Seismological Expression of the Iron Spin Crossover in Ferropericlase in the Earth's Lower Mantle

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1 Abstract

- The two most abundant minerals in the Earth's lower mantle are bridgmanite and ferroper-
- 3 iclase. The bulk modulus of ferropericlase (Fp) softens as iron d-electrons transition from
- a high-spin to low-spin state, affecting the seismic compressional velocity but not the shear
- velocity. Here, we identify a seismological expression of the iron spin crossover in fast re-

gions associated with cold Fp-rich subducted oceanic lithosphere: the relative abundance of fast velocities in P- and S-wave tomography models diverges in the \sim 1,400-2,000 km depth range. This is consistent with a reduced temperature sensitivity of P-waves throughout the iron spin crossover. A similar signal is also found in seismically slow regions below \sim 1,800 km, consistent with broadening and deepening of the crossover at higher temperatures. The corresponding inflection in P-wave velocity is not yet observed in 1-D seismic profiles, suggesting that the lower mantle is composed of non-uniformly distributed thermochemical heterogeneities which dampen the global signature of the Fp spin crossover.

14 2 Introduction

Mineral physics experiments^{1–3} and theory^{4,5} consistently predict that the d-electrons of Fe²⁺ in Fp, (Mg,Fe)O, change from a high-spin to low-spin (HS-LS) state at mid-lower mantle conditions (Fig. 1). However, the compressional velocity of a homogeneous pyrolitic mantle (Fig. 1d) does not fit global seismic reference profiles when the effects of the iron spin crossover are included in the predicted seismic velocity computations⁶. Confirmation of the existence and observation of the iron spin crossover in the Earth's mantle is relevant because it is expected to alter material properties such as density, viscosity, elasticity, thermal conductivity, and elemental partitioning in the lower mantle⁷. The rheological consequences of such material changes mean that subducted slab, mantle plume, and deep mantle dynamics are thought to be affected by the crossover, including reduced viscosity, enhanced vertical flow, and slab stalling^{8–10}. In spite of its potential importance, the spin crossover in Fp has thus far eluded seismological detection, suggesting that the predictions

are inaccurate, the signature is below the detection threshold, and/or the lower mantle has a lower (Fe+Mg)/Si ratio than the shallower mantle.

The distinct effects of the Fp spin crossover on compressional (P-wave) and shear (S-wave) 28 velocities offer a promising target for geophysical observation (Fig. 2). In particular, a volume reduction during the spin crossover⁴ inevitably increases the compressibility of Fp and decreases its bulk modulus¹¹. Both the onset pressure as well as pressure interval of the mixed 31 spin region (where both high- and low-spin states coexist) are predicted to increase at higher 32 temperatures^{7,11–13}. The temperature dependence of the pressure onset and pressure range of the HS-LS crossover results in an anomalous dependence of the bulk modulus on temperature¹⁴, with little influence on the shear modulus (Fig. 2a). The significance of this effect increases for higher iron contents and abundance of Fp⁷. Specifically, the transition pressure does not change significantly for FeO concentrations below 20 mol% in Fp, which is representative for the lithological range from fertile peridotite to harzburgite¹⁵. The magnitude of our predicted velocity reductions are supported by experimental data⁵, especially from Brillouin scattering^{13,16}, and motivate investigation of thermal anomalies in the lower mantle.

One consequence of the bulk modulus softening during the iron spin crossover in Fp is that
the P-wave velocity is generally reduced while the S-wave velocity remains unaffected. While
pyrolitic model compositions have been found to be consistent with 1-D seismic models^{17,18} (i.e.
global seismic reference/average profiles), Fig. 2 demonstrates that the Fp content of pyrolitic rock
is sufficient to significantly reduce P-velocity across the mid-mantle iron spin crossover when the

effects of the iron spin crossover are included. The velocities are computed using *ab initio* mineral physics calculations¹⁵ on a simplified pyrolite composition listed in Table 1. The P-wave and S-wave velocities for the full range of Fp-bearing rock (from Fp-free model composition to Fp-rich harzburgite, Supplementary Fig. 1) reveal the influence of variable Fp abundances on mid-mantle seismic velocities. Most domains in the lower mantle likely contain Fp in the range bounded by these two compositions. Fig. 2 and Supp. Fig 1 reveal that mid-mantle thermal anomalies in Fp-bearing rock are predicted to produce a measurable S-wave seismic anomaly while the predicted P-wave seismic anomaly would be greatly diminished. Thus, we survey P-wave and S-wave velocity tomography models for the distinctive seismic signal of the iron spin crossover in Fp: S-velocity anomalies produced by lateral temperature variations persist but P-velocity anomalies weaken within the expected mixed spin region (see Fig. 2c).

In the lower mantle, regions with fast seismic anomalies are commonly interpreted as cold, sinking oceanic lithosphere^{19,20}. These subducted slabs typically comprise 5-7 km of basaltic crust underlain by ~60-80 km of mantle. The lithospheric mantle is depleted in Si due to the extraction of basaltic melt, increasing its Mg/Si ratio and thus the relative amount of Fp in the lithospheric mantle (at lower mantle conditions). Because the magnitude of the velocity reduction due to the iron spin crossover depends on the abundance of Fp (Supplementary Fig. 1), these fast seismic regions should host the strongest spin crossover-related seismic signals. Slow regions in the mid-mantle may be due to return flow of former oceanic plates after becoming warm and buoyant near the core-mantle boundary²¹. Depending on wavelength and depth, previous comparisons of P- and S-wave tomography models suggest different seismic characteristics in the lower mantle, including

changes in the ratio and correlation of S- and P-wave velocity variations and apparent disruption
of imaged fast/slow features^{22–26}. Direct P- and S-waves and additional phases such as PP, PPP, SS, and SS-S provide nearly uniform coverage across the mid-mantle²⁷. Hence, both P-wave
and S-wave models are well-resolved vertically and laterally in the mid-mantle^{28,29}. Given the
similarities in P- and S-wave resolution in the mid-mantle, we focus on characteristics within fast
and slow velocity regions in P-wave and S-wave models using both individual tomography models
and combined through tomographic vote maps.

Here, we identify the seismological expression of the iron spin crossover in the mid-lower mantle by investigating fast and slow regions in P- and S-wave tomography models. The identified signal (below \sim 1,400 km in fast and below \sim 1,800 km in slow regions) corresponds to mineral physics predictions, including a temperature dependence of the pressure onset and pressure range of the high-to-low spin crossover in Fp.

79 3 Results and Discussion

Individual tomography models With the rapid expansion of data acquisition and improvements in inversion and modelling techniques in recent decades, numerous global P- and S-wave seismic tomography models are now available^{30–32}. Here we use 4 P-wave models (DETOX-P01³³, GAP-P4^{34,35}, HMSL-P06²⁸, MITP-2011³⁶), and 4 S-wave models (HMSL-S06²⁸, S40RTS³⁷, savani³⁸, SEMUCB-WM1³⁹) that capture a range of global, whole mantle tomographic data and techniques. Fig. 3 shows the overall methodology we use to determine the vertical and lateral extent of fast and

slow regions. The percentage of the surface area at each depth that is identified as a fast (or slow) seismic anomaly is calculated as derived from a contour threshold. We define the threshold for fast/slow as seismic wave speed anomalies that deviate by more than one standard deviation (σ) in the central portion of the seismic velocity distribution over a reference depth range of 1,000-2,200 km (i.e., $\geq 1\sigma$ for fast, $\leq -1\sigma$ for slow, see Methods). Supplementary Figs. 2-4 show the resiliency of alternative thresholds for defining fast/slow anomalies of the depth-dependent trends.

The surface area of fast and slow wave speed anomalies, plotted at depth intervals of 50 km across the lower mantle, reveals distinct patterns between P-wave and S-wave models (Fig. 4), including that there is more variability between the P-wave models than between the S-wave models, as also noted in 40 . Furthermore, when viewed collectively (Fig. 4), these individual tomography models indicate that the area covered by fast P-wave velocities decreases in the lower mantle across the depth range of $\sim 1,400-2,200$ km relative to S-wave velocities. The overall trend of fast areas in the S-wave models increases with depth (from $\sim 15\%$ coverage at 1200 km depth to $\sim 40\%$ coverage near the core-mantle boundary).

Vote maps The differences in the characteristics and distribution of seismic anomalies, both within and between the P-wave and S-wave models, and as illustrated in Fig. 4, lead us to further inspect the geographic similarity of these patterns. Thus, we employ a vote map method to examine the surface area of fast and slow regions that are common to all of these models ⁴¹ (Fig. 3a-c, see Methods). The highest count (4 votes; Fig. 1b-c) indicates regions where all four models (for P-waves or S-waves) agree on the existence of fast anomalies (i.e. $>= 1\sigma$) at a given depth

interval. For example, the pattern of fast anomaly vote maps (Fig. 5) reveals north-south trending subducted slabs under North America, related to long-lived subduction along eastern Panthalassa, as well east-west trending slabs related to palaeo-subduction within the Tethys Ocean⁴¹. Likewise, the cluster analysis-based vote map technique ^{40,42} illuminated the common morphology of large low shear velocity provinces (LLSVP) in the lowermost mantle.

The vote map procedure does not add any features not already present in the constituent 111 tomography models; it rather highlights the features that are common to multiple models. For 112 example, when analysing global, whole mantle models, it is difficult to know if any given patch 113 of anomalously fast or slow velocity is due to imperfect input data, inversion artefacts, or is a 114 genuine signal present in the lower mantle. Each tomography model utilizes different types of 115 input data, parameterization, regularization, and other subjective choices in their construction (e.g. 116 see model compilations^{25,32,41,43}). Therefore, we expect that features introduced into individual 117 tomography models due to unique tomographic data and/or modeling approaches will not have a 118 strong influence in the highest count of the vote maps (e.g. 42). Furthermore, our contour analysis 119 is global and is therefore less susceptible to locally-restricted seismic anomalies. By the same token, vote maps offer a framework for unique, localized anomalies to be identified and evaluated between tomography models. 122

Similar to the individual models shown in Fig. 4, the surface area of fast velocity regions in P- and S-wave vote maps (Fig. 1b) diverges in the mid-mantle beginning at \sim 1,400 km depth. This observed depth is similar to that predicted for the mixed spin region in Fp for a pyrolitic compo-

regardless of the analysis type; contour threshold, highest vote counts, or model combinations.

For example, we also test the influence of sequentially adding in the tomography models (from 1 to 4 models) in Supplementary Fig. 5, as well as alternative combinations of 3 of the 4 models in Supplementary Fig. 6. The decorrelation signal of fast P-waves and S-waves was previously examined⁴¹ using an expanded set of 14 tomography models. Furthermore, in Supplementary Fig. 7 we compare the depth-dependent signal for lower vote counts rather than just the maximum vote count of 4 in Fig. 1b,c. These tests demonstrate the robustness of the P- versus S-wave signal.

To further test the hypothesis that the decoupling of the fast velocity signals in P-wave and 134 S-wave models reflects a spin crossover in Fp, we examine seismically slow, and presumably 135 warm, portions of tomographic models. The surface area of slow velocity regions in the vote 136 maps (Fig. 1c) reveals that the onset of divergence shifts to greater depths (i.e. below $\sim 1,800$ 137 km) consistent with the deepening of the spin crossover as temperature increases (Fig. 1a). It also demonstrates the predicted broadening of the spin transition at higher temperatures (Fig. 1a), 139 leading to a more diffuse seismic signal. The divergence in slow velocity regions between Pand S-wave models is likewise more subtle than that observed in fast velocity regions, see also Supplementary Fig. 5-6. The vote maps are a useful tool for examining these types of subtle but 142 consistent and geographically coherent velocity anomaly patterns, i.e., the common signal derived from slow anomalies in the individual tomography models (Fig. 4) is more discernible in the vote maps (Fig. 1b,c). 145

Figs. 5-6 show horizontal and vertical cross-sections, respectively, through vote maps of fast 146 and slow velocity regions. All vote values are shown in these images (i.e. 0-4 votes). We can 147 qualitatively observe a divergence in the agreement among P-wave models compared to S-wave 148 models in the mid mantle (see 1500 km depth) for both fast and slow anomalies. For example, fast anomalies attributed to subducted slabs under North America and SE-Asia appear contiguous 150 through the mid-mantle in S-wave vote maps. However, the P-wave vote maps show a weakening 151 of the fast seismic signal in the mid-mantle (coherent fast anomalies at the top and bottom of the 152 lower mantle are still observed). Likewise, the slow mantle domain under Africa and the Afar 153 hotpot region is more readily apparent in S-wave than in P-wave vote maps towards the lowermost 154 mantle (below ~ 2000 km depth). This observed interference is what is predicted for the spin 155 crossover in Fp¹⁴. The disruption of slab and plume images in the mid-mantle has also been 156 noted in other studies ^{23,26,44–47}. Fig. 7 shows difference maps, highlighting the spatial and depth-157 dependent differences between the P- and S-wave vote maps. There is a dominance of S-wave 158 votes over P-wave votes in the lowermost mantle, especially for the fast anomalies in regions of 159 long-lived subduction (Figs. 5 and 6), and in the slow anomalies for regions corresponding to 160 the LLSVP domains. Note that our definition of anomalous material is based on characteristic 161 behaviours in the depth range 1,000-2,200 km (see Methods), and any discussion of anomalies 162 outside of this depth range should be considered relative to these standards.

We note that the abundance of fast velocity regions in both P-wave and S-wave models (Fig. 1b, 4) increases between \sim 2,500-2,800 km depth. This could reflect a build-up of slab material and/or a change in the globally averaged subduction flux, as estimated from mantle sinking rates

^{41,48}. Furthermore, the area of fast S-wave anomalies increases more rapidly toward the base of the mantle than the P-wave anomalies. This relative difference could (in addition to potential 168 slab-volume changes) be caused by the appearance of post-perovskite in cold mantle, which is expected to increase S-wave velocity by \sim 1-2% but has notably smaller effect on P-waves⁴⁹⁻⁵¹. The difference maps between P-wave and S-wave votes at 2,800 km depth, shown in Fig. 7, reveal 171 regions of potential post-perovskite (dark purple regions indicating higher S-wave votes than P-172 wave votes). The antipodal LLSVPs, beneath the Pacific and Africa, are areas where the S-wave 173 velocity is more strongly reduced relative to the P-velocity. The divergence between S- and P-wave 174 behaviours within the LLSVPs has been used to argue for the presence of dense chemically distinct 175 piles in these regions⁵². Below \sim 2,800 km we expect the trends to be complicated by core-mantle 176 boundary layer dynamics^{40,53,54}. 177

Effect of iron partitioning The spin crossover is expected to influence the iron partitioning (K_D)
between bridgmanite (Bm), (Mg,Fe,Al,Si)O₃, and Fp^{1,55} by increasing the iron concentration in Fp,
thus decreasing K_D^{55} . Since the spin crossover may shift to higher pressures as K_D decreases⁷, the
pressure range over which the crossover occurs could be wider than that predicted for the constant
partitioning value of K_D =0.5 which we assign in our calculations. We also investigated how the
onset and depth range of the spin crossover changes with variable K_D^{55} values (Supplementary Fig.
8). The velocities with variable K_D are barely distinguishable from the constant K_D case due to a
very weak dependence on the crossover depth on FeO concentrations below ~20 mol.% (e.g.^{56,57}).
This prediction is consistent with our observation that the effects of the crossover on P-velocities
in fast velocity regions does not extend below ~2500 km depth even for Fp-rich compositions,

Supplementary Fig. 1.

Implications for lower mantle composition A reduction in the area of mid-mantle fast velocity regions in P-wave models compared to S-wave models is consistent with the predictions of an iron spin crossover in Fp. To investigate the 1-D signal, we compare our predicted P- and S-wave 191 velocities for pyrolite to the Preliminary Reference Earth Model (PREM)⁵⁸ radial P-wave profile, 192 Fig. 1d. Due to uncertainties in the average mantle geotherm⁶, we calculate the temperature profile 193 which aligns our predicted S-wave velocity to PREM (Supplementary Fig. 9.). We demonstrate 194 that the different behavior of P- and S-wave velocities during the spin crossover could be detected 195 by 1-D seismic profiles for a uniform Fp-bearing mantle where S-wave velocity is a proxy for 196 temperature since it is not effected by the iron spin crossover. However, the intensity of the P-197 wave velocity reduction depends on the Fp abundance and the abundance of iron in the Fp which 198 could be different than our model composition. Since Bm has a similar spin crossover for ferric 199 iron (Fe³⁺) located in the octahedral B-site⁵⁹, the lack of a distinct iron crossover signal in 1-D seismic profiles⁶⁰ suggests that aluminium replaces a majority of the Fe³⁺ on the B-site⁶¹. While 20 there are still uncertainties on the spin crossover pressure range and magnitude of the seismic 202 signal at relevant mantle temperatures, the general agreement between theoretical predictions⁵ and 203 experimental measurements¹³ at room temperature compels us to consider how to reconcile the 204 patterns observed here, in both the fast and slow regions, with those from the 1-D average profiles. 205

The observed divergence in P-wave and S-wave models in the fastest and slowest regions of
the mid-mantle indicates that the iron spin crossover signal is seismically detectable in the deeply

subducted Fp-enriched oceanic lithosphere. Variable composition, such as regions with less Fp or less iron in the Fp, could disrupt and reduce the spin crossover signal^{6,12}. Variations of lateral temperature with pressure introduce a depth-dependence to the P-wave seismic velocity inflection 210 (i.e. causing a potential vertical smearing of the signature), which could reduce the globally averaged signal. Geodynamically, the lack of a ubiquitous signal of the iron spin crossover in the 212 lower mantle may indicate that sluggish mantle mixing has yet to erase large-scale heterogeneities. Suppression of a global (1-D) signature of the spin crossover might be explained if significant por-214 tions of the lower mantle are depleted in Fp (i.e., enriched in bridgmanite), while Fp-bearing rock 215 that circulates between the shallow and deep mantle is concentrated in upwelling and downwelling 216 channels. This situation is similar to the bridgmanite-enriched ancient mantle structures (BEAMS) 217 model²¹ in which Fp-poor regions exhibit a higher viscosity and resist convective mixing⁶². In 218 addition, 1-D seismic models using low-order polynomial parameterizations of radial velocities 219 may have smoothed the seismic signal of the iron spin crossover which becomes more subdued 220 as the shape and distribution of thermochemical provinces becomes more varied. High resolution 221 regional 1-D profiles are challenging to construct but could reveal the presence or absence of Fp 222 outside of regions with large lateral temperature variations such as those identified in this study. 223 It is possible that more complicated combinations of thermal, phase, and/or chemical composition 224 variations could provide an alternate explanation for Vs-Vp decorrelation. However, the pressuretemperature dependence of the Fp spin crossover provides a unified explanation for why this occurs at these particular distinct depths in slow and fast regions, and does so without the need to invoke 227 depth-dependent changes in the chemical composition of downwelling and upwelling materials.

Our study qualitatively identifies the predicted seismic expression of the iron spin crossover in lower mantle Fp in fast and slow regions of global tomography models. The effects of the iron spin crossover on seismic velocities are subtle⁶³ but most discernible in the presence of lateral temperature variations in Fp-bearing regions that extend across the depths that span the iron spin crossover range. Our detection of Fp in the fastest and slowest regions without a strong signal in the global average mantle suggests the presence of a mosaic of large-scale thermal and compositional domains in the lower mantle.

236 4 Methods

Predictions of the Spin Crossover in Fp. Fig. 1a was calculated for $Mg_{1-y}Fe_yO$ with y=18.75%, also labelled Y_{Fe} in equation (1), using published models^{5,14}. The low spin fraction is calculated as:

$$n(P,T) = \frac{1}{1 + m(2S+1) \exp\left[\frac{\Delta G_{\text{HS-LS}}^{\text{st+vib}}}{Y_{\text{Fe}}k_BT}\right]}$$
(1)

where m=3 for the three possible orientations of minority electron d orbital (xy, yz, or zx) and S=2. $\Delta G_{\rm HS-LS}^{\rm st+vib}$ includes only static and vibrational energy, without electronic entropy. Our elastic moduli and densities are also taken from published models^{5,15,64,65}. These calculations used the rotationally invariant local density approximation LDA+U_{SC} method calculated with a self-consistent Hubbard U⁶⁶. Results for Fp were obtained using a 64-atom supercell with an iron concentration of y=0.1875 (24 Mg, 32 O, and 6 Fe maximally separated from each other). Thermoelastic properties were then obtained for other concentrations by linearly interpolating between y=0 and y=0.1875. The vibrational density of states (VDOS) was computed using the vibrational

virtual-crystal model¹¹, and then used in conjunction with the quasiharmonic approximation to predict high temperature effects. The magnitude of the predicted effects are in good agreement with experimental measurements¹³. Thermoelastic properties from^{64,65} are used for Fe²⁺- and Albearing bridgmanite. While our calculations do not include Fe³⁺, the velocities for Fe³⁺-bearing Bm^{65,67} are similar and thus do not effect our estimates of the temperature-dependence of the iron spin crossover in ferropericlase. Here we consider the effects of a spin crossover in Fp, proposed spin changes in Fe in Bm are not considered.

The mantle is thought to be a lithological mix of depleted peridotite and separate slivers and lenses of recycled oceanic crust (ROC). Whereas the current subduction zones have an average ROC to depleted peridotite ratio of about 1/10, this ratio has probably decreased steadily from larger ROC fractions in the Archean⁷⁰. Although a depleted peridotite has higher Fp-content and lower Fe/Mg ratio than a fertile (pyrolitic) peridotite⁵⁵, it may have a slightly stronger spin crossover signal. This effect will be weakened by the diluting ROC content.

The shear and bulk modulus (Fig. 2a), S-wave (Fig. 2b) and P-wave velocity (Fig. 1d, 2c) are calculated for a pyrolite¹⁵ composition. The self consistent geotherms are calculated by setting the starting temperature of the calculation at the top of the lower mantle to 1373 K (the -500 K case), 1873 (the average case), and 2373 K (the +500 K case) (Supplementary Fig. 8 and 9). The mineralogy of four different bulk composition models are reported in Table 1. They are the same as those derived in¹⁵. The Earth's actual mantle geotherm is uncertain, and fitting PREM requires non-adiabatic gradients and/or variations in composition with depth in the lower mantle⁷¹.

	Bm	Fp	Сри	x	y	z
Harzburgite	55.99	42.74	1.27	0.0693	0.1315	0.0149
Peridotite	60.4	34.42	5.19	0.0747	0.1458	0.0492
Pyrolite	62.93	31.58	5.49	0.0779	0.1523	0.0553
Fp-free model	94.18	0.0	5.82	0.1220	0.0	0.0453

Table 1: Compositions in mol.% used in this paper expressed as Bm $(Mg_{1-x-z}Fe_xAl_z)(Si_{1-z}Al_z)O_3 + Fp$, $(Mg_{1-y}Fe_y)O + Ca$ -perovskite (Cpv), $CaSiO_3$. These simplified compositions were also used in ref.¹⁵. The simplified peridotite composition based on ref.^{68,69} is included to demonstrate its similarity to pyrolite used in Fig. 1-2. In our calculations we used a partitioning coefficient $K_D = [Fe/Mg]Bm / [Fe/Mg]Fp = [x/(1-x-z)] / [y/(1-y)] = 0.5$

Here the P-wave velocity in Fig. 1d is calculated using temperatures that align pyrolite S-wave velocity to PREM⁵⁸ at each depth, thus highlighting the inability to match both S-wave and P-wave constraints simultaneously when the effects of a spin crossover are included (S-wave velocities are not significantly affected by the spin crossover, Fig. 2b). Note, that this calculation is performed for an uniform chemical composition without lateral temperature variations.

Fast and slow mapping Most tomography models agree on the large-wavelength structure of seismic velocity anomalies in the mantle e.g. 37,42,44. However, the amplitudes of the anomalies, as well as smaller scale-features such as individual subducted slabs, sometimes vary owing to differences in parameterization, data processing, regularization, and other subjective influences²³. There are also few joint P- and S-wave models that do not include some type of scaling of the P-wave model to the S-wave model in the lower mantle. Finally, wide disparities in amplitudes have been noted between various models⁴³, which may reflect volume and coverage of data, choice of regularization parameters, volume discretization, and other influences (Supplementary Fig. 10).

Instead of relying on particular P- and S-wave model pairs and their stated amplitudes, we set a uniform grid in the mantle and generate a contour based on a given positive/negative σ deviation for fast/slow anomalies, respectively. We define σ for each model by combining and binning all values between 1,000 km and 2,200 km depth (by area) to produce a mid-mantle reference distribution. We use only the mid-mantle to avoid more complex behaviours that appear in the shallow and deep portions of the lower mantle. We then perform an iterative Gaussian fitting procedure⁴³ on the mid-mantle reference distribution, utilizing values only within the interval

 $1 < \sigma < 1$. This procedure avoids the influence of more extreme velocity values on determining the threshold, as these may exhibit non-normal characteristics that would otherwise exert a large influence on the usual arithmetic measure of standard deviation (Supplementary Fig. 10). If the 290 distribution is perfectly normal, then the σ value obtained using this procedure would be identical to the usual measure of standard deviation. Note that this procedure also excludes what will come 292 to be defined as "fast" or "slow" anomalies from the determination of what constitutes fast or slow 293 velocities; only the dominant modal variation of relatively modest velocity variations is used to 294 obtain σ for each model. Supplementary Fig. 10 shows the mid-mantle reference distributions 295 for all of the models used in this study, along with the Gaussian fits we obtain in the -1 < σ < 1 296 intervals. 297

The differing extent of mid-mantle fast anomalies in Vp and Vs requires the simultaneous 298 effect of temperature, composition, and phase. Any temperature effect alone would be expected to 299 manifest in Vs and Vp to a similar extent and magnitude. Since fast anomalies are often interpreted 300 as cold subducted oceanic lithosphere, the next property to consider is composition. Subducted 301 slabs are composed of a thin basaltic crust and a Fp-rich mantle lithosphere. The thin basaltic 302 crust may host anomalous seismic characteristics, but these seismic anomalies are not expected to 303 be detected by seismic tomography at scales of 1000s of km in the mid-mantle. If Fp exists in 304 higher quantities in fast velocity regions, then the bulk rock would have slightly reduced velocity 305 since Fp has slower Vp and Vs than Bm. However, the fast velocity anomaly observed in seismic 306 tomography indicates that temperature dominates the seismic signal even in these more Fp-rich 307 subducting slabs. Since variations in Fp concentration have a similar effect on Vp and Vs, it is 308

difficult to decouple Vp and Vs even with temperature and composition. Fp concentration in slabs
opens up the possibility of the iron spin transition which reduces Vp and not Vs in the presence of
a thermal anomaly.

Vote maps Vote maps are a simple tool, developed to detect the existence and map the distribution
of material exhibiting particular seismic characteristics in the lower mantle. Lekic et al.⁴² and
Cottaar and Lekic⁴⁰ developed a k-means cluster analysis-style vote map for the lower mantle.
This was expanded in Shephard et al.⁴¹, who developed an alternative vote map technique using
tomography and depth-dependent metrics which aimed at surveying individual model depths across
the whole mantle and retaining geometric features (see also Hosseini et al.³²).

The tomography models used in this study were chosen to capture a variety of data types and processing techniques that are employed in tomographic inversions. The 4 P-wave models are DETOX-P01³³, GAP-P4^{34,35}, HMSL-P06²⁸, MITP-2011³⁶, and the 4 S-wave models are HMSL-S06²⁸, S40RTS³⁷, savani³⁸, SEMUCB-WM1³⁹. An earlier vote maps paper⁴¹ applied a similar process to an expanded set of 7 P-wave and 7 S-wave tomography models. The original models are not filtered to exclude any spherical harmonic degrees, and can be accessed via the SubMachine website³² http://submachine.earth.ox.ac.uk/.

The individual tomography models are linearly interpolated along a 0.5° grid with a depth increment of 50 km. Processing was done with Generic Mapping Tools (GMT, version 5.3.1⁷²).

The vote map methodology uses sigma values (standard deviation) as the contour metric for each tomography model at each depth (i.e.⁴³). Each model contributes one vote at each grid cell ac-

cording to whether the model value lies inside (vote=1) or outside (vote=0) the specified contour. Supplementary Fig. 4 shows an example of the vote map contouring procedure for each tomography model (also applicable to the non-vote maps). Votes for each of the 4 models are tabulated 331 to generate the final vote map grid as shown in Fig. 5. The resulting abundance profiles (in % of area) of agreement (i.e. how many models agree at a given depth, where 4 votes is the maxi-333 mum agreement) for alternative sigma thresholds for the individual seismic tomography models are 334 shown Supplementary Figs. 2-3. Two additional tomography models TX2019⁷³ and SP12RTS⁷⁴ 335 which show higher variability than the models chosen in our analysis, are included for comparison 336 (Supplementary Fig. 11). They were constructed with different data and with different purposes, 337 to image the core-mantle boundary at long wavelengths for SP12RTS and to test the influence on 338 subducting slabs in the reference model for the TX2019 inversion, which make them less suitable 339 for our focus on the mid-mantle. Scientific, perceptually uniform colour gradients 75,76 were used 340 in all figures. 341

Data Availability The data generated in this study have been deposited via Zenodo:

http://folk.uio.no/gracees/Shephard_etal_2020_Submitted/

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Author contributions G.E.S., C.H., J.W.H., R.G.T. and R.M.W. instigated the study. G.E.S. and J.W.H. undertook the vote map preparation, C.H. and R.M.W. undertook the seismic velocity calculations, R.M.W. and J.J.V-C. computed elastic moduli and seismic velocities. All authors contributed to the scientific discussion and preparation of the manuscript.

Competing interests The authors declare no competing interests.

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Competing Interests The authors declare that they have no competing financial interests.

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Figure 1 Comparison of mineral physics predictions and seismological observations of the Fe spin crossover in Fp. (a) The depth-temperature distribution of low-spin Fe and three schematic mantle geotherms. The onset of the mixed spin region occurs at shallower depths for relatively colder temperatures and at greater depths and over a broader range at higher temperatures. Surface area of fast (b) and slow (c) velocities in the lower mantle imaged by unanimous consensus (4/4 models) corresponding to the vote maps shown in Figs. 5 and 6. A divergence in the seismic signal between P-wave models relative to S-wave models is revealed below the respective "onset" depths of approximately 1,400 km and 1,800 km. (d) The calculated profile of P-wave velocities for pyrolite (see Supp. Fig.9) reveals a significant departure suggesting that the signature of the spin crossover is not a globally-averaged feature. See Methods. Colour gradients from 75.

Figure 2 Depth dependence of elastic moduli and seismic velocities for pyrolite composition listed in Table 1¹⁵. (a) Shear and bulk moduli. The anomalous behaviour of the bulk modulus, K¹¹ (K = -V(dP/dV), where V is volume and P is pressure) is due to the iron octahedron volume collapse during the spin-state change⁴ associated with the spin crossover. As previously shown¹¹, the pressure onset, the pressure range of the HS-LS crossover, and associated anomalies in K are temperature dependent (same legend all panels). The shear modulus, G, ($G = \tau/\gamma$, where τ is the shear stress and γ is the shear strain) is not significantly affected by the octahedron volume reduction and increases monotonically with increasing pressure and decreasing temperature. (b) Swave ($V_s = \sqrt{G/\rho}$) and (c) P-wave ($V_p = \sqrt{(K+4/3G)/\rho}$) velocity for pyrolite at different

the starting temperature to 1873 K at 660 km, and integrating the adiabatic temperature gradient¹⁵ through the lower mantle. The blue/magenta curves were calculated using the same technique, but decreasing/increasing the temperature at 660 km by ±500 K. In the mixed-spin region, the softening of K¹¹ causes a reduction in P-wave velocity sensitivity to isobaric temperature variations¹⁴, while the S-wave velocity remains sensitive to such temperature variations. Consequently, the expected seismic signal of iron-bearing Fp in the lower mantle consists of a disruption of vertically coherent thermal structures in P-velocities, whereas a coherent thermal structure is apparent in the S-velocities^{12,14}. Additional compositions shown in Supplementary Fig. 1 demonstrate the calculated seismic velocities dependence on Fp proportion.

Figure 3 Workflow used in this paper. Step 1: select tomography model. Step 2: a gaussian fitting procedure is applied (see Methods). Step 3: a contour metric is chosen e.g. fast ($>+1\sigma$ from the mean), and slow ($<-1\sigma$ from the mean) and binary grids are created. Step 4: surface area coverage of the contour is extracted across the lower mantle. For the vote map methodology additional steps are applied between Steps 3-4. Step 3a: binary grids from additional tomography models are created as per Steps 1-3. Step 3b: at each grid point the constituent models (here 4 models) are summed. Step 3c: difference vote maps can be generated, for example by subtracting the S-wave votes from the P-wave votes.

Figure 4 The depth-dependent changes in surface area for the (a) fast ($>+1\sigma$ from the mean), and (b) slow ($<-1\sigma$ from the mean) regions, as applied individually to each of the the 4 P-wave, and 4 S-wave tomography models. The individual model names and details are shown in Supplementary Figs. 2-3. The bold lines are the average of each panel, which are extracted and shown in the rightmost panels. This procedure is similar to that shown in Fig. 1b-c except without the vote map analysis.

Figure 5 Vote maps of mantle tomography models. Variable depth vote maps for fast $(>+1\sigma)$ from the mean), and slow $(<-1\sigma)$ from the mean) mantle for all (a) 4 P-wave and (b) 4 S-wave tomography models (see Methods) considered here. In general, lower mantle vote maps of fast velocity regions reveal subducted slabs, and slow maps reveal plumes and antipodal large low shear wave velocity provinces (LLSVPs). In this map view, the P-wave model vote maps appear less coherent than the S-wave model vote maps in the fast velocity regions of the mid-mantle. Colour gradients from 75 .

Figure 6 Vertical cross sections through the vote maps. All 4 S-wave models (left) and 4 P-wave models (right) are used for profiles through (a) SE Asia and (b) the Farallon slab regions (vote maps for fast velocities), and (c) the African-Afar large low shear wave velocity province (LLSVP) and plume region (vote maps for slow velocities). Location maps are overlain with palaeo-subduction zones between 0-200 Ma as extracted from a global plate reconstruction⁷⁷. Panels (a) and (b) identify vertically coherent fast regions that are common to S-wave models in the mid-mantle indicating the presence of subducted slabs

whereas the slab signal is weak amongst P-wave models. This is more clear in the fast rather than (c) slow regions because at higher temperatures the HS-LS crossover shifts to greater depths where the seismic signal is dominated by the LLSVPs, and also occurs over a broader depth range.

Figure 7 Difference maps between P-wave and S-wave models. Difference maps for the fast (left panels) and slow (right panels) vote maps constructed by subtracting the S-wave model votes (constructed with 4 models) from P-wave model votes (constructed with 4 models). Yellow areas indicate high votes (i.e. the identification of robust features) in P-wave models but not S-wave models, darker purple areas indicate high votes for S-wave models relative to P-wave models, and central colours indicate regions of mutual agreement.

Figure 1

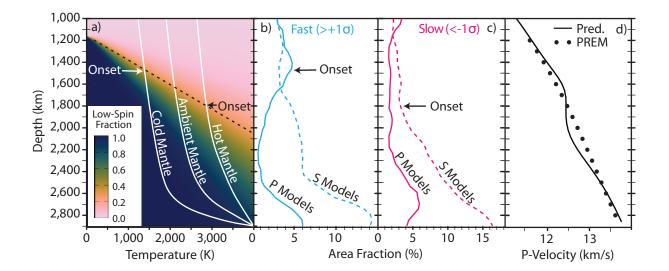


Figure 2

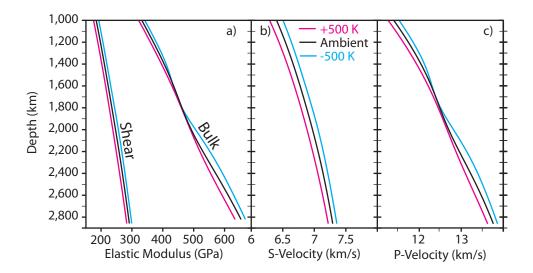


Figure 3

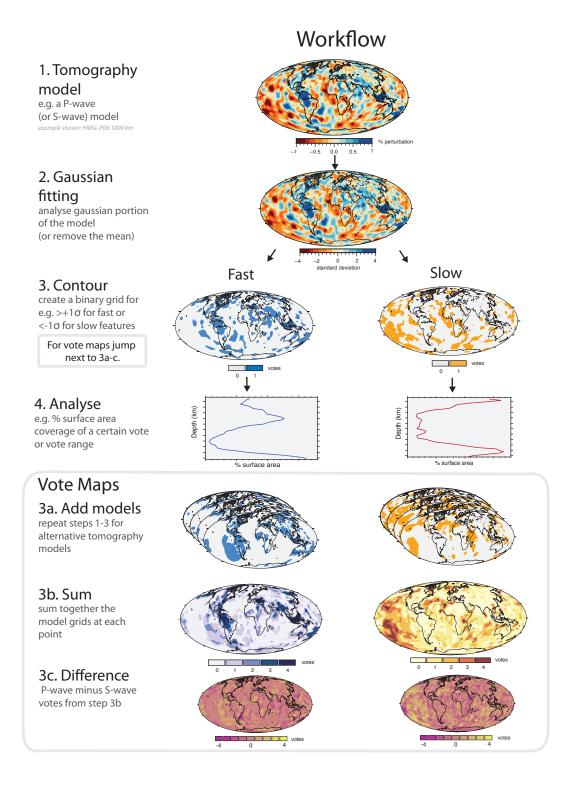


Figure 4

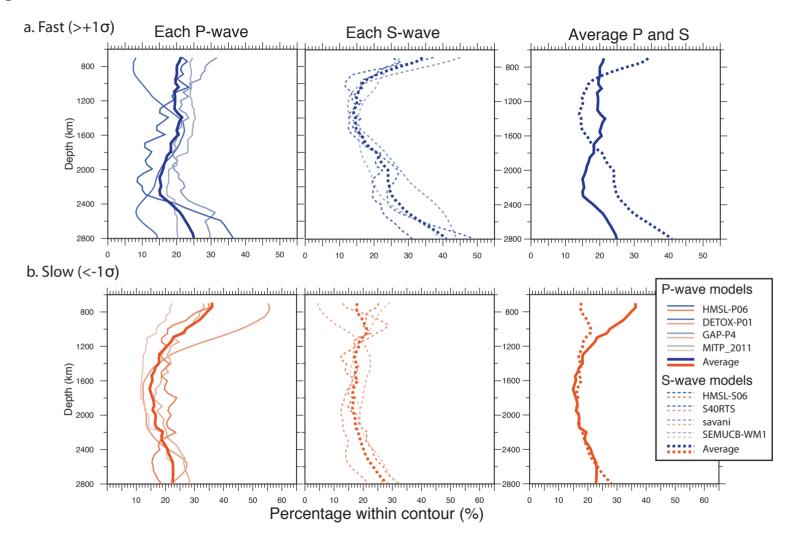


Figure 5

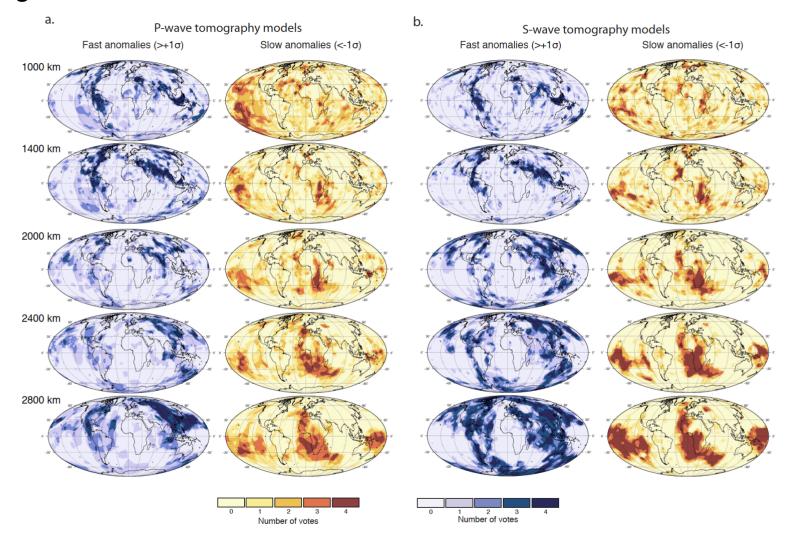


Figure 6

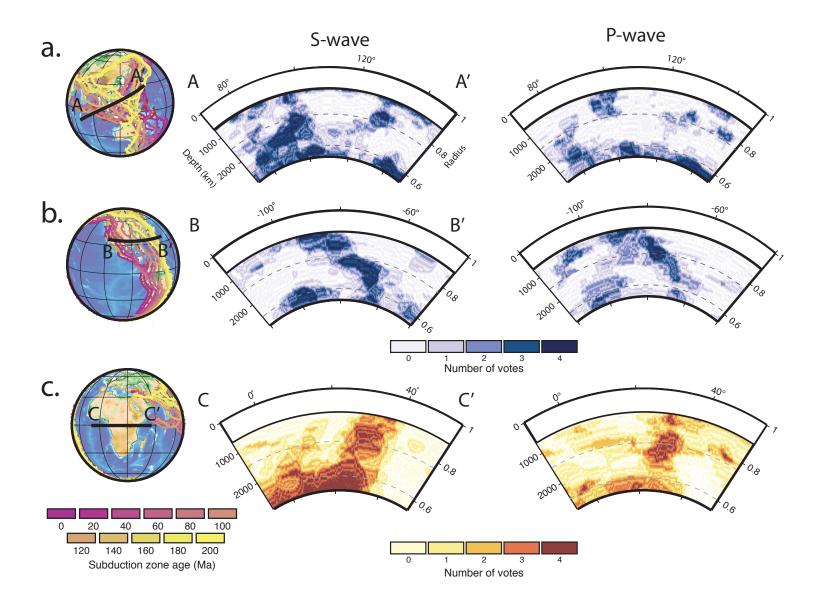
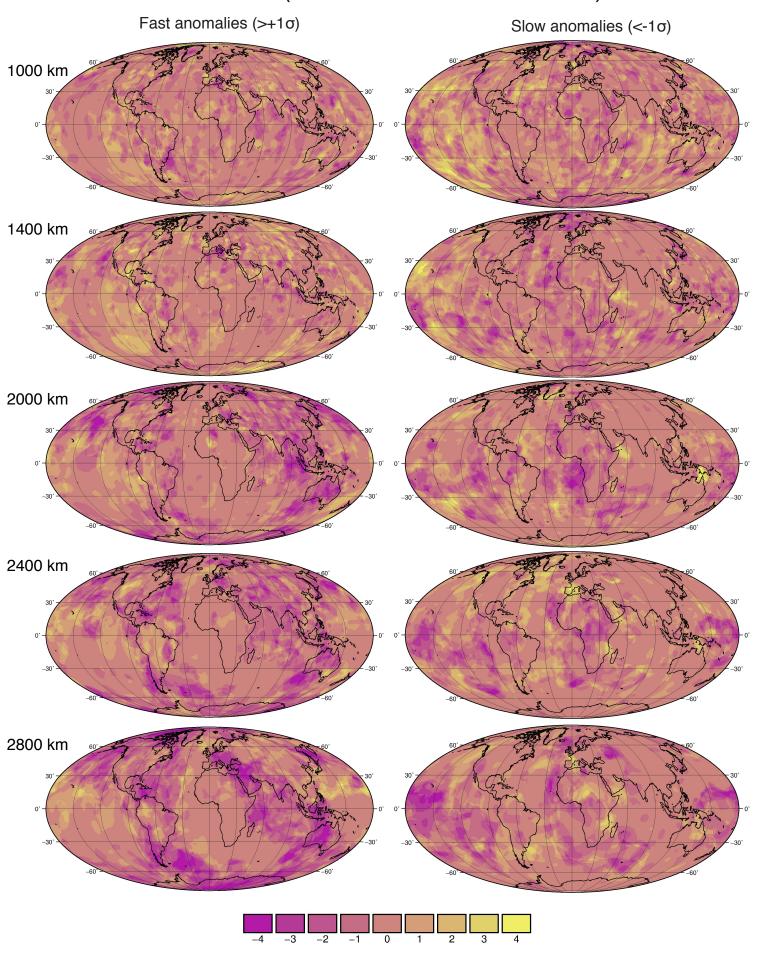


Figure 7

Difference (P-wave minus S-wave votes)



Number of votes (Vp minus Vs)

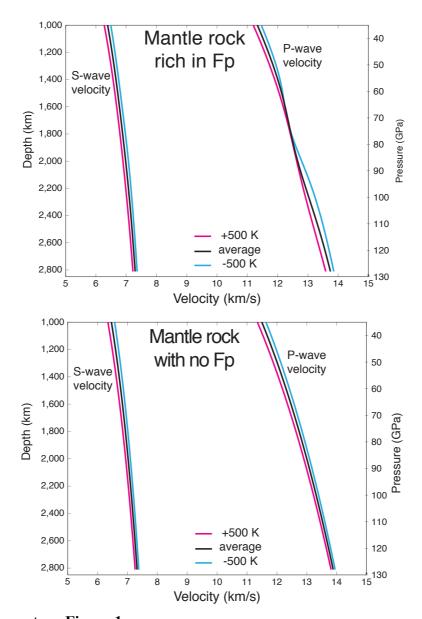
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Supplementary Information: Seismological Expression of the Iron Spin Crossover in Ferropericlase in the Earth's Lower Mantle

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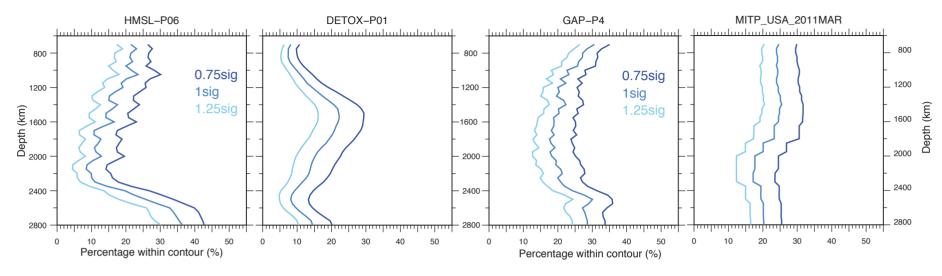
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- 6. Department of Applied Physics and Applied Mathematics, Columbia University, New York City, USA

Supplementary Figures

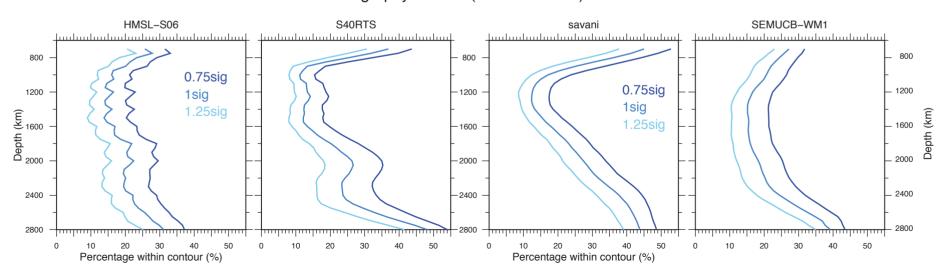


Calculated shear and compressional velocities using the ab initio technique described in Methods section for harzburgite (top) and an Fp-free model composition (bottom). The ab initio calculations were performed for each composition with the self consistent geotherm anchored at 1873 K at the top of the lower mantle (black) along with the same calculation anchored at 500 K below (blue) and a 500 K above (magenta). The properties of individual minerals were calculated using an ideal solid solution formalism, where the end-members were the Mg-compound and a (Mg,Fe) solid solution with Mg = 0.875 and Fe = 0.125 for bridgmanite 1 and Mg = 0.8125 and Fe = 0.1875 for ferropericlase 2. Aggregate elastic properties were obtained using the Voigt-Reuss-Hill average for the Fp-free mantle model composition, consisting of 94 wt.% bridgmanite and 6 wt.% calcium perovskite and Fp-rich harzburgite consisting of 74 wt.% bridgmanite, 24 wt.% ferropericlase, and 2 wt.% calcium perovskite

P-wave tomography models (fast anomalies)



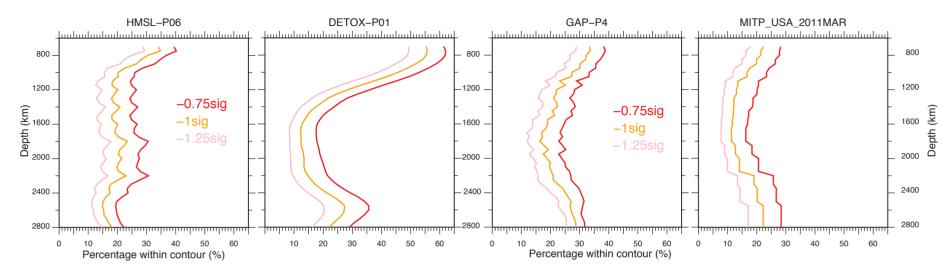
S-wave tomography models (fast anomalies)



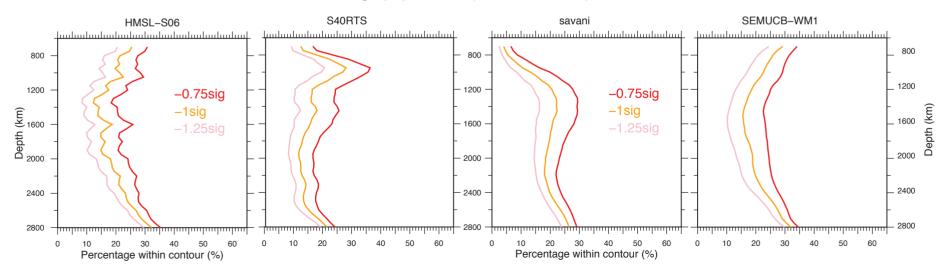
Supplementary Figure 2 (previous page)

Surface area coverage for individual models and for variable sigma contours, for fast anomalies. Area fraction of fast (>+0.75, >+1, >+1.25 σ) anomalies as a function of depth for the 8 tomography models individually. This is similar to Fig. 1b and 4a (and Supplementary Fig. 5 for HMSL₃), but presented here for the individual tomography models (4 P-wave and 4 S-wave) prior to being summed into the vote map. There is high variability between and within the individual tomography models, including the joint HMSL models. While a decorrelation between P- and S-wave models is apparent between some model combinations, it is not in others, which is why a single pair of tomography models in isolation may not render a robust signal of the spin transition. Other features in these models, such as the oscillatory behaviour in HMSL, are not well understood and can also distract from the broader trends in P-wave and S-wave velocity.

P-wave tomography models (slow anomalies)



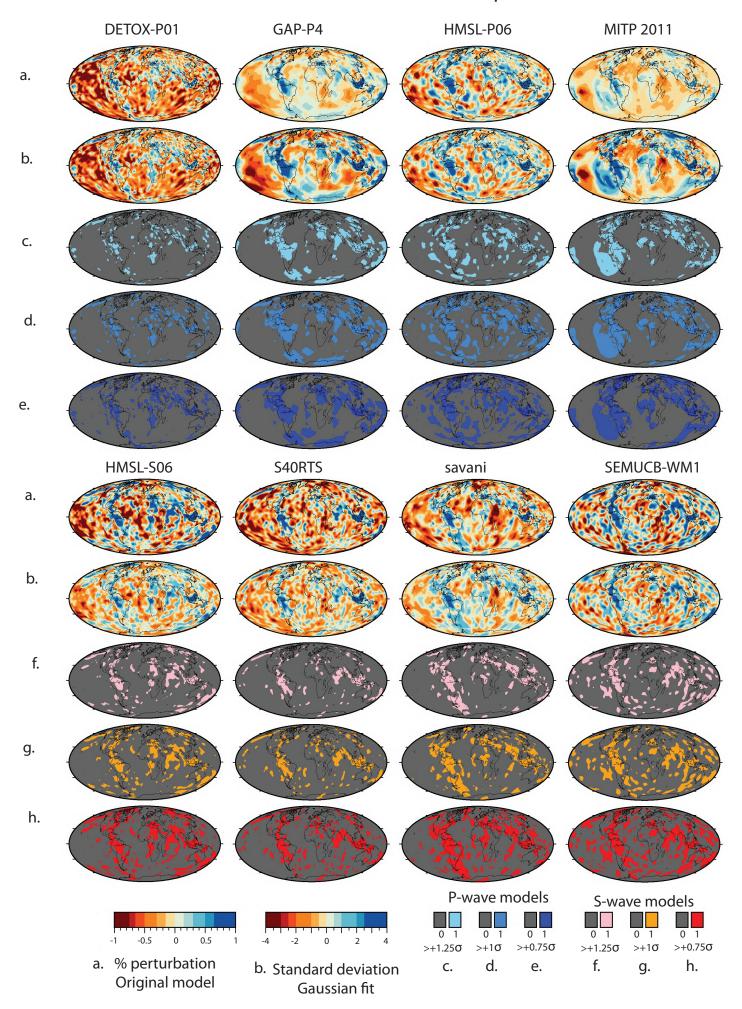
S-wave tomography models (slow anomalies)



Supplementary Figure 3 (previous page)

Surface area coverage for individual models and for variable sigma contours, for slow anomalies. Area fractions of slow (<-0.75, <-1, <-1.25 σ) anomalies as a function of depth for the 8 tomography models. Similar to Fig. 1c, but here presented for the individual tomography models (4 P-wave and 4 S-wave) prior to being summed into the vote map. As with the fast anomalies (Supplementary Figure 2), there is high variability between the tomography models. Other features in these models, such as the oscillatory behaviour in HMSL, are not well understood and can also distract from the broader trends in P-wave and S-wave velocity.

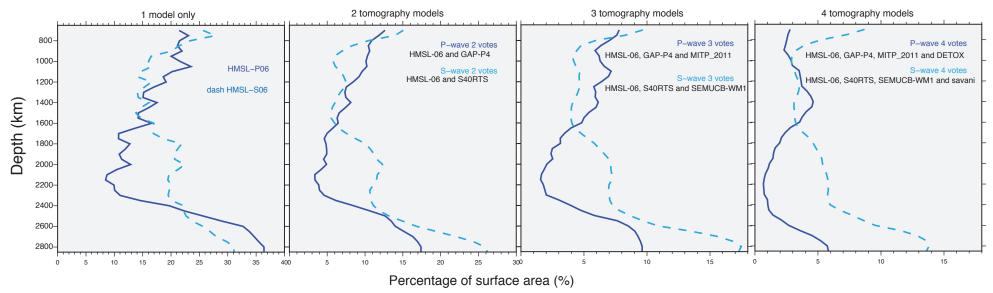
Fast anomalies at 1000 km depth

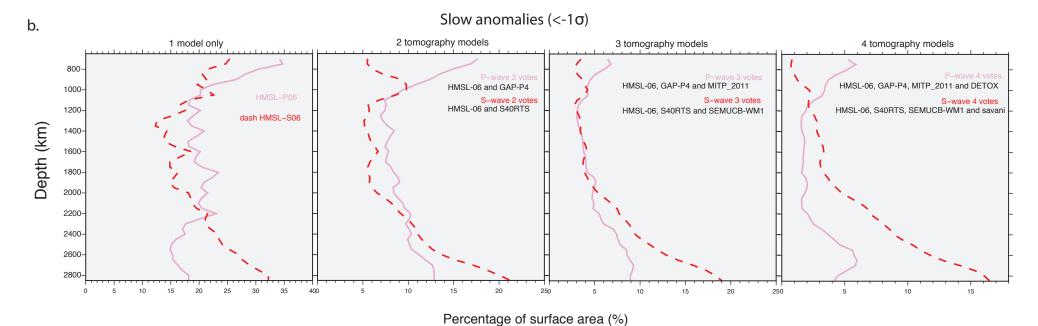


Supplementary Figure 4 (previous page)

A graphical example figure of the contouring procedure for fast anomalies at 1000 km depth. This step occurs before the models are added into vote maps and are equivalent to what is shown in Supplementary Figures 2-3, and Figure 3 Steps 1-3. Each of the 8 tomography models are shown in their original format (panel a) and after the gaussian fitting is applied to 1000-2200 km depth (panel b; See Supplementary Figure 10). The models are contoured for values equal to or higher than +0.75, +1, +1.25 σ) anomalies for the P-wave models (panels c, d, e) and S-wave models (panels f, g, h), respectively. The fast vote maps in the main manuscript were constructed from the >+1 sigma vote maps. Shephard et al. (2017)4 presents further details of the vote map methodology.



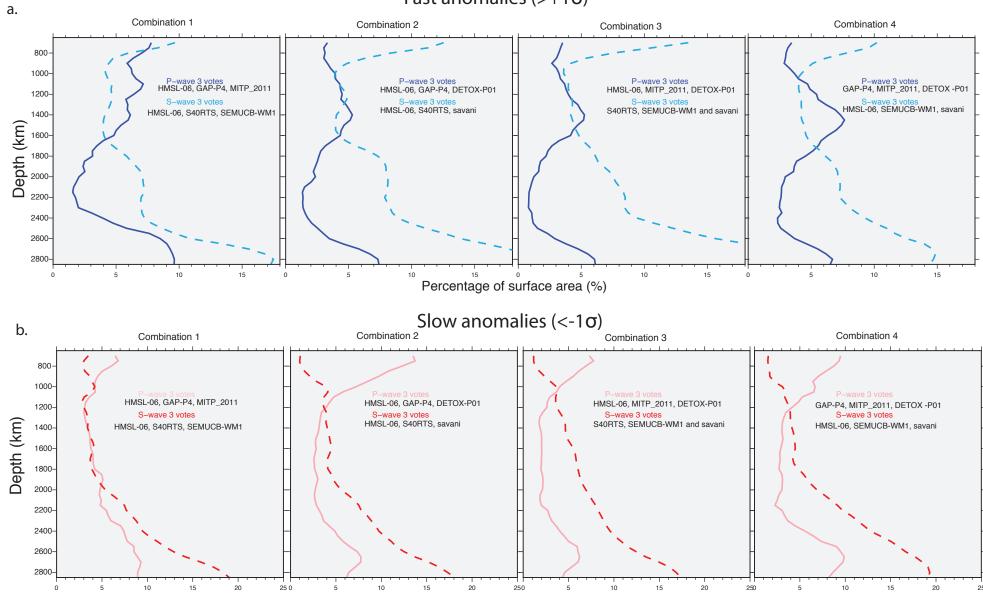




Supplementary Figure 5 (previous page)

The influence of using fewer tomography models. Area coverage as a function of depth for the sequential addition of tomography models used in this study. P-wave models (solid) and S-wave models (dashed), top panels (a) show fast anomalies, and bottom (b) panels show slow anomalies. Models used are listed within each panel (the HMSL profiles (1 model) are the same as shown in Supplementary Figures 2 and 3). There is an apparent decorrelation of P-wave and S-wave profiles in all combinations. However, the signal becomes more apparent when the models are summed into the vote maps, which identify the most common features between tomography models.

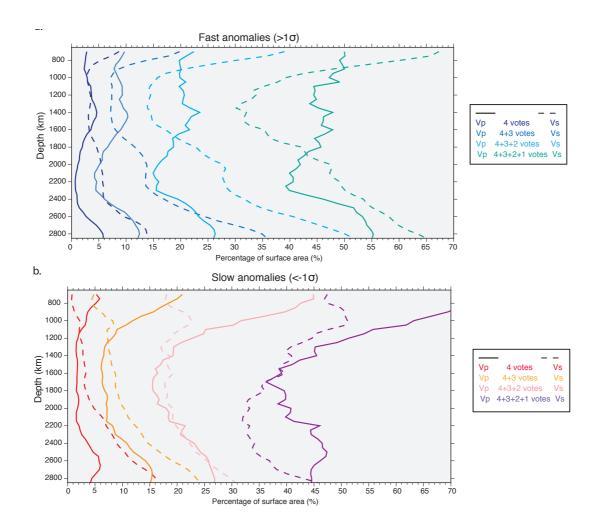




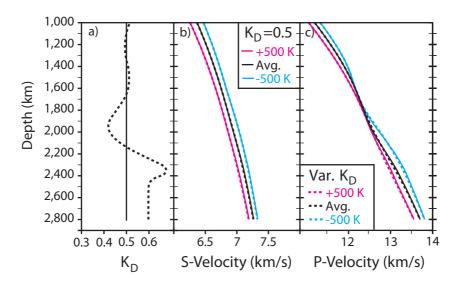
Percentage of surface area (%)

Supplementary Figure 6 (previous page)

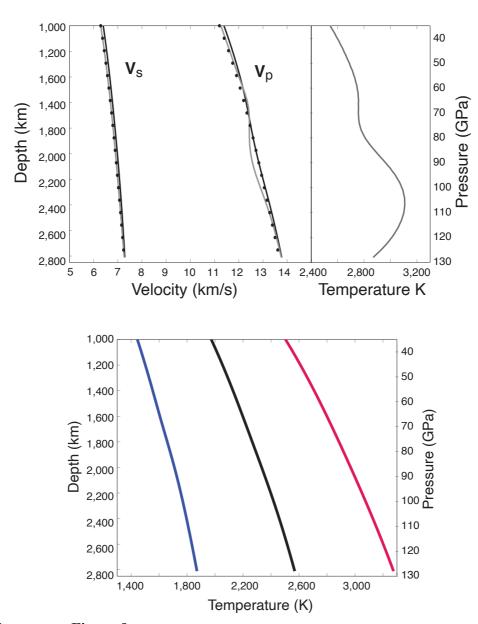
Comparison of the vote map procedure for alternative combinations using 3 of the 4 alternative tomography models used in the manuscript, for Vp (solid) and Vs (dashed). The combination models are listed within each panel. The surface area is the coverage for the (maximum) 3 votes, and is complementary to Figure 1b and 1c which shows the maximum 4 votes. Fast velocities are shown in the top panels (a) and slow velocities in the lower panels (b). While there is some variability between the combinations, the observed decorrelation between P and S-wave velocity models is consistent at ~ 1400 km for fast velocities and ~ 1800 km for the slow velocities. This suggests that, regardless of which three models are used (conversely, the one model which is excluded), the effects of the iron spin cross-over in ferropericlase can be observed.



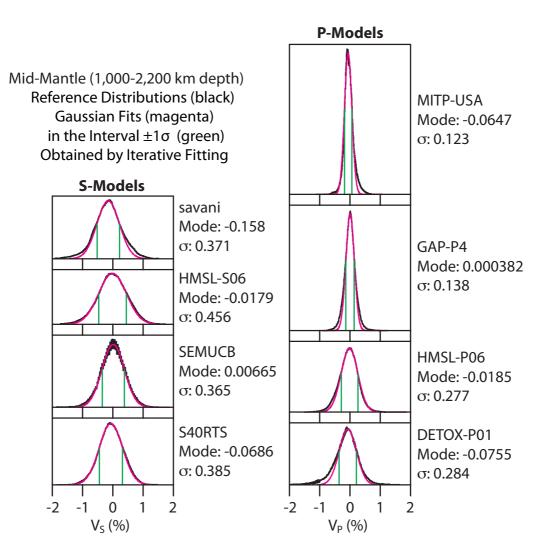
Comparison of depth-dependent changes in surface area for alternative vote combinations, Vp (solid) and Vs (dashed). In Figure 1, only the area corresponding to the maximum vote of 4 was shown; "4+3 votes" indicates that the area corresponding to votes of 3 and 4 are summed and plotted, "4+3+2" indicates votes of 2, 3 and votes are summed and plotted etc. Fast velocities are shown in the top panels (a) and slow velocities in the lower panels (b). The vote counts are listed in the inset panel. For the combination of 4 and 4+3 votes (and 4+3+2 for the fast anomalies), the decorrelation signal is very similar. However, when 2 and 1 votes are also added the signal becomes more complicated; this is due to the potential inclusion of noise/artefacts which may not be robust features (because only one model captured it; see Shephard et al. (2017)4 for further details). Nonetheless, the robustness of the signal suggests that the effects of the iron spin cross-over can be observed.



The change in the seismic velocities using constant versus depth dependent partitioning of iron between Br and Fp, Kd. Panel (a): Depth-dependent Kd 5 curve (dashed line) and the constant 0.5 value (solid line) used in the main text. Panels (b and c): Shear and compressional velocities for the depth-dependent Kd 5 case (dashed lines) and the constant value 0.5 case (solid lines, same as Figure 2). A higher proportion of Fe in the ferropericlase (lower Kd) may increase the crossover pressure6. We find that the FeO content in ferropericlase remains below 25 mol%, which is the threshold for observing substantial increases in the crossover transition pressure7 for the depth-dependent Kd case. Thus, depth-dependent Kd does not have a significant influence on the crossover depth/pressure range over which we observe the anomalous signal in compressional velocity in the tomographic models.

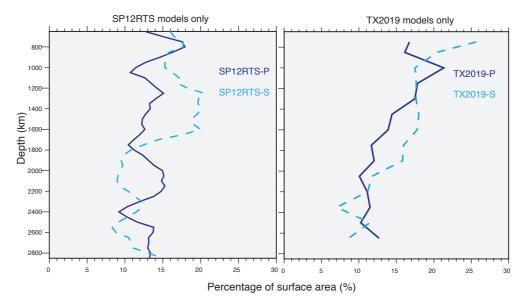


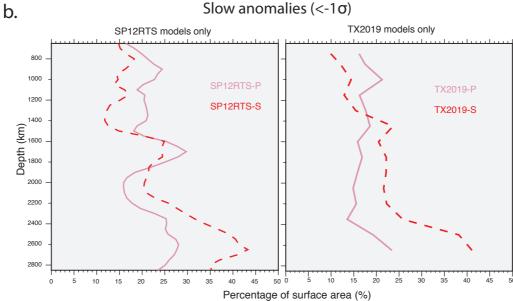
Plots related to velocity, temperature and pressure/depth calculations. Top panel: Development of Figure 1d. PREM8 is shown in black circles and the black lines are the calculated velocities for pyrolite9. Figure 1d demonstrates the spin transition effect on Vp for the case in which predicted Vs matches PREM (grey lines). Since Vs for pyrolite does not fit PREM with an adiabatic temperature gradient10, 11, the temperature profile that shifts Vs to align with PREM (grey line right panel) undulates in the lowermost mantle. Bottom panel: The self-consistent geotherms from our pyrolite calculations9 for the elastic moduli and velocity profiles plotted in Figure 2. The calculations start by setting the temperature at the top of the lower mantle to 1373 K (blue, the -500 K case), 1873 K (black, the average case), and 2373 K (red, the +500 K case) and allowing the temperature to increase adiabatically as the calculations proceed to higher pressures across the lower mantle.



The results of our Gaussian-fitting procedure (see Methods) for all 8 tomography models used in this study. Analysis of velocity-frequency distributions of a variety of tomographic models reveals that they exhibit significant differences that confound intermodal comparisons₁₂. These differences can be categorized as scale/amplitude (e.g., caused by variability in tomographic model data, design, regularization), shift/alignment (e.g., caused by reference to different 1-D global models), and shape of the distributions (variations in distribution morphology that remain even after accounting for linear shift and scale differences). By analyzing distributions we find that all models yield Gaussian-like variations in Vp and Vs in the depth range 1,000-2.000 km, however, there are particularly large discrepancies in amplitude between the different models₁₂. These scale differences must be normalized to a reference standard in order to establish a useful definition for fast and slow anomalies that can be compared across the suite of models. We do this by combining each model from 1,000-2,200 km depth, and performing iterative Gaussian fitting to the central portion (i.e., within $\pm \sigma$) of the resultant distribution as described in Methods. The value of σ obtained in this manner is then used to define what qualifies as fast and slow anomalies in the models).







Surface area calculations for two additional tomography models. In addition to the eight models used in the paper, depth-dependent change in surface areas for the joint tomography models of SP12RTS₁₃ and TX2019₁₄ are also included for reference. The trend between P- and S-wave models is somewhat variable between the individual model pairs of SP12RTS, TX2019, (as for HMSL₃, Supplementary Figure 5) but do hint at a mid-mantle decorrelation similar to the models analyzed in the main text. However, aspects of their construction such as inclusion of subducting slabs in the starting model for TX2019 and the long-wavelength SP12RTS make them less ideal for the mid-mantle focus in this study.

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