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1 Magmas trapped at the continental lithosphere-asthenosphere
2 boundary

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12 **Abstract**

13 The lithosphere-asthenosphere boundary (LAB) beneath the continents is a key
14 interface in plate tectonics, yet its nature remains elusive. A partial melt layer
15 has been advocated to explain its geophysical characteristics. However, the main
16 counter-argument is that such a layer can not be stable as melts should rise through
17 the lithosphere. Density measurements of volatile-containing alkali basalts taken
18 as a proxy for LAB melts show that they are neutrally buoyant at the pressure (P)-
19 temperature (T) conditions of the LAB under continents. Complementary X-ray
20 diffraction and Raman data provide structural insights on melt compaction mecha-
21 nisms. Basalts generated below the lithosphere may thus be gravitationally trapped
22 and accumulate over time. Their presence provide answers to key questions on
23 continental lithosphere geodynamics, and in particular on cratonic keels stability.
24 This buoyancy trap would cease to exist at higher mantle T such as those relevant
25 of the Archean, and as such, could be linked to the onset of plate tectonics.

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27 **1. Introduction**

28 Several geophysical observables define the continental LAB: 1) the Lehmann
29 discontinuity at constant depth (200-250 km) across the Archean and proterozoic
30 units in North America (Yu and Romanowicz, 2010); 2) the low velocity zone in
31 global tomographic models of shear-wave velocity (Cammarano and Romanowicz,
32 2007); 3) a shear wave radial anisotropy with horizontally polarized shear waves
33 traveling faster than those that are vertically polarized, anomaly present under most
34 cratons in the depth range 250-400 km (Yu and Romanowicz, 2010) with East-
35 West flow in the convective mantle, and North-South fast direction in the LAB; 4)
36 an electrical resistivity drop (Jones, 1999; Jones et al., 2010). Only observable 2
37 is common to oceanic and continental LAB, the former being significantly shal-
38 lower (circa 90 km). It has long been suggested that all characteristics given above
39 for the continental LAB may be caused by small amounts of partial melt (Eaton
40 et al., 2009; Anderson and Sammis, 1970). Petrological models of the continental
41 lithosphere describe its lowest part as enriched by melts from below (Foley, 2008),
42 consistently with melts having ponded in the asthenosphere (O'Reilly and Grif-
43 fin, 2010). Magnetotelluric observations suggest that the partial melt layer is of
44 finite thickness, which implies that partial melting ceases at greater depths (Jones,
45 1999), and/or that melts are trapped at this particular depth as suggested by Agee
46 (1998) and Chen et al. (2002). A stable partial melt layer in the LAB would have
47 major geodynamical consequences such as lithosphere-asthenosphere decoupling

48 (Doglioni et al., 2011) and explain why cratonic roots survive so long while nu-
49 merical models predict that they should be eroded (King, 2005) by shielding them
50 from the mantle stress field. However, this suggestion requires the presence of ma-
51 terials that will: 1) melt at the P-T conditions of the LAB, and 2) be retained at that
52 depth by some mechanism.

53 **2. Why the choice of an alkali basalt?**

54 There has been a strong focus on carbonatites as candidates for LAB melts,
55 essentially as they can be generated as deep as 250 km from partial melting of
56 carbonated peridotite, and have been proposed to explain the oceanic low-velocity
57 zone (Gaillard et al., 2008; Dasgupta et al., 2013). However, their low density (2.2-
58 2.3 g/cc) discards them for the continental LAB as they would not be retained at
59 depth. Instead, alkali basalts combine a higher density with a relatively low melting
60 point. The solidus of an alkali basalt is lower than that of a typical mid-ocean ridge
61 basalt (MORB) at depth with a maximum depression of 200 K at 6 GPa (Tsuruta
62 and Takahashi, 1998), and in contrast to the MORB solidus, the alkali basalt solidus
63 becomes very steep around 6-7 GPa (Fig.1), i.e. at or around the conditions of the
64 continental LAB.

65 Alkali basalts have been dragged in the Japanese sea and interpreted as origi-
66 nating from the asthenosphere (Hirano et al., 2006), with a high vesicularity sug-
67 gesting high CO₂ content in the pre-eruptive melt. The contribution of high pres-
68 sure eclogites, the crystallized high pressure equivalent of an alkali basalt, to the
69 source of mafic magmatism has been recognized from the isotopic and geochemi-

70 cal characteristics of some basalts, in particular of ocean island basalts (Hofmann,
71 2003; Pertermann and Hirschmann, 2003; Sobolev et al., 2005, 2007). The impor-
72 tance of volatile-rich alkali basalts in the asthenosphere may however not be limited
73 to the oceanic contexts. Silica enrichment of some cratonic peridotites compared to
74 what would be expected for simple partial melt residues (Carlson et al., 2005) has
75 been interpreted by percolation of Si-rich melts derived from subducted slabs (Rud-
76 nick et al., 1994; Kelemen et al., 1998). Similarly, eclogitic melts may have lead
77 to the refertilisation of the lithosphere at depths of circa 170-220 km beneath cra-
78 tons (O'Reilly and Griffin, 2010). Finally, diamond inclusions originating from the
79 asthenosphere are of metabasite (i.e. eclogitic) affinity (Harte, 2010), and the gen-
80 esis of diamondites, polycrystalline diamonds, has been linked to the presence of
81 volatile saturated eclogitic melts in the sub-cratonic mantle (Mikhail et al., 2013).

82 The presence of eclogite in the cratonic mantle as a whole has been quantified
83 from seismology to about 1%, and locally to as much as 15% (Schultze, 1989),
84 as mafic magmatic rocks may be returned to the mantle via plate subduction or
85 through delamination of the lower crust after contributing to the formation of cra-
86 tonic roots (Lee, 2006). This motivated the investigation of the eclogite dry solidus
87 up to 5 GPa (Spandler et al., 2008). The composition used in this study, a primary
88 alkali basalt (Pichavant et al., 2009), contains 1.5 wt% more K_2O than the GA2
89 composition used by Spandler et al. (2008). The eclogite dry solidus can be de-
90 pressed by circa 250 K for our alkali- and volatile-rich composition (0.9 wt% CO_2 -
91 1.04 wt % H_2O), accounting for the effect of dissolved carbonate ions and water
92 observed on altered MORB at high pressure – respectively circa -25 K per wt%

93 CO₂ (Gerbode and Dasgupta, 2010) and -150 K for 0.87 wt % H₂O in the glass
94 (Kiseeva et al., 2012) – and for the effect of excess K₂O assuming a similar ef-
95 fect to that observed for a hydrated and carbonated peridotite in the 4-6 GPa range
96 (Foley et al., 2009).

97 T estimates at the LAB under cratons range from 1573 K to 1773 K at 200 km
98 (~ 6.6 GPa) from the study of xenoliths in the Kaapvaal craton in South Africa
99 (James et al., 2004). The solidus of our composition will thus be about 200 K
100 below petrological T estimates for the LAB, which corresponds to 70-85% of melt
101 fraction (Pertermann and Hirschmann, 2003; Spandler et al., 2008) as required to
102 generate an alkali basaltic melt. Consistently, a melt with a similar composition to
103 ours was obtained by bringing an eclogite+3wt%(H₂O-CO₂)+3wt%KCl at 5 GPa
104 and 1573 K (Butvina et al., 2009). The high alkali content is thus efficient in both
105 lowering the melting point and increasing melt productivity, and it is important in
106 that respect that alkalis are not leached out of the subducted slabs, as supported by
107 examination of eclogites from paleo-subduction zones (Spandler et al., 2004).

108 A few studies have investigated the reactivity of eclogite-derived melts with
109 peridotite, some finding that all melt is consumed (Yaxley and Green, 1998), oth-
110 ers that once a reaction band of pyroxene is produced, it will prevent further contact
111 between melt and mantle, thereby trapping melt in peridotite/pyroxenite reaction
112 zones (Kogiso et al., 2004). Latest reaction experiments between peridotite (KLB-
113 1) and MORB-eclogite-derived carbonated melts (2.6 wt% CO₂) (Malik and Das-
114 gupta, 2013) produced between 11 and 24 % sustainable melt at near equilibrium
115 conditions, while melt composition spanned the range of most alkali basalts. Malik

116 and Dasgupta (2013) noted that their experiments are relevant beneath continental
117 lithosphere as generation of the first carbonated-eclogite melt might be triggered
118 by conversion of graphite to carbonate at the redox front, constrained to occur at
119 250 km depth (Rohrbach et al., 2007, 2011).

120 Volatile-containing alkali basalts can thus thermally be present in the LAB but
121 the physical mechanism for retention is still to be discovered as magmas are ex-
122 pected to percolate through the silicate matrix after formation. Wetting experi-
123 ments at high P suggest that, in contrast to low P conditions, very little amounts
124 are needed for the melt to totally wet olivine crystals and hence have a large influ-
125 ence on the electrical conductivity of the upper mantle (Yoshino et al., 2009). But
126 another consequence of this high melt connectivity is that it will be even harder to
127 prevent it from moving through the mantle. An alternative to mechanical retention
128 of melts at depth is gravitational trapping. This idea was suggested (Agee, 1998)
129 based on shock-wave density data on basalts (Rowan, 1993). However, the scat-
130 ter in the shock-wave data was too large to be conclusive and an ex situ sink-float
131 density measurement on molten MORB at 6 GPa did not confirm it either (Agee,
132 1998). Additional sink-float data have been collected on molten MORB with and
133 without water in the 15-20 GPa/2573 K-2673 K range (Sakamaki et al., 2006),
134 but these conditions are largely above the estimates for the LAB discussed above,
135 especially for T, and that makes extrapolations back difficult.

136 **3. Experimental procedures**

137 *3.1. Generation of high P-T conditions*

138 High pressure conditions were generated by a VX5 Paris-Edinburgh press. The
139 cell-assembly used is detailed in Van Kan Parker et al. (2010); it consists in a
140 7/2.4 mm boron epoxy gasket, a graphite heater and an hBN pressure transmitting
141 medium, while P-T conditions are derived from the cell volumes of internal cali-
142 brants, hBN and Pt (Pt ribbon inserted between hBN and the sample capsule). Es-
143 timated error bars are ± 0.25 GPa on P, and ± 50 K on T. The starting composition
144 (Table 1) used in this work had been previously synthesized at ISTO (Pichavant
145 et al., 2009). Sample was hand-packed in a single crystal diamond capsule and
146 covered by Pt-10%Rh caps. Single crystal diamond is the best capsule material
147 for these experiments as it provides the lowest absorption back-ground possible
148 and hence considerably reduces the error bar on the density measurements, and
149 it preserves a cylindrical shape upon compression. Last but not least, diamond is
150 the stable phase of carbon at the P-T-oxygen fugacity conditions of the continental
151 LAB. The diamond capsules were 1.5 mm in height and either 1.0 mm inner di-
152 ameter (6.25 GPa run) or 0.75 mm inner diameter (3.9 GPa run). P transmission to
153 the sample inside the rigid diamond capsule is fully achieved for T above 1200 K,
154 as demonstrated by calibration experiments (Van Kan Parker et al., 2010).

155 *3.2. Ex situ chemical, Raman and IR measurements*

156 The sample recovered from the 6.25 GPa run was lost upon extraction from
157 the diamond capsule. The analyses reported here for this pressure point (Table

158 1) were done on a sample synthesized ex situ using a Paris-Edinburgh press at
159 IMPMC with the same cell-assembly and ran for 40 minutes at identical power
160 and oil pressure conditions. Chemical analyses were done using a Cameca SX100
161 electron microprobe at the EMMAC centre, University of Edinburgh. Conditions
162 were 15 keV and 4 nA current for analysis of Ca and Na, and 15 keV and 40
163 nA current for all other elements. We used a 20 μm beam size for glass analyses
164 and a 8 μm beam size for crystals analyses. For both samples, the glass is very
165 homogeneous (Table 1), and crystals are sedimented at the bottom of the capsule
166 (Fig.2). Pyroxene crystals are observed in both runs, with a small addition of garnet
167 at 6.25 GPa. Hence only the melt was irradiated through the 100 μm to 200 μm
168 window defined by the vertical space between the press anvils.

169 For the purpose of infrared and Mössbauer spectroscopic measurements, the
170 samples were removed from the epoxy after electron microprobe analyses and
171 double-polished down to 550 μm (3.9 GPa run) and 300 μm (6.25 GPa run). In-
172 frared spectroscopic measurements were performed under vacuum using a Bruker
173 IFS 66v/S Fourier transform infrared (FTIR) spectrometer, set with resistive Mid-
174 dle Infrared Globar SiC source with 3 mm optical aperture; a KBr beamsplitter and
175 a N_2 -cooled MCT detector. Micro-focalisation was obtained by setting the sam-
176 ple in a homemade sample chamber at the focal point of two cassegrain reflectors.
177 Transmission spectra were recorded in the range 550-9000 cm^{-1} with resolution
178 of 4 cm^{-1} and accumulation of 64 scans. Analyzed spot is around 100 μm . Total
179 water concentration (Table 1) was determined from the sum of structurally bonded
180 hydroxyl groups and molecular water concentrations, using the Beer-Lambert law

181 from the absorbances of the 4470 and 5210 cm^{-1} bands respectively, the baseline
182 being fitted as a straight line (Fig.3 right). Molar absorption coefficients for OH and
183 H_2O bands were taken from Ohlhorst et al. (2001), and glass density taken from
184 the present measurements (see below). Carbonate ions IR bands were saturating,
185 thus requiring further polishing down of the sample. Instead, and to preserve the
186 sample, CO_3^{2-} concentration was quantified by Raman spectroscopy using previ-
187 ously established calibration (Morizet et al., 2013). Raman spectra were collected
188 in CSEC, University of Edinburgh, and at ISTO, University of Orléans. The Ra-
189 man systems consisted of an argon laser (488 nm excitation in CSEC, 514 nm
190 excitation at ISTO), a CCD detector and the spectra were collected using either a
191 1800 (CSEC) or 2400 (ISTO) grooves/mm grating, a laser power of 20 mW, and a
192 x50 objective. Although variations of the CO_2 content are observed in the vicinity
193 of the capsule walls, the bulk of the sample is characterized by a concentration
194 of 0.9 ± 0.1 wt% (middle curve, Fig.3 left) and 2.1 ± 0.5 wt% at respectively 3.9
195 GPa and 6.25 GPa. The uptake of reduced Fe by the Pt-Rh caps and concomitant
196 oxidation of C from the capsule contributed to the formation of CO_3^{2-} units. For
197 instance at 3.9 GPa, 2.1 wt% FeO (corresponding to 0.34 at% Fe, i.e. 17% of the
198 total Fe content) was reduced to metallic Fe during the course of the experiments,
199 thus potentially forming 0.65 wt% CO_3^{2-} which is consistent with the estimates ob-
200 tained from Raman spectroscopy. Our initial starting composition was carbonate-
201 and water-free. The volatile uptake by the melt occurred by equilibration at high
202 P-T with the single-crystal diamond capsule for carbonate, and by diffusion from
203 the epoxy gasket through the Pt-10%Rh caps for water. Water contamination has

204 been reported in previous experiments using the same cell-assembly (Perrillat et al.,
205 2013).

206 Finally, the sample was analyzed by Mössbauer spectroscopy at the Bayerisches
207 GeoInstitut. The Mössbauer spectra were collected in transmission mode with a
208 beam diameter of 500 μm using a ^{57}Co in Rh point source. There is no evidence
209 for the presence of Fe^{3+} species within the experimental uncertainty (estimated
210 detection limit $\sim 2\%$).

211 3.3. Density of the melt from x-ray absorption scans

212 X-ray absorption data were collected in situ using a monochromatic beam at 20
213 keV. The observation of diffuse rings with the simultaneous disappearance of all
214 crystalline diffraction peaks is used as the criterion to determine melting. Molten
215 state of the sample was also systematically checked after the density measurement
216 that takes 10 min.

217 The absorption method consists of measuring the intensity of the X-ray beam
218 with two ionization chambers before (I_0) and after (I) the crossing of the whole cell
219 assembly. The absorption profile is recorded while moving the press perpendicular
220 to the x-ray beam axis. The intensity ratio obeys the Beer-Lambert law:

$$\frac{I}{I_0} = \int_{x,y} \exp(-(\mu\rho d)_{liq} - (\mu\rho d)_{env}) dx dy \quad (1)$$

221 where μ is the mass absorption coefficient, ρ the density, d the X-ray path
222 length, x and y respectively the horizontal and vertical size of the x-ray beam (50
223 μm width \times 50 μm height). The subscript *env* stands for the environment sur-
224 rounding the sample. Each absorption scan is simulated with relation (1) leading

225 to values of $(\mu\rho)_{liq}$ (Fig.4). Due to CO_3^{2-} and water dissolution in the melt, the
226 value of μ_{liq} could not be measured before melting from the density measured by
227 x-ray diffraction and the $\mu\rho$ product inferred from the absorption scans. Fe loss to
228 the Pt-Rh caps is corrected for by assuming that only the mean molecular mass is
229 affected, thus neglecting the effect on the volume. This results in a correction of
230 +0.9% at 3.9 GPa and +1.4% at 6.25 GPa. The ambient P density is obtained using
231 the diffraction-based method (see below) on the sample recovered from 6.25 GPa,
232 removed from the cell-assembly but still in its diamond capsule. This value, 2930
233 $\text{kg}\cdot\text{m}^{-3}$, was used to calculate μ from $(\mu\rho)_0$ ($\mu = 0.2916 \text{ m}^2\cdot\text{kg}^{-1}$). We note that
234 this density corresponds to a densified glass, as it was recovered from 6.25 GPa,
235 consistently with the reported densification after decompression of samples melted
236 at 6 GPa (Kelsey et al., 2009).

237

238 3.4. Structure and density of the melt from x-ray diffraction data

239 The energy of the x-ray beam was switched to higher values, 46.8 keV, for
240 x-ray diffraction measurements in order to increase the accessible $2\text{-}\theta$ angle and
241 consequently enlarge the reciprocal space. Diffraction data were recorded on a
242 MAR350 image plate, with typical acquisition times of 2 min. Contribution to the
243 diffraction signal from parts surrounding the sample was filtered out by a multi-
244 collimator slit system (Morard et al., 2011).

245 The intensity data, $I(2\theta)$, are converted into the structure factor, $S(q)$, using the
246 Ashcroft-Langreth formalism (Ashcroft and Langreth, 1966). Note that in Fig.5,

247 $S(Q)$ functions have been renormalized to 1 at infinite q , for the sake of clarity.

$$S(q) = \frac{\alpha I(q)}{Z^2 f(q)^2} \quad (2)$$

$$\text{with } q = \frac{4\pi}{\lambda} \sin(\theta), \quad Z = \sum_i x_i Z_i \quad \text{and} \quad f(q) = \frac{\sum_i x_i f_i(q)}{Z}$$

248 where λ is the x-ray beam wavelength (0.26472 Å), x_i is the atomic fraction of the
 249 i^{th} atom, $f_i(q)$ its form factor as tabulated by (Hajdu, 1972), Z_i its atomic number
 250 and α is the Krogh-Moe and Norman normalization factor (Norman, 1957).

251 The radial distribution function, $g(r)$ is obtained from $S(q)$:

$$g(r) = 1 + \frac{1}{4\pi r n} \int_0^{q_{max}} q(S(q) - S_\infty) \sin(qr) dq \quad (3)$$

252 where q_{max} is the maximum experimental q-range, $n = \frac{\rho N_A}{M}$, M the mean atomic
 253 molar mass (cf Table 2), and ρ the density. Fe loss to the Pt-Rh caps is corrected
 254 for by using the mean atomic molar mass calculated with the starting FeO content.

255 The method to derive density from x-ray diffraction data on melts was estab-
 256 lished for liquid mercury (Kaplow et al., 1965) and adapted to high pressure data
 257 (Eggert et al., 2002), and consists in minimizing the oscillations in $g(r)$ were there
 258 should not be any signal, i.e. below the minimum interatomic distance. We have
 259 applied this method here and the density found are in good agreement with those
 260 obtained from the x-ray absorption method (Table 2), albeit with a larger error bar
 261 at high P, ± 0.002 atoms/Å³ on n that translates into ± 2 % on density.

262 The radial distribution functions obtained here are the sum of all ion-ion con-
 263 tributions. In order to evaluate the coordination number for Si-O and Al-O contri-

264 butions (Table 2), we have simulated the experimental $g(r)$ against a sum of gaus-
 265 sians (where each gaussian corresponds to a particular ion-ion partial distribution
 266 function) with the following equation:

$$g(r) = \frac{1}{nS_\infty} \sum_i \frac{A_i}{\sigma_i \sqrt{2\pi}} \exp\left(-\frac{(r - d_i)^2}{2\sigma_i^2}\right) \quad (4)$$

267 where

$$A_i = \frac{CN_i}{\int \frac{4\pi r^2}{\sigma_i \sqrt{2\pi}} \exp\left(-\frac{(r - d_i)^2}{2\sigma_i^2}\right) dr} \quad (5)$$

268 where CN_i is the coordination number of the i^{th} ion-ion contribution, d_i the cor-
 269 responding inter-atomic distance, and σ_i a parameter depending on structural dis-
 270 order (Hosemann and Bagchi, 1962), $\sigma_i = k\sqrt{d_i}$. k is an adjustable parameter
 271 (typically 0.15-0.17). We want to determine the coordination number of the two
 272 first contributions, Si-O and Al-O, that make most of the first peak in $g(r)$ at 1.6 Å.
 273 For this purpose, only ion-ion contributions with d_i up to 3 Å need to be considered
 274 as further contributions does not contribute to the first peak. Those contributions
 275 are Si-O, Al-O, Mg-O, Fe-O, Ca-O, O-O and (Si-O)₂. Note that the contribution of
 276 Mg-O is almost identical to that calculated at ambient pressure for molten An_{0.36}-
 277 Di_{0.64} with a similar MgO content (Vuilleumier et al., 2009).

278 4. Results

279 Density measurements using both methods, absorption and diffraction, were
 280 done successively at high P-T conditions and are summarized on Fig.6. Data were
 281 collected at 3.9 GPa-1850 K and 6.25 GPa-1910 K (Fig.1), i.e. at subliquidus

282 conditions as confirmed by the presence of crystals in the quench samples (Fig.2).
283 Data were then reduced to the 1673 K isotherm relevant for the LAB using 7.4
284 10^{-5} K^{-1} for the thermal expansion coefficient, value calculated at 5 GPa (Guil-
285 lot and Sator, 2007a). The obtained density are in the lower range of previous
286 shock-wave data (Rowan, 1993) but above the shock-wave equation of state mea-
287 sured for molten $\text{An}_{0.36}\text{-Di}_{0.64}$ and applied to basaltic composition (Rigden et al.,
288 1984), and 2.3% higher than the sink-float data point on dry MORB (Agee, 1998).
289 A recurrent difficulty for volatile-containing magmas is to determine their ambi-
290 ent pressure density, due to the fact that the dissolved volatile content is strongly
291 pressure dependent. As discussed by Agee (2008), recent studies on the density of
292 hydrous silicate melts (Sakamaki et al., 2006, 2009) have anchored their high pres-
293 sure data to the ambient density value calculated using the partial molar volume
294 of H_2O and its temperature derivative derived at 1000°C from 1-bar density mea-
295 surements on hydrous SiO_2 -rich and Fe-free silicate glasses synthesized at 1 GPa
296 (Ochs III and Lange, 1999). It is unclear if such values can be extrapolated to more
297 mafic compositions and higher temperatures; we instead calculated the partial vol-
298 ume of H_2O from the lowest P density measurements on mafic melts (Agee, 2008)
299 at 1.4 GPa-1773 K (i.e. 11.24 cc/mol), a temperature reasonably close to 1673 K,
300 and applied it to the density of dry molten basalt (Rigden et al., 1984). This value at
301 1.4 GPa and our high pressure data points obtained from both x-ray absorption and
302 x-ray diffraction methods were fitted with a third order Birch-Murnaghan equa-
303 tion of state, with $K_{0,1673K}=18.1\pm 1.2$ GPa assuming $K'_{0,1673K}=5$ for the sake of
304 comparison with previous data. These values, when compared to those obtained

305 for a MORB+2 wt% H₂O at higher P-T conditions (14-20 GPa and 2573 K), i.e.
306 $K_{0,2573K}=13.8\pm 2.2$ GPa assuming $K'_{0,2573K}=5$ (Sakamaki et al., 2006), imply
307 $\partial K/\partial T=4.8 \cdot 10^{-3}$ GPa·K⁻¹. The H₂O component is very compressible in silicate
308 melts (Ochs III and Lange, 1999; Sakamaki et al., 2006; Agee, 2008). Conse-
309 quently, its effect on the density is very strong at low P but decreases a lot under
310 increased compression, rapidly leveling off above a few GPa.

311 The expected effect of dissolved water and carbonate ions in basalts is an in-
312 crease of ^VAl and ^{VI}Al at the expense of ^{IV}Al, as suggested from NMR studies
313 on quenched glasses for water (Malfait et al., 2011; Xue and Kanzaki, 2008), and
314 by molecular dynamic calculations (Guillot and Sator, 2011) and infra-red spec-
315 troscopy (Taylor, 1990) for carbonate ions. As our experiments were conducted
316 not only in situ at high P-T but also at pressures higher than those of the NMR and
317 IR studies (0.2 GPa for Xue and Kanzaki (2008) and up to 3.5 GPa for Malfait et al.
318 (2011)), we might expect this effect to be more pronounced as Al of higher coordi-
319 nations are favoured by high pressure (Allwardt et al., 2007). Indeed, increased
320 Al-O coordination number is observed in our structural data (Fig.5 and Table 2),
321 reaching 5.3 at 6.25 GPa while MD calculations predict 4.6 only for a dry MORB
322 at 5 GPa (Guillot and Sator, 2007b). In contrast, our observed Si-O coordination
323 number, 4.15 at 6.25 GPa, is similar to the MD calculated value of 4.1 at 5 GPa.
324 Both carbonate and water components might increase the network polymerization
325 of basaltic melts (Xue and Kanzaki, 2008). The Si-O-Si vibrational modes are
326 observed at low frequencies in the quenched glass (Fig.4), in the 450-550 cm⁻¹
327 region, although the quenched glass might not be an appropriate proxy for the high

328 P melt. The frequency of these modes normally ranges from 400 to 700 cm^{-1}
329 depending on glass composition, and has been related to the degree of polymer-
330 ization, the lower the frequency the more polymerized the glass (McMillan, 1984).
331 The increased polymerization is also reflected in the x-ray diffraction data as the
332 the first sharp diffraction peak gets more intense while shifting to slightly lower
333 q -values between the starting and quenched glasses (Fig.5 left). These increased
334 Al-O coordination number and melt polymerization might therefore compensate
335 for the slight mass deficit induced by the presence of volatiles, hence providing an
336 explanation for the matched density with dry MORB at high pressures.

337

338 **5. Discussion: nature of the continental lithosphere-asthenosphere boundary**

339 To assess the buoyancy of volatile-containing alkali basalts, our density data
340 are compared to petrological density profiles (Poudjom Djomani et al., 2001; James
341 et al., 2004), and to the radially averaged PREM mantle density profile (Dziewon-
342 ski and Anderson, 1981) (Fig.6). Regional seismically-derived density profiles
343 exist westwards of the North American craton (Ito and Simons, 2011) but not for
344 intracratonic contexts. Nonetheless, petrological density data on xenoliths (James
345 et al., 2004) do overlap with PREM values for the deep lithosphere. Compared to
346 PREM and concordant petrological data, the alkali basalt is just neutrally buoyant
347 at the LAB, trapped between the depleted lithosphere and the fertile and denser
348 asthenosphere. It is also clear from this comparison that such melts will not be
349 neutrally buoyant at the conditions of the oceanic LAB (Fig.6). The PREM model

350 probes the current-day Earth, the petrological profiles established from xenoliths
351 are relevant for the last Gy or so. Because the melt is just neutrally buoyant at the
352 continental LAB, that means that for pre-proterozoic ages when the mantle was
353 hotter, they likely were positively buoyant. Indeed, the thermal expansion coef-
354 ficient of lithospheric and sub-lithospheric mantle is approximately $3 \cdot 10^{-5} \text{ K}^{-1}$
355 (cf Korenaga (2007) and refs. therein), i.e. 2.5 times less that of the basaltic melt
356 (Guillot and Sator, 2007a). Using that value for the mantle thermal expansion and
357 the asthenospheric PREM density value, we calculate that alkali basalts will cease
358 to be neutrally buoyant for temperatures hotter by 270 K than present-day ones.
359 Such high temperatures existed during the Archean about 3 Ga ago (Herzberg et al.,
360 2010), time at which different geochemical indicators point to the initiation of plate
361 tectonics (Shirey and Richardson, 2011; Dhuime et al., 2012). Essential to the es-
362 tablishment of plate tectonics is their lubrication. Although water has long been
363 held responsible for viscosity softening in the asthenosphere, latest experimental
364 work showed that water has in fact very little effect (Fei et al., 2013), and neither
365 has a tiny melt fraction (1% level). Thin pockets or a layer of molten basalt could
366 thus provide a better explanation for lithosphere/asthenosphere decoupling below
367 continents from mid-Archean on. As such, they could have plaid a major role in
368 the initiation of plate tectonics.

369 This is yet another example of density trap playing a key role in planetary
370 evolution. Partial melts layers or pockets have been evidenced at the bottom of
371 the Earth's and lunar mantles (Williams and Garnero, 1996; Weber et al., 2011;
372 Van Kan Parker et al., 2012), where they likely trap incompatible heat producing

373 elements and as such blanket the core. A partial melt layer has been reported
374 at the terrestrial 410-km discontinuity from seismology (Tauzin et al., 2010) and
375 electrical resistivity measurements (Toffelmier and Tyburczy, 2007), i.e. in the
376 present-day Earth, and its existence has also been postulated in the early Archean
377 (Lee et al., 2010). These dense liquids would constitute hidden enriched reservoirs
378 at depth. The occurrences of stable layers of magmas at depth could therefore prove
379 more widespread than previously thought both in time and space, and must have
380 exerted a strong control on the structure, geochemistry and dynamics of planetary
381 silicate mantles.

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390 **Figure captions.**

391

392 Figure 1. Experimental P-T conditions compared to melting relationships for alkali
393 basalt (Tsuruta and Takahashi, 1998), mid-oceanic ridge basalts (MORB) (Yasuda
394 et al., 1994), GA2 eclogite (Spandler et al., 2004), and geotherm estimates covered
395 by the orange shading (James et al., 2004). The effect of added K₂O (+1.5 wt%),
396 CO₂ and H₂O on the solidus of the GA2 eclogite is shown (-250 K). N.B.: alkali
397 basalt and MORB have a very similar liquidus curve.

398 Figure 2. Scanning electron microscope image of the sample quenched from 3.9
399 GPa-1850 K, and annotated sketch; the grey square represent the x-ray window.

400 Figure 3. Left: Raman spectra taken on the quenched samples (black lines: 3.9
401 GPa, grey line: 6.25 GPa); bottom curve: spectrum representative of the bulk of
402 the sample, top and middle curves: spectra taken close to the capsule walls. Right:
403 IR spectra (black line: 3.9 GPa, grey line: 6.25 GPa); note that the samples have
404 different thicknesses (550 μm for the 3.9 GPa run, 300 μm for the 6.25 GPa run).

405 Figure 4. X-ray absorption scans collected in situ on the melt at 6.25 GPa-1850 K
406 (top) and ex situ on the quenched sample still in its diamond capsule but removed
407 from the cell-assembly (bottom). Red curves: data, black dashed curves: fit with
408 the Beer-Lambert law. The strong absorption signal on the left-hand side of the

409 sample is due to the platinum foil inserted for P-T calibration purposes.

410 Figure 5. Structure of the starting glass, high pressure melts and quenched glass.
411 Left: structure factor, $S(q)$. Right: radial distribution function, $g(r)$, of the melt at
412 6.25 GPa-1910 K (solid black curve) and fit to the data with ion-ion contributions
413 up to 3 Å. Are represented only the main ion-ion contributions significant before
414 1.8 Å, i.e. below the first peak in $g(r)$.

415 Figure 6. Density of melt as a function of pressure at 1673 K (black full squares:
416 density from x-ray absorption, black full diamonds: density from x-ray diffraction,
417 full circle: calculation at 1.4 GPa for 1.04 wt% dissolved H₂O in MORB), com-
418 pared to seismological models (green solid line: PREM model (Dziewonski and
419 Anderson, 1981), blue line: Pacific profile (Ito and Simons, 2011)), density model
420 for cratons (green dashed line (Poudjom Djomani et al., 2001)), and petrological
421 values of the density for surrounding rocks (full green circles: harzburgite xeno-
422 liths, empty green circles: lherzolite xenoliths (James et al., 2004)). Black solid
423 line: third order Birch-Murnaghan equation of state through our density data+ 1.4
424 GPa estimate; the grey zone illustrates the effect on this equation of state of T
425 variations of ± 100 K, reflecting the range of T reported for the continental LAB;
426 open diamonds: shock-wave data on molten MORB (Rowan, 1993), black dashed
427 line: shock-wave equation of state measured on Anorthite₃₆-Diopside₆₄ melt and
428 applied to a MORB composition (Rigden et al., 1984), empty square: sink-float

429 data on molten MORB (Agee, 1998).

Oxide	Starting composition (Pichavant et al., 2009)	Quenched glass	
		3.90 GPa	6.25 GPa
SiO ₂	50.2(3)	50.1(2)	50.9(5)
TiO ₂	0.84(4)	0.82(2)	0.66(2)
Al ₂ O ₃	15.2(3)	15.6(1)	15.4(6)
FeO	7.81(12)	5.68(9)	4.41(30)
MnO	0.16(5)	0.15(8)	0.10(2)
MgO	7.87(12)	6.97(3)	6.65(15)
CaO	12.4(2)	11.0(3)	11.88(16)
Na ₂ O	2.29(5)	2.46(1)	2.47(3)
K ₂ O	1.86(6)	1.99(4)	1.91(2)
P ₂ O ₅	0.64(6)	0.49(2)	0.47(2)
Cr ₂ O ₃	0.05(5)	not det.	not det.
NiO	0.03(3)	not det.	not det.
CO ₃ ²⁻ *	–	0.9(1)	2.1(5)
H ₂ O **	–	1.04(4)	1.4(2)
Total	99.1	97.24	98.35

Table 1: Composition of the starting material and of the recovered glass samples. Data given in wt%, one standard deviation given in parentheses in terms of last digit. * Carbonate ions concentration is derived from Raman spectra. ** Water content is derived from infra-red spectra.

Technique	X-ray absorption			X-ray diffraction				
P-T conditions	run duration at T	$\rho\mu$ at T (\AA^{-1})	ρ at 1673 K ($\text{kg}\cdot\text{m}^{-3}$)	ρ at T ($\text{atoms}\cdot\text{\AA}^{-3}$)	M g/mole	ρ at 1673 K ($\text{kg}\cdot\text{m}^{-3}$)	Si-O CN	Al-O CN
3.90 GPa-1850 K	33 min	900	3154±30	0.088±0.0020	21.126	3128±70	4.10	4.3
6.25 GPa-1910 K	43 min	950±5	3361±31	0.0925±0.0020	21.015	3315±70	4.15	5.3
quenched sample	-	850	-	0.0835±0.0005*	21.015	2930±20*	4.05	4.4

Table 2: Summary of absorption and diffraction data. CN stands for coordination number.*: for the quenched sample density values are given at room T.

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