Mapping the Thermal Lithosphere and Melting across the Continental US

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Abstract

The thermal regime of continental lithosphere plays a fundamental role in controlling the behavior of tectonic plates. In this work, we assess the thermal state of the North American upper mantle by combining shear-wave velocity models calculated using data from the EarthScope facility with empirically-derived anelasticity models and basalt thermobarometry. We estimate the depth to the thermal lithosphere-asthenosphere boundary (LAB), defined as the intersection of a geotherm with the 1300° C adiabat. Results show lithospheric thicknesses across the contiguous US vary between $\tilde{}40 \text{ km}$ and > 200 km. The thinnest thermal lithosphere is observed in the tectonically active western US and the thickest lithosphere in the mid-continent. By combining geotherm estimates with solidus curves for peridotite, we show that a pervasive partial melt zone is common within the western US upper mantle and that partial melt is absent in the eastern and central US without significant metasomatism.

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5 ABSTRACT

6 The thermal regime of continental lithosphere plays a fundamental role in controlling the 7 behavior of tectonic plates. In this work, we assess the thermal state of the North American upper 8 mantle by combining shear-wave velocity models calculated using data from the EarthScope 9 facility with empirically derived anelasticity models and basalt thermobarometry. We estimate 10 the depth to the thermal lithosphere-asthenosphere boundary (LAB), defined as the intersection 11 of a geotherm with the 1300° C adiabat. Results show lithospheric thicknesses across the 12 contiguous US vary between ~ 40 km and > 200 km. The thinnest thermal lithosphere is observed 13 in the tectonically active western US and the thickest lithosphere in the mid-continent. By 14 combining geotherm estimates with solidus curves for peridotite, we show that a pervasive 15 partial melt zone is common within the western US upper mantle and that partial melt is absent 16 in the eastern and central US without significant metasomatism.

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18 PLAIN LANGUAGE SUMMARY

19 The lithosphere, which is the upper most mechanical layer of the earth, makes up tectonic 20 plates and can vary in thickness laterally. Thickness variations influence the location of 21 volcanoes and where deformation occurs when forces act on the lithosphere. Lithospheric 22 thicknesses can be estimated by examining the thermal properties of the uppermost mantle. We integrate seismic observations and lab results to calculate temperatures for the upper mantle in the continental US and compare these to geochemical proxies for temperature. We then use these temperature results to estimate lithospheric thickness and map where melt is predicted within the upper mantle. Results show thin lithosphere and the presence of melt in the western US. Thicker lithosphere and an absence of melt are observed in the central and eastern US.

28

29 INTRODUCTION

30 The lithosphere-asthenosphere boundary (LAB) is a fundamental rheological boundary in 31 the earth, separating the rigid lithosphere, which makes up the earth's tectonic plates, from 32 ductile asthenosphere below. The decrease in seismic velocity with respect to depth often 33 observed at this boundary is attributed to changes in rheology due to increased temperatures at 34 depth, the presence of melt, and/or the transition from a chemically depleted mantle lithosphere 35 to a more enriched asthenosphere [e.g. Jordan, 1975; Fischer et al., 2010; Yuan and 36 *Romanowicz*, 2010]. Understanding the thermal state of the upper mantle is important for better 37 understanding of the nature of the LAB in regions of both active tectonism and tectonic 38 quiescence, and the behavior of lithosphere in general. To better understand the physical state of 39 the mantle beneath North America, we utilize experimentally derived anelasticity data to convert 40 shear velocities calculated using data from the EarthScope Transportable Array to temperatures 41 and compare these results with basalt equilibration pressures and temperatures based on 42 thermobarometry. We then present a new three-dimensional temperature model for the 43 uppermost mantle beneath the continental US, which allows for a better understanding of upper-44 mantle rheology and the nature of the LAB across the continent.

45

46 **METHODOLOGY**

47 Shear Velocities

To calculate upper-mantle temperatures, we utilize a shear velocity model where 48 49 velocities were calculated by inverting ambient noise and wave gradiometry data at periods 50 between 8 and 150 seconds [Liu and Holt, 2015; Porter et al., 2016]. We use a linearized least 51 squares inverse method where all phase velocity measurements are weighted equally to invert 52 from phase velocity to shear velocity [Herrmann and Ammon, 2002]. The use of phase velocity 53 measurements out to a period of 150 seconds allows for the calculation of a shear velocity model 54 that extends down to ~200 km depth, which is deeper than many other existing surface wave 55 measurements for the region allow for. In the shear velocity inversion, crustal and basin 56 thicknesses are constrained using data from the Earthscope Automatic Receiver function Survey 57 (EARS) [Crotwell and Owens, 2005], and the Laske and Masters [1997] global sediment 58 thickness map.

59

Seismic Temperature Calculations

60 We use seismic velocities and pressure estimates to calculate temperatures for the upper 61 mantle across the continental US. Within the mantle, the dominant control on seismic velocity is 62 thought to be temperature, with the roles of factors such as composition, melt, and grain size 63 debated and less constrained. Experimentally derived data from Isaak [1992] are used to 64 calculate the effects of temperatures on the unrelaxed shear modulus for olivine. At high 65 temperatures (>~900° C) anelastic effects are pronounced and a linear relationship between 66 increased temperature and anharmonic decreases in elastic moduli no longer holds [Goes et al., 67 2000; Cammarano et al., 2003; Faul and Jackson, 2005; Priestley and Mckenzie, 2006; Jackson 68 et al., 2008; Jackson and Faul, 2010; McCarthy et al., 2011; Priestley and Mckenzie, 2013]. To

69 account for this, data from McCarthy et al. [2011] are used to relate velocities to temperature. 70 Using these anharmonic and anelastic velocity/temperature relationships, we apply a Newton-Raphson iterative methodology to minimize the difference between predicted and observed 71 72 velocities to calculate temperature as in Porter et al. [2019]. In our calculations, pressure is 73 estimated using the crustal thickness model from Porter et al. [2016] and assuming a density of 74 2700 kg/m³ for the crust. For calculating mantle densities, we follow the methodology of Goes et 75 al. [2000], which accounts for the effects of pressure and temperature on upper mantle densities. 76 Grain size is not well constrained within the mantle and may strongly influence the relationship 77 between seismic velocities and temperatures, especially at elevated temperatures [Jackson and 78 Faul, 2010; McCarthy et al., 2011; e.g. Dannberg et al., 2017]. As grain size may vary laterally 79 and with depth within the upper mantle [e.g. Karato and Wu, 1993; Behn et al., 2009], we 80 assume a grain size of 1 mm in our estimates and show LAB estimates assuming grain size of 0.1 81 mm in the Supplemental Data.

82 In our seismic temperature calculations, we assume that all velocity variations in the 83 mantle are associated with temperature, which does not account for the effects of composition, 84 melts, fluids, etc. on shear velocities. The relative effects of these factors on seismic velocity are 85 variable and debated [Anderson and Sammis, 1970; Karato, 1995; van der Lee, 2002; 86 Cammarano et al., 2003; Dunn and Forsyth, 2003; Artemieva et al., 2004; Kreutzmann et al., 2004; Priestley and Mckenzie, 2006; Schutt and Lesher, 2006; Aizawa et al., 2007; Schutt and 87 88 Dueker, 2008; Karato, 2010b; Schutt and Lesher, 2010; Priestley and Mckenzie, 2013; 89 Cammarano and Guerri, 2017; Cline et al., 2018]. While attributing all mantle seismic 90 variations to temperature is a simplification of upper mantle conditions, this allows for a baseline 91 estimate of thermal conditions under the continent. For a more detailed discussion of these
92 compositional assumptions and the methodology refer to Porter et al. [2019].

- We use our seismically derived estimates of temperatures to calculate geotherms at every gridpoint within the shear velocity model. In order to estimate the thickness of the thermal lithosphere, we use the depth of the intersection of the 1300° C adiabat and seismically derived geotherms as a proxy for the location of the LAB (Figure 1). We also use these data to calculate the geothermal gradient in the upper mantle by measuring the vertical gradient of the estimated temperatures.
- 99

Basalt Thermobarometry

100 We calculate melt equilibrium pressure and temperatures using the major element 101 thermobarometer described in Plank and Forsyth [2016]. Major oxide chemistries from basaltic 102 rocks are downloaded from the EarthChem Portal (www.earthchem.org/portal) for all samples younger than 6 Ma within the western US and converted to molar percentages. The ratio of Fe³⁺ 103 to Fe²⁺ is estimated assuming buffering of oxygen fugacity at the QFM buffer [Kress and 104 105 *Carmichael*, 1991]. Whole rock compositions are converted to primary melt compositions by the 106 sequential addition of olivine to obtain a melt in equilibration with Fo₉₀, as in *Lee et al.* [2009]. 107 For our calculations, samples with less than 8% MgO, and/or 12% Al₂O₃, or those with 108 unnormalized compositions of less than 97.5% by weight are deemed unlikely representative of 109 near-primary mantle melts and were discarded. We estimate equilibrium P-T conditions assuming 1.5 wt % H₂O in the melt because water measurements are not available for most 110 samples. The 1.5% value was chosen as a rough average based on the water contents observed by 111 112 Plank and Forsyth [2016], which ranged from 1-3.2%. To account for the range of possible 113 magmatic water contents, the error bars in Figures 3, and 4 show the range of temperatures

(horizontal) and pressures (vertical) that are calculated when water contents were varied between 0.5 wt % and 3 wt %. We compare our results to Plank and Forsyth [2016], who use vanadium to constrain oxygen fugacity and estimate Fe^{3+} to Fe^{2+} ratios. Resulting pressure-temperature estimate differences between our estimates and those of Plank and Forsyth [2016] are < 0.06 GPa and < 14° C when calculations were run for the same compositions assuming the same magmatic water contents.

120

Seismic Mantle Melting Estimates

121 In order to better understand the physical state of the upper mantle across the continent, 122 we combine our seismic temperature estimates with experimental data that constrain solidi to 123 map out where partial melt is present in the upper mantle across the contiguous US, assuming a 124 peridotite upper mantle [Katz et al., 2003]. The solidus was calculated for upper mantle depths 125 assuming 75 ppm H₂O. We do not account for CO_2 in these melting estimates, which has a 126 considerably smaller effect than H₂O and is negligible for melt equilibration pressures <2 GPa 127 [*Plank and Forsyth*, 2016]. At temperatures above the solidus, the presence of partial melt is 128 expected within the upper mantle, which would lower seismic velocities, and lead to an 129 overestimation of seismically derived temperatures. Because of the uncertainty in this 130 relationship, instead of estimating melt fractions based on temperature, we subtract solidus 131 temperatures from our seismically derived temperatures estimates. This allows us to predict 132 where partial melting is expected within the upper mantle.

The value of 75 ppm water was selected as a wet average for "damp" upper mantle. Previous geophysical estimates are consistent with 0-100 ppm water within the upper mantle outside of subduction zones [*Khan and Shankland*, 2010]. In actuality, hydration is likely variable both vertically and horizontally within the upper mantle [*Karato*, 2010a]. At a 137 continental scale, higher water contents are likely present in the western US than in the eastern

138 and central parts of the country due to the recent history of subduction across the region

139 [Humphreys et al., 2003]. At a finer scale, hydration is likely variable regionally due to

140 variations in geologic settings including lateral heterogeneity in slab dehydration [Dixon et al.,

141 2004], the extent of fluid introduction into the upper mantle during continental formation

142 [Selverstone et al., 1999], and post-formational processes such as cratonic rejuvenation [Rudnick

143 *et al.*, 1998; *Carlson*, 2005; *Griffin et al.*, 2009; *Lee et al.*, 2011; *Eeken et al.*, 2018].

144 Compounding this uncertainty in the efficacy of hydration, mantle dehydration due to heating

and related volcanism is likely inconsistent across the continent. The results reported here should

146 help guide where expanded constraints on mantle hydration are imperative for better constraining

147 the thermal and viscosity structure of the upper mantle.

148

149 **RESULTS**

Results of the seismic temperature calculations show large variations in the thermal regimes within the upper mantle across the continental US. As expected, cooler temperatures are observed throughout the uppermost mantle within the tectonically quiescent eastern and central US relative to tectonically active western US (Figures 1, 2, and 3). The hottest temperatures and thinnest lithosphere within the western US correspond to regions of recent extension and/or hypothesized mantle upwelling.

Melt thermobarometry estimates are primarily for generation of recently emplaced basalts in the Snake River Plain, the Basin and Range/Colorado Plateau margins, and the Cascade Arc (Figure 3). We show results from all samples though a few give erroneous results that result in pressure estimates less than that at the Moho (e.g. the low-P CP sample in Figure 3). Pressure-

160 temperature estimates from the Snake River Plain and Colorado Plateau generally exhibit 161 relatively high equilibrium temperatures and deeper depths than those within the Cascades, even 162 before the higher water contents likely present under the Cascades are considered (Figures 3 and 163 4). Our seismically derived thermal estimates generally agree well with the melt 164 thermobarometry results (Figures 3 and 4). Where seismic geotherms do not agree with 165 thermobarometry estimates, it is often in places where sharp lateral changes in upper mantle 166 temperature occur (e.g. the edges of the Snake River Plain). In the seismic model, these 167 boundaries may appear gradational due to smoothing. At pressures > 2 GPa, the Plank and 168 Forsyth [2016] estimates plot closer to the 1300° C adiabat, likely because of the higher water 169 contents in those samples (> 2 wt. % for many) than the fixed value used here. When we assume 170 greater degrees of hydration (indicated by the horizontal error bars in Figures 3 and 4) the 171 temperature estimates are relatively consistent between our estimates and Plank and Forsyth 172 [2016]. In comparing our seismic estimates of temperature to basalt equilibrium estimates, it is 173 apparent that volatiles are required to produce melts at depth > 2 GPa, as few seismically derived 174 geotherms show conditions hot enough to match PT estimates for basalts containing 1.5 wt % 175 water. This is consistent with hydration of the upper mantle beneath the Colorado Plateau and 176 parts of the western US due to the dehydration of a flat-slab during present beneath the region 177 during the late Cretaceous/Early Cenozoic.

In our seismic results, thinned thermal lithosphere (< 100 km thick) is observed across much of the Basin and Range Province, beneath the Snake River Plain/Yellowstone hotspot trace, and in the backarc of the Cascade Mountains in Washington and Oregon (Figures 1 and 2). The thickest lithosphere (> 180 km thick) is observed in the central US where the cratonic core of the continent is located. The shear model used to derive temperatures only has resolution

183 down to ~ 200 km depth; as such, estimates of ~ 200 km are likely a minimum thickness for 184 thermal lithosphere in cratonic regions and are not well-constrained. Intermediate lithospheric thicknesses are observed along the eastern margin of the continent where rifting occurred during 185 186 the opening of the Atlantic Ocean in the Jurassic. A west-east cross section of temperature across 187 the continent highlights these variations in temperatures and depth to the thermal LAB (Figure 188 2). These results agree with body-wave tomography results which show a high-velocity keel 189 beneath the cratonic region of North America that extends down to ~200 km depth [Schmandt 190 and Lin, 2014], and with previous temperature estimates for the uppermost mantle [Goes and van 191 der Lee, 2002; Schutt et al., 2018]. Thermal estimates also show slightly increased 192 temperatures/thinned thermal lithosphere along the eastern seaboard in the vicinity of New 193 England and western Virginia (Figure 1). These high temperature zones align with areas where 194 recent tectonism has been proposed [van der Lee et al., 2008; Mazza et al., 2014; Schmandt and 195 Lin, 2014; Menke et al., 2016].

Zones of partial melting were mapped by identifying regions where seismically derived geotherms exceed the predicted pressure-dependent solidus for peridotite with 75 ppm water.
Figure 3 shows the maximum difference between the seismically derived temperature estimates and the peridotite solidus at all depths for gridpoints using the parameterization of Katz et al.
[2003]. Results show that partial melt is likely present within the mantle across much of the western US, where thin lithosphere is observed, and absent within the eastern and central US where the lithosphere is thicker.

Within the western US, the LAB may be defined by a zone of significant partial melting,
which would lower both mantle viscosity and, if enough partial melt were present, seismic
velocities. This sharp velocity gradient would result in a relatively sharp LAB conversion in

206 receiver functions. Basaltic volcanism in the western US is most commonly observed within the 207 Basin and Range province where widespread extension, large-scale mantle upwelling, and small-208 scale convection have been proposed, and within the Snake River Plain where mantle upwelling 209 associated with the Yellowstone hotspot is driving volcanism. In the eastern and central US, 210 melts are predicted to be absent at the LAB for mantle containing 75 ppm water and the 211 transition from lithosphere to asthenosphere may involve a gradual transition in viscosity. 212 A cross section of geothermal gradient highlights the varying temperature regimes within 213 the upper mantle across the continental US (Figure 2). Higher gradients (> 2° C/km) are 214 observed within the thermally defined (< 1300° C) lithospheric mantle than within areas mapped 215 as asthenosphere (> 1300° C). These variations are consistent with conduction as the dominant 216 mechanism of heat transfer in the lithosphere and advection or convection as the dominant 217 mechanisms of heat transfer in the asthenosphere (Figure 2). In a few locations in the western 218 US, low geothermal gradients are observed in regions where observed mantle temperatures are 219 below 1300° C. Low gradients in these regions can be explained by uncertainty in the model 220 and/or the presence of partial melt in these regions (Figure 2), which would likely allow for 221 advective heat transfer. It is also possible that partial melting of these regions may lower the 222 viscosity of the mantle enough for convective heat transfer to occur. In these cases, the 1300° C 223 isotherm would likely be an inaccurate proxy for rheological lithospheric thickness.

224

225 **DISCUSSION**

226

Nature of the Lithosphere-Asthenosphere Boundary

In this work, we show that upper-mantle thermal conditions within much of the western US are near or above the solidus for partially hydrated peridotite (Figure 2), consistent with the

229 hypothesis that partial melt may play a role in controlling the thickness of mantle lithosphere in 230 this region [Hopper and Fischer, 2018]. The presence or absence of partial melt in the upper 231 mantle may influence how the rheological LAB, which separates viscous lithosphere from the 232 lower viscosity asthenosphere [e.g. Fischer et al., 2010], is observed seismically. In the western 233 US, Sp receiver function work shows a laterally extensive high-amplitude negative conversion 234 interpreted as the LAB, which can be explained by the presence of partial melt at this boundary 235 and an abrupt boundary between lithosphere and asthenosphere [Abt et al., 2010; Hopper and 236 Fischer, 2018]. In the central cratonic US, mid-lithosphere seismic discontinues are observed in 237 receiver functions, however, there is no conversion that can be clearly associated with the LAB. 238 This lack of a clear boundary is consistent with a gradual transition from lithosphere to lower-239 viscosity asthenosphere in these regions [Abt et al., 2010; Hopper and Fischer, 2018]. Within the 240 eastern US, receiver function amplitudes are consistent with partial melt at the LAB [Hopper and 241 Fischer, 2018], however, we do not observe temperatures high enough to result in melting 242 without volatile addition (Figure 4).

243 Based on our seismically derived temperature estimates and the timing of tectonism, 244 extensive upper mantle melting is expected only in areas with recent thermotectonic activity. 245 This is highlighted in Figure 4 which shows geotherms taken from our model at gridpoints 246 located at 1° latitude and longitude intervals. These geotherms are shaded using the 247 thermotectonic age model of Porter et al. [2019], which is based on dating of surface volcanic 248 rocks. Of these geotherms, the 75 ppm solidus is only exceeded by those with nearby young (< 249 10 Ma) volcanism. Figure 4 highlights the importance of thinned lithosphere in the occurrence of 250 melting. In all but the hottest geotherms, melting with moderate hydration can only occur at 251 relatively shallow depths ($\leq \sim 100$ km) within the mantle. Given this constraint, partial melt is

likely to define and yield a sharp LAB, observable in receiver functions, within regions of
relatively thin and recently modified lithosphere or in areas carbonated and/or hydrated by
extensive metasomatism.

255 Carbon dioxide-assisted melting is hypothesized as a mechanism for controlling the LAB 256 by lowering the peridotite solidus in cratonic regions [*Tharimena et al.*, 2017]. The presence of 257 carbon dioxide (in addition to water) can significantly lower the peridotite solidus [Foley et al., 258 2009] and has been hypothesized as especially important for producing small-degree melting at 259 depth within the mantle beneath mid-ocean ridges [Dasgupta and Hirschmann, 2006]. Our 260 results are consistent with temperature exceeding the carbonated peridotite solidus at depths 261 between 100-180 km in cratonic regions. However, this depth is shallower than our thermally 262 derived LAB under the cratonic region of the US. Modeling work shows that, if the LAB is 263 defined rheologically, the viscosity contrast at this boundary is between 3 and 10 orders of 264 magnitude [Doglioni et al., 2011; Rolf et al., 2018]. To produce a velocity contrast of this 265 magnitude between a solid and partially molten rock, a melt fraction, φ , > 0.2 is required 266 [Kohlstedt and Hansen, 2015]. Such a melt fraction, even if arising from magma pooling, would 267 require widespread carbonization and/or hydration of the upper mantle to produce an extensive 268 region with this degree of melting. Because of this, we prefer a thermal rather than melt-related 269 explanation for the LAB under the cratonic US that results in a gradational boundary.

270

271 CONCLUSIONS

272 Results from this work highlight the varied thermal states of the upper mantle across the 273 continental US and shed insight into the nature of the lithosphere-asthenosphere boundary within 274 the region. In our measurements, we observe hotter temperatures and zones of extensive melting

275	in the western US that are absent in the central and eastern US. These zones of mapped melts
276	align well with recently emplaced basalts at the surface. Melt within the tectonically active
277	western US likely defines the LAB while this is less likely in cratons where melts would only
278	form in zones of concentrated metasomatism.
279	
280	ACKNOWLEDGMENTS
281	This work was funded by NSF Award EAR-1829520. Seismic data were collected as part
282	of the EarthScope experiment and downloaded from the IRIS DMC.
283	
284	DATA AVAILABILITY STATEMENT
285	Data from the TA network were made freely available as part of the EarthScope USArray
286	facility, operated by Incorporated Research Institutions for Seismology (IRIS) and supported by
287	the National Science Foundation, under Cooperative Agreements EAR-1261681. No new data
288	were collected as part of this work, the seismic data used can be accessed at:
289	https://ds.iris.edu/ds/nodes/dmc/. The geochemical data are available at:
290	www.earthchem.org/portal.
291	

292 FIGURE CAPTIONS





Figure 1. Map of depth to the 1300° C adiabat, which is interpreted as the base of the thermal
lithosphere. Bold lines are physiographic provinces modified from Fenneman [1917]. Thick
dashed line denotes the Grenville Front and eastern limit of Cordilleran strain [*DeCelles*, 2004; *Whitmeyer and Karlstrom*, 2007]. Line X-X' shows the location of the cross section in Figure 2.
Hill shade shows topography.



300 Figure 2. Thermal profiles along line X-X'. Panel A shows seismically derived upper mantle 301 temperature estimates. The dashed black line is where the modeled temperatures reach the 1300° 302 C adiabat, which we interpret as the thermal LAB. The thin blue lines are the estimated solidi 303 assuming anhydrous conditions (dark blue), 75 ppm water (medium blue), and 150 ppm water 304 (light blue). Melt is expected in the regions above these curves. Diamond are basalt melt 305 equilibrium P-T conditions from this study. Fill colors indicate temperature estimates. Stars are 306 P-T conditions from Plank and Forsyth [2016] and squares are from Klöcking [2018]. Panel B 307 shows smoothed geothermal gradient for cross section X-X'. Higher geothermal gradients are 308 observed in cratonic areas with thick lithosphere relative to areas of thinned lithosphere. Dashed 309 line is the thermal LAB.

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311





the location, temperature and pressure of melt thermobarometry data. Black regions are mapped
Pliocene and younger volcanic units from the Decade of North American Geology: Geologic
Map of North America [*Reed et al.*, 2005]. Physiographic provinces modified from Fenneman
[1917]. Inset shows the melt equilibrium estimates (diamonds) and the closest seismically
derived geotherm (dotted lines) from the Colorado Plateau (blue) and Snake River Plain (red).
The spread in Snake River Plain seismic geotherms is due to the sharp boundaries of the
province.





Figure 4. Pressure-temperature plots of seismic and basalt melt equilibrium data. Dotted lines are seismically derived geotherms for the continental US taken at 1° intervals. Geotherms colors are based on thermotectonic age for their location using the model of Porter et al. [2019]. Orange diamond are basalt melt equilibrium P-T conditions from this study. Error bars show the effects of varying water contents between 0.5 wt % and 3 wt % on temperature (horizontal) and pressure (vertical) for each sample. Blue stars are P-T conditions from Plank and Forsyth [2016]. Solid

331	black line is the solidus and labeled dashed contour lines are melt fractions based on Katz et al.
332	[2003] for 75 ppm water in the upper mantle. The sub-vertical dashed black line is the 1300° C
333	adiabat. Background shading and additional lines are CO ₂ solidi modified from Foley et al.
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