



Thomson, A. R., Walter, M. J., Kohn, S. C., & Brooker, R. A. (2016). Slab melting as a barrier to deep carbon subduction. *Nature*, *529*(7584), 76-79. https://doi.org/10.1038/nature16174

Peer reviewed version

Link to published version (if available): 10.1038/nature16174

Link to publication record in Explore Bristol Research PDF-document

© 2015 Macmillan Publishers Limited. All Rights Reserved.

University of Bristol - Explore Bristol Research General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available: http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/

1 2

3

SLAB MELTING AS A BARRIER TO DEEP CARBON SUBDUCTION

AR Thomson^{1,2}, MJ Walter^{1,} SC Kohn¹ and RA Brooker¹

¹School of Earth Sciences, University of Bristol, BS8 1RJ. ²Department of Earth Sciences, UCL, WC1E 6BT.

4 Interactions between crustal and mantle reservoirs dominate the surface inventory of volatile elements 5 over geological time, moderating atmospheric composition and maintaining a life-supporting planet¹. 6 Whilst volcanoes expel volatile components into surface reservoirs, subduction of oceanic crust is responsible for replenishment of mantle reservoirs^{2,3}. Many natural, 'superdeep' diamonds originating 7 in the deep upper mantle and transition zone host mineral inclusions indicating an affinity to 8 subducted oceanic crust⁴⁻⁷. Our experiments show that the majority of slab geotherms will intersect a 9 10 deep depression along the melting curve of carbonated oceanic crust at depths of ~ 300 to 700 km, 11 creating a barrier to direct carbonate recycling into the deep mantle. Low-degree partial melts are 12 alkaline carbonatites that are highly reactive with reduced ambient mantle, producing diamond. Many 13 inclusions in superdeep diamonds are best explained by carbonate melt - peridotite reaction. A deep 14 carbon barrier may dominate the recycling of carbon in the mantle and contribute to chemical and 15 isotopic heterogeneity of the mantle reservoir.

16

17 Altered oceanic crust incorporates appreciable carbon, which is added by magmatic and

hydrothermal processes⁸, and by addition of CO_2 during interaction of basalt with seawater⁹. 18

Together, these alteration processes result in subducting lithosphere that contains an average of ~ 2 19

20 wt.% CO₂ in the uppermost volcanic section and 100 - 5000 ppm CO₂ throughout the remaining 7

km of crust⁸. Crustal carbon initially contains a mixture of reduced hydrocarbons⁸ and oxidised 21

22 carbonates⁹. However, metamorphic re-equilibration of slab carbon with ferric iron and/or oxidizing

fluids produced during serpentine dehydration at sub-arc conditions, likely converts most slab 23

carbon to carbonate¹⁰. Some of this carbon is returned to the exosphere in volcanic arcs, but both 24

theoretical¹¹ and experimental¹² studies suggest that a significant quantity of carbon may survive 25

26 beyond slab dehydration, and be subducted into the mantle.

27

Carbon is insoluble in mantle silicate minerals¹³ and is stored either as carbonate, carbide or 28 29 diamond depending on the oxidation state. Under oxidising conditions carbonate lowers the melting 30 point (solidus) of mantle peridotite by some five hundred degrees compared with volatile-free mantle¹⁴. However, at the more reducing conditions prevailing deeper in the upper mantle and 31 transition zone, carbon will be stored as diamond or carbide minerals¹⁵, where it does not 32 appreciably influence melting.

33

35 Superdeep diamonds originate from depths beneath the lithospheric mantle ($\gtrsim 200$ km) and are the 36 only direct samples of the deep mantle carbon reservoir. Inclusions in these diamonds are 37 dominated by upper mantle and transition zone minerals, which are mostly associated with subducted mafic lithologies rather than peridotite^{4-7,16}. Many superdeep diamonds are made of 38 39 isotopically light carbon^{6,7} and, where measured, their inclusions contain isotopically heavy $oxygen^{17}$, unambiguously indicating an origin from recycled surface material^{6,7,17}. The elevated 40 41 trace element abundances of many silicate inclusions suggest crystallization from a low-degree melt, thought to be generated from melting of subducted oceanic crust^{7,18}. Here we examine the fate 42 of subducting carbonated MORB (mid-ocean ridge basalt) as it reaches the transition zone, and the 43 44 potential for melt-mantle reactions to reproduce superdeep diamonds and their distinctive inclusion 45 assemblages.

46

47 Previous experimental studies have investigated the melting behaviour of carbonated basalt at elevated pressures, but only one extends beyond 10 GPa¹⁹. These studies show a remarkable 48 49 diversity in melting behaviour making extrapolation to higher pressures difficult. In addition, the 50 bulk compositions employed in previous studies often contain considerably more CO₂ than mean 51 oceanic crust, and fall outside the compositional field of natural MORB rocks (see Methods, EDF1 52 and EDT1). To better understand the melting behaviour of deeply subducted oceanic crust we have 53 determined the melting phase relations of a synthetic MORB composition containing 2.5 wt.% CO₂ 54 between 3 and 21 GPa (Methods). Our starting composition replicates the major element composition of basaltic rocks from IODP hole $1256D^{20}$ and falls within the range of natural crust 55 compositions²¹ (EDF1). 56

57

We observe subsolidus phase assemblages containing garnet, clinopyroxene, an SiO₂ polymorph, and Ti-rich oxide at all pressures. The carbon component was either CO₂, dolomite, magnesite or magnesite plus Na-carbonate depending on pressure, and the positions of solid carbonate phase boundaries are consistent with previous studies^{22,23}. Near-solidus partial melts are CO₂ bearing silicate melts below 7 GPa, and silica-poor calcic carbonatites above 7 GPa. The alkali component of carbonatite melts increases with pressure (EDF4), and all melts have high TiO₂/SiO₂ (see Methods and extended data items for detailed results).

65

66 The melting temperature of carbonated oceanic crust is tightly bracketed from ~ 3 to 21 GPa (figure

67 1). Melting temperatures increase steadily with increasing pressure until about 13 GPa, when the

solidus dramatically drops over a narrow pressure interval by ~ 200 °C. This drop in solidus

69 temperature is caused by a change in clinopyroxene composition towards a more Na-rich

70 composition above 13 GPa due to dissolution of Na-poor pyroxene components into coexisting 71 garnet. Eventually, clinopyroxene becomes so sodium-rich that a coexisting Na-carbonate mineral 72 $([Na_{0.97}K_{0.03}]_{0.33}[Ca_{0.86}Mg_{0.11}Fe_{0.03}]_{0.67}CO_3)$ stabilizes in the subsolidus assemblage, causing the depression along the solidus. The loss of Na-poor clinopyroxene component, and the extended 73 74 stability of sodic clinopyroxene in the absence of an alternative Na-bearing silicate phase, is consistent with previous studies²⁴. Above 16 GPa the solidus changes little with pressure, remaining 75 76 at ~ 1150 °C, consistent with the solidus observed in a sodium-rich simplified system where sodic carbonate ($[Na,K]_{0.33}Ca_{0.67}CO_3$) controls melting temperatures²⁵. The major difference between this 77 work and the previous study of carbonated MORB above 8 GPa¹⁹ is the different phase assemblage 78 79 resulting from the lower and more realistic CO₂ and CaO contents of our bulk composition. 80 Previous bulk compositions with higher CaO contents (EDF1 and 5) are located on the Ca-rich side 81 of the majorite-clinopyroxene tie-line and stabilise aragonite as the carbon-hosting phase, which can 82 incorporate considerable Na₂O. The lower CO₂ content in our bulk composition results in a smaller 83 proportion of carbonate, of which the dominant species is Na-poor magnesite. Thus, sodic clinopyroxene remains stable as an alkali-host, coexisting with stoichiometric Na-carbonate to high 84 85 pressures.

86

87 The deep solidus depression in carbonated oceanic crust at uppermost transition zone conditions 88 creates a key control on the recycling of mantle carbon. Extrapolation of the range of modern-day oceanic crustal geotherms into the transition $zone^{26}$ reveals that the majority of slabs will intersect 89 90 our solidus for carbonated recycled MORB (figure 1), producing carbonatite melt. Given the expected temperature profile in the average subducted slab²⁶ we estimate that melting would occur 91 92 to depths of at least 7 km into the crustal section. Only the coldest modern day slabs escape the 93 solidus depression and are able to carry their carbonate cargo beyond the transition zone. If ancient slabs were hotter³, it appears likely that carbonate subduction through the transition zone and into 94 95 the lower mantle has been limited throughout Earth's history. Whilst the natural variability of 96 subducting slabs (e.g. composition, age, temperature) will have created some range in melting 97 behaviour, the depression of the carbonated eclogite solidus will remain an efficient barrier. Thus, 98 direct recycling of carbon into the lower mantle may have been highly restricted throughout most of 99 Earth history, instead being redistributed throughout the upper mantle.

100

Carbonatitic melts are predicted to be mobile at mantle conditions due to their low viscosity and
 ability to wet silicate minerals²⁷, so should percolate out of the slab and infiltrate the overlying

103 peridotitic mantle²⁵. Experiments suggest that below ~ 250 km, ambient mantle oxygen fugacity is

reducing, and a free metal phase may be present in the mantle²⁸. Under such conditions carbonate
 melt is unstable and will reduce to diamond plus oxygen by a 'redox-freezing' reaction²⁸ such as:

- 100
- 107

$$MgCO_3 + 2Fe^0 = 3(Mg_{0.33}, Fe^{2+}_{0.67})O + C$$

108

109 Thus, the expulsion of carbonatite melts due to melting of oceanic crust along the solidus 110 depression provides an ideal environment for diamond growth across a depth interval of $\sim 300 -$ 111 700 km. We predict that the interaction between MORB-derived carbonatite melt and ambient 112 peridotite is capable of reproducing many of the characteristics of superdeep diamonds and the mineral inclusions that they capture from this depth interval^{4,5}. The most common silicate minerals 113 identified in superdeep diamonds are majorite garnet, and a titanium-bearing, calcium-silicate phase 114 commonly interpreted as retrogressed 'calcium perovskite'^{4,6,7,18}. Barometric estimates of the 115 crystallization pressures for these majorite inclusions indicate they crystallised between 10 and 16 116 GPa⁵, and inclusions of calcium perovskite are constrained by their chemistry to have formed 117 between ~ 10 and 20 GPa^{6,18}. These pressures are remarkably consistent with the range of pressures 118 119 at which slab crustal geotherms are predicted to intersect the carbonated solidus depression (figure 120 1).

121

122 Redox reactions in the mantle are complex and involve silicates, many containing iron that exists in both ferrous (Fe^{2+}) and ferric form (Fe^{3+}). To test the melt-mantle interaction model we recreated 123 124 the infiltration process in a second set of experiments by partially equilibrating a model slab melt 125 with an iron-metal-bearing transition zone peridotite assemblage at 20 GPa (see Methods for 126 details). We observe a reaction zone between the alkaline carbonatite melt and the initial peridotitic 127 assemblage of majorite, wadsleyite, calcium-silicate perovskite and iron metal that consists of 128 sodium-rich majoritic garnet, Ca[Si,Ti]O₃ perovskite, ferrous ringwoodite (Mg $\# \sim 75$), 129 ferropericlase (Mg $\# \sim 0.4$) and diamond (EDF6, 7 and EDT3). We compare the resulting mineral 130 compositions with previous experimental data for peridotite and MORB systems to investigate 131 whether natural inclusion assemblages might preserve a record of mineral-melt reactions. 132 The compositions of the majority of superdeep majoritic garnet inclusions are not typical of those 133 134 expected in either peridotitic or eclogitic bulk compositions (figure 2) and instead lie between these two end-members. Kiseeva et al.¹⁶ described these intermediate compositions as pyroxenitic, and 135 136 suggested that the transition zone may harbour a large component of this rock type. Our results 137 suggest an alternate explanation. In figure 2 the majoritic garnets produced during the experimental 138 melt-mantle interaction are intermediate between peridotitic and eclogitic compositions, and cover

- 139 much of the range seen in the diamond inclusions. The chemical imprint imparted by the MORB-
- 140 carbonatite on the peridotitic mantle is recorded in the inclusions as elevated Ca#, Na and Ti
- 141 contents alongside depleted Mg#. Our experiments only demonstrate the composition of garnets
- 142 produced near the beginning of melt-mantle interaction sequence, and we suggest that the
- 143 intermediate character of the natural inclusions records a snap shot of the infiltration and reaction of
- 144 slab-derived carbonatite melt with peridotite.
- 145
- 146 Experimental Ca-perovskites have high titanium (~ 40 60 mol% CaTiO₃) and are essentially
- 147 magnesium free, features observed throughout the global range of 'Ca-perovskite' inclusions
- 148 (EDF8). Thus, our reaction experiments reproduce the unique chracteristics of diamond-hosted 'Ca-
- 149 perovskite' inclusions. Crystallisation by reaction between a low-degree carbonated melt and
- 150 peridotite is also consistent with the extremely elevated trace element contents of diamond-hosted
- 151 'Ca-perovskites' inclusions²⁴.
- 152

153 Probably the most abundant inclusions in superdeep diamonds are magnesium-iron oxide ([Mg,Fe]O), which are often interpreted to indicate diamond growth in the lower mantle⁴. However, 154 155 our experiments demonstrate that ferropericlase can be produced in reactions between carbonatitic 156 melt and reduced mantle peridotite at upper mantle pressures rather than requiring a lower mantle origin²⁹. Figure 3 demonstrates that natural ferropericlase inclusions are almost all iron-rich relative 157 158 to ferropericlase expected in mantle peridotite, and their compositions form arrays toward higher 159 NiO and lower Na₂O with increasing magnesium number. Our experimental ferropericlase 160 compositions lie at the end of the arrays and are iron-rich because the peridotite starting material 161 was initially iron-saturated. We suggest that, like the majorite inclusions, the array of intermediate 162 ferropericlase compositions record the progressive reaction of carbonatite melt and ambient mantle. 163

164 The melting phase relations of recycled oceanic crust suggest that slabs should undergo melting and 165 loss of carbonate components in the transition zone (figure 4), a process that has considerable 166 implications for the deep carbon cycle. The compositions of diamond-hosted inclusions provide 167 strong evidence of this process and confirm that carbon must survive subduction beyond sub-arc 168 dehydration reactions. We predict that carbon is rarely transported beyond the transition zone and 169 instead refertilises the upper mantle as diamond. Oxidation of diamond-bearing mantle upon upwelling can lead to redox melting¹⁵ beneath the lithosphere and contribute significantly to the 170 171 generation and geochemical signature of surface layas. This process also likely contributes to the formation of distinctive chemical and isotopic reservoirs in the mantle³⁰. Superdeep diamonds 172 173 provide a physical record of carbon recycling above subducting slabs, which can be used to infer

- the residence time of carbon in the mantle. This residence time is regulated by rates of subduction,
- 175 convective mantle upwelling and melting beneath the lithosphere, and could occur over a range of
- 176 timescales, perhaps as short as tens to hundreds of millions of years, suggesting the mantle carbon
- 177 cycle can be significantly more vigorous than previously estimated^{2,3}.
- 178

179 **References**

- 180 1. Zahnle, K. et al. Emergence of a habitable planet. Space Sci. Rev. 129, 35–78 (2007).
- Sleep, N. H. & Zhanle, K. Carbon dioxide cycling and implications for climate on ancient Earth. *J. Geophys. Res.* **106**, 1373–1399 (2001).
- 183 3. Dasgupta, R. & Hirschmann, M. M. The deep carbon cycle and melting in Earth's interior. *Earth Planet. Sci. Lett.*184 298, 1–13 (2010).
- Harte, B. Diamond formation in the deep mantle: the record of mineral inclusions and their distribution in relation to
 mantle dehydration zones. *Mineral. Mag.* 74, 189–215 (2010).
- 187 5. Stachel, T. Diamonds from the asthenosphere and the transition zone. *Eur. J. Mineral.* 13, 883–892 (2001).
- 188 6. Thomson, A. R. *et al.* Origin of sub lithospheric diamonds from the Juina 5 kimberlite (Brazil): constraints from
 189 carbon isotopes and inclusion compositions. *Contrib. to Mineral. Petrol.* 168, 1081 (2014).
- 190 7. Bulanova, G. *et al.* Mineral inclusions in sublithospheric diamonds from Collier 4 kimberlite pipe, Juina, Brazil:
 191 subducted protoliths, carbonated melts and primary kimberlite magmatism. *Contrib. to Mineral. Petrol.* 160, 489–
 192 510 (2010).
- Shilobreeva, S., Martinez, I., Busigny, V., Agrinier, P. & Laverne, C. Insights into C and H storage in the altered
 oceanic crust: Results from ODP/IODP Hole 1256D. *Geochim. Cosmochim. Acta* **75**, 2237–2255 (2011).
- 195 9. Alt, J. & Teagle, D. The uptake of carbon during alteration of ocean crust. *Geochim. Cosmochim. Acta* 63, 1527–
 1535 (1999).
- 10. Debret, B. *et al.* Redox state of iron during high-pressure serpentinite dehydration. *Contrib. to Mineral. Petrol.* 169,
 1-18 (2015).
- 199 11. Kerrick, D. M. & Connolly, J. A. D. Metamorphic Devolatilization of Subducted Mid-Ocean Ridge Metabasalts:
 200 Implications for Seismicity, Arc Magmatism and Volatile Recycling. *Earth Planet. Sci. Lett.* 189, 19-29 (2001).
- 12. Poli, S., Franzolin, E., Fumagalli, P. & Crottini, A. The transport of carbon and hydrogen in subducted oceanic
 crust: An experimental study to 5 GPa. *Earth Planet. Sci. Lett.* 278, 350–360 (2009).
- 203 13. Shcheka, S.S., Wiedenbeck, M., Frost, D.J. & Keppler H. (2006) Carbon solubility in mantle minerals. *Earth* 204 *Planet. Sci. Lett.* 245, 730-742.
- 14. Ghosh, S., Ohtani, E., Litasov, K. & Terasaki, H. Solidus of carbonated peridotite from 10 to 20 GPa and origin of
 magnesiocarbonatite melt in the Earth's deep mantle. *Chem. Geol.* 262, 17–28 (2009).
- Stagno, V., Ojwang, D. O., McCammon, C. A. & Frost, D. J. The oxidation state of the mantle and the extraction of
 carbon from Earth's interior. *Nature* 493, 84–8 (2013).
- 209 16. Kiseeva, E. S. *et al.* Metapyroxenite in the mantle transition zone revealed from majorite inclusions in diamonds.
 210 *Geology* 41, 883–886 (2013).
- 17. Ickert, R. B., Stachel, T., Stern, R. A. & Harris, J. W. Extreme ¹⁸O-enrichment in majorite constrains a crustal origin
 of transition zone diamonds. *Geochem. Persp. Lett.* 1, 65-74 (2015).
- 213 18. Walter, M. J. et al. Primary carbonatite melt from deeply subducted oceanic crust. Nature 454, 622–625 (2008).

- 214 19. Kiseeva, E. S., Litasov, K. D., Yaxley, G. M., Ohtani, E. & Kamenetsky, V. S. Melting and phase relations of
- carbonated eclogite at 9-21 GPa and the petrogenesis of alkali-rich melts in the deep mantle. J. Petrol. 54, 1555–
 1583 (2013).
- 20. Expedition 309/312 Scientists in Teagle et al. Proceedings of the integrated Ocean Drilling Program, Volume
 309/312 (2009).
- 219 21. Gale, A., Dalton, C. A., Langmuir, C. H., Su, Y. & Schilling, J.-G. The mean composition of ocean ridge basalts.
 220 *Geochemistry, Geophys. Geosystems* 14, 489–518 (2013).
- 22. Martin, A. M., Laporte, D., Koga, K. T., Kawamoto, T. & Hammouda, T. Experimental study of the stability of a
 dolomite + coesite assemblage in contact with peridotite: Implications for sediment-mantle interaction and diamond
 formation during subduction. *J. Petrol.* 53, 391–417 (2012).
- 224 23. Luth, R. W. Experimental determination of the reaction aragonite + magnesite = dolomite at 5 to 9 GPa. *Contrib. to* 225 *Mineral. Petrol.* 141, 222–232 (2004).
- 226 24. Okamoto, K. & Maruyama, S. The Eclogite Garnetite transformation in the MORB + H₂O system. *Phys. Earth* 227 *Planet. Inter.* 146, 283–296 (2004).
- 228 25. Litasov, K., Shatskiy, A., Ohtani, E. & Yaxley, G. Solidus of alkaline carbonatite in the deep mantle. *Geology* 41,
 79–82 (2013).
- 26. Syracuse, E. M., van Keken, P. E. & Abers, G. A. The global range of subduction zone thermal models. *Phys. Earth Planet. Inter.* 183, 73–90 (2010).
- 232 27. Hammouda, T. & Laporte, D. Ultrafast mantle impregnation by carbonatite melts. *Geology* 28, 283–285 (2000).
- 233 28. Rohrbach, A. & Schmidt, M. W. Redox freezing and melting in the Earth's deep mantle resulting from carbon-iron
 234 redox coupling. *Nature* 472, 209–12 (2011).
- 29. Brey, G. P., Bulatov, V., Girnis, A., Harris, J. W. & Stachel, T. Ferropericlase a lower mantle phase in the upper
 mantle. *Lithos* 77, 655–663 (2004).
- 30. Jackson, M. G. & Dasgupta, R. Compositions of HIMU, EM1 and EM2 from global trends between radiogenic
 isotopes and major elements in ocean island basalts. *Earth Planet. Sci. Lett.* 276, 175–186 (2008).
- 239
- Acknowledgements A.R.T acknowledges the support of NERC grant NE/J500033/1. M.J.W. and
- 241 S.C.K acknowledge the support of NERC grant NE/J008583/1. We thank S. Kearns and B. Buse for
- their assistance performing EPMA analyses and J. Blundy for contributing ideas and expertise
- 243 during discussions with the authors.
- 244
- Author Contributions A.R.T designed, performed and analysed the experiments, gathered data
- from the literature and wrote the manuscript as part of his Ph.D. studies. M.J.W. and S.C.K.
- 247 provided training in experimental techniques, assisted during interpretation of results, provided
- advice and assisted with manuscript preparation in their roles as A.R.T.'s Ph.D. supervisors. R.A.B.
- 249 provided training and assistance with experimental techniques and sample preparation alongside
- 250 contributing to the scientific content and preparation of the manuscript.
- 251

- 252 Author Information Reprints and permissions information is available at
- 253 www.nature.com/reprints. The authors declare no competing financial interests. Correspondence
- and requests for materials should be addressed to A.R.T. (a.r.thomson@ucl.ac.uk).

255 Main text figure legends

- 256 Figure 1: The melting curve of carbonated MORB (this study) compared to hot and cold
- 257 **subduction geotherms**²⁶. The stability fields of carbon-bearing phases are identified in different
- 258 colours. Experiments performed marked by filled triangles indicating their relationship to the
- 259 solidus, larger symbols mark solidus brackets. The solidus ledge creates a narrow depth interval
- 260 where slab temperatures intersect the melting curve, producing a focussed region of melt generation
- at the top of the transition zone.
- 262

263 Figure 2: Composition of majoritic garnet minerals from previous experimental studies,

264 inclusions in diamonds and reaction experiments (this study). The red field outlines the

approximate range of peridotitic majorite compositions, the blue field outlines the range of MORB

266 majorites from pressures above the carbonated MORB solidus ledge ($> \sim 9$ GPa). Data and

- 267 corresponding references for this figure are provided in the online source data file.
- 268

269 Figure 3: Composition of ferropericlase minerals from previous experimental studies,

270 inclusions in diamonds and reaction experiments (this study). Blue arrows indicate the

271 compositional evolution expected as melt-mantle interactions progress. Data and corresponding

- 272 references for this figure are provided in the online source data file.
- 273

Figure 4: Schematic of the deep mantle carbon cycle as described in the text. Arrows represent paths and estimates of the relative magnitudes of carbon fluxes. Downwelling slabs dehydrate at sub-arc depths but retain the majority of their carbon cargo. Upon reaching the transition zone they produce carbonatite melts (this study) along the solidus ledge that infiltrate [28] and react with the overlying mantle (this study). This causes diamond production, refertilisation and associated metasomatism of the surrounding mantle. The melting of recycled crust in the transition zone essentially prevents carbon transport into the lower mantle.

- 281
- 282

283 Methods

- 284 **Starting materials.** The starting material for experiments to determine the melting phase relations 285 of carbonated MORB (ATCM1) replicates basalts from the IODP 1256D from the Eastern Pacific Rise²⁰ (the reported composition of IODP 1256D basalts is the average of all analyses presented in 286 287 table T17 of the cited issue) with an added 2.5 wt.% CO₂ (EDT1). This material was formed by 288 mixing high purity SiO₂, TiO₂, Al₂O₃, FeO, MnO, MgO, Ca₃(PO₄)₂ and CaCO₃, that were fired 289 overnight at temperatures of 400 – 1000 °C, of appropriate weights in an agate mortar under 290 ethanol. This mixture was decarbonated and fused into a crystal-free glass in a one-atmosphere tube 291 furnace by incrementally increasing temperature from 400 to 1500 °C prior to drop quenching into 292 water. Subsequently weighed amounts of $CaCO_3$, Na_2CO_3 and K_2CO_3 were ground into the glass, 293 introducing the alkali and CO₂ components. After creation the starting material was stored at 120 294 °C to avoid absorption of atmospheric water. Starting material ATCM2 replicates the near-solidus 295 melt composition measured in melting experiments at 20.7 GPa and 1400/1480 °C. This was 296 created by grinding natural magnesite and synthetic siderite with high purity CaCO₃, Na₂CO₃, 297 K_2CO_3 , SiO₂, TiO₂, Al₂O₃ and Ca₃(PO₄)₂. Synthetic siderite was created in a cold-seal pressure 298 vessel experiment run at 2 kbar and 375 °C for 7 days. A double Au capsule design containing iron 299 (II) oxalate dehydrate in the inner and a 1:1 mixture of $CaCO_3$ and SiO_2 in the outer capsule 300 produced a pale beige powder confirmed as siderite using Raman spectroscopy. The material for a 301 sandwich experiment, to ensure near-solidus melt compositions were accurately determined at 20.7
- 302 GPa, was formed of a 3:1 mixture of ATCM1:ATCM2.
- 303
- The transition zone peridotite mineral assemblage in reaction experiments was synthesised at 20.7
- 305 GPa and 1600 °C for 8 hours from a mixture of KR4003 natural peridotite³¹ with an added 2.5 wt.%
- 306 Fe metal. In reaction runs the recovered synthetic peridotite was loaded in a second capsule,
- 307 surrounded by the ATCM2 near-solidus melt composition. Additional reaction-type experiments
- 308 were performed on ground mixtures of peridotite and melt compositions. In these experiments PM1
- 309 pyrolite³² was used as the peridotite component and mixed with ATCM2 melt in 9:1, 7:3 and 1:1
- 310 weight ratios in Fe capsules. A single mixed experiment was performed in a Au capsule and used a
- 311 starting mix of PM1:Fe:ATCM2 in 16:1:4 molar ratio.
- 312
- 313 Experimental techniques. High-pressure experiments were performed using a combination of end-
- 314 loaded piston cylinder (3 GPa) and Walker-type multi anvil (5 21 GPa) experiments at the
- 315 University of Bristol. Piston cylinder experiments employed a NaCl-pyrex assembly with a straight
- 316 graphite furnace and Al₂O₃ inner parts. Temperature was measured using type D thermocouple
- 317 wires contained in an alumina sleeve and positioned immediately adjacent to the Au₈₀Pd₂₀ sample

- capsule that contained the powdered starting material. We assume that the temperature gradient across the entire capsule (< 2 mm) was smaller than 20 °C^{33,34}. The hot piston-in technique was used with a friction correction of 3% applied to the theoretical oil pressure to achieve the desired
- 321322

run conditions³⁵.

323 Multi-anvil experiments were performed using Toshiba F-grade tungsten carbide cubes bearing 11, 324 8 or 4 mm truncated corners in combination with a pre-fabricated Cr-doped MgO octahedron of 18. 325 14 or 10 mm edge length respectively. The relationship between oil-reservoir and sample pressure 326 for each cell was calibrated at room and high temperature (1200 °C) by detecting appropriate room 327 temperature phase transitions of Bi, ZnTe and GaAs and bracketing transformations of SiO_2 328 (quartz-coesite and coesite-stishovite), Mg₂SiO₄ (α - β and β - γ) and CaGeO₃ (garnet-perovskite). 329 Calibrations are estimated to be accurate within ± 1 GPa. In all experiments desired run pressure 330 was achieved using a slow, Eurotherm controlled, pressure ramp of ≤ 50 tonnes/hour. Experiments 331 were heated after high pressure was reached with high-temperatures generated using stepped 332 graphite (18/11 cell) or straight LaCrO₃ furnaces (14/8 and 10/4 cells) and monitored with type C 333 thermocouple wires. Two 10/4 experiments, performed during a period of repeated LaCrO₃ heater 334 failures, used rolled 40 µm thick Re furnaces. Temperature was quenched by turning off the furnace 335 power prior to a slow decompression ramp (half the rate of experiment compression) to ambient 336 conditions. Samples were contained in Au capsules unless temperatures exceeded its thermal 337 stability, in which case $Au_{80}Pd_{20}$ or $Au_{75}Pd_{25}$ capsules were used. Run durations all exceeded 600 338 minutes and are reported in extended data tables 2 and 3. Temperature uncertainties were believed 339 to be less than $\pm 20, 30$ or 50 °C for 18/11. 14/8 and 10/4 cells respectively^{36,37}. 340

Recovered samples were mounted longitudinally in epoxy, polished under oil and repeatedly reimpregnated with a low viscosity epoxy (Buelher EpoHeat) in order to preserve soft and watersoluble alkali carbonate components present in run products.

344

345 Analytical techniques. Polished and carbon coated run products were imaged in backscatter 346 electron mode (BSE) using a Hitachi S-3500N SEM microscope with an EDAX Genesis energy 347 dispersive spectrometer to identify stable phases and observe product textures. Subsequently, 348 wavelength dispersive spectroscopy (WDS) was performed using the Cameca SX100 Electron 349 Microprobe or the Field Emission Gun Jeol JXA8530F Hyperprobe at the University of Bristol to 350 achieve high precision chemical analyses of run products. Analyses were performed using an 351 accelerating voltage of 15 or 12 kV on the respective instruments, with a beam current of 10 nA. 352 Calibrations were performed during each session using a range of natural mineral and metal

- 353 standards and were verified by analysing secondary standards (as in [6]). Silicate phases were
- 354 measured using a focused electron beam whereas carbonates and melts were analysed using an
- 355 incident beam defocussed up to a maximum size of 10 µm. Count times for Na and K were limited
- to 10 seconds on peak and 5 seconds on positive and negative background positions. Peak count
- times for other elements were 20 40 seconds. Additional analyses of the calcium perovskite phases
- 358 grown during reaction experiments, measuring only SiO₂ and MgO content, were made using the
- 359 Jeol instrument at 5 kV and 10 nA to ensure reported MgO contents were not influenced by
- 360 secondary fluorescence from surrounding material.
- 361

The identity of experimental-produced minerals was determined using Raman spectroscopy as a fingerprint technique. Spectra were collected using a Thermo Scientific DXRxi Raman microscope equipped with an excitation laser of either 455 or 532 nm.

365

366 Choice of bulk composition and comparison with previous studies. Studies that investigate the 367 alteration of oceanic crust have demonstrated that carbon incorporation does not simply occur by the addition of a single carbonate species to MORB⁹. It instead appears to occur by a complex 368 amalgamation of hydrocarbon and graphite deposition related to hydrothermal fluxing above 369 magma chambers at the mid-ocean ridge⁸ and underwater weathering^{9,38-40} where seawater-derived 370 371 CO₂ reacts with leached crustal cations, often in veins. It is believed that the quantity of biotic 372 organic carbon in the crustal assemblage is negligible compared with abiotic organic compounds and inorganic carbonates⁸. These processes result in a layered crustal assemblage that, in the 373 uppermost few hundred metres can contain up to a maximum of 4 wt.% CO₂ in rare cases^{9,39} but 374 more commonly < 2 wt.% CO₂ [8, 9, 39]. Beneath 500 m depth the carbon content drops to between 375 376 100 and 5000 ppm CO₂ throughout the remainder of the 7 km thick basaltic section⁸, and is mostly 377 organic hydrocarbon species. The upper 300 m are regularly altered and can be generally thought to have compositions similar to the altered MORB rocks analysed by Kellev et al.⁴¹. Deeper portions 378 379 of the MORB crust retain their pristine MORB compositions. It is therefore apparent that 380 carbonated eclogite bulk compositions used in previous studies, where at least 4.4 wt.% CO₂ was 381 added to an eclogite by addition of ~ 10 wt.% carbonate minerals, may not be good analogues of naturally subducting crustal sections. The compositions of these starting materials from previous 382 studies^{19,42-46} can be found in EDT1. We do not include the composition of the starting material 383 384 used by [47] or [48] as these studies were conducted in simplified chemical systems so are not 385 directly comparable with these natural system compositions.

387 However, as some of the previous studies rightly identify and discuss, the composition of deeply 388 subducted MORB is not likely to be the same as that entering the subduction system. One process 389 widely believed to alter the composition of downwelling MORB is sub-arc slab dehydration. PT paths of subducted slabs²⁶ can be compared with experimental studies of hydrous, carbonated and 390 H_2O-CO_2 -bearing eclogite compositions^{12,24,42,43,49} and thermodynamic models^{11,50} to conclude that 391 392 slabs experience dehydration at sub-arc conditions (i.e. 1-5 GPa) but will generally not reach high 393 enough temperatures to undergo melting. Therefore, they will by-in-large retain their carbon components although some fraction may be lost by dissolution into aqueous fluids^{51,52}. It is believed 394 395 that sub-arc dehydration is capable of removing SiO₂ from the subducting assemblage, and previous 396 carbonated MORB compositions were therefore designed to be significantly silica undersaturated (relative to fresh/altered MORB)^{19,43-45}. Whilst studies^{e.g. 53-56} do indicate that SiO₂ can become 397 soluble in H₂O at high-pressures, they infer that the solubility of silica in hydrous fluids only 398 399 exceeds ~ 1 wt.% at T > 900 °C at 1 GPa (higher T at higher P). In contrast, slab dehydration occurs on all prograde slab paths at T < 850 °C. Additionally, Kessel et al.⁵⁷ measured the composition of 400 401 quenched hydrous fluids coexisting with MORB at 4 GPa and 800 °C; their data indicates a 402 maximum of ~ 12 wt.% SiO₂ can dissolve in the fluid. Given that there should be considerably less 403 than 10 wt.% H₂O (more likely ≤ 5 wt.% H₂O) in subducting assemblages this suggests a 404 maximum SiO₂ loss in subducting MORB lithologies of $\sim 0.6 - 1.2$ wt.%. The compositions used in 405 previous studies have SiO₂ depletions ranging from 3 wt.% up to, more commonly, 6 - 10 wt.% 406 SiO₂ relative to MORB.

407

408 We further investigated the effect of oceanic crust alteration and sub-arc dehydration on the 409 composition of subducted MORB rocks by compiling a dataset of altered MORB⁴¹ and exhumed 410 blueschist, greenschist and eclogite facies rocks from exhumed terrains worldwide to compare them with fresh MORB²¹, our starting material and previous starting materials. We then assess the 411 412 relevance of our starting material based on the composition of natural MORB rocks, rather than 413 using models of the subduction process that contain few observable constraints. Results of this 414 comparison are plotted in EDF1. This analysis confirms that relative to fresh MORB, altered 415 MORB and exhumed crustal rocks are somewhat depleted in SiO₂, up to a maximum of 6 wt.% 416 SiO_2 in the most extreme case, but more commonly 0 - 3 wt.% SiO_2 . Thus, many previous starting 417 materials are too silica undersaturated to be good analogues of subducting MORB. Furthermore, 418 this analysis reveals that altered and exhumed MORB are not enriched in CaO compared with fresh 419 MORB, if anything they actually contain lower CaO on average. In contrast, all previous starting 420 materials are enriched in CaO compared with fresh MORB. This is because most previous studies 421 introduced the carbon component to their experiment by adding ~ 10 wt.% calcite to an eclogite-

base composition. We note that SLEC1⁴³ was not created in this manner, but instead this 422 423 composition falls far from the MORB field as the authors used an eclogite xenolith erupted by a 424 Hawaiian volcano as a base material. By plotting the position of the maj-cpx join, defined by the 425 composition of our experimental phases plotted in EDF5, onto EDF1a we demonstrate that our bulk composition (ATCM1), ALL-MORB²¹, the vast majority of the fresh MORB field, altered⁴¹ and 426 427 exhumed MORB samples fall on the CaO-poor side of this join, i.e. on the Mg+Fe rich side. 428 Therefore, magnesite will be the stable carbonate phase in these compositions at high pressure 429 (above dolomite breakdown). In contrast, all previous bulk compositions plot on the Ca-rich side of 430 this join, and therefore in a different phase field to the overwhelming majority of subducted MORB. 431 This difference causes a significant difference in the phase relations of our starting material relative 432 to those used in previous studies.

433

We acknowledge that no single bulk composition can be a perfect analogue for the entire range ofsubducting MORB compositions, however ATCM1 is a good proxy for sections of the MORB crust

436 between ~ 300 m and 7 km depth that have unaltered major element compositions and low CO₂

437 contents. Additionally, ATCM1 remains a better analogue for the uppermost portions of the MORB

438 crust than starting materials employed in previous studies because its CO₂ content is within the

range of natural rocks whilst it is also not oversaturated in CaO or over depleted in SiO₂. This is
despite it falling towards the SiO₂ rich end of the compositional spectrum of subducting MORB

441 442

rocks.

443 Slab *f*O₂ and carbonate survival to transition zone conditions.

444 Recent experiments have suggested that carbonate in eclogitic assemblages may be reduced to elemental carbon, either graphite or diamond, at depths shallower than 250 km⁵⁸. However, 445 446 subducting slab geotherms are much colder than the experimental conditions investigated by this 447 study, and additionally they are believed contain significant ferric iron that is further increased during de-serpentinisation¹⁰. Indeed, several observations of carbonate inclusions in sub-448 lithospheric diamonds^{e.g. 6,7,59} require that slab carbon remains oxidised and mobile until diamond 449 450 formation, far deeper than 250 km. Given the numerous observations from natural diamond 451 samples, the general uncertainty in the mantle's fO_2 structure and the lack of any conclusive 452 experimental evidence that subducting carbon becomes reduced prior to reaching the transition zone 453 we posit that nearly all subducting carbon is stable as carbonate throughout the upper mantle in 454 subducting MORB assemblages.

Experimental Results – Carbonated MORB melting. EDT2 presents the run conditions, 456 457 durations and phase proportions in all carbonated MORB melting experiments, which are also 458 summarised in EDF2. Phase and melt compositions are presented in the supplementary tables. 459 Phase proportions are calculated by mass balance calculations that use the mean composition of 460 each phase as well as the reported 1σ uncertainty in this mean as inputs. We note that the 1σ 461 uncertainty for some oxides in garnet and clinopyroxene minerals occasionally exceeds 1 wt.%, 462 although it is normally much smaller than this. These large uncertainties are a function of the small 463 crystal sizes present in some runs, and not a function of sluggish reaction kinetics. Phase proportion 464 calculations were run in a Monte Carlo loop of 10.000 calculation cycles where a varying random 465 error was added to each oxide in each mineral phase during each iteration. Overall the distribution 466 of varying random errors for each oxide form a Gaussian distribution with standard deviation equal 467 to the reported 1σ uncertainty of measurements. The reported proportions are the numerical mean of 468 all calculation cycles and the r^2 value reports the average squared sum of residuals. Low r^2 values indicate that chemical equilibrium is likely to have been achieved and that mineral and melt 469 470 compositions have been accurately determined.

471

472 Representative BSE images of the polished experiments are shown in EDF3. Garnets in 473 experiments at all pressures contain abundant SiO₂ inclusions. In subsolidus experiments the 474 number of inclusions increases and the definition of mineral boundaries deteriorates, which makes 475 accurate analysis of garnet compositions increasingly challenging. In supersolidus runs, garnet 476 minerals adjacent, or near to, carbonatite melt pools have well defined edges and contain fewer 477 inclusions. However, far from guenched melts the textures of garnets remain small and pervasively 478 filled with inclusions, indicating the influence of melt fluxing on mineral growth. With increasing 479 pressure, garnets become increasingly majoritic, with increasing quantities of octahedral silicon. 480

Clinopyroxene was observed in all subsolidus experiments, as euhedral crystals that are often spatially associated with the carbon-bearing phase. Cpx abundance falls with increasing pressure and their compositions becoming increasingly dominated by sodic components (jadeite, aegerine and NaMg_{0.5}Si_{2.5}O₆) at high pressure (EDF5). Cpx only disappears from the stable phase assemblage in supersolidus experiments at 20.7 GPa. SiO₂ is observed in all runs and are small, often elongated tabular-shaped crystals. An oxide, either TiO₂ at low pressure or an Fe-Ti oxide above 13 GPa (as in [24]) are observed in all subsolidus runs.

The carbon-bearing phase in subsolidus experiments changes with increasing pressure. At 3 GPa
CO₂, marked by the presence of voids in the polished sample, is stable. This converts to dolomite at

491 7.9 GPa, consistent with the position of the reaction $2cs + dol = cpx + CO_2$ [22]. Beyond ~ 9 GPa dolomite becomes unstable and breaks down into magnesite + aragonite²³. Therefore, because the 492 493 ATCM1 bulk composition lies on the Mg+F e^{2+} -rich side of the garnet-cpx join (EDF5 and EDF1a), 494 magnesite replaces dolomite as the carbon host in the experimental phase assemblage. This differs 495 from experiments in previous studies, where aragonite was dominant because bulk compositions 496 fall on the opposite side of the garnet-cpx join. It is clear from the ternary diagrams (EDF5) that 497 while the tie-line between garnet and cpx remains magnesite and aragonite cannot coexist in a 498 MORB bulk composition. Finally, at pressures above 15 GPa, Na carbonate becomes stable in the 499 subsolidus phase assemblage. This is chemographically explained by the rotation of the garnet-cpx 500 tie-line with increasing pressure (EDF5). Its appearance can also be justified as a necessary host of 501 sodium at increasing pressure, since aside from clinopyroxene there is no other Na-rich phase stable 502 on the Mg+Fe side of the maj-cpx join.

503

504 The appearance of silicate melt, containing dissolved CO_2 (estimated by difference), defines the 505 solidus at 3 GPa. This may initially appear to contradict the results of some previous studies, which 506 find carbonatite melts are produced near the solidus of carbonated eclogite at pressures lower than 7 GPa^{e.g. 43,45,46}. However, this is easily explained by the differences in CO₂ and SiO₂ content used in 507 508 these studies. The higher CO₂ and lower SiO₂ contents of previous studies stabilise carbonate melt 509 to lower temperatures relative to silicate melts. Indeed, we note that our results are consistent with those of Yaxley and Green⁴⁴ and Hammouda⁴² (the two previous studies with the least depleted 510 511 SiO₂) who also observed near solidus melts below 5 GPa were basaltic to dacitic silicate melts containing dissolved CO₂. The results of Kiseeva et al.¹⁹ are not entirely self-consistent, in that at 512 513 some pressures between 3.5 and 5.5 GPa they observed silicate melts prior to carbonate melts (4.5 514 and 5 GPa), whereas this relationship is sometimes reversed (5 GPa in AuPd capsules) or both melts 515 were observed together (3.5 GPa). The observation of two immiscible melts in previous studies 516 likely reflects the maximum CO₂ solubility in silicate melts. Since our bulk composition has less 517 CO₂, akin to natural rocks, we do not observe liquid immiscibility.

518

In all experiments above 7 GPa near-solidus melt compositions are carbonatitite and essentially silica-free. This result is notably different from [19] who reported that near solidus melts were a mixture of silicate, carbonated silicate and carbonatite melts. We believe this contrast is caused by the interpretation of experimental run textures. Whereas [19] identified regions of fine-grained material consisting of mixtures of stable phases from elsewhere in the capsule as quenched melts, we have not followed the same interpretation of these features. Although we do recognise similar features in some run products we have interpreted these features as a consequence of poor crystal 526 growth in regions far from the influence of melt fluxing. In all supersolidus experiments we 527 observed regions of carbonatite material (typically < 1 wt.% SiO₂) that is fully segregated from 528 surrounding silicate minerals and possesses a typical carbonate-melt quench texture (EDF3). 529 Silicate minerals in close-proximity to these melt pools are larger than those elsewhere in the same 530 experiment, have well-defined crystal boundaries and contain few inclusions. Therefore, we 531 attribute the variable texture and regions of fine-grained material present in experiments to the 532 location of melt within experiments, which has a tendency to segregate to isolated regions of 533 capsules under influence of temperature gradients. Although melt segregation occurs in all 534 supersolidus experiments, the efficiency of segregation and size of melt pools significantly 535 increases with rising temperature above the solidus. EDF4 shows the highly systematic evolution of 536 the melt compositions reported from our study with increasing pressure, strongly supporting our 537 interpretations.

538

539 Carbonatite melts are calcic, Ca# > 0.5 (Ca# = Ca/[Ca+Mg+Fe]), despite subsolidus carbonates 540 being dominated by magnesite (EDF4). Melts have high concentrations of TiO₂ (typically 1 - 3.5 541 wt.%), P₂O₅ (0.4 - 1.5 wt.%) and K₂O (0.3 - 1.5 wt.%) and a variable Mg# (0.33 - 0.7 defined as 542 Mg/[Mg+Fe]). The alkali content of melts, strongly dominated by Na₂O due to the bulk 543 composition, increases with pressure (from 1 to ~ 15 wt.% Na₂O at 7.9 and 20.7 GPa respectively; 544 EDF4). This increasing Na₂O content is driven by the decreasing compatibility of Na₂O in the 545 residual mantle phase assemblages as the abundance of stable clinopyroxene falls. At 20.7 GPa the 546 melt composition, as evidenced both by constant phase proportions and consistent melt/majorite 547 compositions, remains constant over a temperature interval of ~ 350 °C above the solidus. It is only 548 when temperature reaches 1530 - 1600 °C (runs #16 and #31) that the silica content of the melt 549 begins to increase (to 8.7 wt.%) and CO₂ content falls as melts start to become silica-carbonatites. 550

551 One experiment (#33) aimed to verify that measured low-degree melt compositions are accurate, 552 and are not affected by analytical problems related to the small size of melt pools, was conducted at 553 20.7 GPa. In this experiment the abundance of carbonate melt was increased by adding a mix 554 replicating the low degree melt composition ATCM2 to ATCM1 in a mass ratio of 1:3. If the 555 composition of low-degree melts has been accurately determined in 'normal' experiments then this 556 addition will have a negligible affect on phase relations or the compositions of the garnet, SiO_2 or melt; it would simply increase the melt abundance. The result of this experiment has a similar 557 558 texture to all other experiments, where carbonatite melt segregates to one end of the capsule and is 559 adjacent to large, well-formed majoritic garnets. The far end of the capsule has a much smaller 560 crystal size, crystals have ragged edges, garnets are full of inclusions and SiO₂ is present along

- 561 grain-boundaries and triple junctions (EDF3h). Mineral and melt compositions, although not
- 562 exactly identical, are similar to those measured in 'normal' experiments (to achieve identical
- 563 compositions an iterative approach would be required that was not deemed to be necessary) thus
- 564 confirming that near-solidus melt compositions have been accurately determined. The presence of
- 565 fine-grained material away from segregated melt also acts to further confirm our hypothesis
- 566 regarding the vital importance of melt presence for growing large crystals during experiments.
- 567

568 Subsolidus carbonate species at high pressure.

- 569 Comparing our starting material and results with those of previous studies using ternary and 570 quaternary projections (EDF5) reveals that it is not possible for both magnesite and aragonite to 571 coexist alongside majorite and clinopyroxene due to stable mineral phase fields (see above). Thus, 572 in Mg-Fe dominated compositions, such as our starting material, magnesite is the stable carbonate 573 at high-pressure subsolidus conditions. Whereas, in Ca dominated compositions aragonite will be 574 the stable carbonate beyond the pressure of dolomite dissociation. Natural subducting MORB 575 compositions, which contain, at most, a similar quantity of CO_2 to our bulk composition¹¹, almost 576 all lie on the Ca-poor side of the majorite-clinopyroxene join (EDF1 and EDF5). In this situation, as 577 our experiments demonstrate, cpx remains an important Na-host in MORB assemblages to high 578 pressures alongside [Na,K]_{0.33}Ca_{0.67}CO₃ structured carbonate. Ca-rich compositions containing 579 subsolidus CaCO₃ experience different phase relations because aragonite can dissolve significant 580 Na₂O and so is the sole Na-host in these compositions. We conclude that because the majority of 581 natural MORB rocks fall on the Mg+Fe side of the maj-cpx join, like our bulk composition, that the 582 phase relations determined in this study are applicable to the case of natural subduction. Therefore, 583 the melting point depression we observe along the carbonated MORB solidus at uppermost 584 transition zone pressures is generally applicable to subducted oceanic crust.
- 585

586 **Experimental Results – Melt-mantle reactions.** Without the influence of slab-derived melts the 587 anhydrous transition zone peridotite assemblage at 20.7 GPa and 1600 °C (experiment G168 and 588 G176) is dominated by Na-poor majorite and wadsleyite (Mg# = 0.90) (EDF6, EDT3 and 589 supplementary tables). Upon reaction with the near solidus alkaline carbonatite defined during 590 melting experiments, ATCM2, a clearly defined reaction zone is observed between this ambient 591 peridotite assemblage and the infiltrating melt (EDF6). The products of this reaction are garnet containing a notable $Na_2X^{2+}Si_5O_{12}$ majorite component, $Ca(Si,Ti)O_3$ perovskite, ringwoodite, 592 593 ferropericlase and diamond. All of these phases were identified using Raman spectroscopy (EDF7) 594 and their compositions are presented in the supplementary tables. Raman spectroscopy alone, which 595 was performed prior to any sample polishing using diamond-based products, confirms the creation

- of diamond during these reactions. We have not observed diamond using SEM techniques and
- 597 believe that it resides as sub-micron sized inclusions in the various reaction-product minerals where
- 598 it is seen by spectroscopic methods. The experiments performed on intimately mixed powders of
- 599 melt and pyrolite also form the same phase assemblages (EDT3) and mineral compositions from
- 600 those runs are also presented in the supplementary tables.
- 601

602 We observed the reaction products as new crystals floating in the residual carbonatite melt and/or

- nucleated on the relics of the peridotite assemblage, thus creating zoned minerals. We have
- 604 demonstrated that the composition of majorite minerals crystallising during the reactions lie
- between those expected for peridotitic and eclogitic minerals at a similar pressure and possibly
- 606 explain intermediate-composition diamond-hosted majorites (figure 2). We suggest that the full
- range of intermediate inclusion compositions might be created by the gradual shift in phase
- 608 compositions, from those we observe towards more peridotitic minerals as the melt composition
- reacts with increasing quantities of mantle material. Additionally we have shown that the
- 610 compositions of calcium perovskite (EDF8) and ferropericlase (figure 3) formed during the
- 611 reactions are consistent with diamond-hosted minerals of those species. Further experiments, across
- the solidus ledge and into the uppermost lower mantle pressure range are required to test whether
- 613 melt-mantle interactions account for all diamond-hosted inclusions.
- 614

615 References

- 616 31. Walter, M. J. Melting of Garnet Peridotite and the Origin of Komatiite and Depleted Lithosphere. J. Petrol. 39,
 617 29–60 (1998).
- 618 32. Walter, M. J., Nakamura, E., Trönnes, R. G. & Frost, D. J. Experimental constraints on crystallization
- 619 differentiation in a deep magma ocean. *Geochim. Cosmochim. Acta* 68, 4267–4284 (2004).
- Watson, E., Wark, D., Price, J. & Van Orman, J. Mapping the thermal structure of solid-media pressure
 assemblies. *Contrib. to Mineral. Petrol.* 142, 640–652 (2002).
- Schilling, F. & Wunder, B. Temperature distribution in piston-cylinder assemblies: Numerical simulations and
 laboratory experiments. *Eur. J. Mineral.* 16, 7–14 (2004).
- McDade, P. *et al.* Pressure corrections for a selection of piston-cylinder cell assemblies. *Mineral. Mag.* 66, 1021–
 1028 (2002).
- 626 36. Walter, M. J., Thibault, Y., Wei, K. & Luth, R. W. Characterizing experimental pressure and temperature
 627 conditions in multi-anvil apparatus. *Can. J. Phys.* **73**, 273–286 (1995).
- 628 37. Hernlund, J., Leinenweber, K., Locke, D. & Tyburczy, J. A. A numerical model for steady-state temperature
 629 distributions in solid-medium high-pressure cell assemblies. *Am. Mineral.* 91, 295–305 (2006).
- 630 38. Nakamura, K. & Kato, Y. Carbonatization of oceanic crust by the seafloor hydrothermal activity and its
- 631 significance as a CO₂ sink in the Early Archean. *Geochim. Cosmochim. Acta* **68**, 4595–4618 (2004).

- 632 39. Coogan, L. a. & Gillis, K. M. Evidence that low-temperature oceanic hydrothermal systems play an important role
 633 in the silicate-carbonate weathering cycle and long-term climate regulation. *Geochemistry, Geophys. Geosystems*
- **634 14,** 1771–1786 (2013).
- 635 40. Coogan, L. a. & Dosso, S. E. Alteration of ocean crust provides a strong temperature dependent feedback on the
 636 geological carbon cycle and is a primary driver of the Sr-isotopic composition of seawater. *Earth Planet. Sci. Lett.*637 415, 38–46 (2015).
- Kelley, K. A., Plank, T., Ludden, J. & Staudigel, H. Composition of altered oceanic crust at ODP Sites 801 and
 1149. *Geochemistry, Geophys. Geosystems* 4, (2003).
- 42. Hammouda, T. High-pressure melting of carbonated eclogite and experimental constraints on carbon recycling and
 storage in the mantle. *Earth Planet. Sci. Lett.* 214, 357–368 (2003).
- 642 43. Dasgupta, R., Hirschmann, M. M. & Withers, A. C. Deep global cycling of carbon constrained by the solidus of
 643 anhydrous carbonated eclogite under upper mantle conditions. *Earth Planet. Sci. Lett.* 227, 73–85 (2004).
- 44. Yaxley, G. M. & Green, D. H. Experimental demonstration of refractory carbonate-bearing eclogite and siliceous
 melt in the subduction regime. *Earth Planet. Sci. Lett.* **128**, 313–325 (1994).
- 646 45. Dasgupta, R., Hirschmann, M. M. & Dellas, N. The effect of bulk composition on the solidus of carbonated
 647 eclogite from partial melting experiments at 3 GPa. *Contrib. to Mineral. Petrol.* 149, 288–305 (2005).
- 648 46. Gerbode, C. & Dasgupta, R. Carbonate-fluxed melting of MORB-like pyroxenite at 2.9 GPa and genesis of HIMU
 649 ocean Island basalts. *J. Petrol.* 51, 2067–2088 (2010).
- 47. Litasov, K. & Ohtani, E. The solidus of carbonated eclogite in the system CaO-Al₂O₃-MgO-SiO₂-Na₂O-CO₂ to 32
 GPa and carbonatite liquid in the deep mantle. *Earth Planet. Sci. Lett.* 295, 115–126 (2010).
- 48. Keshav, S. & Gudfinnsson, G. H. Experimentally dictated stability of carbonated oceanic crust to moderately great
 depths in the Earth: Results from the solidus determination in the system CaO-MgO-Al₂O₃-SiO₂-CO₂. *J. Geophys. Res.* 115, B05205 (2010).
- 49. Molina, J. F. & Poli, S. Carbonate stability and fluid composition in subducted oceanic crust: An experimental
 study on H₂O-CO₂ bearing basalts. *Earth Planet. Sci. Lett.* **176**, 295–310 (2000).
- 657 50. Connolly, J. A. D. Computation of phase equilibria by linear programming: A tool for geodynamic modeling and
 658 its application to subduction zone decarbonation. *Earth Planet. Sci. Lett.* 236, 524–541 (2005).
- 51. Manning, C. E. Geochemistry: A piece of the deep carbon puzzle. *Nat. Geosci.* 7, 333–334 (2014).
- 660 52. Ague, J. J. & Nicolescu, S. Carbon dioxide released from subduction zones by fluid-mediated reactions. *Nat.*661 *Geosci.* 7, 2–7 (2014).
- 53. Manning, C. E. The chemistry of subduction-zone fluids. *Earth Planet. Sci. Lett.* 223, 1–16 (2004).
- 54. Newton, R. C. & Manning, C. E. Quartz solubility in H₂O-NaCl and H₂O-CO₂ solutions at deep crust-upper
- mantle pressures and temperatures: 2-15 kbar and 500-900 °C. *Geochim. Cosmochim. Acta* 64, 2993–3005 (2000).
- $665 \qquad 55. \quad \text{Newton, R. C. \& Manning, C. E. Solubility of enstatite + forsterite in H_2O at deep crust/upper mantle conditions: 4}$
- to 15 kbar and 700 to 900 °C. *Geochim. Cosmochim. Acta* **66**, 4165–4176 (2002).
- 56. Newton, R. C. & Manning, C. E. Thermodynamics of SiO₂-H₂O fluid near the upper critical end point from quartz
 solubility measurements at 10 kbar. *Earth Planet. Sci. Lett.* 274, 241–249 (2008).
- Kessel, R., Schmidt, M., Ulmer, P. & Pettke, T. Trace element signature of subduction-zone fluids, melts and
 supercritical liquids at 120 180 km depth. *Nature* 437, 724–727 (2005).
- 671 58. Stagno, V. et al. The oxygen fugacity at which graphite or diamond forms from carbonate-bearing melts in
- 672 eclogitic rocks. *Contrib. to Mineral. Petrol.* **169**, 1-18 (2015).

- 673 59. Zedgenizov, D. A., Kagi, H., Shatsky, V. S. & Ragozin, A. L. Local variations of carbon isotope composition in
- diamonds from São-Luis (Brazil): Evidence for heterogenous carbon reservoir in sublithospheric mantle. *Chem.*
- 675 *Geol.* **363**, 114–124 (2014).

676 Extended Data Captions

677 Extended Data Figure 1: Comparison of experimental compositions with natural rocks.

678 'Fresh' MORB rocks (red field), ALL-MORB ([21]; red circle), altered MORB rocks ([41]; pale

- blue circles), exhumed blueschist, greenschist and/or eclogitic rocks (yellow circles) and starting
- 680 material from this (dark blue circle) and previous studies (green circles) of carbonated MORB
- 681 compositions. In **a** rocks altered MORB and exhumed rock compositions that fall on the Mg-Fe side
- of the maj-cpx join from EDF5 plot below the dashed line, compositions that lie on the Ca side of
- this join are plotted with as orange circles with yellow outlines or purple circles with blue outlines
- and sit above the dashed curve. This confirms that magnesite will be the stable carbonate phase at
- high pressure in vast majority of natural crustal rocks, as is the case for ATCM1. Data and
- 686 corresponding references for this figure are provided in the online source data file.
- 687

688 Extended Data Figure 2: Experimental results/phase diagram and interpreted solidus

position. The reactions $cpx+CO_2=dol+2cs$ and dol=mag+arag are from [22] and [23] respectively.

- 690 The upper left curve is the anhydrous MORB solidus. N.B due to temperature gradients in
- 691 experiments at 8 GPa, a small quantity of dolomite is observed coexisting with melt in one

692 experiment above the solidus, present at the cold end of the capsule.

693

Extended Data Figure 3: BSE images of experimental products. a 7.9 GPa, 1250 °C, b 7.9 GPa,
1350 °C, c 13.1 GPa, 1350 °C, d 13.1 GPa, 1450 °C, e 20.7 GPa, 1100 °C, f 20.7 GPa, 1480 °C, g
20.7 GPa, 1600 °C, h sandwich experiment, 20.7 GPa, 1400 °C. The scale bar in each image is 10 μm.

698

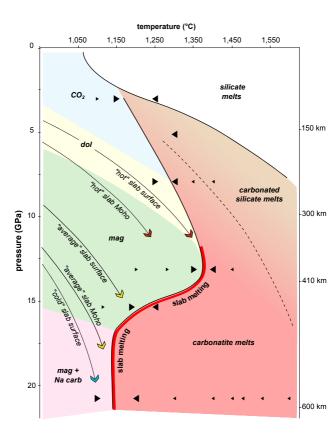
Extended Data Figure 4: Composition of experimental melts from this study. Experimental
melts from selected previous studies marked with semi-transparent greyscale symbols. The effects
of increasing pressure, temperature and the effect of contamination due to partial analysis of silicate
minerals surrounding small melt pools are shown in b.

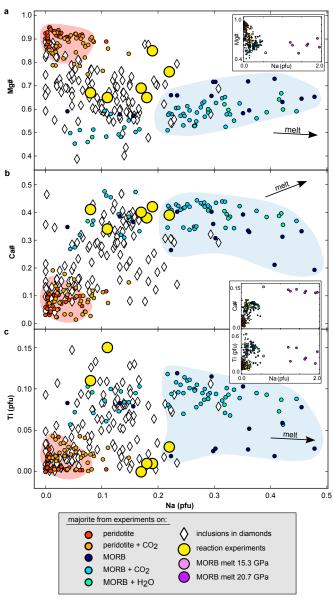
703

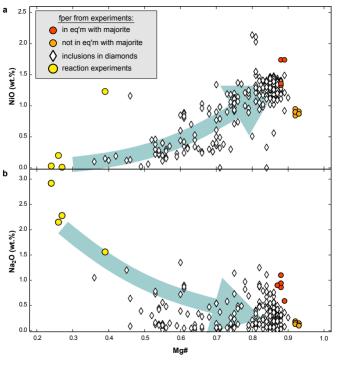
704 Extended Data Figure 5: The composition of experimental phases from this study projected

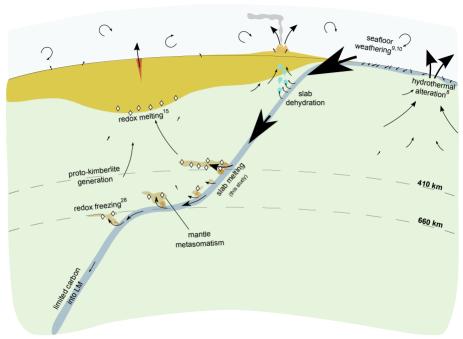
- into two quaternary plots. **a** [Ca]-[Mg+Fe²⁺]-[Si+Ti]-[Na+K] and **b** [Mg+Fe²⁺]-[Ca]-[Al+Fe³⁺]-
- [Na+K]. In both diagrams the grey fields are the compositional data projected onto the basal
- ternary. The red field is the range of natural MORB compositions projected onto the basal ternary.

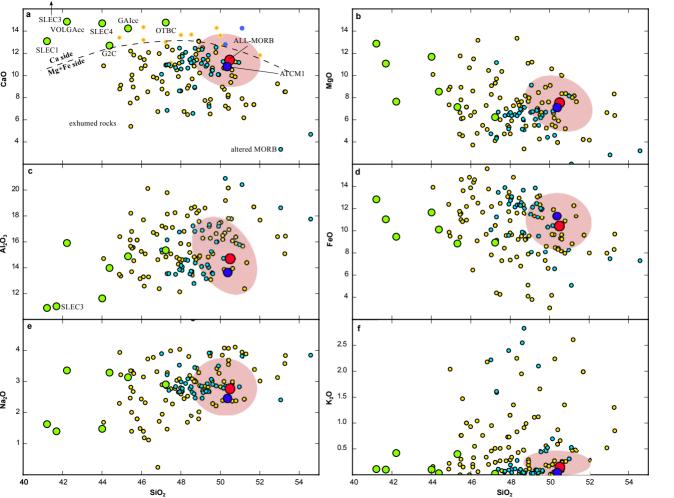
708	The yellow star plotted in the 4-component system and projected onto the basal ternary is ATCM1
709	(our bulk composition) whilst the black stars are bulk compositions from previous studies ²⁵⁻²⁷ .
710	
711	Extended Data Figure 6: BSE images of reaction experiments. a, b G169 and c, d G177. In both
712	experiments a reaction zone and remaining carbonatite melt surrounds the unreacted peridotite
713	region. a An overview of G169. b A close up of the reaction in G169 containing newly crystallised
714	calcium perovskite, majorite, ferropericlase and ringwoodite minerals. c A close up of the reaction
715	products in G177, which consist of small bright calcium perovskites, new majorite that is often
716	observed as a rim on relic peridotitic garnet and ringwoodite. d An overview of G177.
717	
718	Extended Data Figure 7: Raman spectra of minerals from reaction experiment G177
719	measured using a blue 455 cm ⁻¹ excitation laser. The position of the main peaks in each collected
720	spectrum have been labelled with their shift from the excitation laser in cm ⁻¹ .
721	
722	Extended Data Figure 8: Comparison of diamond-hosted calcium perovskite inclusions with
723	experimental mineral compositions in MgO vs Ti# space. Data and corresponding references for
724	this figure are provided in the online source data file.
725	
726	Extended Data Table 1: Starting materials used in this and previous studies. $Ca\# =$
727	Ca/[Ca+Mg+Fe]. $Mg# = Mg/[Mg+Fe]$.
728	
729	Extended Data Table 2: Summary of run conditions and products for carbonated MORB
730	melting experiments. Mass balance calculations were performed as described in the supplementary
731	information. Mineral abbreviations are as follows: gt = garnet; cpx = clinopyroxene; cs = coesite;
732	rut = rutile; maj = majoritic garnet; st = stishovite; FeTi oxide = iron-titanium-rich oxide phase; SM
733	= silicate melt; CM = carbonatite melt; dol = dolomite; mag = magnesite; Na carb = sodic
734	carbonate. Phase proportions are in wt. %.
735	
736	Extended Data Table 3: Summary of reaction experiments run conditions and experimental
737	products
738	
739	

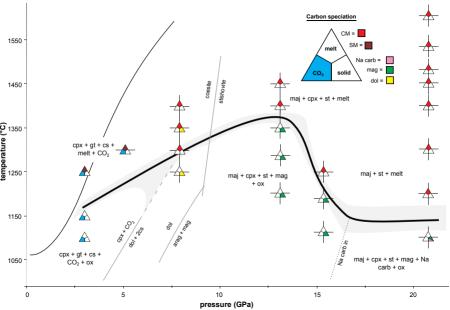


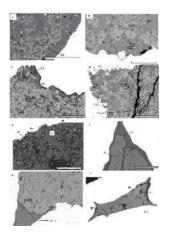


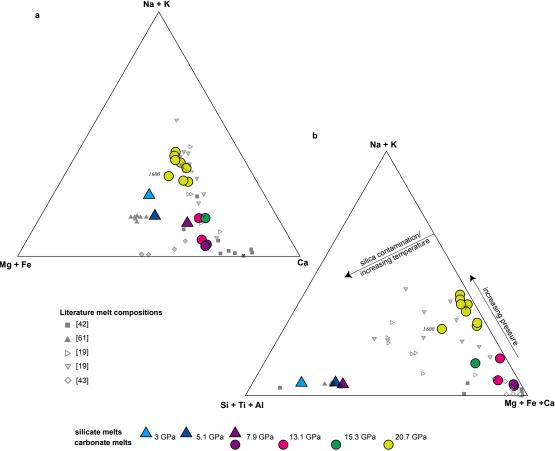


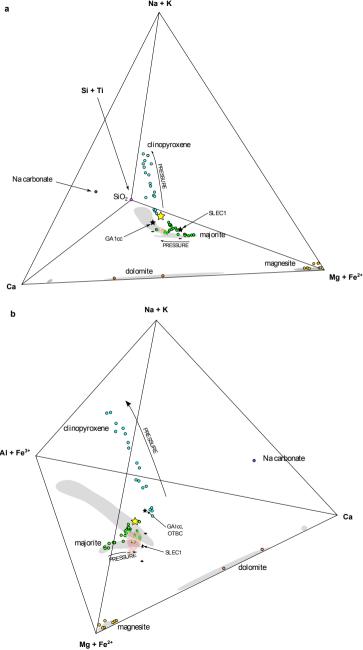


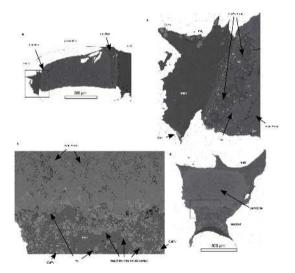


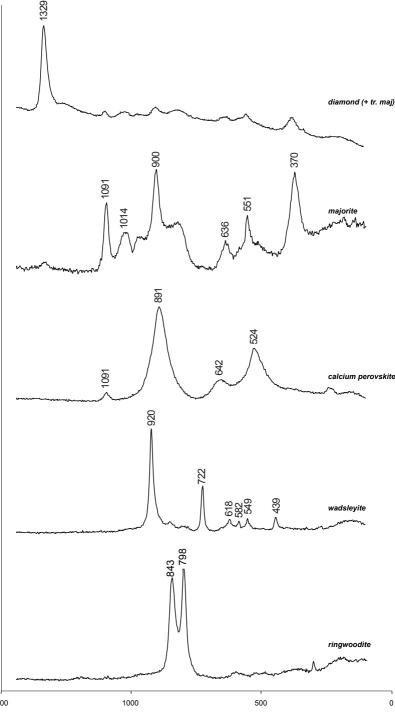






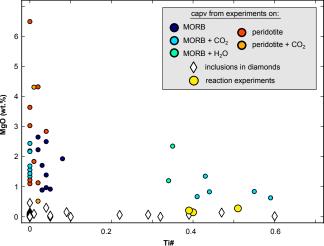






Raman shift (cm-1)

intensity



	.21	38	15	-	-	10	- No.	-	-		14	
Ψ.	÷,	1.			-		10	- 10		۰.	Τ.	
			-			1.5						

	 1.45				
		10.00			

hinter the is in house	
a settion of the left and the	