

D'' reflection polarities inform lowermost mantle mineralogy

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Abstract

Polarities of seismic reflections at the discontinuity atop the D'' region (PdP and SdS) indicate the sign of the velocity contrast across the D'' reflector. Recent studies found PdP polarities matching and opposite those of P and PcP. While anisotropy could explain this behavior, we find that the ratio of the change in S-wave velocity over change in P-wave velocity (R-value) can influence polarity behavior of D'' reflected P-waves. For R-values exceeding 3 the P-wave reverses polarity in the absence of anisotropy while S-wave polarity is not influenced by the R-value. Using sets of 1 million models for normal mantle and MORB with varying minerals and processes across the boundary, we carry out a statistical analysis (Linear Discriminant Analysis) finding that there is a marked difference in mantle mineralogy to explain R values larger and smaller than 3, respectively. Based on our results we can attribute different mineralogy to a number of cases. In particular, we find that when velocities increase across D'' and polarities of PdP and SdS are opposite the post-perovskite phase transition is still the best explanation while MORB is the best explanation when PdP and SdS are the same. When the velocities are decreasing, the post-perovskite phase transition within MORB is the best explanation if PdP and SdS polarities are the same but if PdP and SdS are opposite in regions of velocity decreases, our results indicate that primordial material or mantle enriched in bridgmanite can explain the polarity behavior, further constraining mineralogy within the LLSVPs.

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1 **D" reflection polarities inform lowermost mantle mineralogy**

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14 **Key Points:**

- 15 • Ratio (R) of S- over P-wave velocity changes (%) controls polarity of P-wave reflections
16 at D" reflector.
- 17 • Thermochemical modelling and statistical analysis show specific minerals contributing to
18 large R values.
- 19 • Polarity observations indicate that part of the Pacific LLSVP is due to bridgmanite
20 enrichment.

21

22

Abstract

Polarities of seismic reflections at the discontinuity atop the D" region (PdP and SdS) indicate the sign of the velocity contrast across the D" reflector. Recent studies found PdP polarities matching and opposite those of P and PcP. While anisotropy could explain this behavior, we find that the ratio of the change in S-wave velocity over change in P-wave velocity (R-value) can influence polarity behavior of D" reflected P-waves. For R-values exceeding 3 the P-wave reverses polarity in the absence of anisotropy while S-wave polarity is not influenced by the R-value. Using sets of 1 million models for normal mantle and MORB with varying minerals and processes across the boundary, we carry out a statistical analysis (Linear Discriminant Analysis) finding that there is a marked difference in mantle mineralogy to explain R values larger and smaller than 3, respectively. Based on our results we can attribute different mineralogy to a number of cases. In particular, we find that when velocities increase across D" and polarities of PdP and SdS are opposite the post-perovskite phase transition is still the best explanation whereas MORB is the best explanation when PdP and SdS are the same. When the velocities are decreasing, the post-perovskite phase transition within MORB is the best explanation if PdP and SdS polarities are the same but if PdP and SdS are opposite, our results indicate that primordial material or mantle enriched in bridgmanite can explain the polarity behavior, further constraining mineralogy within the LLSVPs.

Plain Language Summary

The polarities of seismic waves (P and S) reflecting at structures in the Earth's mantle indicate seismic velocity changes across those structures. For the lowermost mantle reflector (called D" reflector, approx. 300 km above the core-mantle boundary), a velocity increase for P- and S-waves across the boundary generates a polarity that is the same for the main wave and the core-reflected wave. If, however, the percentage change of the velocity of the S-wave increases at least three times as much as that of the P-wave velocity (expressed as the R-value, the ratio dV_s/dV_p), the polarity of the D"-reflected PdP wave changes polarity, becoming opposite to both the main P-wave and the reflection from the core-mantle boundary below it. Here we analyse sets of one million models with variable compositions of mantle material and mid-ocean ridge basalt and use an advanced statistical method to identify those combinations of minerals that produce large positive R-values. Two scenarios are distinguished: P- and S-velocity both increasing, and both decreasing. In each of these, the reflected P-wave polarity can be either the same as, or opposite to, the S-wave polarity, yielding four cases in total. We find that previous explanations for three of these cases concur with our analysis. However, for regions where velocities decrease over the D" reflector but polarities of P and S-wave reflections are opposite, our analysis shows that enrichment with the lower-mantle mineral bridgmanite is mainly responsible for the observed polarity behaviour. This suggests that for regions such as large low-velocity anomalies in the lowermost mantle, primitive or bridgmanite-enriched material is the preferred explanation. More generally, this study shows that waveforms and polarities of seismic waves are useful in constraining lowermost mantle mineralogy.

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65 1 Introduction

66 The lowermost mantle of the Earth, the D" region (Bullen, 1949), is characterised by a range of
67 seismic structures that have been studied with a variety of seismic methods, in order to
68 understand their formative processes and mineralogy in the deep Earth (for overviews, see
69 Garnero, 2000; Lay, 2015). One prominent feature of the lowermost mantle is a seismic
70 discontinuity at the top of the D" region that generates reflections for S- and P-waves (see
71 reviews by Wysession et al., 1998; Lay, 2015; Cobden et al., 2015; Jackson and Thomas, 2021).
72 Several explanations for this reflector at the top of D" have been discussed, such as subducted
73 slabs (e.g., Lay and Garnero, 2004), scatterers (Scherbaum et al., 1997), and the post-perovskite
74 phase transition (e.g., Murakami et al., 2004; Oganov and Ono, 2004; Tsuchiya et al., 2004;
75 Shim, 2008).

76
77 The D" reflector has been found in many regions at approximately 300 km above the CMB,
78 constrained mostly by travel times of the reflected waves off the top of D" (Lay and Helmberger,
79 1983; Weber, 1993; Wysession et al., 1998; Cobden et al., 2015) with depth variations of about
80 ± 100 km. But whereas in the past travel times of seismic data were most commonly used for
81 studying the reflector, recently wave amplitudes and polarities have also been used to extract
82 details about D" structures (e.g., Cobden and Thomas, 2013; Thomas et al., 2011; Thorne et al.,
83 2007; Pisconti et al., 2019). For example, complexity in waveforms can indicate layering (e.g.
84 Moore et al., 2004; Thomas et al., 1998; Rost et al., 2005; Schumacher et al., 2018), and wave
85 amplitude behaviour has provided information on attenuation (e.g., Lay and Helmberger, 1981;
86 Cormier, 1982) or gradients of seismic reflectors in the Earth (e.g., Lay, 2008; Weber 1993). In
87 addition, polarities of seismic waves can provide information about velocity and density
88 variations, i.e., the impedance contrast, across a reflector (Zoeppritz, 1919).

89
90 Previous work on D" reflections (e.g., Weber, 1993; Lay and Helmberger, 1983; Cobden et al.,
91 2015; Cobden and Thomas 2013) has shown that the polarities of these reflected P- or S-waves
92 correlate with the velocity jump across the reflector. This means that for a P-wave velocity
93 increase across D", the reflection off this layer (PdP, see Figure 1a) will show the same polarity
94 as both the direct P-wave travelling above it and PcP, the P-wave reflection off the core-mantle
95 boundary. The same is true for S-waves. Lay et al. (2004) stated that the density has little
96 influence on amplitudes of the reflected waves at epicentral distances exceeding 60 degrees,
97 therefore models have often been calculated based only on the change in V_p and V_s (e.g., Lay
98 and Helmberger, 1983; Young and Lay, 1990; Weber, 1993). The magnitude of the velocity
99 jump is generally determined by comparing the observed amplitude of the reflected wave with
100 synthetic predictions, often using 1D modelling (e.g. Weber 1993; Lay and Helmberger, 1983).
101 The estimated wave-velocity jumps usually range from 1-3%, but can occasionally reach 5%
102 (Bréger and Romanowicz, 1998; Thomas and Laske, 2015).

103
104 Interestingly, recent observations of PdP-wave polarities have in some cases shown opposite
105 polarities to PcP- and P waves (e.g., Thomas et al., 2011; Hutko et al., 2008; Pisconti et al.,
106 2019), which would suggest a seismic velocity reduction across the reflector, while SdS waves in
107 these regions show polarities that agree with S and ScS, indicating a positive velocity jump
108 across D" (e.g., Chaloner et al., 2009; Cobden and Thomas, 2013; Thomas and Laske, 2015).
109 This discrepancy between PdP and SdS polarities excludes a purely thermal origin, since one
110 would expect both velocities to increase given a temperature reduction. The mineral phase

111 transition of bridgmanite to post-perovskite in MgSiO₃ (Murakami et al., 2004; Oganov and
112 Ono, 2004; Shim et al., 2004; Tsuchiya et al. 2004), which occurs near the core-mantle boundary
113 (CMB), has been shown in theoretical mineral physics calculations to be potentially associated
114 with a small change in P wave-velocity (which can be either positive or negative) and a larger
115 increase (of up to 3%) in S wave-velocities (Wookey et al., 2005; Tsuchiya and Tsuchiya, 2006;
116 Wentzcovitch et al., 2006; for a compilation of published wave velocity changes in D" related to
117 the post-perovskite phase transition, see Cobden et al., 2015). Hence the presence of post-
118 perovskite could potentially explain these discrepant PdP- and SdS polarity observations. In
119 other regions, however, the PdP wave exhibits the same polarity as P and PcP, while SdS also
120 shows the same polarity as S and ScS (Weber, 1993; Thomas et al., 1997; Cobden and Thomas
121 2013). This would make pure MgSiO₃ post-perovskite (Wookey et al., 2005) an unlikely
122 explanation for the D" reflector in those places (e.g., Cobden and Thomas, 2013), but the latter
123 could still be caused by post-perovskite if the P-wave velocity change is positive across the
124 phase transition (e.g., Tsuchiya and Tsuchiya, 2006).

125

126 It has been shown (Thomas et al., 2011; Pisconti et al. 2019) that in some areas P-wave polarity
127 depends on the direction of wave propagation (i.e., azimuth) and that deformation, i.e.,
128 anisotropy in D", can change the polarity of P-waves and potentially also S-waves (Thomas et
129 al., 2011; Creasy et al., 2019; Pisconti et al., 2019). To our knowledge, array observations of SdS
130 waves with an opposite polarity to S and ScS have not been reported, but stacks of seismic data
131 (e.g., Lay et al., 2006) and inversions (Kawai and Geller, 2010; Konishi et al., 2009) suggest that
132 velocity decreases for S-waves also exist. Using azimuthal as well as distance dependence of the
133 polarities of P- and S-wave D" reflections can help to further constrain mineralogy in D"
134 (Creasy, et al., 2019; Pisconti et al., 2019, 2022).

135

136 Most aforementioned observations have been made in regions where tomographic inversions
137 suggest above-average velocities (Ritsema et al., 2011; Hosseini et al., 2018, 2020; Li et al.,
138 2008). If deep subduction is responsible for the D" reflector in these cases, a post-perovskite
139 phase transition would be a good explanation, since post-perovskite would preferably be found in
140 colder mantle regions (e.g. Hernlund et al., 2005; Cobden and Thomas, 2013; Cobden et al.,
141 2015). Moreover, this would also agree with the mineralogical best fit for anisotropy in post-
142 perovskite (Pisconti et al., 2019; Creasy et al., 2019; Romanowicz and Wenk, 2017; Thomas et
143 al., 2011).

144

145 For regions associated with below-average wave speeds, it has been suggested that observations
146 of PdP and SdS reflections may not be due to a simple Mg-bridgmanite to post-perovskite phase
147 transition, due to the positive Clapeyron slope of the phase transition (Murakami et al., 2004;
148 Oganov and Ono, 2004), and the possibility that slower-than-average regions may be warmer
149 (e.g. Hernlund et al., 2005). However, when this phase transition takes place in Fe- and Al-
150 bearing bridgmanite, or in a multi-mineral assemblage, then the depth and strength of the
151 discontinuity can change, as well as introducing a broad depth interval over which the transition
152 occurs (e.g. Grocholski et al., 2012, Catalli et al., 2009, Cobden et al., 2015, Hernlund, 2010,
153 Kuwayama et al., 2022), even moving the phase transition to pressures inside the core. A broad
154 phase transition region may make observations of the seismic reflector off this phase transition
155 more difficult to observe since it results in small amplitudes of D" reflected waves. Interestingly,
156 in some of these low-velocity regions, P (and S, respectively) wave reflections off D" show the

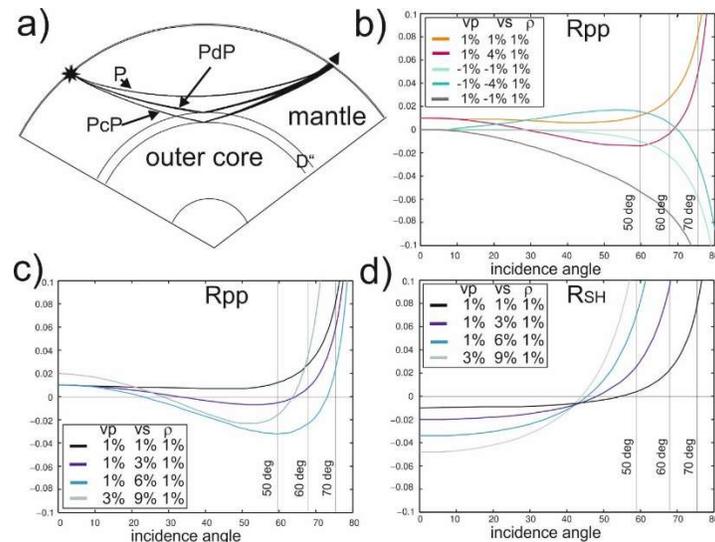
157 same polarity as the direct P-wave (S) and core reflected PcP wave (ScS). This indicates an
 158 increase in seismic wave velocity across D", even though a tomographic model might suggest
 159 slow wave velocities regionally, which would lead to an opposite polarity for a reflection from
 160 these regions (e.g. Jackson and Thomas, 2021, Cobden et al., 2013). However, one should be
 161 cautious when comparing D" reflection points with tomographic models in detail, since the latter
 162 is concerned with large-scale lateral variations in wave velocity, and a lack of model resolution
 163 and other uncertainties limit the interpretation of structures at the relatively small length scale of
 164 D" reflection points. Also, lateral homogeneity in a tomography model does not preclude vertical
 165 changes in wave velocity.

166
 167 In summary, polarity observations of P and S-waves reflecting off the D" region seem variable,
 168 and while anisotropy could potentially explain these variations, here we investigate whether an
 169 alternative explanation could also produce polarity changes of D" reflections.

170
 171 **2 Modelling of polarities**
 172

173 The reflection coefficient is controlled by the impedance contrast (density \times velocity) for P- and
 174 S waves across a discontinuity, and the angle of incidence of the wave at the discontinuity
 175 (Zoeppritz, 1919, see also descriptions and approximations in Aki and Richards, 1980; Bortfeld,
 176 1961). The amplitudes of reflected and transmitted waves for an incoming P- or S-wave are
 177 governed by the velocities of P- and S-waves, by density (impedance) contrasts and also ratios of
 178 P- and S-wave velocities above and below the boundary. For a reflection off the top of the
 179 discontinuity, the reflection coefficient will, for sufficiently large angles of incidence, enter the
 180 overcritical range (e.g., Weber, 1993), causing a phase change and strongly enhancing the
 181 amplitude of the reflection (see Figure 1b-d). For this reason, most previous D" reflection studies
 182 favour a distance range of 65 to 85 degrees (e.g., Wysession et al., 1998; Lay, 2015; Cobden et
 183 al., 2015 for reviews) to benefit from large amplitudes.

184



185
 186 *Figure 1: a) wave paths of P waves, the reflection off the D" discontinuity PdP, and PcP, the*
 187 *CMB-reflected phase. Same paths for S, SdS and ScS. b) Reflection coefficient for P to P*
 188 *reflections (Rpp) at the D" discontinuity with variable changes in Vp, Vs and density across the*
 189 *reflector as given in the legend. c) Same as for b but for different (but only positive) values of the*

190 *changes in V_p and V_s across D'' . d) Same as c) but for SH to SH reflection coefficient (R_{SH}). The*
 191 *distance corresponding to the incidence angle at the discontinuity is given by the vertical lines in*
 192 *b, c, and d.*

193

194 To investigate polarities of D'' reflections (PdP and SdS, Figure 1a), we vary P- and S-wave
 195 velocity jumps (dV_p and dV_s) as well as the density jump across the boundary, compute the
 196 reflection coefficient for P and SH wave reflections. We verify the results using three different
 197 methods (Reflectivity method, Müller, 1985; Zoeppritz explorer (Crewes Explorer programs
 198 2022) and Javascript solver for Zoeppritz equations (Frederiksen 2022). For completeness we
 199 also tested converted waves (PdS and SdP waves) and SV reflections, although those have not
 200 been used extensively for D'' studies. We express the velocity changes of V_p and V_s through the
 201 (R)atio of percent V_s change over percent V_p change, the so-called R-value (similar to the
 202 concept of R in seismic tomography, e.g., Masters et al., 2000; Karato and Karki, 2001;
 203 Koelemeijer et al., 2016). Thus a 1% change in V_p in combination with a 3% change in V_s would
 204 yield an R-value of 3.

205

206 We confirm that for the distance ranges often used for D'' reflection observations (65-85 degrees
 207 distance), which correspond to incidence angles above 70 degrees (Figure 1b-d), a velocity
 208 increase in V_p produces the same polarity as that of P and PcP (and ditto for S-waves). However,
 209 we find that from an R-value of 3, which means that the %-change of V_s is at least 3 times that of
 210 the %-change of V_p , the reflection coefficient for the P-wave becomes negative for part of the
 211 incidence angle range (Figure 1b and 1c). The size of the reflection coefficient increases with
 212 increasing P-wave velocity jump (blue and grey lines compared with black line in Fig 1c), but
 213 the R-value determines whether for part of the incidence angle range the P-wave reflection
 214 coefficient becomes smaller than zero, resulting in a PdP wave polarity opposite to that of P and
 215 PcP (black line versus blue and grey lines in Figure 1c). The same is true for P-wave reflection
 216 coefficients for negative V_p and negative V_s changes (Figure 1b).

217

218 However, if either V_p or V_s increases while the other velocity decreases, this effect does not
 219 occur. Taking the case of a small P-wave velocity reduction with an S-wave velocity increase
 220 (negative R-value, dark grey line in Figure 1b), as is expected for the bridgmanite to post-
 221 perovskite phase transition in $MgSiO_3$ (e.g., Wookey et al., 2005), this yields a PdP-wave
 222 polarity opposite to that of P waves, as expected for velocity reductions, but no polarity change
 223 over the entire incidence angle range occurs for all R-values. But such a case of opposite changes
 224 for P- and S-wave contrasts causes amplitudes to be slightly larger than for changes with the
 225 same signs (see also Cobden et al., 2015).

226

227 Due to the reflection coefficient becoming negative for part of the incidence angle range, as
 228 shown in Figure 1b-d, the reflection coefficient also has up to two angles (Brewster angles, in
 229 analogy to optics, Yang et al., 2021; Tatham and Kreil, 2012; Červený, 2001) where no P-wave
 230 is reflected in case of an incident P-wave. The same is true for an incident S-wave, however,
 231 only one Brewster angle is usually found there (e.g., Müller, 2007, Červený, 2001). Waves do
 232 behave non-intuitively at interfaces (see also Malcolm and Trampert 2011; Sollberger et al.,
 233 2017), so it is not straightforward to explain the physical reason behind the behaviour of
 234 reflection coefficients, but it is likely that it arises due to the interaction (and production) of the

235 SV wave at the interface, as well as the reflected and transmitted P-wave, together with the
236 relevant boundary conditions (Červený, 2001).

237

238 Looking at the SH-wave reflection coefficient, we find that an R-value smaller or larger than 3
239 does not affect the polarity of the S-wave reflection much in the distance range used for
240 observing D" reflections; it mostly changes the amplitude of the wave (Figure 1d) and, to a small
241 degree, the incidence angle at which the polarity change occurs, which always happens for the S-
242 wave reflection coefficient (e.g., Müller, 2007). The S-wave reflection coefficient shows a
243 polarity change for incidence angles smaller than 50 degrees, which translates into small
244 epicentral distances (< 40 to 45 degrees, depending on P and S-velocity changes, see Figure 1d),
245 so usually it is not tested for D" studies. For the larger epicentral distances often used in D"
246 studies (i.e. 65 degrees and above), the SdS-wave will therefore always show a polarity that is
247 the same as the S-wave for velocity increases. We also found that that PdS and SdP waves and
248 vertically polarised SdS waves show no change in polarity with varying R-values, only a change
249 in the size of the reflection coefficient, leading to amplitude changes of the waves. Thus, we
250 concentrate in the following on the polarity behaviour of PdP waves only.

251

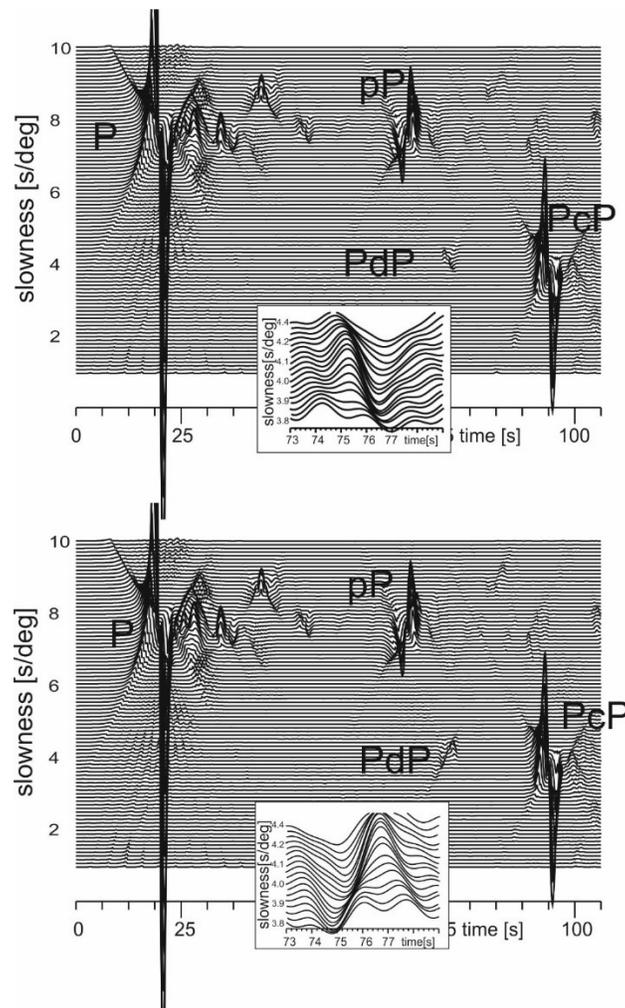
252 So far, we have only looked at changes in V_p and V_s . Lay et al. (2004) mention that the density
253 has little effect on the amplitude of the reflected wave and therefore on the reflection coefficient
254 for epicentral distances of 70 degrees and larger, and in our studies this is indeed the case, even
255 for large R-values. Regarding smaller distances, the change in density does not influence the
256 incidence angle at which the reflection coefficient changes polarity, but it does affect the
257 amplitude of the wave at short incidence angles, i.e., at distances below 10-20 degrees.

258

259 For R-values of 3 and 4, the epicentral distance that corresponds to the incidence angle at which
260 the PdP wave reverses polarity is smaller than that used in most studies, and only short-distance
261 data of 40 to 65 degrees would allow detection of this reflection coefficient polarity behaviour
262 (Figure 1b). Few observed steep-angle D" reflections have been reported so far (e.g., Schimmel
263 and Paulssen, 1996 (using S-waves), Thomas and Laske, 2015 (using P-waves)), mostly because
264 the amplitudes are so small that the reflections have to be detected using stacking methods (e.g.,
265 Weber 1993; Thomas et al., 2004a,b; Kito et al., 2007; Cobden and Thomas 2013). Increasing
266 the size of the R-value shifts the transition from a negative to a positive reflection coefficient
267 (i.e., from opposite to same polarity of PdP with respect to P) to larger epicentral distances,
268 allowing this behaviour to also be observed at larger distances; however, very large R-values (R
269 > 5) may be unrealistic for the Earth.

270

271



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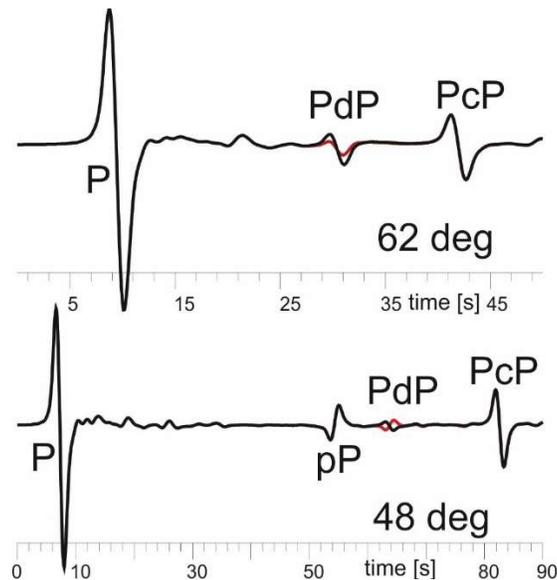
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274 *Figure 2: 4th root vespagrams for two synthetic data examples: top: an R-value of 2, bottom: an*
 275 *R-value of 6. The insets show the PdP wave for a better comparison with P and PcP waveforms*
 276 *and polarities. The arrival at 75 sec with P-slowness is the pP wave.*

277

278 The behaviour of the reflection coefficient allows us to test the ratio of changes in P-velocity
 279 versus S-velocity, which may help to constrain the mineralogy of the D" region and the cause for
 280 the observed D" reflector. But because the reflection coefficient is very small, it is necessary to
 281 test whether a D" reflection would still be visible in seismic data. To confirm our reflection
 282 coefficient findings, we use the reflectivity method (Müller, 1985) to generate synthetic data for
 283 R-values larger and smaller than 3. Since PdP arrivals are usually small in a seismogram, we
 284 generate 4th root vespagrams (e.g., Davies et al., 1971; Muirhead and Datt, 1976; Rost and
 285 Thomas, 2002; Schweitzer et al., 2002) in which these arrivals can be detected and distinguished
 286 by their slowness values. Vespagram processing has been used in many studies to detect P- and
 287 S-wave reflections off the D" discontinuity (e.g., Weber, 1993; Thomas and Weber, 1997; Kito
 288 et al., 2007; Thomas et al., 2004a,b; Cobden and Thomas, 2013, Piscconti et al., 2019). Figure 2a
 289 shows an example vespagram for synthetic data generated by a model with a velocity increase
 290 across D" and an R-value of 2. Contrastingly, Figure 2b shows a vespagram for a model with a
 291 velocity increase across D" and an R-value of 6. The inset shows the PdP wave; one can clearly

292 see that the polarity of PdP of Figure 2b is opposite to that of P and PcP, while in Figure 2a the
 293 PdP polarity is the same as that of P and PcP. The vespagrams are generated for stations in an
 294 epicentral distance of 45 to 52 deg. To demonstrate that the change in polarity is distance-
 295 dependent, Figure 3 shows the traces for 62 and 48 degrees for the case of an R-value of 1 (black
 296 curve) and an R-value of 4 (red curve). The wave at 48 degrees arriving at 52 s is the depth phase
 297 pP, which can be distinguished by its slowness in the vespagram in Figure 2.
 298



299
 300
 301
 302 *Figure 3: Seismogram section for the model with R-value of 2 (black line) and R-value of 6 (red*
 303 *line) for two different distances, indicating the distance dependency of the polarity reversal. The*
 304 *P and PcP waves are clearly visible in both examples, the arrival at 52 sec in the seismogram*
 305 *for 48 deg is the pP wave.*

306 307 **3 Comparison with Data**

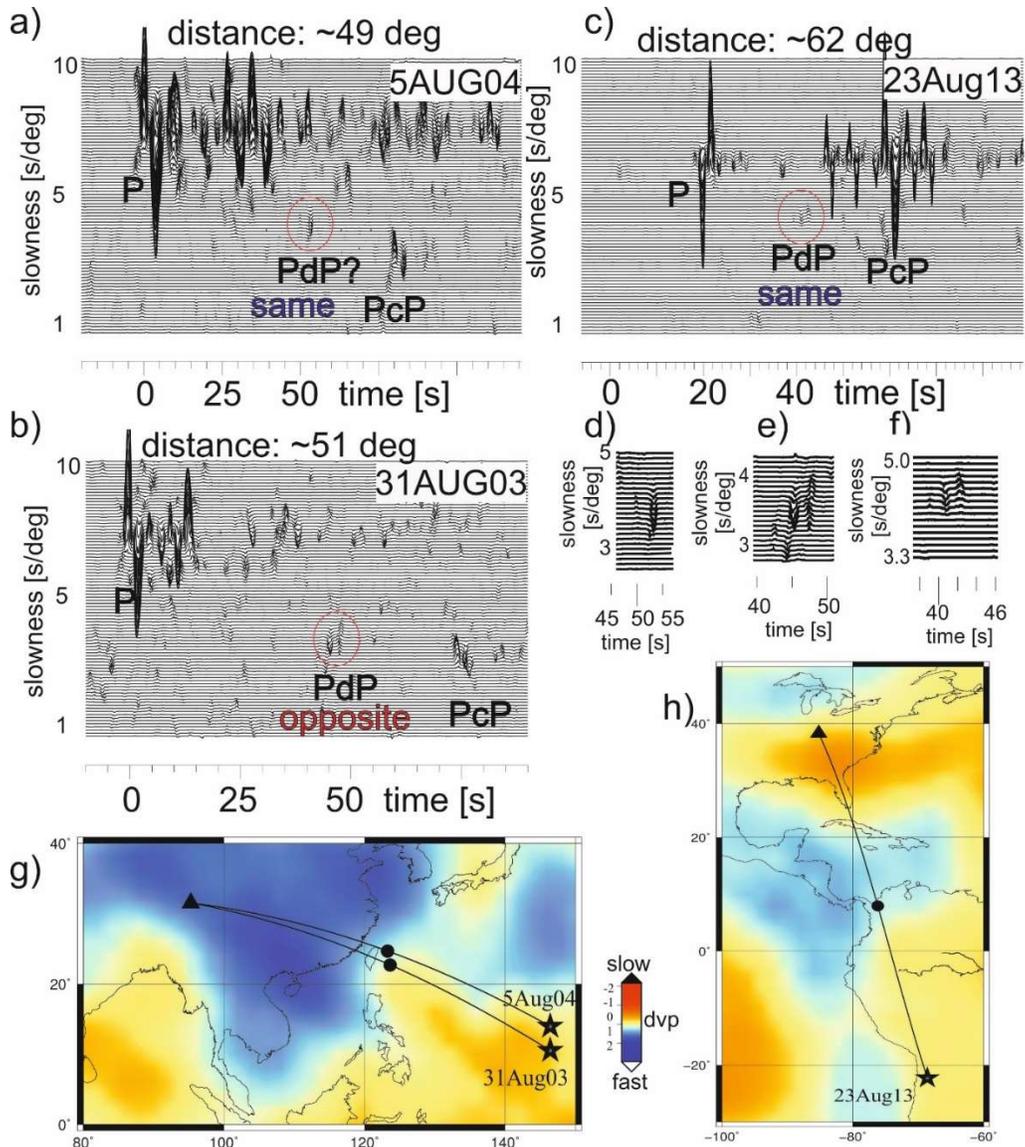
308
 309 Our modelling shows that an observation of the effect of R-values larger than 3 on seismic
 310 polarities is theoretically possible. We searched the literature for evidence of published R-values
 311 greater than 3 in the lower mantle, but found most published velocity ratios for the D" region in
 312 the range of 1 to 3, where a ratio of 3 is often interpreted as melt (Williams and Garnero, 1996;
 313 Jackson and Thomas, 2021; Dobrosavljevic et al., 2019, Rost et al., 2005). Tomographic
 314 inversions show R-values ($d \ln V_s / d \ln V_p$ in this case) of up to 5 in the lowermost mantle
 315 (Koelemeijer et al., 2016, 2018) and even higher (Cobden et al., 2012). Mineralogically, R-
 316 values larger than 3 are possible (Deschamps & Trampert, 2003; Hernlund & Houser 2008;
 317 Cobden et al., 2012; Karato and Karki, 2001) and should generate polarity reversals for part of
 318 the distance range. In fact, high P-T experiments suggest that for Fe-rich (Mg,Fe)O, the R-value
 319 could be up to 6-9 if Reuss-bound mixing models are employed (e.g., Dobrosavljevic et al.,
 320 2019). It is therefore necessary to assess the polarity of PdP waves at short distances in real data,
 321 to verify our modelling results.
 322

323 Most PdP wave reflections have been detected for large epicentral distances (larger 60 degrees)
324 and cases of opposite as well as the same PdP polarity compared with the main phases (PcP and
325 P) have been found. In contrast, most SdS reflections seem to have the same polarity as ScS and
326 S, except for the Pacific (Lay et al., 2006; Ohta et al., 2008). An overview of previously
327 observed polarities for PdP waves can be found in Cobden and Thomas (2013) or Cobden et al.
328 (2015). A recent study (Pisconti et al., 2019) detected PdP and SdS waves beneath the Central
329 Atlantic near the edge of the large velocity anomaly beneath Africa. In their work, the PdP waves
330 for shorter distances showed opposite polarities with respect to P, while the SdS-waves had the
331 same polarity as S for all distances. This polarity behaviour is possible for an R-value exceeding
332 3, but is more likely for an R-value of about 5, since the angle of incidence at which the polarity
333 changes sign (Fig. 1) occurs at larger epicentral distances for $R = 5$ than for $R = 3$. Pisconti et al.
334 (2019) showed that deformation of post-perovskite, i.e., anisotropy, could be responsible for
335 those variations in polarity of PdP, especially since they also used splitting measurements for the
336 same region. It would be of interest to investigate a crossing path for this particular region to test
337 their interpretation of anisotropy versus the possibility of large R-values.

338
339 To examine other locations, we collected data from a number of seismic arrays to find D"
340 reflections at short distances (between 40 and 60 degrees) where we would expect a change in
341 polarity of PdP if the R-value is larger than 3. Despite a large number of source-receiver
342 combinations, we found only a small number of events that show an additional arrival in
343 vespagram analysis (e.g., Rost and Thomas, 2002; Schweitzer et al., 2002) with a slowness and
344 travel time that agree with a D" reflection. Since reflection coefficients for the selected distance
345 range of 40-60 degrees are small (Figures 1), the reflection is often very small in the vespagram
346 or might be buried in noise. Nevertheless, we were able to find a few cases where the polarity of
347 the D" reflection can be extracted and compared with PcP and P (Figure 4). We verify that the
348 D" reflections travel in plane by performing slowness-backazimuth analyses, as shown for one
349 example event in Figure S1. It is possible that reflections that travel out-of-plane could arrive
350 with an opposite polarity due to the radiation pattern or reflections at different structures, i.e., not
351 D" (Schumacher and Thomas, 2016; Schumacher et al., 2018; Rochira et al., 2022), therefore, in
352 our study, we ensure that all waves travel in plane.

353
354 Two examples of D" reflections shown are from events in the Mariana region, detected at an
355 array in Tibet (Tables S1 and S2), for which the distances are 49 and 51 degrees. One of these D"
356 reflections, located beneath the western Pacific, shows a polarity that is the same as PcP and P
357 (Figure 4a, d), while the other shows an opposite polarity (Figure 4b, e). The region in D" where
358 these two events reflect is associated with high to average P-wave velocities in most
359 tomographic models (e.g. Hosseini et al., 2020; Simmons et al., 2010), or a change from high- to
360 low velocity as shown in Figure 4g for the tomographic model of Li et al. (2008). The third data
361 example in Figure 4 is an event in Chile recorded at the Transportable Array (TA) stations in
362 Kentucky (Tables S1 and S2), with an epicentral distance of 62 degrees. The vespagram of this
363 event shows a reflection with the same polarity as P and PcP (Figure 4c, f). This event is
364 reflecting in an area characterised by past subduction (Figure 4h), and tomographic inversions
365 for P-waves show mostly fast velocities here (e.g. Hosseini et al., 2020; Li et al., 2008; Simmons
366 et al., 2010).

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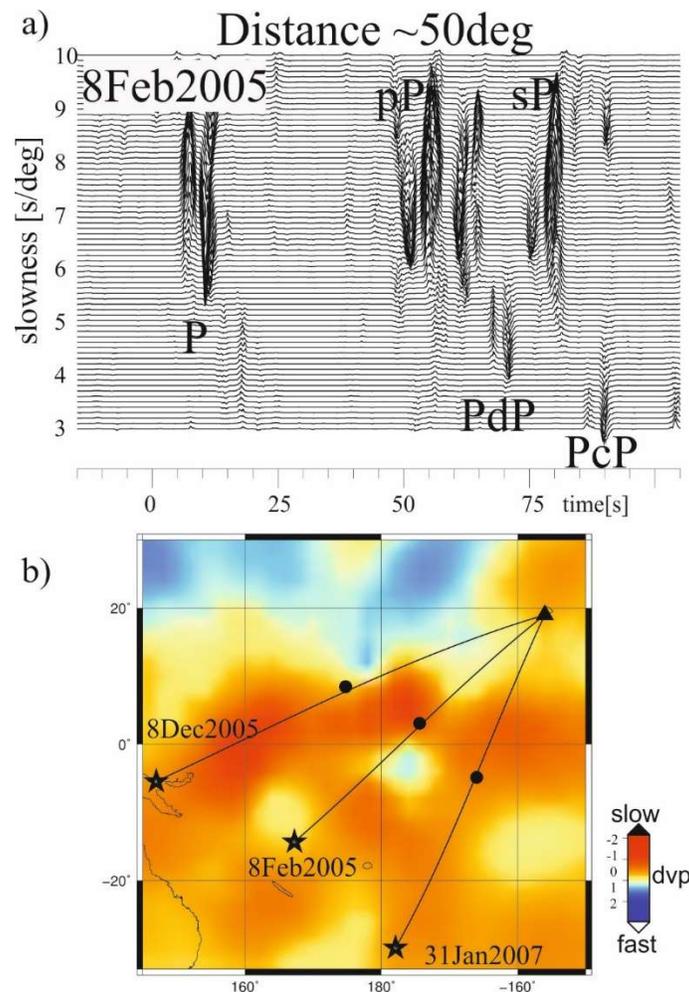


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Figure 4: Three examples for 4th root vespagrams showing PdP (circled in red) at short distances. The distance to the central station is given above the vespagrams. a) Event 5-August 2004 recorded at the array in Tibet, b) event 31-August-2003 recorded at the array in Tibet and c) event 23-August 2013 recorded at stations of the TA in Kentucky (Table S2). The polarities are indicated in each vespagram. d), e) and f) show insets around the PdP wave for events in a), b) and c). g) Sources (stars), central station of the array (triangle), great circle path and reflection points (circles) superimposed on a tomographic model MITP08 (Li et al., 2008) for the events in a) and b). h) Same as in g) but for the event in c).

380 We also re-examined some of the events from Thomas and Laske (2015), who used Ocean
381 Bottom Seismometer (OBS) data of instruments installed around Hawaii, and detected PdP
382 waves at short distances (Tables S1 and S2). These data suffered from noise: however, the
383 polarity of the few events where a D" reflection could be determined, was often the same as PcP

384 and P. Several of the source-receiver combinations were reflected from tomographically fast
 385 regions (see Thomas and Laske, 2015) where we might expect the same polarity of PdP
 386 compared with P and PcP, but some slow regions were also tested, and the reflections there also
 387 showed the same polarity for PdP compared with P and PcP. Figure 5a shows the vespagram for
 388 one event where the PdP polarity is clearly visible and is the same as the P and PcP wave. The
 389 D" reflection point for this event is in the large low seismic velocity province (LLSVP) as
 390 outlined in the P-wave tomography by Li et al. (2008) in Figure 5b. The data for the other two
 391 reflection points of the events presented in Thomas and Laske (2015) that reflect nearby (Figure
 392 5b) also show a polarity of PdP matching those of PcP and P.
 393
 394



395
 396 *Figure 5: a) As Figure 4a-c) but for event 8-February-2005 recorded at the PLUME array*
 397 *(Table S2). b) As Figure 4f-g) but for the event 8-February-2005. In addition, event locations*
 398 *and reflection points for 8-December-2005 and 31-January-2007 that were analysed and shown*
 399 *in Thomas and Laske (2015) are also indicated.*

400

401

402 Taking these new observations into account and looking at published D" reflections, we find that
 403 D" reflections for P waves show both positive and negative polarities, not necessarily related to
 404 the velocity variations in the mantle mapped by tomography. S-wave reflections from the D"

405 reflector in most regions show the same polarity as the main waves (S and ScS) except for the
 406 Pacific (Lay et al., 2006; Ohta et al., 2008). While anisotropy can explain some of this behaviour
 407 (e.g., Thomas et al., 2011; Pisconti et al., 2019; 2022), large R-values can also be due to changes
 408 in mineralogy. We will explore this scenario here.

409

410 **4 Thermochemical models and Linear Discriminant Analysis**

411

412 To understand which parameters are most important in producing large R-values we re-analysed
 413 the seismic properties of the thermo-chemical models presented in Cobden and Thomas (2013)
 414 and Cobden et al. (2012). The background to the models is explained in Methods 1 in the
 415 supplementary material and the parameters are listed in Table 1. We call these models the Mantle
 416 simulation. In addition, we also tested models which include a layer of 100 percent MORB
 417 below the reflector, where post-perovskite is able to exist (see supplementary material, Table
 418 S3). For each simulation, one million unique thermochemical models were produced.

419

420 In order to evaluate the R-values, we need to know the velocities and density of each model.
 421 First, bulk and shear moduli of the individual minerals were calculated from the elastic
 422 parameters published in Stixrude & Lithgow-Bertelloni (2011), using the equation of state in
 423 Stixrude & Lithgow-Bertelloni (2005). This involves a 3rd order Birch-Murnaghan equation of
 424 state to calculate properties at high pressure, with a Mie Grüneisen correction for thermal
 425 pressure (Stixrude and Lithgow-Bertelloni, 2005). All calculations were performed at a pressure
 426 of 119 GPa, corresponding to a mantle depth of ~2600 km. The P- and S-wave velocities of both
 427 starting (above D") and end (below D") model were then calculated from a Voigt-Reuss-Hill
 428 average of the bulk and shear moduli of the individual minerals, and a Voigt average of the
 429 density. We pinned the starting model above D" such that the velocities and density fall within
 430 5% of 1D reference model ak135 (Kennett et al., 1995) to avoid extreme outliers. For each
 431 model run, we subtract the absolute percentages of the constituent minerals above the reflector
 432 from those below it, which yields the changes in composition downward across the boundary.
 433 We then evaluated the calculated wave velocities for each model, and performed a detailed
 434 analysis of those that produced a ratio of dV_s/dV_p of 3 and larger across the boundary.

435

436 *Table 1: Ranges of the thermochemical parameters (modelling parameters) as varied between*
 437 *models (Mantle model). See supplementary material (Method 1) for explanation.*

438

Parameter	Minimum value	Maximum value
X. vol% (Mg,Fe)(SiO ₃ + O)	85	100
Y. vol% (Mg,Fe)SiO ₃ within X	60	100
Z. vol% FeSi O ₃ within Y	0	20
K. Fe-Mg part. coeff bm-mw	0.0001	2.0
A. vol% CaSiO ₃ within (100-X)	0	100
B. vol% SiO ₂ within (100-X-A)	0	100
P. vol % bm and Al ₂ O ₃ which converts to ppv	0	100
Temperature (K)	1800	3100

439

440 Since one million models is too large a number to consider individually, we turned to Linear
 441 Discriminant Analysis (LDA), a powerful statistical technique for classifying existing and new
 442 data into predefined discrete groups ("classes"). It is similar to Principal Component Analysis

443 (PCA) in that it involves data reprojection into an eigenspace with useful properties; in this case:
444 maximising the separability of known classes while taking into account their internal (i.e., class-
445 specific) variance. LDA is different from PCA in that the axes of this eigenspace are non-
446 orthogonal because the eigenvectors are based upon the between-class data scatter scaled by the
447 within-class scatter (Martinez & Kak 2001), rather than the data covariance used in PCA. The
448 technique was first published by Fisher (1936, in Duda & Hart 1973); for a recent treatment, see
449 for example McLachlan (2005). Applying PCA instead would be unsuitable here, as the aim of
450 this study is not to define abstract independent components (comprised of various positive or
451 negative contributions from many inputs), but instead to identify predefined R value-based
452 classes in terms of specific combinations and regimes of the original modelling parameters.

453
454 Here, we use LDA as a class "filter" on the full data sets (of modelling and chemical composition
455 parameters, respectively), in order to identify which original model parameters contribute most
456 to class separability, more specifically in distinguishing between low- and high R regimes (i.e.,
457 below/above $R = +3$). That is, after LDA reprojection we reject those data that are misclassified
458 in terms of those subsets, thereby reducing the error in the subsequent statistical significance
459 assessment of the input parameters. We also only keep cases for which $R > 1$ (see Method 2 in
460 Supplementary material). The final objective is to construct balanced, distinct profiles of these
461 parameters for low- and high R-values respectively, while distinguishing between two
462 seismological cases: changes in P and S velocity being both positive, or both negative (both of
463 which yield a positive R value). A flow diagram of the process is shown in supplementary
464 Figure S2. The relevant numbers for the datasets and more information on the LDA process are
465 provided in Methods 2 in the supplementary material and in Figure S3.

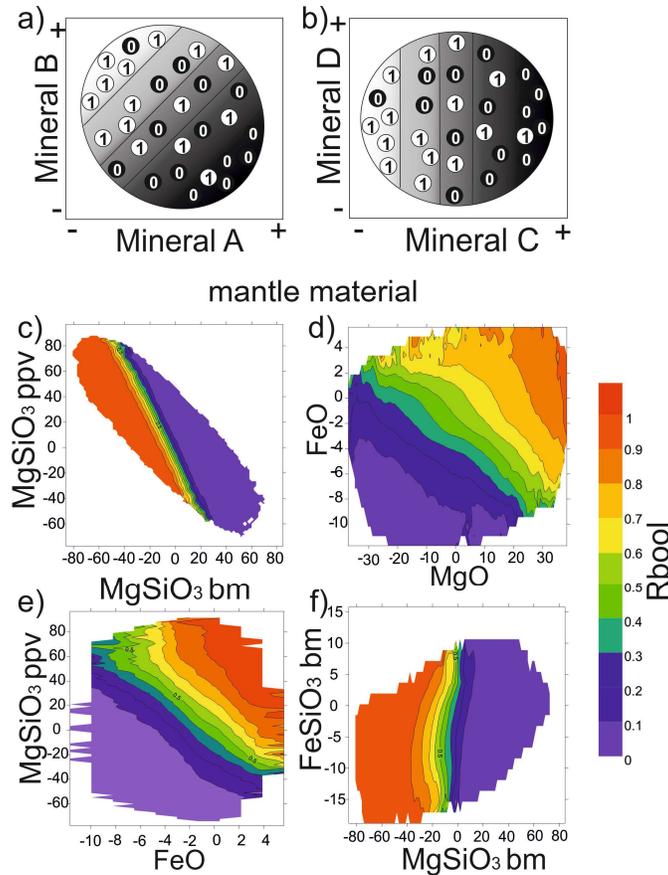
466
467 To simplify subsequent analysis and visualisation of the results, we encoded the two R regimes
468 in the LDA results as variable *Rbool*(ean), with 0 and 1 representing low and high R
469 respectively. Whereas correctly-classified LDA results are discrete, that is, either zero (low-R) or
470 unity (high-R), *Rbool* is the continuous spatial average of a large number of these points, with
471 equal numbers of low- and high-R cases, when plotted in multidimensional modelling parameter
472 space (Figure 6a, b). Wherever low values dominate (black regions in Figure 6a, b, purple
473 regions in other plots) $R < 3$ is predominantly produced, whereas *Rbool* values close to unity
474 (white regions in Figure 6a, b, orange regions in the other plots) indicate $R \geq 3$ is dominant.

475
476 The *Rbool* data sets form the basis for the figures in the following section and the supplementary
477 material (Figures 6, 7, S5-S7). To determine which parameters are most relevant for generating
478 large R-values, we also look at the boundary between high and low R-values. If a boundary is
479 vertical, as shown in Figure 6b, mineral C is important for generating large R values while
480 mineral D is not important (likewise for horizontal boundaries, but then mineral C is not
481 important while mineral D is). If the boundary is slanted (Figure 6a) both minerals have to
482 change for generating large R-values. The aim is to thereby identify a) which parameters are
483 most and least relevant for producing $R \geq 3$, b) which combinations of parameter ranges are
484 necessary and sufficient for this, and c) to what extent transitions between low and high-R
485 regimes are sharp boundaries (steep gradients).

486 487 **5 Large R-values**

488

489 Firstly, we look at the case of both P- and S-velocities increasing across the discontinuity for the
 490 mantle model (dV_p and $dV_s > 0$): our analysis shows that a change from MgSiO₃-bridgmanite
 491 (bm) to MgSiO₃-post-perovskite (ppv) is most important for the generation of R values ≥ 3
 492 (orange-red colours in Figure 6). Figure 6c shows that a decrease of bm is balanced with an
 493 increase in ppv for large R-values; however, when comparing the change of MgSiO₃ bm to
 494 FeSiO₃ bm across the boundary, we find that the reduction of MgSiO₃ bm is the important
 495 parameter, since the dividing line between high and low R-values is almost vertical in Figure 6f.
 496 The same is true for MgSiO₃-ppv and FeSiO₃-ppv in that the MgSiO₃-ppv increase is more
 497 important than the FeSiO₃ increase (Figure S5e).
 498



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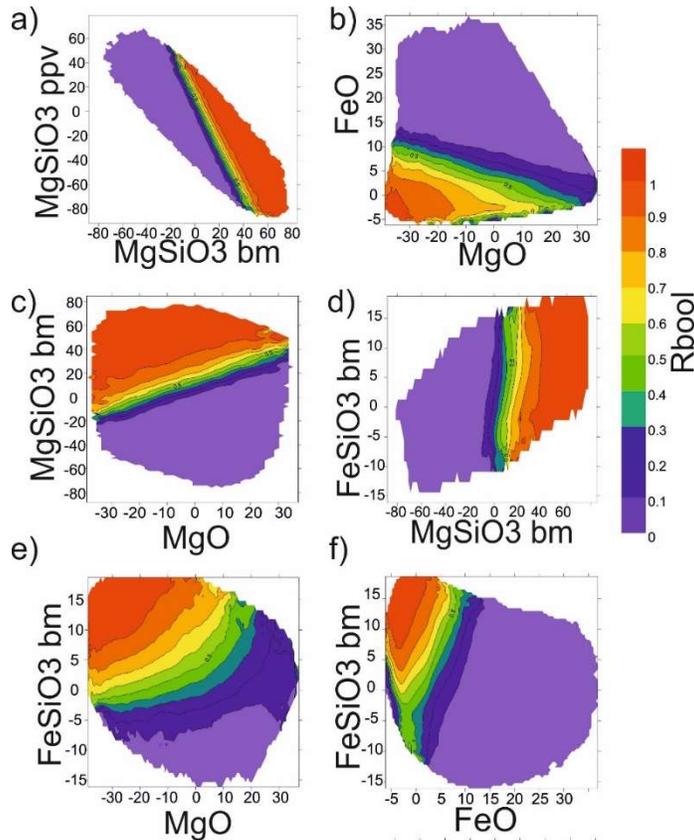
501 *Figure 6: a, b) Explanation for the following plots and the calculation of the local average*
 502 *Rbool, derived from the point cloud of correctly-classified LDA results containing an equal*
 503 *number of low- (0) and high-R cases (1). Black regions mean most values are 0, while in white*
 504 *regions most values are 1. a) For the case that both mineral changes are important for*
 505 *generating large R-values (here decreasing A and increasing B percentages). b) example of*
 506 *mineral C being important for generating large R-values but not mineral D. c) to f) Colour*
 507 *coded Rbool (0, purple: low R-values, i.e., smaller than 3; 1, red: high R-value, i.e., 3 and*
 508 *above) for different combinations of minerals of mantle material (Table 1) as indicated on the*
 509 *diagrams for the case of both V_p and V_s increasing across the D'' reflector.*
 510

511

512 We find that a large increase of MgO across the boundary and a moderate increase of FeO across
 the boundary can generate large R-values (Figure 6d). But if an increase of FeO is found, then a

513 small increase of Mg-ppv is sufficient for producing large R-values (Figure 6e). Since we find
 514 that an increase of MgO can generate R-values ≥ 3 , we map MgO, MgSiO₃-ppv and MgSiO₃-
 515 bm and find that the region of high (≥ 3) and low R-values is separated by a steep and narrow
 516 boundary (Figure S6). The figure shows that high R-values are possible for an increase in ppv
 517 while bm is decreasing (i.e., a phase transformation) if at the same time MgO is also increasing.
 518

519 Looking at other parameters (Figure S5), we find that varying temperature does not cause large
 520 R-values, since temperature changes seem to induce changes in V_p and V_s that are comparable in
 521 size. Indeed, Deschamps and Trampert (2003) show that temperature variations can lead to an R-
 522 value of 1.5 to 2. In our models, the partitioning of iron between bm and ferropericlase also
 523 seems to have little influence. Andraut et al. (2010) showed that Fe partitions preferably into bm
 524 and leaves post-perovskite Fe-poor. However, we only looked at partitioning between
 525 [Mg,Fe]SiO₃ and [Mg,Fe]O in our models, and therefore the case described by Andraut et al.
 526 (2010) is not represented in our models. Lastly, we find that an increase or decrease of pure SiO₂
 527 phase (seifertite), or Al in bridgmanite and/or post-perovskite, do not produce large R-values
 528 either.
 529



530

531

532 *Figure 7: same as Figure 6, but for the case that both V_p and V_s decrease across the D''*
 533 *reflector.*

534

535 The above-mentioned results were for cases with dV_p and $dV_s > 0$. Contrastingly, for dV_p and
 536 $dV_s < 0$ across the boundary, we find the opposite behaviour: a reduction of FeO and MgO or a
 537 decrease of post-perovskite (either FeSiO₃-ppv or MgSiO₃-ppv) while increasing bm is needed

538 to have large R-values (Figure 7a,b). However, a reduction of ppv across the boundary is
 539 unrealistic, since post-perovskite is inferred to be at a depth corresponding to the D'' region
 540 rather than above it (e.g., Grocholski et al. 2012). This suggests that the most relevant
 541 explanation for generating large R-values in regions where the P- and S-velocity are both
 542 decreasing is an increase of b_m and a reduction of MgO and FeO, with the effect of reducing
 543 MgO being stronger than that of reducing FeO.

544

545 The dataset of mantle models containing a MORB component (Table S3, Figure S7) shows
 546 similar results: For cases where V_p and V_s both increase across the D'' reflector, an increase of
 547 ppv and a decrease of b_m is the important scenario for producing large R-values. In the case of
 548 both velocities decreasing, a reduction of MgO and FeO or a decrease of the amount of ppv with
 549 increase of b_m across the reflector would generate R-values of 3 and higher. Note that the
 550 amount of FeO and MgO come from the non-MORB component in the bulk assemblage, since
 551 MORB does not contain MgO or FeO.

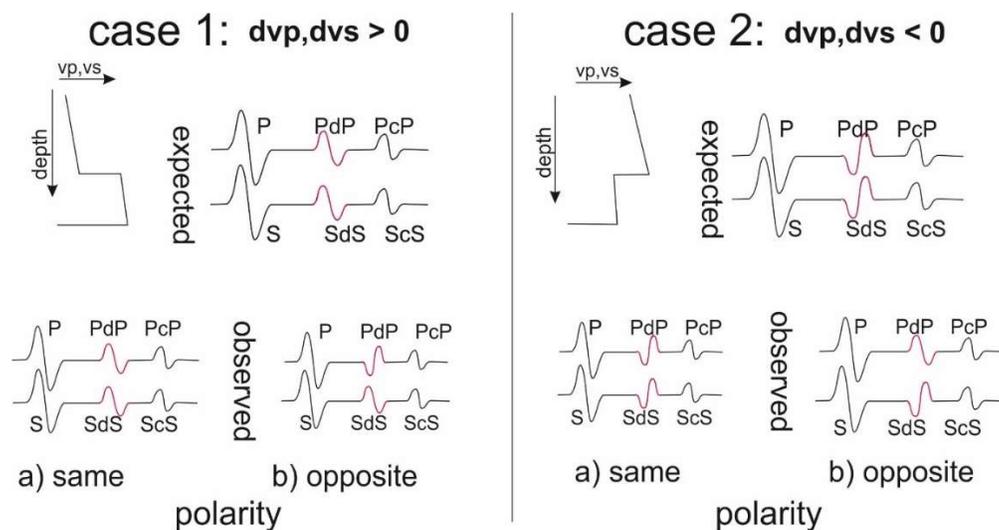
552

553 6 Discussion

554

555 The exact mineralogy of the lowermost mantle is still being debated (e.g., Vilella et al., 2021;
 556 Houser et al., 2020; Davies, et al., 2015; Trønnes, 2010; Cobden et al., 2009) and seismological
 557 mapping of structures near the core-mantle boundary has helped to test several possibilities of
 558 mantle mineralogy. While the mineral phase transition from bridgmanite to post-perovskite
 559 seems to be a good explanation for regions of past subduction (e.g. Trønnes, 2010, Hernlund et
 560 al., 2005), the mineralogy in the LLSVPs where slower-than-average velocities exist is still not
 561 well understood (e.g., Koelemeijer et al., 2021; McNamara, 2019; Deschamps et al., 2012,
 562 2015). In several cases, waves reflecting from layers inside these large low-velocity structures
 563 have been used to determine the velocity change across the reflectors (e.g., Lay et al., 2006;
 564 Schumacher et al., 2018), which provides a constraint on mineralogy (e.g., Ohta et al., 2008). We
 565 use our thermochemical modelling results in combination with PdP and SdS polarity information
 566 to constrain mineralogy and causes for the D'' reflector.

567



568

569

570 *Figure 8: Overview of the different cases: left hand side: V_p and V_s both increasing across the*
 571 *reflector, Case 1, with expected waveforms, right hand side: V_p and V_s both decreasing across*
 572 *the reflector, Case 2, with expected waveforms. The possibilities of observed polarities of PdP*
 573 *(SdS) as (a) same and (b) opposite to P(S) and PcP(ScS) are shown in the bottom row, referring*
 574 *to Cases 1a and 1b and Cases 2a and 2b, respectively, in Table 2.*

575

576 When interpreting polarity variations in P- and S-waves while ignoring those cases where
 577 changes in P-wave and S-wave velocity have opposite signs, there are essentially four possible
 578 cases (Figure 8 and Table 2). These four cases separate into two groups where V_p and V_s both
 579 increase (Case 1), and two groups where V_p and V_s decrease (Case 2), with either the same or
 580 opposite polarity of PdP- and SdS-waves.

581

582 If V_p and V_s both increase, and the ratio (R) between S-wave velocity change and P-wave
 583 velocity change is between 1 and 3 (Figure 8, case 1a), D" reflection polarities for P- and S-
 584 waves are the same as the main phase (P or S) and the CMB reflection. This case been observed
 585 in several seismic datasets using P- and S-waves together (e.g. Weber, 1993; Thomas and Weber,
 586 1997; Cobden and Thomas, 2013; Pisconti et al., 2019). Such a scenario could be produced by a
 587 thermal anomaly (e.g., Lay et al., 2004; Thomas et al., 2004a), or alternatively, by subducted
 588 mid-ocean ridge basalt, MORB (Cobden and Thomas, 2013; Hirose, et al., 1999; Deschamps et
 589 al., 2012; Vilella et al., 2021), which is silica-saturated and does not contain ferropericlasite. Our
 590 modelling shows that an R-value between 1 and 3 can be generated by an increase of bm or a
 591 decrease of FeO and MgO (Figure 6, purple colours), and this reduction in bulk (Mg,Fe)O can be
 592 indicative of the presence of MORB. Our analyses of mantle models containing a MORB
 593 component support this assumption and we therefore conclude that the event shown in Figure 4c
 594 is most likely reflections off MORB residing in the D" region, since S-wave observations in this
 595 region also show polarities consistent with a velocity increase (Kendall and Nangini, 1996; Lay
 596 et al., 2004). For the two events in Figure 4a and b no clear explanation is possible, since we are
 597 missing S-wave polarity information for this region.

598

599 If, for an S-velocity increase across D", the PdP polarity would indicate a velocity decrease,
 600 there are two explanations: Either there is indeed a P-velocity decrease with an associated S-
 601 wave velocity increase across the D" reflector, as indicated by e.g., Wookey et al. (2005) for the
 602 ppv phase transition in pure MgSiO₃. Alternatively, an R-value larger than 3 could generate the
 603 same effect (case 1b in Table 2 and Figure 8). Our thermochemical modelling shows that the ppv
 604 phase transition is again a good explanation for this scenario (Figure 6, Table 2). Indeed, the
 605 contrast of the P-wave velocity across the post-perovskite phase transition has been reported to
 606 be between $\pm 1\%$, while the S-wave change is between 1 and 4% (Oganov and Ono, 2004;
 607 Tsuchiya and Tsuchiya, 2006; for an overview see e.g., Cobden et al., 2015).

608

609 There is potentially another mechanism that could generate the polarities shown in case 1b: an
 610 increase of MgO and FeO across the boundary would also generate large R-values. While the
 611 decomposition of (Mg,Fe)-bm into (Mg,Fe)O and SiO₂ has been suggested in early experimental
 612 studies (e.g., Saxena et al., 1996; Dobrovinsky et al., 1998), more recent studies indicate that the
 613 decomposition could have arisen through a problem with the experimental setup (Mao et al.,
 614 1997; Gong et al., 2004). Hence, we suggest that the post-perovskite phase transition is the best

615 explanation for observations of PdP polarities opposite those of P and PcP together with SdS
 616 polarities the same as S and ScS (case 1b).

617

618 *Table 2: The four cases shown in Figure 8 with their previous interpretation. In the 3rd row, we*
 619 *provide the R-value associated with the polarities PdP vs SdS in the 1st row and the 4th row*
 620 *explains the mineralogy changes that cause the R-values in row 3. The last row gives our*
 621 *interpretation for each case.*

	Case 1a	Case 1b	Case 2a	Case 2b
Polarities, PdP vs. SdS	same	opposite	same	opposite
previous interpretation	MORB, cold slab	ppv (in MgSiO ₃)	ppv in MORB, seifertite trans.	
R-value range	$1 < R < 3$	$R \geq 3$	$1 < R < 3$	$R \geq 3$
mineralogy change across D"	+bm, -ppv -MgO, -FeO	-bm, +ppv +MgO, +FeO	+ppv, -bm +FeO	+bm, -ppv -MgO, (-FeO)
interpretation with R-value	consistent with MORB	consistent with ppv phase trans.	consistent with ppv phase trans in MORB	primordial material, BEAMs

622

623 The mineralogy in low-velocity regions, especially in the LLSVP beneath Africa and the Pacific,
 624 is less well constrained, and different mechanisms for velocity discontinuities within LLSVPs
 625 have been discussed. Ohta et al. (2008) show that the post-perovskite phase transition in MORB
 626 could generate a reflector, but the stishovite to seifertite transition could also be a candidate for
 627 this observation (Andrault et al., 2014; Tsuchiya et al. 2004), although the depth of the transition
 628 is still debated (Ohta et al., 2008; Grocholski et al., 2013; Sun et al. 2019). Both cases would
 629 show polarities of PdP and SdS consistent with a velocity decrease as represented by case 2a in
 630 Table 2. Our modelling shows that an R-value below 3 is consistent with the ppv phase transition
 631 within MORB while bm decreases.

632

633 A velocity decrease for both, P- and S-waves with a ratio of dV_s/dV_p of ~ 3 is, on the other hand,
 634 indicative of melt in the lower mantle (e.g., Hier-Majumder, 2008; Berryman, 2000), but melt
 635 has previously been discussed as cause for ultra-low velocity zones (e.g. Rost et al., 2005, 2006;
 636 Yu and Garnero 2019) rather than for a 300 km thick D" layer, and it is still discussed whether
 637 melt would stay at the CMB (Thomas et al., 2012; Garnero, 2000). It is difficult to envisage a
 638 dynamic mechanism in which thin melt layers would pond 300 km above the CMB, although
 639 seismically it would not be incompatible with our observations. A 300 km thick layer of (partial)
 640 melt is incompatible with observations of the P and S-wave speed structure within D" (e.g.
 641 Cobden et al. 2012).

642

643 Lastly, case 2b, where a velocity decrease across the D" reflector is expected in S-waves, but
 644 where the PdP polarity suggests a velocity increase (Figure 8, Case 2b), is possibly the rarest
 645 observation up to now. We find such a case in the region beneath the western Pacific (Figure 5,
 646 see also Thomas and Laske 2015) with PdP waves showing a polarity that is the same as P and
 647 PcP in a part of the Pacific LLSVP (Figure 5). Near this region, the S-wave study of Konishi et
 648 al. (2009), on the other hand, found a velocity decrease at the top of D" (interpreted there as a
 649 phase transition within MORB). While not exactly in the same region, the results by Konishi et
 650 al. (2009) together with our results would suggest that our observed P-wave polarity is due to

651 large R-values, and hence would confirm that S-wave velocity reductions are at least 3 times as
652 strong as P-wave velocity reductions in this part of the LLSVP, as also indicated by Koelemeijer
653 et al. (2016, 2018). The reduction of S-wave velocity suggests that MORB itself is not a good
654 explanation for this region (Deschamps et al., 2012), and the P-wave polarity results (Figure 5)
655 indicate that the ppv phase transition is not satisfactory either. Instead, our thermochemical
656 modelling shows that an increase in *bm* or a decrease in MgO (and to a smaller degree FeO)
657 would generate large R-values.

658
659 Ballmer et al. (2016) model the Pacific LLSVP with a combination of MORB and primordial
660 material, which generates a velocity discontinuity at depths consistent with the D" reflector
661 within an LLSVP-like region (Schumacher et al., 2018). Furthermore, Deschamps et al. (2012)
662 and Vilella et al. (2021) show that an increase of *bm* with an increase of Fe has been suggested to
663 be responsible for the LLSVPs. Their composition is similar to BEAMs (bridgmanite enriched
664 ancient material, Ballmer et al., 2017) and if the BEAMs exists near the CMB (Gülcher et al.,
665 2020) this could explain case 2b in Table 2. Our thermochemical modelling suggests that an
666 increase in *bm* has the largest effect, but it may also be accompanied with a decrease of FeO
667 (Figure 7f). Interestingly, the studies by Chandler et al. (2021) and Pisconti et al. (2022),
668 although aimed at constraining anisotropy near the edges of an LLSVP, also find that outside the
669 LLSVP ppv is a good explanation, while inside the LLSVP *bm* explains their observations better.

670
671 Our modelling has shown that the different polarity information of P and S-waves, when jointly
672 considered, can aid to constrain the mineralogy of the D" region in different settings. While we
673 are focussing here on isotropic minerals and combinations of minerals above and below the D"
674 reflector to explain polarities, we have to keep in mind that anisotropy is another mechanism that
675 causes polarity changes in seismic waves. For example, Thomas et al. (2011), Pisconti et al.
676 (2019; 2022) and Creasy et al. (2019; 2021) show that polarity variations, especially of P-waves
677 reflected at the D" layer, can also be generated by anisotropy of the D" minerals (ppv, *bm*, and
678 even ferropericlase), even over small azimuth ranges. The anisotropy, generated by the flow of
679 anisotropic minerals in D", will, however, cause polarity observations that vary with azimuth as
680 shown in Pisconti et al. (2019; 2022); these are unlike the results here, where polarity variations
681 are isotropic. In addition, when anisotropy is present in the D" region, ScS-waves will experience
682 directionally dependent splitting (Nowacki et al. 2011). It has been shown that a combination of
683 splitting measurements together with PdP and SdS polarity observations (Pisconti et al., 2019;
684 2022), and including discrepant SKS and SKKS splitting measurements (e.g., Creasy et al.,
685 2021) can further constrain mineralogy in the D" region, but the observations vary with azimuth
686 due to the directional velocity variations of the deformed minerals. Therefore, a mapping of
687 regions such as beneath the Caribbean or the western Pacific with crossing paths and taking
688 shear wave splitting of ScS waves into account would help to discriminate between the
689 alternative hypotheses of anisotropy versus large R-values.

690 691 **7 Conclusion**

692
693 We have shown that distance-dependent polarity observations of P-wave reflections depend on
694 the ratio of change of S-wave velocity with respect to change in P-wave velocity across the D"
695 reflector, referred to here as the R-value. Linear discriminant analysis (LDA) of mineral
696 composition paired with a set of velocities derived from thermochemical modelling enables us to

697 generate a profile of distinct observable classes (namely, R-values smaller or larger than 3 for
698 regions with velocity increases or decreases), allowing the seismological observables to inform
699 the characterisation of regions in terms of typical mineralogical constituent ratios.

700

701 The statistically significant results derived from the thermo-chemical modelling data suggest
702 different causes for large R-values. The post-perovskite phase transition is the best explanation
703 for regions where a velocity increase is detected with S-waves while the P-wave has a polarity
704 that would indicate an apparent velocity decrease. In regions where both D"-reflected P- and S-
705 waves have polarities opposite to the main phases, the ppv phase transition within MORB is
706 likewise the best explanation, as already reported in previous work. A reflection at a MORB
707 layer is consistent with P- and S-wave polarities both suggesting a velocity increase. The last
708 case of an SdS-wave with a polarity opposite to S and ScS but with a PdP-wave suggesting a
709 positive velocity jump across D", as seen in one region of the Pacific LLSVP, can be explained
710 by a reflection off bridgmanite-enriched material, thereby further constraining mineralogy in the
711 LLSVP regions.

712

713 Analysing polarities of P- and S-waves, together with extending the epicentral distance range to
714 lower values than previously, and for different regions, thus allows a better classification of the
715 mineralogy change across a reflector. Since variable polarities of P-waves and S-waves can also
716 be generated by anisotropy in the D" region, as shown by Thomas et al. (2011) and Pisconti et al.
717 (2019), a detailed analysis of P- and S-wave observations covering a variety of distances and
718 azimuths is necessary to discriminate between these two hypotheses of large R-values versus
719 anisotropy. Where the former is supported and the latter is absent, inferences can be drawn
720 regarding the most likely mineralogical constituent ratios across the reflector.

721

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731 C++ template library for linear algebra (<https://eigen.tuxfamily.org>).

732

733

734 **Open Research**

735 All data used here are freely accessible through IRIS (Incorporated Research Institutions for Seismology).
736 The dois and references for the datasets are given in the supplementary material Table S2, the events
737 parameters are shown in Table S1.

738

739

740

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