1  **Explosive eruptions at mid-ocean ridges driven by $CO_2$-**

2  **rich magmas**

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18      **The abundance of volatile compounds, and particularly $CO_2$, in the upper**

19      **oceanic mantle affects the style of volcanic eruptions. At mid-ocean ridges,**

20      **eruptions are generally dominated by the gentle effusion of basaltic lavas with a**

21      **low volatile content. But, explosive volcanism has been documented at some ocean**

22      **spreading centres[1-3], indicative of abundant volatile compounds. Estimates of the**

23      **initial $CO_2$ concentration of primary magmas can be used to constrain the $CO_2$**

24      **content of the upper oceanic mantle, but these estimates vary greatly[4,5]. Here we**

25      **present ion microprobe measurements of the $CO_2$ content of basaltic melt trapped**

26      **in plagioclase crystals. The crystals are derived from volcanic ash deposits erupted**

27      **explosively at Axial Seamount, Juan de Fuca Ridge, in the northeast Pacific Ocean.**

28      **We report unusually high $CO_2$ concentrations of up to 9,160 ppm, which indicate**

29      **that the upper oceanic mantle is more enriched in carbon than previously thought.**

30      **And we furthermore suggest that $CO_2$ fluxes along mid-ocean ridges[4,5] vary**

31      **significantly. Our results demonstrate that elevated fluxes of $CO_2$ from the upper**

32      **oceanic mantle can drive explosive eruptions at mid-ocean ridges.**

33      Mid-ocean ridges (MOR) are the most active and voluminous volcanic systems on

34      Earth, forming nearly 60 % of the Earth's crust. Owing to its large volume, MOR

35      volcanism is a key contributor to the total $CO_2$ flux from the mantle to the Earth's

36      surface. Recent work has documented the widespread existence of volcaniclastic ash

37      deposits comprising basaltic glass fragments at MOR sites[1-3]. Although widely

38      interpreted as primary products of submarine explosive eruptions[1,2,6], some researchers

39      argue for lava-seawater interaction[7,8]. Due to its low solubility, $CO_2$ is the only

40      magmatic volatile phase undergoing significant exsolution as basaltic magma ascends to

41      the seafloor[9], hence the only volatile which can drive explosive eruptions at these

42  depths. Pyroclastic activity in MOR environments therefore is controlled by the primary

43  $CO_2$ content of basaltic liquids, and consequently by the carbon budget of the mantle

44  source. Initial $CO_2$ contents of variously enriched basalts from the Mid-Atlantic Ridge,

45  including so-called "popping rock", are inferred to be between 660 and 57,600 ppm,

46  based on their vesicularity and extent of carbon isotope fractionation[5,10]. However, such

47  elevated $CO_2$ levels have never been measured directly. By contrast, dissolved $CO_2$

48  concentrations in vapour-undersaturated melt inclusions from an East Pacific Rise MOR

49  basalt (MORB) suite, which are thought to represent the initial MORB volatile contents,

50  show very low $CO_2$ contents of 44-244 ppm (ref. 4). This large discrepancy poses a

51  significant problem to our understanding of $CO_2$ abundances in the MORB mantle and

52  derived magmas.

53      We analysed the dissolved volatile concentration of 47 melt inclusions entrapped

54  in plagioclase ($An_{81-91}$) prior to eruption as well as host glass shards sampled from five

55  pyroclastic ash sequences on Axial Seamount (Supplementary Tables S1, S2), to assess

56  the pre-eruptive volatile inventory of the local MORB. The Axial caldera system is part

57  of the intermediate-rate spreading Juan de Fuca Ridge (JdFR) between 45° 50' N and

58  46° N. A present-day magma reservoir is present at 2.5-6 km beneath the volcanic

59  edifice[11]. Widespread ash deposits up to 2 m thick on the volcano's flanks include

60  angular glass fragments, thin platy glass shards interpreted as bubble walls and termed

61  limu o Pele (Supplementary Fig. S1), and plagioclase phenocrysts. This volcanic ash is

62  evidence for explosive activity accompanying effusive lava flows.

63      The melt inclusions are generally more primitive (7.85 to 10.85 wt % MgO) and

64  more variable in their trace element composition than the host glass (Supplementary

65  Fig. S2a, Supplementary Tables S1, S3). Incompatible trace element compositions

66  (Supplementary Fig. S2b) fall within the overall range of JdFR basalts[12] indicating some

67  variations in the mantle source chemistry. The melt inclusions exhibit an extremely

68  large range of $CO_2$ concentrations, from 262 ppm up to 9,159 ppm (Fig. 1), with ~30 %

69  of the inclusions >1,000 ppm ("high-$CO_2$" inclusions). Corresponding saturation

70  pressures range from ~ 60 MPa to 1.2 GPa (using ref. 13). These are the highest $CO_2$

71  concentrations ever measured in a MORB, and are consistent with previous predictions

72  of initial, undegassed volatile contents of MORB liquids[5,10,14,15]. Variations of other

73  volatile elements are much more restricted. $H_2O$ concentrations are 0.12-0.38 wt %, S

74  825-1,379 ppm , Cl 14 – 144 ppm, and F 74-222 ppm. For comparison, melt inclusions

75  from similar volcaniclastic deposits at the Gakkel Ridge record lower $CO_2$

76  concentrations between 170-1,600 ppm[16].

77      Decompression degassing of $CO_2$-rich, $H_2O$-poor magma results in exsolution of

78  $CO_2$ with restricted $H_2O$ partitioning into the vapour phase[9]. Within $CO_2$-$H_2O$ space, the

79  melt inclusions define a vertical trend (Fig. 1), indicating volatile saturation and

80  decompression degassing of $CO_2$-rich vapour from mantle to crustal depths (40 km to 2

81  km, calculated from the range of $CO_2$-$H_2O$ saturation pressures, and a crustal density of

82  2,360 kg m$^{-3}$, ref. 17). $H_2O$ variability exceeds that expected from purely degassing

83  trends. The excellent positive correlation between $H_2O$ and F in the melt inclusions

84  (Fig. 2a) indicates their similar geochemical behaviour and a constant $H_2O$/F of the

85  local mantle source of 14.3±0.1. Hence, the $H_2O$ variability reflects some heterogeneity

86  of the mantle source.

87      The ratio also allows us to assess post-eruptive alteration in MORBs, as hydration

88  by seawater will cause the ratio to vary as a function of $H_2O$. Moreover, Cl/$H_2O$ in the

89  melt inclusions varies only as a function of Cl (Fig. 2b). Cl is accordingly assimilated

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90   within the magma reservoir, while $H_2O$ is not. Figure 2 reveals that the host glasses

91   show both hydration and Cl assimilation. Hence $Cl/H_2O$ and $H_2O/F$ combined can be

92   used to assess both the degree of pre-eruptive Cl assimilation and post-eruptive

93   seawater-alteration in MORBs.

94        During melting, volatiles such as $CO_2$ behave highly incompatibly and partition

95   strongly into the melt phase, similar to elements such as Nb (ref. 4). The melt inclusion

96   with the highest $CO_2$ concentration (9,159 ppm) is volatile-oversaturated at any pressure

97   below 1.2 GPa (calculated using ref. 13). Subsequent evolution of primitive $CO_2$-rich

98   melts, as they ascend from the upper mantle to the shallow magma reservoir, can be

99   evaluated in terms of three conceptual $CO_2$ degassing scenarios. First, degassing during

100  ascent in the mantle without crystallisation would not entrap high-$CO_2$ melts and can be

101  ruled out. Second, the melt inclusions show no correlation between the degree of

102  fractionation in terms of their Ca-number or Mg-number and $CO_2$ content

103  (Supplementary Fig. S3), which would be expected for continuous coeval degassing and

104  crystallisation of plagioclase or olivine during magma ascent in the mantle. We

105  therefore propose a third scenario where melt entrapment occurs over shallower mantle

106  to crustal depths, in agreement with the calcic composition of the plagioclase crystals

107  (Supplementary Table S4),which is commonly associated with crystallisation at lower

108  pressures[18,19]. Following the model in ref. 19, melt is entrapped as magma rises through

109  a calcic plagioclase-rich zone within the magma plumbing system. This implies that

110  significant volatile exsolution is delayed during the ascent of melt batches from the

111  deeper mantle, introducing strong degrees of supersaturation. The $CO_2$ bubble

112  nucleation rate depends on the extent of supersaturation, with the degree of

113  supersaturation necessary for bubble nucleation increasing at lower pressures as magma

114   rises[20]. As the supersaturated magma arrives and stagnates at constant pressures within

115   the magma reservoir system at ~6 km depth, it will then experience strong $CO_2$

116   exsolution. In a similar fashion, strong degrees of supersaturation are achieved during

117   the ascent of magma from the reservoir to the seafloor, as clearly demonstrated by our

118   $CO_2$ data from the host glasses (Fig. 1b) and previous studies[5,9].

119        Our documentation of high $CO_2$ levels in primitive MORB liquid has far-reaching

120   implications. The data provide insights into the physical evolution of the magma as it

121   passes through the mantle into the shallow reservoir and is then erupted. At saturation

122   pressures of ~60 MPa corresponding to a crustal depth of 2 km (using ref. 17), at least

123   8800 ppm $CO_2$ have been exsolved from a magma initially containing 9,160 ppm $CO_2$,

124   translating to a vesicularity of ~10 % of free vapour. At the ocean floor this increases to

125   ~32-34 % vesicularity. Under these conditions, expanding bubbles rising within the

126   conduit can coalesce and drive strombolian explosions. For conditions similar to Axial

127   Seamount, ref. 21 models a maximum magma rise velocity of 0.5-2.0 m s$^{-1}$ and a vent

128   width of 0.3-0.6 m for bubble coalescence to be achieved. Alternatively, bubbles could

129   accumulate against the reservoir roof of the magma reservoir as a foam layer[22]. When a

130   critical thickness of foam is reached, an eruption is triggered by foam collapse at the top

131   of the reservoir, and gas slugs rise through the conduit causing bubble bursts. We

132   compute a minimum gas flux of ~10$^{-1}$ kg s$^{-1}$ for the foam to reach the critical height

133   using a gas fraction in the foam of 0.76 and a bubble radius of 0.3 mm (see

134   supplementary information for calculations). The two models are not mutually

135   exclusive. If an eruption is triggered before the critical foam thickness is reached, the

136   accumulated foam will enhance bubble coalescence within the conduit, resulting in

137   strombolian activity according to the first model. In both scenarios, erupting gas pockets

138  are separated by low vesicularity melt, as syn-eruptive degassing adds less than 4 % to

139  the total vesicularity. Our key conclusion is that the very high $CO_2$ in the mantle and

140  derived magmas gives rise to large amounts of $CO_2$-rich gas bubbles at shallow crustal

141  levels, which in turn drive explosive submarine eruptions.

142      Adopting a $CO_2$/Nb of ~4,000 from the least degassed melt inclusion, a similar

143  geochemical behaviour of both elements during melting[4] and a Nb abundance of the

144  mean upper depleted mantle of 0.3 ppm (ref. 23), we calculate a minimum $CO_2$ content

145  of 1200 ppm for the mantle source beneath Axial Seamount (corresponding to 330 ppm

146  of elemental carbon). For the 100 km spreading segment supplied by Axial Seamount

147  we find a carbon mantle flux of $23 \times 10^8$ mol yr$^{-1}$, using a magma production rate

148  constrained by the thickness of the local crust[24] of 6-8 km and a spreading rate of 6 mm

149  yr$^{-1}$. Likewise, using a global oceanic crust production rate of $20\pm3$ km$^3$ yr$^{-1}$ (ref. 25)

150  and a mean N-MORB Nb content of $3.5\pm1.9$ ppm (ref. 23), we estimate a carbon mantle

151  flux of $19\pm10 \times 10^{12}$ mol yr$^{-1}$ at mid-ocean ridges. This flux agrees with previous high

152  estimates of $15 \times 10^{12}$ mol yr$^{-1}$ (ref. 10) and exceeds the lower range of estimates by

153  nearly an order of magnitude[5,16].

154      $CO_2$ and Nb data from a number of studies from the last ten years[4,5,26,27] suggest

155  variable $CO_2$/Nb in parts of the upper mantle rather than a constant value (Fig. 3). If

156  both elements behave identically during mantle processes[4], their ratio should remain

157  constant and independent from the elemental concentrations. However, $CO_2$ and Nb

158  contents from various locations reveal a strong tendency towards lower $CO_2$/Nb as $CO_2$

159  decreases (Fig. 3). Hence, the $CO_2$ variability is much greater than Nb, suggesting either

160  degassing of volatile-saturated magma, or a heterogeneous carbon distribution in the

161  mantle that is decoupled from non-volatile incompatible elements such as Nb. While the

162    $CO_2$-$H_2O$ data from Axial suggest strong decompression degassing, results for

163    Siqueiros[4] and the North Atlantic ridge[5] (14 °N and 34 °N) are thought to represent

164    undegassed $CO_2$ contents. Only data for the North Atlantic ridge at 14 °N show constant

165    $CO_2$/Nb. All other localities appear to be affected by $CO_2$ degassing, heterogeneous

166    mantle carbon distributions, or both.

167        Our data provide evidence of extremely high dissolved $CO_2$ concentrations in

168    primitive, volatile saturated MORB magmas at depths of 35-40 km. The high $CO_2$

169    content of mantle-derived MORB magmas at Axial Seamount establishes a direct link

170    with explosive eruptions and widespread pyroclastic deposits at MOR spreading

171    centres. We propose that $CO_2$ is decoupled from other incompatible elements in parts of

172    the upper mantle, and $CO_2$ fluxes can vary significantly along mid-ocean ridges.

173

174    **Methods**

175    Volatile ($H_2O$, $CO_2$, S, F, and Cl) analysis was carried out at Woods Hole

176    Oceanographic Institution (WHOI) utilising high mass resolution secondary ion mass

177    spectrometry (CAMECA IMS 1280). Selection of melt inclusions was done carefully

178    through observations under transmitted and reflected light avoiding cracks or shrinkage

179    bubbles within inclusions. Plagioclase grains with exposed inclusions were mounted

180    into indium metal, and a 0.3 µm alumina oxide suspension was used for final polish.

181    Prior to gold-coating, the mounts were dried in a vacuum oven at 110° C and $10^{-3}$ torr

182    for ~12 h and were stored under vacuum at $10^{-7}$ torr for ~24 h. They were further

183    allowed to outgas in the machine airlock at $3 \times 10^{-9}$ torr. Sample chamber pressures

184    during analysis were $<5 \times 10^{-9}$ torr. The principal analytical procedure followed the

185    method as described in ref. 28. The detected secondary ions ($^{12}C$, $^{16}O^{1}H$, $^{19}F$, $^{30}Si$, $^{32}S$,

186　and $^{35}$Cl) were produced by a primary $^{133}$Cs$^+$ beam of 1.2-1.5 nA current and 15 µm

187　diameter. An electron beam was employed to compensate for positive charging of the

188　sample surface. The primary beam was rastered over a $30 \times 30$ µm area, and a

189　mechanical aperture was placed at the secondary ion image plane, such that the central

190　$15 \times 15$um area was analyzed after 3 min of pre-sputtering. Counting times of 10 s were

191　used for $^{12}$C and $^{16}$O$^1$H, and 5 s for $^{19}$F, $^{30}$Si (reference mass), $^{32}$S and $^{35}$Cl. Data were

192　acquired over 10 blocks. Magnet positions were calibrated for every spot and mass

193　resolving power was set to $> 6,700$ to resolve interferences of $^{17}$O from $^{16}$O$^1$H and

194　$^{29}$Si$^1$H from $^{30}$Si. Nine standard glasses, of basaltic and basaltic andesite compositions,

195　were used to establish calibration curves for $^{12}$C/$^{30}$Si, $^{16}$O$^1$H/$^{30}$Si, $^{19}$F/$^{30}$Si, $^{32}$S/$^{30}$Si, and

196　$^{35}$Cl/$^{30}$Si versus the respective volatile component. $CO_2$ content of all standard glasses

197　was determined by Fourier transform infrared (FTIR) spectroscopy after the method of

198　ref. 29. The standard error on the slope of the calibration curves is 2.4 % for $CO_2$ and

199　4.8 % or better for $H_2O$, F, S, and Cl. The 1σ stability of the $^{12}$C/$^{30}$Si signal during

200　analyses was better than 10 %, except for sample PlgM1_3-1 (12.2 %) and PlgM2_7-1

201　(14.1 %). The 1σ reproducibility of the in-run standard glass P1326-2, a JdFR basalt,

202　was 5.3 % or better for $CO_2$, F, S and Cl, and 7.8 % for $H_2O$. Details on standards and

203　quality of analyses are given in Supplementary Tables S5 and S6, and Supplementary

204　Figs S4–S6. Special care was taken to verify high $CO_2$ contents in melt inclusions: first,

205　nine high-$CO_2$ melt inclusions were re-analyzed after removing gold with 0.3 µm $Al_2O_3$

206　suspension. Potential surface contamination was reduced by sputter-cleaning melt

207　inclusions with a stronger ion beam (5 nA) for 5 minutes, instead of a regular cleaning

208　procedure with a 1.5-nA beam. Duplicate analyses confirmed the high $CO_2$

209　concentrations initially obtained. The data reported here are the duplicate values.

210 Second, secondary ion images of $^{12}$C were observed for each melt inclusion, and a

211 homogeneous distribution of $^{12}$C was confirmed for melt inclusions. No enrichment of

212 $CO_2$ in cracks or edges of melt inclusions was observed. Third, $^{12}$C intensity during

213 analysis did not display any sign of surface contamination (Supplementary Fig. S5).

214 Fourth, the $CO_2$ concentration in host plagioclase adjacent to melt inclusions was much

215 less than 30 ppm. This is considered to represent the $CO_2$ background.

216 Subsequent to the volatile analysis, trace element compositions were determined

217 for the melt inclusions using a CAMECA IMS 3f secondary ion mass spectrometer at

218 WHOI[30]. Calibration was carried out using the KL2-G glass standard. Trace element

219 concentrations of the in-run standard P1326-2 were reproducible at a $1\sigma < 8$ %, except

220 for Ba (11 %) (Supplementary Table S6). Major element compositions for the melt

221 inclusions and the host glasses were analysed by electron microprobe (JEOL 8900) at

222 McGill University, using a beam current of 1.5 nA, 15 kV, and defocused beam of 5 µm

223 diameter for the melt inclusions and 10 µm for the host glasses.

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302

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304

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314

**Author contributions**

316    C.H. performed volatile analysis and major element analysis of the melt inclusions and host glasses, and

317    analysed the data. M.-A.L performed the trace element analysis of the melt inclusions, N.S. supervised

318    the volatile and trace element analysis, D.A.C was responsible for the organisation of the cruise and

319    sample collection, and J.S. supervised the work. The manuscript was written primarily by C.H., with

320    contributions from M.-A.L., N.S., D.A.C., and J.S.

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**Additional information**

323    The authors declare no competing financial interests. **Supplementary information** accompanies this

324    paper on **www.nature.com/naturegeoscience**.

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327    **Figure 1** Dissolved $CO_2$ and $H_2O$ contents in melt inclusions and host glasses,

328    measured by SIMS. Isobars calculated using ref. 13. 1σ error bars are shown for

329    representative values. **a**, Melt inclusions exhibit an extremely wide range in $CO_2$

330    contents. The vertical trend indicates decompression degassing from a volatile-

331    saturated melt. **b**, Zoom of the region below 1,000 ppm $CO_2$. The host glasses are

332    volatile-oversaturated for an eruption pressure of 14 MPa (grey isobar). Host glasses

333    are equilibrated at crustal depths between 0.3 and 2 km. The continuity in $CO_2$

334    concentrations from melt inclusions to host glasses indicates limited syn-eruptive

335    degassing.

336    **Figure 2** $H_2O$, F, and Cl contents of the melt inclusions and host glasses. **a**, The

337    excellent correlation between $H_2O$ and F in the melt inclusions indicates similar

338    geochemical behaviour and suggests $H_2O$/F in the mantle of 14.3±0.2 (2σ). The host

339    glasses display increasing $H_2O$ at roughly constant F, indicating hydration and

340    alteration of the erupted basalt. **b**, $Cl/H_2O$ in the melt inclusions is controlled solely by

341    the amount of Cl assimilated within the magma reservoir. By contrast post-eruptive

342    alteration of the host glasses increases both Cl and $H_2O$, causing $Cl/H_2O$ to remain

343    roughly constant. 1σ error bars are shown.


344    **Figure 3** Bilogarithmic plot of $CO_2$/Nb versus $CO_2$. The wide range of observed $CO_2$/Nb

345    is striking, generally decreasing with lower $CO_2$. This trend can be explained by either

346    degassing of $CO_2$ from volatile-saturated magmas, or in cases where degassing can be

347    ruled out, by $CO_2$ distribution in the mantle which is decoupled from Nb. Decoupling of

348    these two elements would result in a range of initial $CO_2$/Nb. *Axial*: degassed,

349    measured dissolved volatile content in melt inclusions; *Siqueiros* [4]: undegassed,

350    measured dissolved volatile content in melt inclusions; *North Atlantic ridge* [5] *14°N* and

351    *34°N* and *Loihi* [27]: reconstructed undegassed volatile contents.

**a**

- ◆ Melt inclusions

Decompression degassing

500 MPa
400 MPa
300 MPa
200 MPa
100 MPa

**b**

200 MPa

- ◆ Melt inclusion
- ○ Host glass

150 MPa
100 MPa
80 MPa
60 MPa
40 MPa
14 MPa

**a**

Legend:
- ◆ Melt inclusions
- ○ Host glasses

Post-eruptive hydration

$H_2O/F = 14.3\pm0.2$ (2$\sigma$)

x-axis: F [ppm] (50 to 250)
y-axis: $H_2O$ [ppm] (1,000 to 5,000)

**b**

Legend:
- ◆ Melt inclusions
- ○ Host glasses

Cl, but <u>no</u> $H_2O$ assimilation (pre-eruptive)

Cl <u>and</u> $H_2O$ assimilation (post-eruptive)

x-axis: Cl [ppm] (0 to 400)
y-axis: $Cl/H_2O$ (0.00 to 0.12)

Popping rock
2πD43