Explosive eruptions at mid-ocean ridges driven by CO$_2$-rich magmas

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The abundance of volatile compounds, and particularly CO$_2$, in the upper oceanic mantle affects the style of volcanic eruptions. At mid-ocean ridges, eruptions are generally dominated by the gentle effusion of basaltic lavas with a low volatile content. But, explosive volcanism has been documented at some ocean spreading centres$^{1-3}$, indicative of abundant volatile compounds. Estimates of the initial CO$_2$ concentration of primary magmas can be used to constrain the CO$_2$ content of the upper oceanic mantle, but these estimates vary greatly$^{4,5}$. Here we present ion microprobe measurements of the CO$_2$ content of basaltic melt trapped in plagioclase crystals. The crystals are derived from volcanic ash deposits erupted explosively at Axial Seamount, Juan de Fuca Ridge, in the northeast Pacific Ocean. We report unusually high CO$_2$ concentrations of up to 9,160 ppm, which indicate that the upper oceanic mantle is more enriched in carbon than previously thought. And we furthermore suggest that CO$_2$ fluxes along mid-ocean ridges$^{4,5}$ vary significantly. Our results demonstrate that elevated fluxes of CO$_2$ from the upper oceanic mantle can drive explosive eruptions at mid-ocean ridges.

Mid-ocean ridges (MOR) are the most active and voluminous volcanic systems on Earth, forming nearly 60% of the Earth’s crust. Owing to its large volume, MOR volcanism is a key contributor to the total CO$_2$ flux from the mantle to the Earth’s surface. Recent work has documented the widespread existence of volcaniclastic ash deposits comprising basaltic glass fragments at MOR sites$^{1-3}$. Although widely interpreted as primary products of submarine explosive eruptions$^{1,2,6}$, some researchers argue for lava-seawater interaction$^{7,8}$. Due to its low solubility, CO$_2$ is the only magmatic volatile phase undergoing significant exsolution as basaltic magma ascends to the seafloor$^9$, hence the only volatile which can drive explosive eruptions at these
depths. Pyroclastic activity in MOR environments therefore is controlled by the primary CO$_2$ content of basaltic liquids, and consequently by the carbon budget of the mantle source. Initial CO$_2$ contents of variously enriched basalts from the Mid-Atlantic Ridge, including so-called “popping rock”, are inferred to be between 660 and 57,600 ppm, based on their vesicularity and extent of carbon isotope fractionation$^{5,10}$. However, such elevated CO$_2$ levels have never been measured directly. By contrast, dissolved CO$_2$ concentrations in vapour-undersaturated melt inclusions from an East Pacific Rise MOR basalt (MORB) suite, which are thought to represent the initial MORB volatile contents, show very low CO$_2$ contents of 44-244 ppm (ref. 4). This large discrepancy poses a significant problem to our understanding of CO$_2$ abundances in the MORB mantle and derived magmas.

We analysed the dissolved volatile concentration of 47 melt inclusions entrapped in plagioclase (An$_{81-91}$) prior to eruption as well as host glass shards sampled from five pyroclastic ash sequences on Axial Seamount (Supplementary Tables S1, S2), to assess the pre-eruptive volatile inventory of the local MORB. The Axial caldera system is part of the intermediate-rate spreading Juan de Fuca Ridge (JdFR) between 45° 50’ N and 46° N. A present-day magma reservoir is present at 2.5-6 km beneath the volcanic edifice$^{11}$. Widespread ash deposits up to 2 m thick on the volcano’s flanks include angular glass fragments, thin platy glass shards interpreted as bubble walls and termed limu o Pele (Supplementary Fig. S1), and plagioclase phenocrysts. This volcanic ash is evidence for explosive activity accompanying effusive lava flows.

The melt inclusions are generally more primitive (7.85 to 10.85 wt % MgO) and more variable in their trace element composition than the host glass (Supplementary Fig. S2a, Supplementary Tables S1, S3). Incompatible trace element compositions
(Supplementary Fig. S2b) fall within the overall range of JdFR basalts\textsuperscript{12} indicating some variations in the mantle source chemistry. The melt inclusions exhibit an extremely large range of CO\textsubscript{2} concentrations, from 262 ppm up to 9,159 ppm (Fig. 1), with \textasciitilde30 \% of the inclusions \textasciitilde1,000 ppm (“high-CO\textsubscript{2}” inclusions). Corresponding saturation pressures range from \textasciitilde60 MPa to 1.2 GPa (using ref. 13). These are the highest CO\textsubscript{2} concentrations ever measured in a MORB, and are consistent with previous predictions of initial, undegassed volatile contents of MORB liquids\textsuperscript{5,10,14,15}. Variations of other volatile elements are much more restricted. H\textsubscript{2}O concentrations are 0.12-0.38 wt \%, S 825-1,379 ppm, Cl 14 – 144 ppm, and F 74-222 ppm. For comparison, melt inclusions from similar volcaniclastic deposits at the Gakkel Ridge record lower CO\textsubscript{2} concentrations between 170-1,600 ppm\textsuperscript{16}.

Decompression degassing of CO\textsubscript{2}-rich, H\textsubscript{2}O-poor magma results in exsolution of CO\textsubscript{2} with restricted H\textsubscript{2}O partitioning into the vapour phase\textsuperscript{9}. Within CO\textsubscript{2}-H\textsubscript{2}O space, the melt inclusions define a vertical trend (Fig. 1), indicating volatile saturation and decompression degassing of CO\textsubscript{2}-rich vapour from mantle to crustal depths (40 km to 2 km, calculated from the range of CO\textsubscript{2}-H\textsubscript{2}O saturation pressures, and a crustal density of 2,360 kg m\textsuperscript{-3}, ref. 17). H\textsubscript{2}O variability exceeds that expected from purely degassing trends. The excellent positive correlation between H\textsubscript{2}O and F in the melt inclusions (Fig. 2a) indicates their similar geochemical behaviour and a constant H\textsubscript{2}O/F of the local mantle source of 14.3\textpm0.1. Hence, the H\textsubscript{2}O variability reflects some heterogeneity of the mantle source.

The ratio also allows us to assess post-eruptive alteration in MORBs, as hydration by seawater will cause the ratio to vary as a function of H\textsubscript{2}O. Moreover, Cl/H\textsubscript{2}O in the melt inclusions varies only as a function of Cl (Fig. 2b). Cl is accordingly assimilated
within the magma reservoir, while H₂O is not. Figure 2 reveals that the host glasses show both hydration and Cl assimilation. Hence Cl/H₂O and H₂O/F combined can be used to assess both the degree of pre-eruptive Cl assimilation and post-eruptive seawater-alteration in MORBs.

During melting, volatiles such as CO₂ behave highly incompatibly and partition strongly into the melt phase, similar to elements such as Nb (ref. 4). The melt inclusion with the highest CO₂ concentration (9,159 ppm) is volatile-oversaturated at any pressure below 1.2 GPa (calculated using ref. 13). Subsequent evolution of primitive CO₂-rich melts, as they ascend from the upper mantle to the shallow magma reservoir, can be evaluated in terms of three conceptual CO₂ degassing scenarios. First, degassing during ascent in the mantle without crystallisation would not entrap high-CO₂ melts and can be ruled out. Second, the melt inclusions show no correlation between the degree of fractionation in terms of their Ca-number or Mg-number and CO₂ content (Supplementary Fig. S3), which would be expected for continuous coeval degassing and crystallisation of plagioclase or olivine during magma ascent in the mantle. We therefore propose a third scenario where melt entrapment occurs over shallower mantle to crustal depths, in agreement with the calcic composition of the plagioclase crystals (Supplementary Table S4), which is commonly associated with crystallisation at lower pressures\textsuperscript{18,19}. Following the model in ref. 19, melt is entrapped as magma rises through a calcic plagioclase-rich zone within the magma plumbing system. This implies that significant volatile exsolution is delayed during the ascent of melt batches from the deeper mantle, introducing strong degrees of supersaturation. The CO₂ bubble nucleation rate depends on the extent of supersaturation, with the degree of supersaturation necessary for bubble nucleation increasing at lower pressures as magma
As the supersaturated magma arrives and stagnates at constant pressures within the magma reservoir system at ~6 km depth, it will then experience strong CO$_2$ exsolution. In a similar fashion, strong degrees of supersaturation are achieved during the ascent of magma from the reservoir to the seafloor, as clearly demonstrated by our CO$_2$ data from the host glasses (Fig. 1b) and previous studies$^{5,9}$. Our documentation of high CO$_2$ levels in primitive MORB liquid has far-reaching implications. The data provide insights into the physical evolution of the magma as it passes through the mantle into the shallow reservoir and is then erupted. At saturation pressures of ~60 MPa corresponding to a crustal depth of 2 km (using ref. 17), at least 8800 ppm CO$_2$ have been exsolved from a magma initially containing 9,160 ppm CO$_2$, translating to a vesicularity of ~10% of free vapour. At the ocean floor this increases to ~32-34% vesicularity. Under these conditions, expanding bubbles rising within the conduit can coalesce and drive strombolian explosions. For conditions similar to Axial Seamount, ref. 21 models a maximum magma rise velocity of 0.5-2.0 m s$^{-1}$ and a vent width of 0.3-0.6 m for bubble coalescence to be achieved. Alternatively, bubbles could accumulate against the reservoir roof of the magma reservoir as a foam layer$^{22}$. When a critical thickness of foam is reached, an eruption is triggered by foam collapse at the top of the reservoir, and gas slugs rise through the conduit causing bubble bursts. We compute a minimum gas flux of ~10$^{-1}$ kg s$^{-1}$ for the foam to reach the critical height using a gas fraction in the foam of 0.76 and a bubble radius of 0.3 mm (see supplementary information for calculations). The two models are not mutually exclusive. If an eruption is triggered before the critical foam thickness is reached, the accumulated foam will enhance bubble coalescence within the conduit, resulting in strombolian activity according to the first model. In both scenarios, erupting gas pockets
are separated by low vesicularity melt, as syn-eruptive degassing adds less than 4% to
the total vesicularity. Our key conclusion is that the very high CO$_2$ in the mantle and
derived magmas gives rise to large amounts of CO$_2$-rich gas bubbles at shallow crustal
levels, which in turn drive explosive submarine eruptions.

Adopting a CO$_2$/Nb of ~4,000 from the least degassed melt inclusion, a similar
genochemical behaviour of both elements during melting$^4$ and a Nb abundance of the
mean upper depleted mantle of 0.3 ppm (ref. 23), we calculate a minimum CO$_2$ content
of 1200 ppm for the mantle source beneath Axial Seamount (corresponding to 330 ppm
of elemental carbon). For the 100 km spreading segment supplied by Axial Seamount
we find a carbon mantle flux of $23 \times 10^8$ mol yr$^{-1}$, using a magma production rate
constrained by the thickness of the local crust$^{24}$ of 6-8 km and a spreading rate of 6 mm
yr$^{-1}$. Likewise, using a global oceanic crust production rate of $20\pm3$ km$^3$ yr$^{-1}$ (ref. 25)
and a mean N-MORB Nb content of 3.5$\pm$1.9 ppm (ref. 23), we estimate a carbon mantle
flux of $19\pm10 \times 10^{12}$ mol yr$^{-1}$ at mid-ocean ridges. This flux agrees with previous high
estimates of $15 \times 10^{12}$ mol yr$^{-1}$ (ref. 10) and exceeds the lower range of estimates by
nearly an order of magnitude$^{5,16}$.

CO$_2$ and Nb data from a number of studies from the last ten years$^{4,5,26,27}$ suggest
variable CO$_2$/Nb in parts of the upper mantle rather than a constant value (Fig. 3). If
both elements behave identically during mantle processes$^4$, their ratio should remain
constant and independent from the elemental concentrations. However, CO$_2$ and Nb
contents from various locations reveal a strong tendency towards lower CO$_2$/Nb as CO$_2$
decreases (Fig. 3). Hence, the CO$_2$ variability is much greater than Nb, suggesting either
degassing of volatile-saturated magma, or a heterogeneous carbon distribution in the
mantle that is decoupled from non-volatile incompatible elements such as Nb. While the
CO₂-H₂O data from Axial suggest strong decompression degassing, results for
Siqueiros⁴ and the North Atlantic ridge⁵ (14 °N and 34 °N) are thought to represent
undegassed CO₂ contents. Only data for the North Atlantic ridge at 14 °N show constant
CO₂/Nb. All other localities appear to be affected by CO₂ degassing, heterogeneous
mantle carbon distributions, or both.

Our data provide evidence of extremely high dissolved CO₂ concentrations in
primitive, volatile saturated MORB magmas at depths of 35-40 km. The high CO₂
content of mantle-derived MORB magmas at Axial Seamount establishes a direct link
with explosive eruptions and widespread pyroclastic deposits at MOR spreading
centres. We propose that CO₂ is decoupled from other incompatible elements in parts of
the upper mantle, and CO₂ fluxes can vary significantly along mid-ocean ridges.

Methods
Volatile (H₂O, CO₂, S, F, and Cl) analysis was carried out at Woods Hole
Oceanographic Institution (WHOI) utilising high mass resolution secondary ion mass
spectrometry (CAMECA IMS 1280). Selection of melt inclusions was done carefully
through observations under transmitted and reflected light avoiding cracks or shrinkage
bubbles within inclusions. Plagioclase grains with exposed inclusions were mounted
into indium metal, and a 0.3 μm alumina oxide suspension was used for final polish.
Prior to gold-coating, the mounts were dried in a vacuum oven at 110° C and 10⁻³ torr
for ~12 h and were stored under vacuum at 10⁻⁷ torr for ~24 h. They were further
allowed to outgas in the machine airlock at 3 × 10⁻⁹ torr. Sample chamber pressures
during analysis were <5 × 10⁻⁹ torr. The principal analytical procedure followed the
method as described in ref. 28. The detected secondary ions (¹²C, ¹⁶O¹H, ¹⁹F, ³⁰Si, ³²S,
and $^{35}\text{Cl}$ were produced by a primary $^{133}\text{Cs}^+$ beam of 1.2-1.5 nA current and 15 µm diameter. An electron beam was employed to compensate for positive charging of the sample surface. The primary beam was rastered over a 30 × 30 µm area, and a mechanical aperture was placed at the secondary ion image plane, such that the central 15 × 15 µm area was analyzed after 3 min of pre-sputtering. Counting times of 10 s were used for $^{12}\text{C}$ and $^{16}\text{O}^1\text{H}$, and 5 s for $^{19}\text{F}$, $^{30}\text{Si}$ (reference mass), $^{32}\text{S}$ and $^{35}\text{Cl}$. Data were acquired over 10 blocks. Magnet positions were calibrated for every spot and mass resolving power was set to > 6,700 to resolve interferences of $^{17}\text{O}$ from $^{16}\text{O}^1\text{H}$ and $^{29}\text{Si}^1\text{H}$ from $^{30}\text{Si}$. Nine standard glasses, of basaltic and basaltic andesite compositions, were used to establish calibration curves for $^{12}\text{C}/^{30}\text{Si}$, $^{16}\text{O}^1\text{H}/^{30}\text{Si}$, $^{19}\text{F}/^{30}\text{Si}$, $^{32}\text{S}/^{30}\text{Si}$, and $^{35}\text{Cl}/^{30}\text{Si}$ versus the respective volatile component. CO$_2$ content of all standard glasses was determined by Fourier transform infrared (FTIR) spectroscopy after the method of ref. 29. The standard error on the slope of the calibration curves is 2.4 % for CO$_2$ and 4.8 % or better for H$_2$O, F, S, and Cl. The 1σ stability of the $^{12}\text{C}/^{30}\text{Si}$ signal during analyses was better than 10 %, except for sample PlgM1_3-1 (12.2 %) and PlgM2_7-1 (14.1 %). The 1σ reproducibility of the in-run standard glass P1326-2, a JdFR basalt, was 5.3 % or better for CO$_2$, F, S and Cl, and 7.8 % for H$_2$O. Details on standards and quality of analyses are given in Supplementary Tables S5 and S6, and Supplementary Figs S4–S6. Special care was taken to verify high CO$_2$ contents in melt inclusions: first, nine high-CO$_2$ melt inclusions were re-analyzed after removing gold with 0.3 µm Al$_2$O$_3$ suspension. Potential surface contamination was reduced by sputter-cleaning melt inclusions with a stronger ion beam (5 nA) for 5 minutes, instead of a regular cleaning procedure with a 1.5-nA beam. Duplicate analyses confirmed the high CO$_2$ concentrations initially obtained. The data reported here are the duplicate values.
Second, secondary ion images of $^{12}$C were observed for each melt inclusion, and a homogeneous distribution of $^{12}$C was confirmed for melt inclusions. No enrichment of CO$_2$ in cracks or edges of melt inclusions was observed. Third, $^{12}$C intensity during analysis did not display any sign of surface contamination (Supplementary Fig. S5). Fourth, the CO$_2$ concentration in host plagioclase adjacent to melt inclusions was much less than 30 ppm. This is considered to represent the CO$_2$ background.

Subsequent to the volatile analysis, trace element compositions were determined for the melt inclusions using a CAMECA IMS 3f secondary ion mass spectrometer at WHOI$^{30}$. Calibration was carried out using the KL2-G glass standard. Trace element concentrations of the in-run standard P1326-2 were reproducible at a $1\sigma < 8 \%$, except for Ba (11 %) (Supplementary Table S6). Major element compositions for the melt inclusions and the host glasses were analysed by electron microprobe (JEOL 8900) at McGill University, using a beam current of 1.5 nA, 15 kV, and defocused beam of 5 µm diameter for the melt inclusions and 10 µm for the host glasses.

References


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**Author contributions**

C.H. performed volatile analysis and major element analysis of the melt inclusions and host glasses, and analysed the data. M.-A.L performed the trace element analysis of the melt inclusions, N.S. supervised the volatile and trace element analysis, D.A.C was responsible for the organisation of the cruise and sample collection, and J.S. supervised the work. The manuscript was written primarily by C.H., with contributions from M.-A.L., N.S., D.A.C., and J.S.

**Additional information**

The authors declare no competing financial interests. *Supplementary information* accompanies this paper on [www.nature.com/naturegeoscience](http://www.nature.com/naturegeoscience).

**Figure 1** Dissolved \(\text{CO}_2\) and \(\text{H}_2\text{O}\) contents in melt inclusions and host glasses, measured by SIMS. Isobars calculated using ref. 13. 1σ error bars are shown for representative values. **a**, Melt inclusions exhibit an extremely wide range in \(\text{CO}_2\) contents. The vertical trend indicates decompression degassing from a volatile-saturated melt. **b**, Zoom of the region below 1,000 ppm \(\text{CO}_2\). The host glasses are volatile-oversaturated for an eruption pressure of 14 MPa (grey isobar). Host glasses are equilibrated at crustal depths between 0.3 and 2 km. The continuity in \(\text{CO}_2\) concentrations from melt inclusions to host glasses indicates limited syn-eruptive degassing.
Figure 2 H₂O, F, and Cl contents of the melt inclusions and host glasses. a, The excellent correlation between H₂O and F in the melt inclusions indicates similar geochemical behaviour and suggests H₂O/F in the mantle of 14.3±0.2 (2σ). The host glasses display increasing H₂O at roughly constant F, indicating hydration and alteration of the erupted basalt. b, Cl/H₂O in the melt inclusions is controlled solely by the amount of Cl assimilated within the magma reservoir. By contrast post-eruptive alteration of the host glasses increases both Cl and H₂O, causing Cl/H₂O to remain roughly constant. 1σ error bars are shown.

Figure 3 Bilogarithmic plot of CO₂/Nb versus CO₂. The wide range of observed CO₂/Nb is striking, generally decreasing with lower CO₂. This trend can be explained by either degassing of CO₂ from volatile-saturated magmas, or in cases where degassing can be ruled out, by CO₂ distribution in the mantle which is decoupled from Nb. Decoupling of these two elements would result in a range of initial CO₂/Nb. Axial: degassed, measured dissolved volatile content in melt inclusions; Siqueiros: undegassed, measured dissolved volatile content in melt inclusions; North Atlantic ridge 14°N and 34°N and Loihi: reconstructed undegassed volatile contents.
Cl and H$_2$O assimilation

Post-eruptive hydration

H$_2$O/F = 14.3±0.2 (2σ)

Cl, but no H$_2$O assimilation (pre-eruptive)

Cl and H$_2$O assimilation (post-eruptive)