 1050°C—fractional crystallization.

Results from all four scenarios are shown in Figure S2 in Supporting Information S1 (Moussallam, 2023c) but in none can the glass composition be derived from the MI compositions. All these observations suggest that the carrier melt was unrelated to the MI population and brought to the seafloor a mostly xenocrystic crystal cargo, potentially following an episode of mixing short enough that embayments sample an unhomogenized melt.

Olivine-hosted MIs have compositions that are unusual when compared with the global MORB database (Figure 3). They record a large spread in MgO from 8 to 4 wt.%, and at any given value of MgO, they have lower

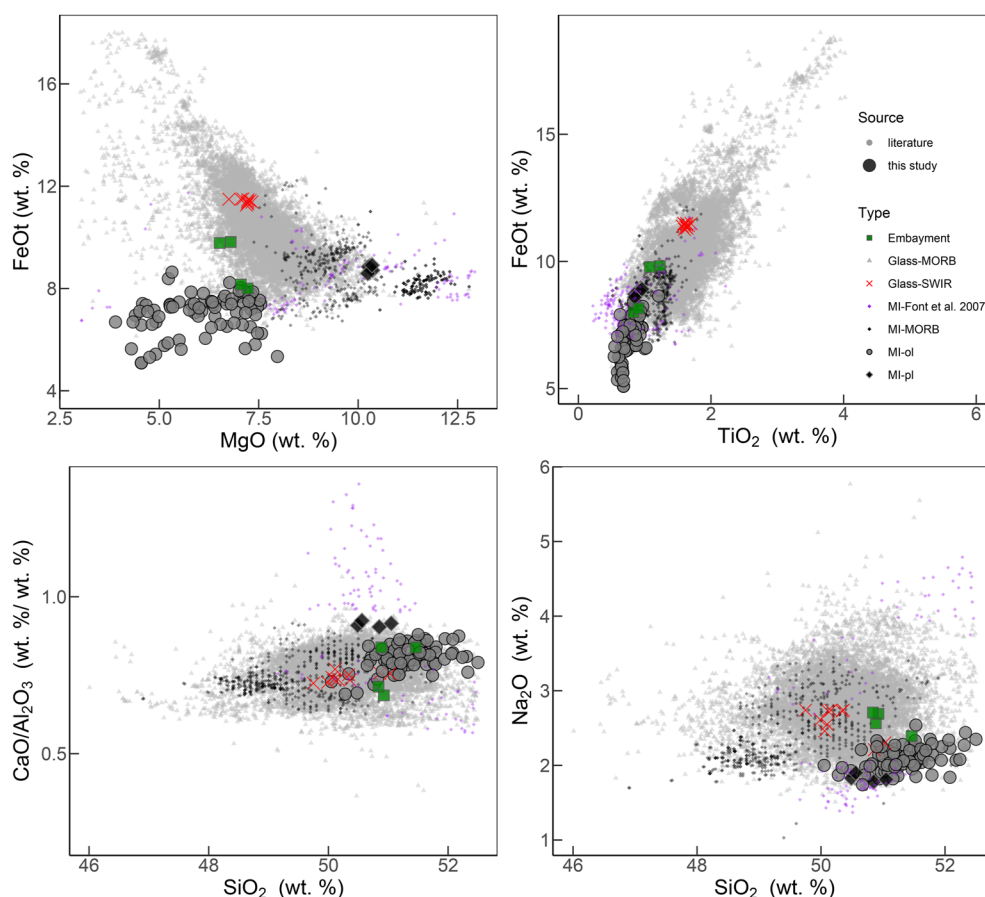


Figure 3. Composition of magmatic MIs compared to global MORB glass data ($n = 13,773$; PETDB and GEOROC databases), and known MORB MIs ($n = 542$; M. Le Voyer et al., 2017; Saal et al., 2002; Shaw et al., 2008; Shimizu et al., 2019; Wanless & Shaw, 2012; Wanless et al., 2014). MI compositions from SWIR by Font et al. (2007) are shown in purple. The host lava compositions of this study are in red crosses and the compositions of embayments are in green squares. Although the MIs of this study are notably low in MgO and FeOt, similar compositions have been reported previously. (a) FeOt total versus MgO, (b) FeOt total versus TiO_2 , and note that the MIs are low in both. (c) $\text{CaO}/\text{Al}_2\text{O}_3$ versus SiO_2 , showing that the MI compositions plot within the global distribution. (d) Na_2O versus SiO_2 showing Na_2O is at the lower end of the global population.

TiO_2 , FeOt, and Na_2O with comparable $\text{CaO}/\text{Al}_2\text{O}_3$ compared to the global MORB database. Similar compositions were found by Font et al. (2007) in olivine-hosted inclusions from other MORB samples dredged along the South West Indian Ridge, but their study focused more on plagioclase-hosted MIs with reported compositions similar to those we report here (Figure 3). Na_2O , TiO_2 , and MgO are at the lower end of the global MORB population. The low Na_2O , TiO_2 , and MgO cannot be derived from crystal fractionation of typical MORB magmas as Na_2O and TiO_2 generally increase with crystal fractionation, which typically decrease MgO concurrently.

3.2. Trace Elements

The trace element compositions of MIs and matrix glasses are given in Table S4 in Supporting Information S2 (Moussallam, 2023b). Trace element systematics can distinguish between fractional crystallization, mixing, or partial melting genetic processes (e.g., Allègre & Minster, 1978; Schiano et al., 2010; Treuil, 1975). From the co-evolution of La and Rb, two highly incompatible elements (Figure 4a), we identify a linear correlation that does not pass through the origin. This observation is consistent with mixing or potentially a partial melting origin but inconsistent with the melts being related to different degrees of fractional crystallization (which would produce a linear trend passing through the origin). In a C^H/C^M versus C^H diagram (where C^H and C^M are the concentrations of highly incompatible and moderately incompatible elements respectively) (Figure 4b) we observe a linear correlation, consistent with partial melting or potentially a mixing origin but inconsistent with

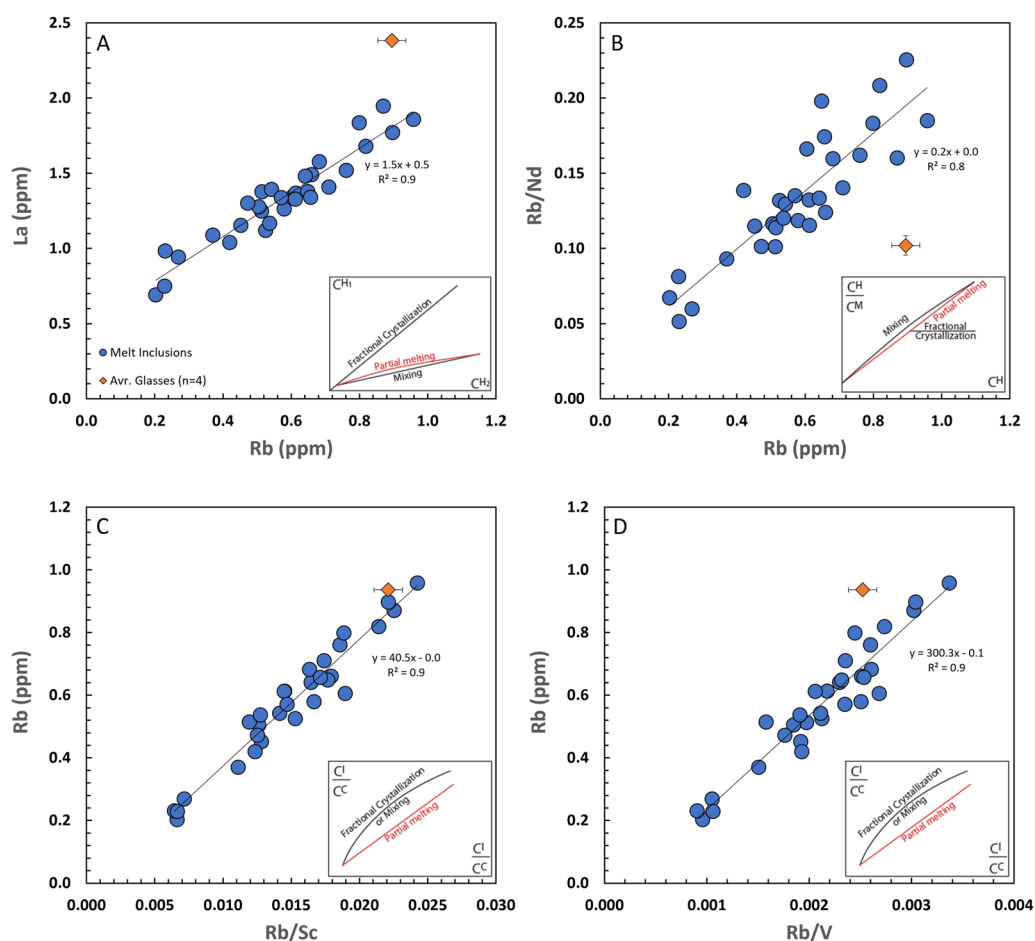


Figure 4. Trace element variation diagrams from MIs and average values of matrix glasses from SWIR. (a) Plot of La versus Rb with inset showing a schematic C^{H_1} versus C^{H_2} diagram (with H_1 and H_2 being two highly incompatible elements) with curves showing theoretical melt compositions produced by fractional crystallization, partial melting, and mixing processes. (b) Plot of Rb/Nd versus Rb with inset showing a schematic C^H/C^M versus C^H diagram (where C^H and C^M are the concentrations of H, a highly incompatible element, and M, a moderately incompatible element) showing theoretical correlation curves during fractional crystallization, partial melting and mixing processes. (c) Plot of Rb versus Rb/Sc, with inset showing a schematic C^I versus C^I/C^C diagram (where C^I and C^C are the concentrations of I, an incompatible element, and C, a compatible element) showing theoretical melt compositions produced by mixing, fractional crystallization and partial melting processes. (d) The plot of Rb versus Rb/V. All inset schematics were redrawn from Schiano et al. (2010). Linear regressions through all MI data are presented on each plot.

the melts being related to different degrees of fractional crystallization (which would produce a near-horizontal line). In a C^I versus C^I/C^C diagram (where C^I and C^C are incompatible and compatible elements respectively) (Figures 4c and 4d), we observe a linear correlation consistent with partial melting but inconsistent with the melts being related to either different degrees of fractional crystallization or by mixing (both of which would produce a hyperbolic curve). The trace element systematics in the SWIR MIs therefore suggest that the melts are related to variable degrees of partial melting. The trace element analyses also reinforce the observation made from the major elements, that the carrier melt is compositionally distinct from the MI population.

3.3. Volatile Elements

The volatile contents of MIs, embayments and matrix glasses are given in Table S2 in Supporting Information S2 (Moussallam, 2023b) together with calculated volatile (H_2O - CO_2) saturation pressures using the model of Iacono-Marziano et al. (2012). Additional SIMS analyses along the two olivine-hosted melt embayments are reported in Table S5 in Supporting Information S2 (Moussallam, 2023b). MIs span a range of concentrations from 68 to 1400 ppm CO_2 , from 0.30 to 0.39 wt.% H_2O , and from 540 to 1150 ppm S, while the matrix

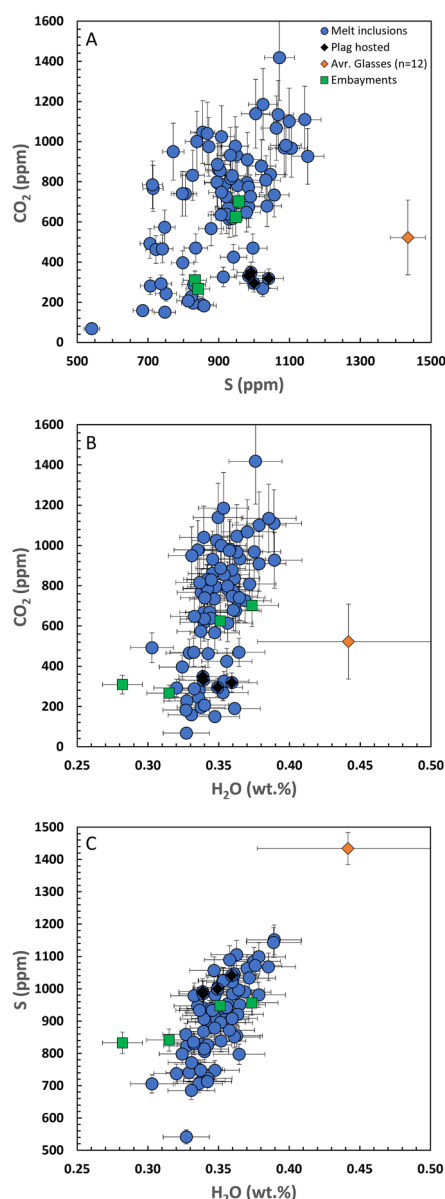


Figure 5. Volatile element abundances in MIs, embayments and matrix glasses from SWIR. Plagioclase-hosted MIs are marked by black diamond symbols, and all other MIs are olivine-hosted. The two embayments were measured at both of their extremities (i.e., the furthest inside and at the mouth). Error bars show one standard deviation from measurement uncertainty except for the average matrix glass where error bars show one standard deviation from $n = 12$ analyses.

glass contains on average 500 ± 200 ppm CO_2 , 0.44 ± 0.06 wt.% H_2O and 1400 ± 50 ppm S (averages and one standard deviation on $n = 12$ analyses) (Figure 5). The volatile element concentrations provide additional evidence supporting the conclusion, based on major and trace elements, that the carrier melt is markedly different from the MIs.

Calculated volatile (H_2O - CO_2) saturation pressures range from 22 to 316 MPa for MIs, corresponding to minimum entrapment pressures down to ~ 10.5 km below the sea floor. For matrix glasses, calculated volatile (H_2O - CO_2) saturation pressures range from 89 to 214 MPa (average $\sim 115 \pm 41$ MPa), which is much higher than the ~ 26 MPa hydrostatic pressure expected at the sample collection depth of ~ 2650 m b.s.l. (where the expected CO_2 content in the glass would be around ~ 90 to 70 ppm). This volatile supersaturation in the glass is significantly higher than that seen in most MORBs (see Figure 5a in Aubaud, 2022) and suggests rapid melt ascent with kinetically limited CO_2 exsolution and small bubble number density preventing efficient degassing (e.g., Gardner et al., 2016; Pichavant et al., 2013). Diffusion profile modeling of the two olivine-hosted embayments (using the EMBER software; Georgeais et al., 2021) yields a decompression rate of 0.001 – 0.005 MPa/s (Table S6 in Supporting Information S2; Moussallam, 2023b).

3.4. Oxidation State

The Fe oxidation states of 38 MIs and five matrix glasses measured by XANES are reported in Table S2 in Supporting Information S2 (Moussallam, 2023b) and shown in Figure 6. MI $\text{Fe}^{3+}/\Sigma\text{Fe}$ ranges from 0.147 to 0.172, with an average of 0.160 and standard deviation of ± 0.006 . Matrix glass $\text{Fe}^{3+}/\Sigma\text{Fe}$ ranges from 0.143 to 0.152, with an average of 0.149 and standard deviation of ± 0.004 . Here and in all figures and remaining text we report $\text{Fe}^{3+}/\Sigma\text{Fe}$ for our analyses based on the calibration using Mössbauer values from Zhang et al. (2018) for the Smithsonian reference glasses. For comparison, we also report the corresponding $\text{Fe}^{3+}/\Sigma\text{Fe}$ values using the calibration based on Mössbauer data from Berry et al. (2018) for the reference glasses (termed “ $\text{Fe}^{3+}/\Sigma\text{Fe}^2$ ” in Table S2 in Supporting Information S2; Moussallam, 2023b). Conversion to deviation from the QFM buffer was performed following Kress and Carmichael (1991) at a fixed pressure of 26 MPa, with individual olivine-hosted MI temperatures estimated using the olivine-melt equilibrium model of Danyushevsky (2001) and plagioclase-hosted MI and matrix glass temperatures estimated using the MORB glass geothermometer of Wallace and Carmichael (1992). This is the ΔQFM value we use in all figures and remaining text. For comparison, in Table S2 in Supporting Information S2 (Moussallam, 2023b) we also report conversion to deviation from the QFM buffer using the equation of O'Neill et al. (2018), termed “ ΔQFM^2 ,” which uses “ $\text{Fe}^{3+}/\Sigma\text{Fe}^2$ ” as input.

MIs range from $\log(f\text{O}_2) = \text{QFM} - 0.17$ to $+0.02$ with an average of -0.07 and standard deviation of ± 0.05 . Matrix glasses range from $\log(f\text{O}_2) = \text{QFM} - 0.22$

to -0.05 with an average of -0.11 and standard deviation of ± 0.06 . It is worth re-stating that the relative precision of our XANES analyses is ± 0.004 on the measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio. MIs show no correlation between their $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios and their volatile element contents (CO_2 , S, and H_2O ; Figures 6a–6c). This remains the case when the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios are converted to deviation from the QFM buffer (i.e., accounting for melt composition and temperature) (Figures 6n and 6o). Correlations do emerge between the measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios and the major element compositions, most notably with MgO , CaO , and SiO_2 contents (R^2 values of 0.6, 0.4 and 0.5 respectively, Figures 6d–6f). However, once converted to deviation from the QFM buffer none of these correlations remain (R^2 values of 0.0; Figures 6p–6r). The MI $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios are uncorrelated with olivine host

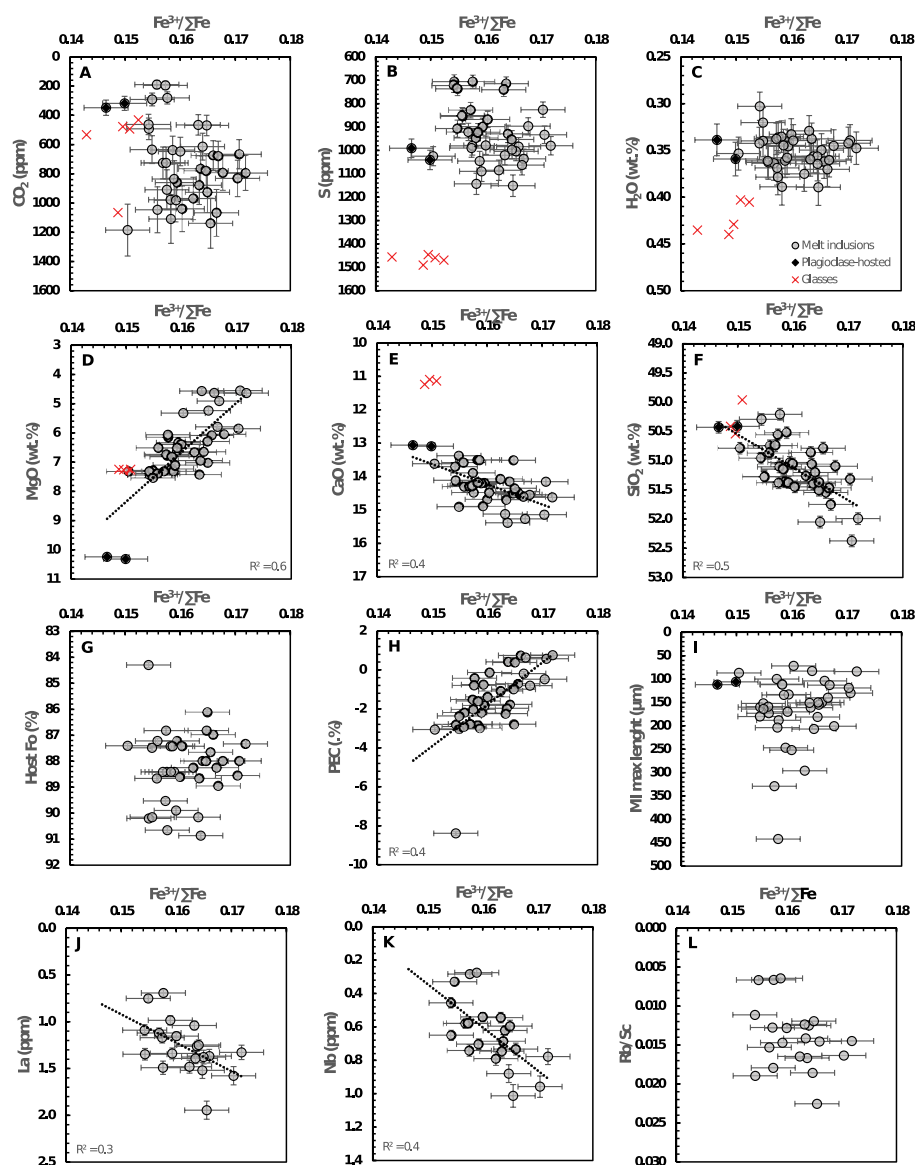


Figure 6. Oxidation states of SWIR MIs and glasses measured by Fe-XANES expressed as measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ (panel A to L) and corresponding oxygen fugacity expressed as log unit deviation from the QFM buffer (panel N to X).

composition and inclusion size (Figures 6g and 6i) but are correlated with the calculated amount of post entrapment crystallization ($R^2 = 0.4$; Figure 6h). This correlation also disappears once converted to deviation from the QFM buffer ($R^2 = 0.0$; Figure 6t). Finally, correlations between $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios and trace elements such as La or Nb (R^2 values of 0.3 and 0.4 respectively, Figures 6j and 6k) also disappear once converted to deviation from the QFM buffer ($R^2 = 0.0$; Figures 6v and 6w). The oxidation states of MIs and matrix glasses from the South West Indian Ridge hence appear extremely uniform despite the large range in major, trace and volatile element concentrations they record.

4. Discussion

4.1. Fast Magma Ascent Rate and Minimal Chemical Exchange

As shown above (IIIa,b,c), the matrix glass composition is distinct from that of the MIs, suggesting that the carrier melt was unrelated to the MI population and brought to the seafloor a mostly xenocrystic crystal cargo.

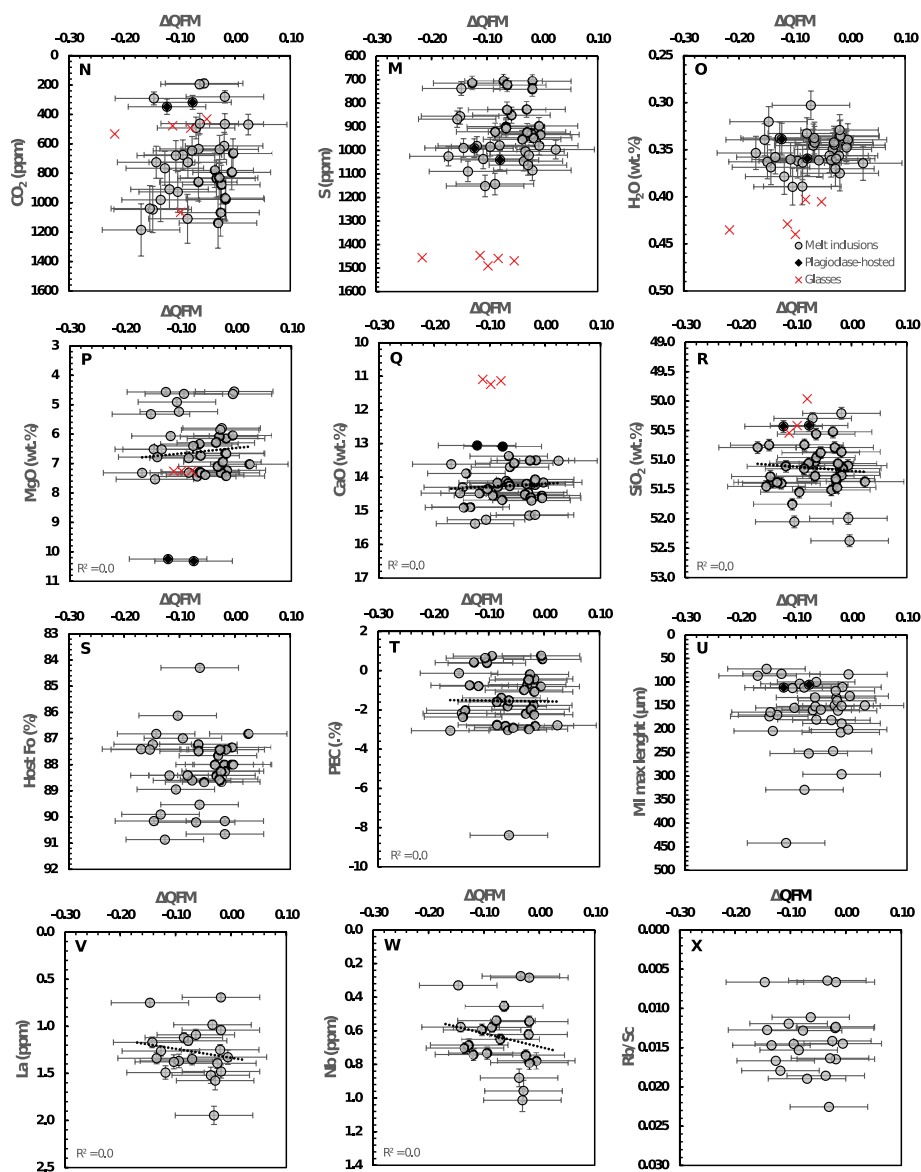


Figure 6. (Continued)

The eruption must have taken place following an episode of mixing short enough not to homogenize the embayment compositions. Such dynamic conditions suggest an explanation for the apparent uniformity in the oxidation state recorded in MIs, namely that any initial redox heterogeneity was overprinted by re-equilibration with the carrier melt via hydrogen diffusion through the olivine hosts, which can occur on timescales of hours to days (Gaetani et al., 2012).

In order to test this scenario, we first modeled the volatile diffusion profiles recorded in two olivine-hosted melt embayments using the EMBER software (Georgeais et al., 2021) to determine the rate and duration of magma ascent (results in Tables S5 and S6 in Supporting Information S2; Moussallam, 2023b). We then modeled MI re-equilibration through hydrogen diffusion using the MATLAB routine of Bucholz et al. (2013). The results suggest that the SWIR magma experienced 5–13 hr of ascent at a rate of 0.03–0.19 m/s (decompression rate of 0.001–0.005 MPa/s; we neglect acceleration) (Figure 7). In contrast, the MI fO_2 re-equilibration timescale was calculated to be about 80 hr with no change in the MI fO_2 in the first 5 hr and little in the first 20 hr (Figure S3 in Supporting Information S1; Moussallam, 2023c). Moreover, if hydrogen diffusion re-equilibration had occurred between MIs and the carrier melt then a relation between the water content and fO_2 of the MIs would

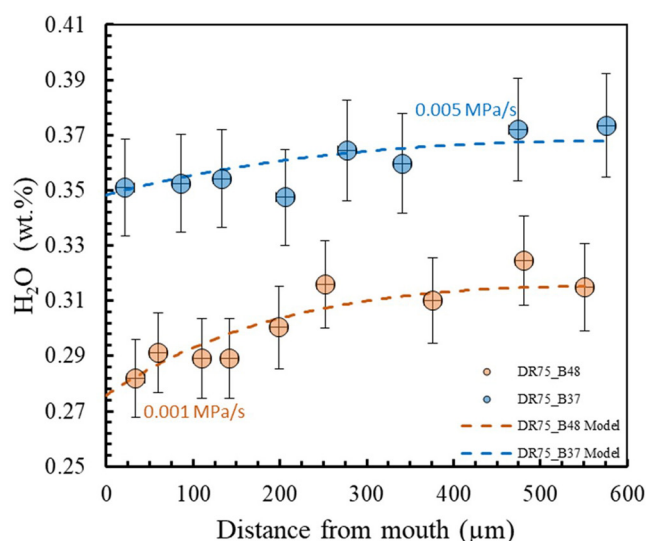


Figure 7. Best-fit diffusion modeling results (calculated using EMBER; Georgeais et al., 2021) compared to H₂O concentrations (measured by SIMS) for two SWIR melt embayments.

be expected, as would a relation between MI size and water content (the smaller MI being more sensitive to H₂O loss), neither of which was evident in our data ($R^2 = 0.0$, Figure S3 and Table S2 in Supporting Information S2; Moussallam, 2023b, 2023c). Finally, the fact that both plagioclase- and olivine-hosted MIs as well as open melt embayments all record similar redox conditions suggests that the Fe-system was not disturbed after MI entrapment.

We consider that the buffering/re-equilibration and post-entrapment modification of the SWIR MI fO_2 during ascent is thus unlikely to have been significant, and therefore the inclusions retain their original fO_2 at the time of entrapment. We cannot entirely exclude the possibility that the MIs equilibrated with yet another melt or magmatic environment at depth prior to their entrainment in the carrier melt that transported them to the surface, but such a scenario would imply the presence of an additional distinct magma which is not found, and should again have resulted in relations between the size, water content and fO_2 of the MIs which are not evident.

4.2. A New Series of CO₂-Undersaturated, Undegassed Melts

MI CO₂ contents are correlated with other highly incompatible elements such as Ba ($R^2 = 0.5$), Rb ($R^2 = 0.4$) and Nb ($R^2 = 0.4$), which indicates that these MIs did not lose their initial carbon through degassing (Figure 8). MI CO₂ and Cl contents are also strongly correlated ($R^2 = 0.8$). This is a strong

indication that the MIs have not been contaminated by seawater, and that both elements behaved as incompatible elements and were unaffected by degassing.

The CO₂/Ba ratio in SWIR MIs is 123 ± 32 , consistent with a depleted mantle value of ~ 140 (Matthews et al., 2017) but slightly higher than the 100 ± 22 ratio found in the Siqueiros MIs (Saal et al., 2002), the 97 ± 10 ratio found in the equatorial MIs (M. Le Voyer et al., 2017) and the 76 ± 8 ratio found in the 2 π D43 popping rock (Cartigny et al., 2008). The CO₂/Rb and CO₂/Nb ratios in SWIR MIs ($1,374 \pm 487$ and $1,134 \pm 415$ respectively) are also higher than those found in the Siqueiros MIs ($\sim 1,219$ and 239 ± 46 respectively), equatorial MIs ($1,105 \pm 104$ and 557 ± 79 respectively), and in the 2 π D43 popping rock (899 ± 91 and 556 ± 56 respectively) (Cartigny et al., 2008; M. Le Voyer et al., 2017; Saal et al., 2002). The CO₂/Cl ratio in SWIR MIs is 78 ± 15 , similar to the 77 ± 26 ratio found in the Siqueiros MIs (Saal et al., 2002) and higher than the ratio of 46 found in the Popping Rock (sample 2 π D43; Cartigny et al., 2008), and the 39 ± 4 ratio found in the equatorial MIs (M. Le Voyer et al., 2017). We note that the SWIR matrix glasses also show CO₂/C_{ITE} ratios significantly higher than other MORBs, which appears consistent with CO₂ being undersaturated in the matrix glass.

Unlike CO₂, the water and sulfur contents of the MIs are uncorrelated with incompatible trace elements (ITE) such as Ce and Dy, respectively ($R^2 = 0.2$). Sulfur abundance in MORBs is widely considered to be controlled by equilibrium with sulfide (e.g., Jenner et al., 2010; Mathez, 1976; O'Neill, 2021; Shimizu et al., 2019). One MI in our suite was found to contain a sulfide globule, and sulfide inclusions were also found in olivine crystals and in the matrix glass, indicating sulfide saturation for at least some and probably most of the melt evolution pathway. The sulfur abundance in the SWIR MIs is not well correlated with their FeO_i contents ($r^2 = 0.3$) but is comparable (on average within $19 \pm 15\%$ or 165 ± 140 ppm) to the predicted sulfur concentrations at sulfide saturation, calculated following O'Neill (2021). Taken together, these observations suggest that the melt S content was at least partially dictated by equilibrium with sulfide liquid. The positive correlation between water and sulfur content ($R^2 = 0.5$) would be expected if both species had been affected by degassing, as is commonly seen in MI suites from subaerial volcanoes (e.g., Stromboli; Métrich et al., 2005). The CO₂-undersaturated nature of our SWIR MI suite should inhibit any significant S and H₂O degassing at >26 MPa pressure. Yet, for water at least, diffusion profiles recorded in melt embayments indicate that some degassing took place (see section a).

4.3. CO₂ Content of the Mantle Source

Experimental work indicates that incompatible element ratios such as CO₂/Nb and CO₂/Ba remain nearly constant during mantle melting and fractional crystallization (Rosenthal et al., 2015). If the initial trace element content

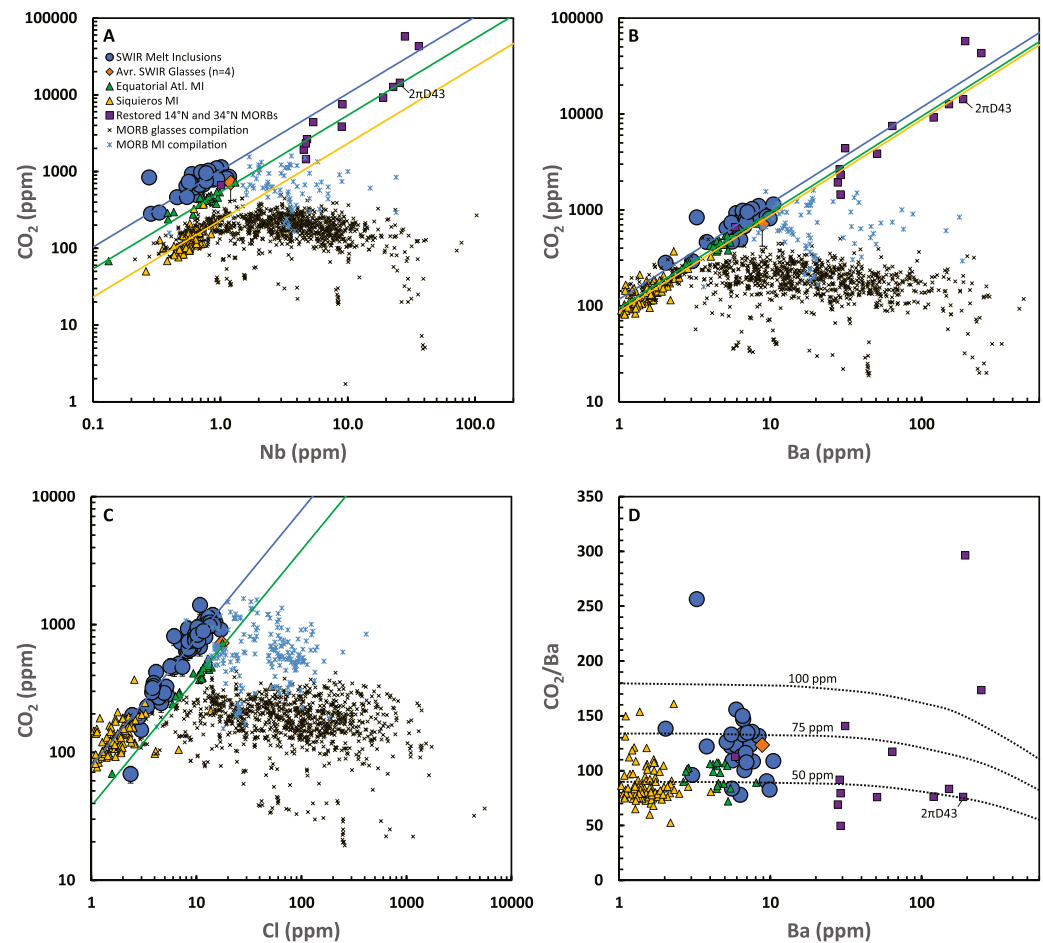


Figure 8. CO_2 versus Nb, Ba and Cl (A–C) and CO_2/Ba versus Ba (D) for MIs and matrix glasses from this study (SWIR) and previous studies of CO_2 -undersaturated MIs and glasses. Equatorial Atlantic MIs are from Le Voyer et al. (2017). Siqueiros MIs are from Saal et al. (2002). 14°N and 34°N mid-Atlantic ridge CO_2 contents are reconstructed values from Cartigny et al. (2008). Sample 2 π D43 is the popping rock (Cartigny et al., 2008). MORB glasses and MORB MI compilations showing partially to mostly degassed samples are from Le Voyer et al. (2017) and references therein. Solid blue, green, and yellow lines represent regressions forced through the origin for the SWIR, equatorial Atlantic and Siqueiros MI suites respectively. Dotted black curves in D are calculated partial melt compositions by Rosenthal et al. (2015) from simple batch melting, using their partition coefficients and assuming a mantle source with Ba = 0.563 ppm (Workman & Hart, 2005), and 50, 75, and 100 ppm CO_2 .

of the mantle source is known, its CO_2 content can be derived. Several estimates of mantle source trace element compositions are found in the literature. For example, assuming a depleted MORB mantle (DMM) source composition with Ba = 0.563 ppm, Rb = 0.050 ppm, and Nb = 0.1485 ppm (values from Workman & Hart, 2005) would give mantle CO_2 abundances of 69 ± 18 ppm (from CO_2/Ba), 69 ± 24 ppm (from CO_2/Rb), and 168 ± 62 ppm (from CO_2/Nb). Using an alternative DMM Nb content of 0.3 ± 0.05 ppm (as quoted in Saal et al., 2002) would give a mantle CO_2 abundance of 340 ± 124 ppm (from CO_2/Nb).

Previous studies do not always clearly indicate which mantle source composition (i.e., Nb, Ba, Rb content) was used to calculate mantle CO_2 content, making comparison between our study and previous estimates difficult. Another difficulty is that some studies base calculations on the average $\text{CO}_2/C_{\text{ITE}}$ ratio measured in a suite of samples, while others use single or highest values. Previous estimates of the mantle source region of MORBs vary from ~ 20 to 1200 ppm CO_2 (e.g., Cartigny et al., 2008; Chavrit et al., 2014; Hauri et al., 2018; Helo et al., 2011; Hirschmann, 2018; Javoy & Pineau, 1991; Le Voyer et al., 2019; Marty & Jambon, 1987; Saal et al., 2002). To make the comparison with previous studies easier, Figure 8d presents the CO_2/Ba versus Ba content calculated

for partial melting of a mantle containing 50, 75, or 100 ppm CO₂ (after Rosenthal et al., 2015, using mantle Ba = 0.563 ppm) with the values measured in the SWIR, equatorial Atlantic (Le Voyer et al., 2017) and Siqueiros (Saal et al., 2002) MI series and in the popping rock and the reconstructed 14°N and 34°N mid-Atlantic ridge MORBs (Cartigny et al., 2008). Using a Ba mantle value of 0.563 ppm, a mantle CO₂ content between 25 and 100 ppm appears most consistent with all these studies, with the SWIR series potentially indicating slightly higher CO₂ in its source compared with the equatorial Atlantic and Siqueiros series.

4.4. The Behavior of Fe³⁺ During Partial Mantle Melting

In most MI and matrix glass suites where oxidation state has been measured, degassing, especially of sulfur species, has been shown to strongly influence the melt oxidation state (Brounce et al., 2017; Hartley et al., 2017; Helz et al., 2017; Moussallam et al., 2014, 2016, 2019; Shorttle et al., 2015), which is also strongly influenced by the removal of chalcophile elements, for example, by sulfide saturation (Jenner et al., 2010). The CO₂-undersaturated MI suite from SWIR, in which S degassing is unlikely to have occurred (and S content is uncorrelated with oxidation state), thus presents an opportunity to consider processes other than degassing which might influence the melt oxidation state.

Fe³⁺ is expected to behave incompatibly to moderately incompatibly during mantle partial melting (e.g., Davis & Cottrell, 2021; Gaetani, 2016; Ghiorso et al., 2002; Jennings & Holland, 2015; Sorbadere et al., 2018), leading to lower Fe₂O₃ contents in higher degree partial melts (e.g., pyroxene/melt Fe³⁺ partitioning experiments of Rudra & Hirschmann, 2022). The undegassed SWIR MIs show variable enrichment in incompatible elements, consistent with origin by variable amounts of partial melting (see result section b). They would therefore be predicted to display a positive correlation between Fe³⁺ and incompatible trace element concentrations.

Because the MIs have all been entrapped at different stages during crystallization, their composition and Fe³⁺/ΣFe need first be corrected. We modeled reverse crystallization paths for our olivine-hosted MIs along olivine control lines using PRIMELT3 (Herzberg & Asimow, 2015) until the melts reached 10 wt.% MgO (Figure 9a). We further estimated the degree of partial melting necessary to produce these melts. We used PRIMELT3 olivine fractionation results to estimate ITE concentrations at 10 wt.% MgO using the olivine-melt partition coefficients of McKenzie and O'Nions (1991). We then calculated the degree of partial melting necessary to reproduce each melt Rb concentration, assuming a source with Rb = 0.050 ppm and bulk partition coefficients of 0.00001 (values from Workman & Hart, 2005). Neither corrected (at MgO = 10 wt.%) nor raw Fe³⁺/ΣFe shows any correlation with incompatible trace element abundance, incompatible trace element ratios such as Ba/La or estimated degree of partial melting (Figures 9b–9d).

The SWIR MI suite therefore does not show any evidence supporting a simple incompatible behavior of Fe³⁺ during partial melting of the upper mantle. If Fe³⁺ was behaving incompatibly, then one would expect a change in Fe³⁺/ΣFe during mantle partial melting, such as shown by Gaetani (2016). The Gaetani (2016) model's initial assumption is that no electron transfer is possible between the melt and residual peridotite, forcing the conservation of Fe³⁺ and Fe²⁺ in the system. Gaetani (2016) predicts a change of Fe³⁺/ΣFe from 0.07 to 0.12 over 12% of partial melting at 1346 °C mantle temperature. SWIR MIs show a range of Fe³⁺/ΣFe from 0.13 to 0.15 (at MgO = 10 wt.%) and no significant geochemical systematics (Figures 9b and 9c).

Our observations are not the first to contradict a simple incompatibility model for Fe³⁺. Bézou and Humler (2005) found a negative correlation between Fe₂O₃ and Na (corrected for fractional crystallization at MgO = 8 wt.%) in MORB glasses, which was later confirmed by Cottrell and Kelley (2011). To reconcile our and previous natural observations with experimental evidence for an incompatible behavior of Fe³⁺ during mantle partial melting of the mantle, we propose two non-mutually exclusive hypotheses. The first is that the oxidation state of partial mantle melts is buffered by the subsolidus mantle rather than dominated by an invariant initial budget of Fe³⁺. Hydrogen, given its mobility in mineral phases and melts at upper mantle temperatures, would likely be the primary agent of electron transfer, giving the mantle a redox buffering capacity and forcing all partial melts to maintain a constant redox state near FMQ = 0. The second hypothesis, as proposed by Cottrell and Kelley (2011) and shown by Sorbadere et al. (2018), is that the bulk peridotite-melt partition coefficient of Fe₂O₃ ($D_{\text{Fe}_2\text{O}_3}^{\text{Peridotite-melt}}$) might not be constant but decreases with increasing degree of partial melting, hence causing the melt Fe³⁺/ΣFe to remain constant over variable degrees of partial melting. Davis and Cottrell (2021) provided additional evidence for this by characterizing the temperature dependency of the spinel-melt partition coefficient (decreasing with increasing temperature).

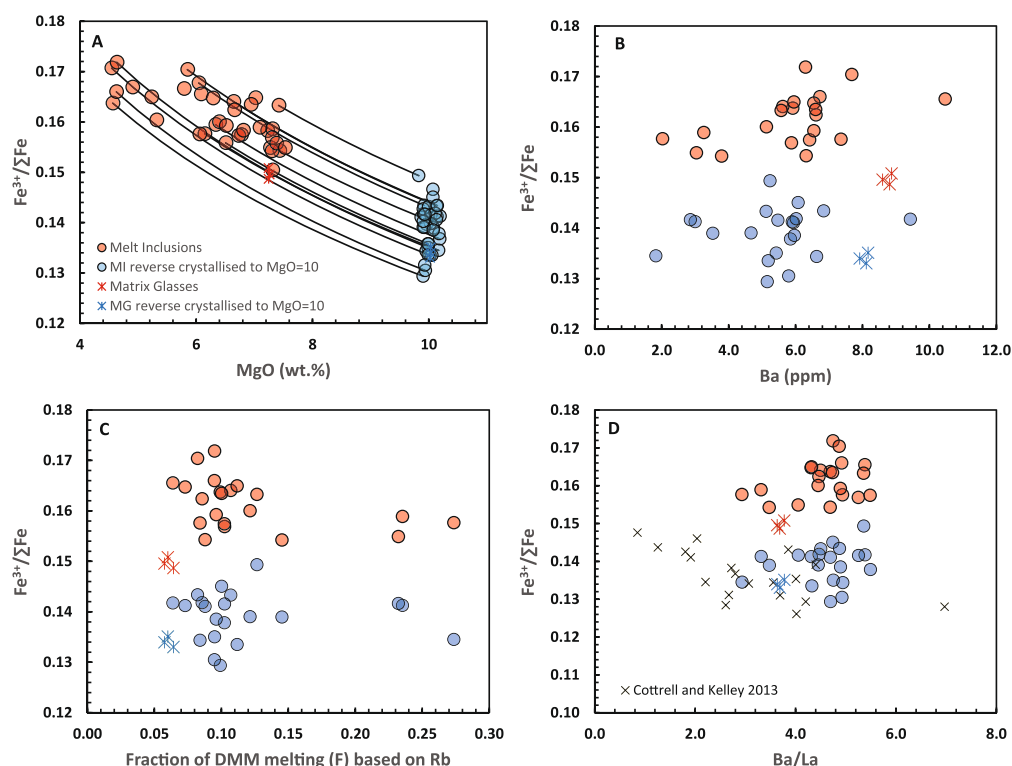


Figure 9. (a) Modeled reverse crystallization paths for SWIR olivine-hosted MIs along olivine control lines using PRIMELT3 (Herzberg & Asimow, 2015) until the melts reach 10 wt.% MgO. Solid black lines show reverse crystallization paths for a subset of inclusions. (b) Raw (red) and corrected to MgO = 10 wt.% (blue) $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in olivine-hosted MIs compared to their Ba content. (c) Raw and corrected $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios compared to the estimated degree of partial melting of a DMM source (note that these calculations are highly assumption-dependent, results are shown only to demonstrate that a range in F is expected). (d) Raw and corrected $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios compared to Ba/La. A global dataset from Cottrell and Kelley (2013) is shown for comparison.

5. Conclusions

We performed major, trace and volatile element measurements on a series of olivine- and plagioclase-hosted melt inclusions and matrix glasses from MORBs of the South West Indian Ridge, together with X-ray absorption near-edge structure spectroscopy measurements at the iron K-edges. We found that both melt inclusions and matrix glasses show clear signs of CO_2 undersaturation, with CO_2 positively correlating with incompatible trace elements. The SWIR CO_2/Ba (123 ± 32), CO_2/Rb ($1,374 \pm 487$) and CO_2/Nb ($1,134 \pm 415$) ratios are amongst the highest measured in MORBs, indicating a CO_2 -rich mantle source containing $69 \pm 18 \text{ ppm CO}_2$, calculated assuming a source composition with 0.563 ppm Ba.

The melt inclusion trace element systematics are consistent with formation by variable degrees of partial melting, and their volatile contents indicate minimum entrapment pressures equivalent to depths up to 10.5 km below the seafloor (i.e., in the upper mantle). Since the melt inclusions are CO_2 -undersaturated, they must have experienced extremely limited amounts of volatile degassing, which would have overprinted their initial oxidation state. The melt inclusion oxidation states show no systematic variation with volatile abundance or composition, and external redox buffering by a carrier melt is unlikely given the rapid magma ascent speed of 0.03–0.19 m/s, determined from water diffusion in embayment profiles.

The MI hence offer a unique sample suite to test the behavior of Fe^{3+} , which is expected to act as an incompatible element during partial melting. We found no correlation between the melt $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio (nor Fe_2O_3 content nor oxidation state as ΔQFM) and other incompatible trace elements even after correcting for the effect of olivine crystallization to a common reference point at MgO = 10 wt.%. We find instead that the oxidation state of all melt inclusions is uniform with a $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio of 0.160 ± 0.006 (giving $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of 0.140 ± 0.005 at MgO = 10 wt.%), corresponding to $\log(f\text{O}_2) = \text{QFM} - 0.07 \pm 0.05$ (giving $\log(f\text{O}_2) = \text{QFM} - 0.30 \pm 0.09$ at MgO = 10 wt.%).

These findings suggest that upper mantle partial melts are effectively buffered by the mantle in which they form/travel or/and that the bulk peridotite-melt partition coefficient of Fe_2O_3 decreases with temperature and increasing degree of partial melting, producing melts with essentially constant $\text{Fe}^{3+}/\Sigma\text{Fe}$. Current models of the behavior of $\text{Fe}^{3+}/\Sigma\text{Fe}$ during partial melting of peridotite may therefore need to be revised. This includes reevaluating the anticipated influence of the extent of mantle partial melting on the oxidation state of volcanic materials and their potential connection to oxygenation of the atmosphere.

Data Availability Statement

Raw X-ray absorption near-edge structure spectra at the iron K-edge are archived as Moussallam (2023a). Table S1–S6 in Supporting Information S2 are archived as Moussallam (2023b). Figures S1–S3 in Supporting Information S1 and text are archived as Moussallam (2023c).

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