Origin of kimberlite from the base of the upper mantle

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2 Abstract:

3

**4 Kimberlite is characterized by explosive eruption powered by excess carbon dioxides
5 (CO₂)¹ and water². Given that diamond is the dominant stable phase of carbon in the
6 upper mantle³, it is obscure where does the excess CO₂ in kimberlite has come from.
7 Here we show that ferric iron oxidizes diamond at 1900K, 20GPa and 2000K, 25GPa,
8 forming CO₂. The lower mantle is dominated by bridgmanite, which is rich in ferric
9 iron⁴. Bridgmanite decomposes once it is brought to the upper mantle, releasing extra
10 ferric iron. Therefore, the oxidation of diamond may have been popularly occurring
11 at the base of the upper mantle, forming CO₂-rich carbonated domains that are the
12 main source of kimberlite. The rising kimberlitic magma reaches the lithosphere
13 mantle of thick cratons before it crosses the solidus line of mantle peridotite, and thus
14 keeps its volatile-rich nature that drives explosive eruptions. When the lithospheric
15 mantle is thinner than ~140 km, kimberlite changes into much less explosive magmas
16 due to partial melting of mantle peridotite, and, consequently, entrained diamond is
17 mostly oxidized during the magma's slower ascension.**

18

19 **Main Text**

20 It has long been established that diamondiferous kimberlites are exclusively distributed
21 in ancient lithospheric mantle, thicker than 140 kilometers (Figure 1), which transport
22 diamond to the surface through volatile-charged highly explosive kimberlite magmas^{5,6}.
23 However, cratons are old (e.g., >2.5 billion years), whereas kimberlites are young (mostly
24 < 0.6 billion years), suggesting that kimberlite is not necessarily coupled with cratons. Plate
25 reconstruction shows that most of the kimberlite were located above one of the two large
26 low shear wave velocity provinces in the lower mantle, suggesting their genetic
27 connections with mantle plumes⁷. Kimberlite has several percent of CO₂ and also H₂O,
28 which are the main components that make kimberlite explosive^{1,2,8,9}. However, cratons
29 have been highly devolatilized, such that the roots of ancient cratons are generally dry¹⁰⁻¹³,
30 which is essential to maintain cratons stable for billions of years. Moreover, carbonate
31 cannot be stored in the asthenospheric mantle at depths shallower than 300 km (Figure 2),
32 because the solidus line of carbonated peridotite is lower than the mantle geotherm¹⁴.

33 Diamond, rather than CO₂, is the dominant carbon species in the upper mantle¹⁵⁻¹⁷.
34 Therefore, conventional models have difficulties to explain the source of large quantities
35 of excess CO₂ in kimberlites. Previous studies showed that oxidation of diamond¹⁸ through
36 redox melting is required to form CO₂ in mid-ocean ridge basalts^{3,19}. Under normal mantle
37 condition, redox melting occurs at depths between 150 to 120 km. For mid-ocean ridge
38 basalts, 30 ppm of C in average should have been oxidized to carbonate at the expense of
39 3% of Fe³⁺/Fe_{Total} in the upper mantle³. However, such redox melting has complications to
40 explain the high abundance of carbonate and excess CO₂ in kimberlite.

41 First of all, formation of kimberlite through redox melting will require ferric iron
42 abundance more than 100 times higher than the estimated value of the upper mantle.
43 Second, the oxygen fugacity decreases with increasing depths^{20,21}, and diamond is the
44 stable carbon species deeper than 170 km in the upper mantle. Therefore, carbonate-
45 induced melting may occur but only at shallow depths of 150-120 km³, whereas kimberlite
46 forms mostly deeper than 140 kilometers^{3,5}. In addition, both the reductant (diamond) and
47 the oxidizing agent (ferric iron) are solid or hosted in solid minerals that are not readily
48 mobile. It is difficult to concentrate the scarce diamond into kimberlite during dispersed
49 small degree redox melting. More importantly, the key point of redox melting is that
50 elemental carbon (diamond or graphite) is oxidized within upwelling. Therefore, the degree
51 of redox melting increases with increasing upwelling distance. In this case, the thicker the
52 lithosphere, the less the redox melting, i.e., melts underneath cratons should have less CO₂.
53 This is exactly the opposite of the distribution of kimberlite.

54 The best place to oxidize diamond is the base of the upper mantle. The lower mantle
55 is rich in ferric iron because of ferrous iron disproportionation that forms native and ferric
56 iron⁴. Native iron is much denser and thus sinks towards the core. Ferric iron is hosted in
57 bridgmanite, the dominant mineral in the lower mantle with high ferric iron contents (up
58 to >60%)^{4,21}. Under the pressure-temperature (*P-T*) conditions of the upper mantle, it
59 transforms into ringwoodite, which has essentially no ferric iron, and releasing ferric iron
60 that reacts with the surrounding mantle. During deep plate subduction that penetrates across
61 the 660 km discontinuity²², some of the bridgmanite is pushed up into the upper mantle
62 through compensational background upwelling, and then decomposes. Therefore, diamond

tends to be oxidized by ferric iron at the base of the upper mantle, forming a CO₂ rich carbonated layer.

To test this model, we performed experiments in a laser-heated diamond anvil cell (DAC) at 20 GPa, 1900 K and 25 GPa, 2000 K (Methods). A mixture of analytically pure Fe₂O₃ and graphite reagent with a mass ratio of 7:3 was used as the starting materials. We investigated the redox reaction between Fe₂O₃ and graphite under the P-T conditions of the bottom of the upper mantle and identified the phase assemblages of the run products by Raman spectroscopy. Raman spectroscopy of the run products shows that CO₂-IV coexists with Fe₃O₄ under 20-25 GPa and 1900-2000 K, indicating that the diamond is oxidized by ferric iron and generated CO₂-IV (Figure. 3).

The reaction equation is as follows:

According to Equation (1), the total amount of cation decreases while the total amount of anion increases during the reaction, resulting in excess CO₂.

High-pressure experiments show that CO₂ is stable in the mantle under pressures higher than 9 GPa¹⁸. It appears as CO₂-IV at the base of the upper mantle. Our experiment results suggest that there should be carbonated domains with excess CO₂-IV at the base of the upper mantle, which is the source of kimberlites and diamond deposits.

This model is supported by Sr, Nd isotopes. Kimberlites are characterized by highly varied Sr and Nd isotopes compared to silicate rocks. Three endmembers are recognized (Figure 4). In addition to the depleted mantle and the continental crust endmembers, kimberlites have a unique endmember with strikingly low ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd (LSN here after). All the kimberlites plot in the mixing field among these endmembers.

86 Considering that the cratonic mantle is highly depleted in terms of Sr-Nd isotopes, the Sr-
87 Nd isotopes suggest that a large proportion of kimberlites were not originated from the
88 cratonic mantle.

89 The continental crust endmember may be plausibly explained by recycling of
90 subducted sedimentary carbonates, whereas the depleted mantle endmember is attributed
91 to assimilation of the depleted mantle by kimberlites during the upwelling.

92 The low $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ (LSN) endmember mantle domains have not been
93 identified in silicate rocks, suggesting that a considerable portion of kimberlites were
94 originated from an unique mantle domain that silicate magmas have rarely sampled.
95 Interestingly, carbonatite also has such an endmember, indicating that this endmember
96 involves only in carbonatic magmas, but not in silicate magmas.

97 Partial melting of mantle peridotite starts at depths of ~ 150 kilometers, depending on
98 temperatures. In contrast, partial melting of carbonated mantle peridotite may start at
99 depths of ~300 kilometers under the current mantle geotherm. It starts to melt even in the
100 lower mantle at elevated temperatures, e.g., mantle plume (Figure 2). Therefore, the most
101 straightforward explanation is that the LSN source is deep.

102 The LSN isotope characteristics require ancient source(s) with very low Rb/Sr and
103 Sm/Nd ratios. Garnet strongly enriches heavy rare earth elements, with high Sm/Nd, so
104 does majorite. Therefore, ringwoodite formed in the presence of majorite should have low
105 Sm/Nd. It transforms into bridgmanite in the upper most lower mantle, while majorite is
106 stable. Consequently, these bridgmanite has low Sm/Nd in the presence of majorite.
107 Similarly, hollandite is stable in the transition zone and the lower mantle²³. Considering
108 that hollandite is a potassium mineral, it should have high Rb/Sr ratios. Therefore,

bridgmanite formed in the presence of hollandite should also have lower Rb/Sr ratios. Once these bridgmanite is pushed into the upper mantle, it decomposes, oxidizes diamond, and forms the LSN endmember of kimberlite.

Our model also plausibly explains the close association of kimberlites with mantle plumes⁷. When an ascending mantle plume head approaches the base of the upper mantle, carbonated mantle domains with excess CO₂ is the first to be partially melted, forming explosive kimberlite melts that may carry diamond with it. At depths below 410 km, diamond is less dense than mantle peridotite in solid state. Therefore, during the formation and upward migration of kimberlite, diamond tends to be preferentially concentrated above the coexisting mantle peridotite, such that it is easier to be sampled by the kimberlite melt (Figure 5).

The upwelling of hot kimberlite melt may cause partial melting of mantle peridotite at depths of ~ 140 km, depending on the mantle temperature. Under cratons that are thicker than 140 km, kimberlite reaches the base of thick refractory cratons without significant partial melting of mantle peridotite, such that it has a better chance to keep its explosive nature that brings diamond to the surface. This plausibly explains the distribution of kimberlite and carbonatite as well as alkalic basalt (Figure 1). Kimberlite is exclusively distributed within cratons thicker than 140 km at the time of eruption^{24,25}. In contrast, carbonatite and alkalic basalt are more abundant in places having thinner lithosphere.

In non-craton regions, the lithospheric mantle is thin and less refractory. Mantle peridotite starts to melt as kimberlite melt ascends to depths of less than ~140 km. Consequently, kimberlite melts are transformed gradually into carbonatite, and then to alkali basalts^{26,27}, and even to normal basalts. Meanwhile, CO₂ reacted with the mantle,

scavenging Na, Mg and Sr, etc. These magmas are far less explosive, and thus ascend more slowly. Meanwhile the density of diamond is higher than mantle peridotite and melts at depths shallower than 410 km. As a result, it sinks to the bottom of the melt. Limited diamond left in the melt should be transformed to graphite when it passes through the graphite stability field, and may consequently be oxidized to carbonate through redox melting^{3,28}.

If the plume head is stronger and rises further, partial melting of carbonated peridotite may also occur at depths of > 140 km, forming carbonatite under cratons (Figure 1). Large igneous provinces form when the plume head successfully penetrates the whole upper mantle, causing large degrees of partial melting^{29,30}. This explains the fact that large igneous provinces are often preceded by carbonatite³¹.

According to our model, kimberlite originates mainly at the base of the upper mantle, with abundant lower mantle material carried up through background upwellings. This plausibly explains inclusions of lower mantle origin³². It also explains the high water contents of kimberlite^{2,18}. Previous studies on ringwoodite inclusions in diamond suggested that the transition zone is hydrous with H₂O content of about 1 weight percent^{33,34}. Therefore, kimberlite may acquire water as it ascending across the transition zone.

At depths of less than 100 km, kimberlite may react with the mantle peridotite on its journey passing through the thick cratonic lithosphere³⁵, forming olivine and clinopyroxene at the expenses of orthopyroxene^{1,36}, providing additional excess CO₂ that further promotes the explosive kimberlite. It also plausibly explains the absence of orthopyroxene in kimberlite¹.

154 This model also feasibly explains the occurrence of diamond and ultrahigh pressure
155 minerals in ophiolite^{37,38}. Oceanic lithosphere is generally thinner than 90 km. As
156 mentioned above, silicates start to melt as kimberlite melt ascends to depths of <140 km,
157 such that kimberlite melts tend to be transformed into basalts. Consequently, diamond
158 carried up by kimberlite disappears due to transformation and oxidation. However, in cases
159 where the kimberlite was located underneath a spreading ridge, and thus was much easier
160 to erupt to the surface, there still could be diamond and other ultrahigh pressure phases left,
161 mostly likely as inclusions. This plausibly explains the occurrence of diamond in ophiolites.

162

163

Methods

Sample preparation and pressure determination

Powder of hematite (99.99%, Alfa Aesar) and graphite (99.99%, Alfa Aesar) was mixed at a mass ratio of 7:3 and ground in an agate mortar for 6 hours.

Boehler-Almax diamond anvils with flat culet diameters of 300 μm were used for the experiments. The starting material was pre-compressed into disks of ~ 15 μm thickness. A thin disk of the starting material was then sandwiched between two layers of quartz which serve as both pressure transmitting medium and thermal insulation and placed in a rhenium (Re) gasket hole preindented to a thickness of about 35 μm . To avoid potential moisture contamination in the sample chamber, before sealing the sample chamber, the DAC was stored in a oven at 120°C for 12 hours. The pressures at room temperature were determined based on the Raman shift of a diamond anvil³⁹.

Raman experiments in laser-heated DACs

High P-T Raman experiments were performed at the Center for High Pressure Science & Technology Advanced Research (HPSTAR). The samples were heated by a Ytterbium fiber laser on both sides⁴⁰. The heating temperature on both sides of the heated sample was determined by fitting the visible part of the gray-body radiation with Planck radiation function^{41,42}. The uncertainty of temperature in the whole heating experiments is $\pm 50\text{K}$.

The Renishaw 2000 type Raman is equipped with a charge-coupled device detector, 2400 line mm^{-1} diffraction grating and holographic filter. The zero shift was calibrated using a 520 cm^{-1} single crystal of silicon. The excitation light was 532 nm, and the acquisition time of each Raman spectrum was 5 minutes to ensure the quality of data

analysis. Gaussian + Lorentzian functions of Peakfit software (Systat Software, San Jose, CA) were used to fit the Raman data. We observed many overlapping peaks in a typical powder Raman pattern of the run products. To identify the phases, we applied the characteristic peaks of these phases for classification.

Competing interests: The authors declare no competing interests.

195

196

197 **Figure 1. The distribution of kimberlite and carbonatite all over the world.** All the
198 kimberlites are distributed in craton thicker than 140 km. In contrast, carbonatite is not
199 selective to lithosphere thickness. Data from the GEOROC database.

200

Figure 2. Density and temperature profiles of the mantle. The solidus line of carbonated mantle peridotite (green dot dash line) is lower than the solid adiabat of the mantle (green solid line) at depths shallower than 300 km¹⁴. This suggests that no carbonate can survive at the bottom of the lithospheric mantle. Diamond (orange solid line) is denser than peridotite melt (orange dotted line) at shallow depths, but is less dense in the lower mantle. The density crossover is close to the 660 km discontinuity. Therefore, diamond has accumulated at the base of the upper mantle in the Magma Ocean. This diamond layer has been oxidized by bridgmanite upwelled from the lower mantle, forming carbonated peridotite⁴³ with excess CO₂.

Figure 3 The run products and CO₂-IV Raman pattern at several high-pressure conditions from this study and previous studies⁴⁴⁻⁴⁶. Raman spectra of the run products of this study show characteristic peaks of CO₂-IV, 108 cm⁻¹ at 20 GPa and 134 cm⁻¹ at 25 GPa, although there are many overlapping peaks between Fe₂O₃ and CO₂ -IV in high pressure Raman spectra. Previous studies found that CO₂ generated CO₂-IV under experimental conditions of 20-25 GPa and 1900-2000 K. All Raman shift to the right with increasing pressures. The Raman shift range of 100-400 cm⁻¹ is consistent with the previous research of CO₂-IV⁴⁴⁻⁴⁶. The Raman peaks of 462 cm⁻¹, 553 cm⁻¹, 707 cm⁻¹ at 20 GPa and 492 cm⁻¹ at 25 GPa of this study are consistent with the high-pressure Raman pattern of Fe₂O₃⁴⁷ (orange triangle), and the Raman peaks of 793 cm⁻¹ at 20 GPa and 865 cm⁻¹ at 25 GPa are consistent with the high-pressure Raman pattern of Fe₃O₄⁴⁸ (blue star), and the Raman peaks of 238 cm⁻¹ and 521 cm⁻¹ at 20 GPa and 246 cm⁻¹ at 25 GPa are consistent with the high-pressure Raman pattern of stishovite⁴⁹ (green diamond). In summary, the experimental results show diamond is oxidized by ferric iron, forming CO₂-IV.

229

230 **Figure 4. Diagram of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ for global kimberlite.** Sedimentary
 231 carbonates are also shown in the Figure (grey square). Kimberlites have highly varied and
 232 mostly enriched isotopes compared to silicate rocks⁵⁰, suggesting that they were originated
 233 from special enriched mantle domains that have not been sampled by silicate melts. This
 234 clearly excludes cratonic mantle, which is depleted in terms of Sr-Nd isotopes. The Sr and
 235 Nd isotope compositions of kimberlites and sedimentary carbonates are obtained from the
 236 GEOROC database.

237

Figure 5 (a) Kimberlite formation model. When a mantle plume approaches the base of the upper mantle, previously formed and stabilized CO_2 is activated, followed by partial melting of carbonated mantle peridotite and water rich phases, forming kimberlite. **(b) Formation of large igneous province.** Large igneous provinces form when the plume head penetrates the transition zone, with most of the melting occurred at shallow depths, forming carbonatite and basalts. Both carbonatites and large igneous province magmas are not as explosive as kimberlite, such that they erupt more slowly, losing diamond during ascent.

248 References and Notes

- 249 1 Russell, J. K., Porritt, L. A., Lavalley, Y. & Dingwell, D. B. Kimberlite ascent by
250 assimilation-fuelled buoyancy. *Nature* **481**, 352-U133, doi:Doi 10.1038/Nature10740
251 (2012).
- 252 2 Kamenetsky, V. S. & Yaxley, G. M. Carbonate-silicate liquid immiscibility in the mantle
253 propels kimberlite magma ascent. *Geochim Cosmochim Ac* **158**, 48-56,
254 doi:10.1016/j.gca.2015.03.004 (2015).
- 255 3 Stagno, V., Ojwang, D. O., McCammon, C. A. & Frost, D. J. The oxidation state of the
256 mantle and the extraction of carbon from Earth's interior. *Nature* **493**, 84-+, doi:Doi
257 10.1038/Nature11679 (2013).
- 258 4 Frost, D. J. *et al.* Experimental evidence for the existence of iron-rich metal in the Earth's
259 lower mantle. *Nature* **428**, 409-412, doi:Doi 10.1038/Nature02413 (2004).
- 260 5 Shirey, S. B. *et al.* Diamonds and the geology of mantle carbon. *Reviews in Mineralogy &*
261 *Geochemistry* **75**, 355-421 (2013).
- 262 6 Wilson, L. & Head Iii, J. W., 3rd. An integrated model of kimberlite ascent and eruption.
263 *Nature* **447**, 53-57, doi:10.1038/nature05692 (2007).
- 264 7 Torsvik, T. H., Burke, K., Steinberger, B., Webb, S. J. & Ashwal, L. D. Diamonds sampled
265 by plumes from the core-mantle boundary. *Nature* **466**, 352-U100, doi:Doi
266 10.1038/Nature09216 (2010).
- 267 8 Price, S. E., Russell, J. K. & Kopylova, M. G. J. J. o. P. Primitive Magma From the Jericho
268 Pipe, N.W.T., Canada: Constraints on Primary Kimberlite Melt Chemistry. 789-808(720)
269 (2000).
- 270 9 Sparks, R. *et al.* The nature of erupting kimberlite melts. **112**, 429-438 (2009).
- 271 10 Taylor, L. A. *et al.* Low water contents in diamond mineral inclusions: Proto-genetic
272 origin in a dry cratonic lithosphere. *Earth Planet Sc Lett* **433**, 125-132,
273 doi:10.1016/j.epsl.2015.10.042 (2016).
- 274 11 Wu, F.-Y., Yang, J.-H., Xu, Y.-G., Wilde, S. A. & Walker, R. J. Destruction of the North
275 China Craton in the Mesozoic. *Annual Review of Earth and Planetary Sciences* **47**, 173-
276 195, doi:10.1146/annurev-earth-053018-060342 (2019).
- 277 12 Peslier, A. H., Schönbächler, M., Busemann, H. & Karato, S.-I. Water in the Earth's
278 Interior: Distribution and Origin. *Space Science Reviews* **212**, 743-810,
279 doi:10.1007/s11214-017-0387-z (2017).
- 280 13 Novella, D., Bolfan-Casanova, N., Nestola, F. & Harris, J. W. H₂O in olivine and garnet
281 inclusions still trapped in diamonds from the Siberian craton: Implications for the water
282 content of cratonic lithosphere peridotites. *Lithos* **230**, 180-183,
283 doi:<https://doi.org/10.1016/j.lithos.2015.05.013> (2015).
- 284 14 Dasgupta, R. Ingassing, storage, and outgassing of terrestrial carbon through geologic
285 time. *Reviews in Mineralogy & Geochemistry* **75**, 183-229 (2013).
- 286 15 Liu, H., Sun, W. D., Zartman, R. & Tang, M. Continuous plate subduction marked by the
287 rise of alkali magmatism 2.1 billion years ago. *Nature Communications* **10**,
288 doi:10.1038/s41467-019-11329-z (2019).
- 289 16 Thomson, A. R., Walter, M. J., Kohn, S. C. & Brooker, R. A. Slab melting as a barrier to
290 deep carbon subduction. *Nature* **529**, 76-79, doi:10.1038/nature16174 (2016).
- 291 17 Drewitt, J. W. E. *et al.* The fate of carbonate in oceanic crust subducted into earth's
292 lower mantle. *Earth and Planetary Science Letters* **511**, 213-222,
293 doi:10.1016/j.epsl.2019.01.041 (2019).

294 18 Stamm, N. & Schmidt, M. W. Asthenospheric kimberlites: Volatile contents and bulk
 295 compositions at 7 GPa. *Earth Planet Sc Lett* **474**, 309-321,
 296 doi:10.1016/j.epsl.2017.06.037 (2017).

297 19 Stagno, V. *et al.* The stability of magnesite in the transition zone and the lower mantle as
 298 function of oxygen fugacity. *Geophys Res Lett* **38**, doi:Artn L19309, Doi
 299 10.1029/2011gl049560 (2011).

300 20 Rohrbach, A. & Schmidt, M. W. Redox freezing and melting in the Earth's deep mantle
 301 resulting from carbon-iron redox coupling. *Nature* **472**, 209-212,
 302 doi:10.1038/nature09899 (2011).

303 21 Frost, D. J. & McCammon, C. A. The redox state of Earth's mantle. *Annu Rev Earth Pl Sc*
 304 **36**, 389-420, doi:DOI 10.1146/annurev.earth.36.031207.124322 (2008).

305 22 van der Hilst, R. D., Widiyantoro, S. & Engdahl, E. R. Evidence for deep mantle circulation
 306 from global tomography. *Nature* **386**, 578-584, doi:Doi 10.1038/386578a0 (1997).

307 23 Deng, L. W., Liu, X., Liu, H. & Zhang, Y. G. A first-principles study of the phase transition
 308 from Holl-I to Holl-II in the composition KAlSi₃O₈. *Am Mineral* **96**, 974-982,
 309 doi:10.2138/am.2011.3689 (2011).

310 24 Giuliani, A. & Pearson, D. G. Kimberlites: From Deep Earth to Diamond Mines. *Elements*
 311 **15**, 377-380, doi:10.2138/gselements.15.6.377 (2019).

312 25 Pearson, D. G., Woodhead, J. & Janney, P. E. Kimberlites as Geochemical Probes of
 313 Earth's Mantle. *Elements* **15**, 387-392, doi:10.2138/gselements.15.6.387 (2019).

314 26 Zhang, G. L., Chen, L. H., Jackson, M. G. & Hofmann, A. W. Evolution of carbonated melt
 315 to alkali basalt in the South China Sea. *Nat Geosci* **10**, 229-U105, doi:10.1038/NCEO2877
 316 (2017).

317 27 Li, S. G. *et al.* Deep carbon cycles constrained by a large-scale mantle Mg isotope
 318 anomaly in eastern China. *Natl Sci Rev* **4**, 111-120, doi:10.1093/nsr/nww070 (2017).

319 28 Stagno, V., Frost, D. J., McCammon, C. A., Mohseni, H. & Fei, Y. The oxygen fugacity at
 320 which graphite or diamond forms from carbonate-bearing melts in eclogitic rocks.
 321 *Contrib Mineral Petr* **169**, doi:ARTN 16, 10.1007/s00410-015-1111-1 (2015).

322 29 Sun, W. D. *et al.* The fate of subducted oceanic crust: a mineral segregation model. *Int*
 323 *Geol Rev* **53**, 879-893, doi:10.1080/00206810903211930 (2011).

324 30 Sobolev, A. V., Hofmann, A. W., Sobolev, S. V. & Nikogosian, I. K. An olivine-free mantle
 325 source of Hawaiian shield basalts. *Nature* **434**, 590-597, doi:Doi 10.1038/Nature03411
 326 (2005).

327 31 Wu, F. Y., Mitchell, R. H., Li, Q. L., Zhang, C. & Yang, Y. H. Emplacement age and isotopic
 328 composition of the Prairie Lake carbonatite complex, Northwestern Ontario, Canada.
 329 *Geol Mag* **154**, 217-236, doi:10.1017/S0016756815001120 (2017).

330 32 Walter, M. J. *et al.* Deep Mantle Cycling of Oceanic Crust: Evidence from Diamonds and
 331 Their Mineral Inclusions. *Science* **333**, 54-57, doi:DOI 10.1126/science.1209300 (2011).

332 33 Pearson, D. G. *et al.* Hydrous mantle transition zone indicated by ringwoodite included
 333 within diamond. *Nature* **507**, 221-+, doi:Doi 10.1038/Nature13080 (2014).

334 34 Druzhbin, D., Fei, H., Katsura, T. J. E. & Letters, P. S. Independent hydrogen
 335 incorporation in wadsleyite from oxygen fugacity and non-dissociation of H₂O in the
 336 reducing mantle transition zone. **557**, 116755 (2021).

337 35 Stone, R. S. & Luth, R. W. Orthopyroxene survival in deep carbonatite melts: implications
 338 for kimberlites. *Contrib Mineral Petr* **171**, doi:ARTN 63, 10.1007/s00410-016-1276-2
 339 (2016).

340 36 Brett, R. C., Russell, J. K., Andrews, G. D. M. & Jones, T. J. The ascent of kimberlite:
341 Insights from olivine. *Earth Planet Sc Lett* **424**, 119-131, doi:10.1016/j.epsl.2015.05.024
342 (2015).

343 37 Yang, J. S. *et al.* Diamond- and coesite-bearing chromitites from the Luobusa ophiolite,
344 Tibet. *Geology* **35**, 875-878, doi:10.1130/G23766a.1 (2007).

345 38 Yang, J. S., Robinson, P. T. & Dilek, Y. Diamonds in Ophiolites. *Elements* **10**, 127-130,
346 doi:10.2113/gselements.10.2.127 (2014).

347 39 Akahama, Y. & Kawamura, H. Diamond anvil Raman gauge in multimegabar pressure
348 range. *High Pressure Research* **27**, 473-482, doi:10.1080/08957950701659544 (2007).

349 40 Shen, G., Mao, H. K. & Hemley, R. J. J. P. n. I. s. o. A. M. Laser-Heated Diamond Anvil Cell
350 Technique: Double-Sided Heating with Multimode Nd:YAG Laser. (1996).

351 41 Benedetti, L. R. & Loubeyre, P. Temperature gradients, wavelength-dependent
352 emissivity, and accuracy of high and very-high temperatures measured in the laser-
353 heated diamond cell. *High Pressure Research* **24**, 423-445,
354 doi:10.1080/08957950412331331718 (2004).

355 42 Prakapenka, V. B. *et al.* Advanced flat top laser heating system for high pressure
356 research at GSECARS: application to the melting behavior of germanium. **28**, 225-235
357 (2008).

358 43 Sun, W. D. *et al.* Carbonated mantle domains at the base of the Earth's transition zone.
359 *Chem Geol* **478**, 69-75, doi:10.1016/j.chemgeo.2017.08.001 (2018).

360 44 Iota, V. & Yoo, C. S. Phase diagram of carbon dioxide: Evidence for a new associated
361 phase. *Phys Rev Lett* **86**, 5922-5925, doi:10.1103/PhysRevLett.86.5922 (2001).

362 45 Yoo, C. S., Iota, V. & Cynn, H. Nonlinear carbon dioxide at high pressures and
363 temperatures. *Phys Rev Lett* **86**, 444-447, doi:10.1103/PhysRevLett.86.444 (2001).

364 46 Park, J. H. *et al.* Crystal structure of bent carbon dioxide phase IV. *Physical Review B* **68**,
365 doi:10.1103/PhysRevB.68.014107 (2003).

366 47 Shim, S. H. & Duffy, T. S. Raman spectroscopy of Fe₂O₃ to 62 GPa. *Am Mineral* **87**, 318-
367 326 (2002).

368 48 Shebanova, O. N. & Lazor, P. Vibrational modeling of the thermodynamic properties of
369 magnetite (Fe₃O₄) at high pressure from Raman spectroscopic study. *Journal of*
370 *Chemical Physics* **119**, 6100-6110, doi:10.1063/1.1602072 (2003).

371 49 Nisr, C., Shim, S. H., Leinenweber, K. & Chizmeshya, A. Raman spectroscopy of water-
372 rich stishovite and dense high-pressure silica up to 55 GPa. *Am Mineral* **102**, 2180-2189,
373 doi:10.2138/am-2017-5944 (2017).

374 50 Hofmann, A. W. Mantle geochemistry: The message from oceanic volcanism. *Nature*
375 **385**, 219-229, doi:Doi 10.1038/385219a0 (1997).