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

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The two most abundant minerals in the Earth are lower mantle bridgmanite and ferropericlase. 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 regions associated with cold Fp-rich subducted oceanic lithosphere: the relative abundance of fast ve-

locities in P- and S-wave tomography models diverges in the ∼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 ∼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 non-uniformly distributed thermochemical heterogeneities are present and dampen the global signature of the Fp spin crossover.

1 Introduction

Mineral physics experiments[1–3] and theory[4,5] consistently predict that Fe^{2+} in Fp, (Mg,Fe)O, undergoes a high-spin to low-spin (HS-LS) crossover at mid-lower mantle conditions (Fig. 1). Confirmation of the existence and observation of the iron spin crossover in the Earth's mantle is relevant because it alters material properties such as density, viscosity, elasticity, thermal conductivity, and elemental partitioning in the lower mantle[6]. Slab, plume, and deep mantle dynamics are all thought to be affected by the crossover[7,8]. 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-waves) and shear (S-waves) wave velocities offer a promising target for geophysical observation (Fig. 2). In particular, a volume reduction during the spin crossover[4] inevitably increases its compressibility and decreases its bulk modulus [9]. Both the onset pressure as well as pressure interval of the mixed spin region (where both high- and low-spin states coexist) are predicted to increase at higher temperatures[6,9–11]. The temperature dependence of the pressure onset and pressure range of the HS-LS crossover result in an anomalous dependence of the bulk modulus on temperature[12], with little influence on the shear modulus (Fig. 2a). The magnitude of this effect increases for higher iron contents and abundance of Fp[6]. Specifically, the transition pressure does not significantly change for iron concentrations below $\sim$20% in Fp, which is the case for most Fp-bearing aggregates in the lower mantle[13].

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. Fig. 2 shows the effect of the iron spin crossover in Fp on the seismic velocities of a hypothetical pyrolite composition rock. Our *ab initio* mineral physics calculations[13] use a simplified pyrolite composition consisting of 78.9 mol% bridgmanite, 14.6 mol% ferropericlase and 6.5 mol% calcium perovskite, with 16 mol% FeO in the Fp. The mantle is thought to be a lithological mix of depleted peridotite and separate slivers and lenses of recycled oceanic crust. Supplementary Fig. 1 shows P-wave and S-wave velocities for Fp-free rock (perovskitite), and Fp-rich harzburgite containing 26 mol% Fp, to demonstrate the influence of variable Fp abundances on mid-mantle seismic velocities. The harzburgite composition represents melt-depleted sub-oceanic mantle lithosphere. Most domains in the lower mantle likely contain Fp in the range bounded by these two compositions. The Fe/Mg ratio of Fp in a pyrolitic model composition has been proposed as representative for 1-D seismic profiles[14,15]. However, the compressional velocity of a homogeneous pyrolitic mantle does not fit 1-D seismic models when the effects of the iron spin crossover are included in the predicted seismic velocity computations[16]. Our predicted velocity reductions are supported by experimental data[5], especially from Brillouin scattering [11,17]. 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 mixed spin region (see Fig. 2c).

In the lower mantle, regions with fast seismic anomalies are commonly interpreted as cold, sinking oceanic lithosphere[18,19]. These subducted slabs typically comprise 5-7 km of basaltic crust underlain by $\sim$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 therefore 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 boundary[20]. Depending on wavelength and depth, previous comparisons of P- and S-wave tomography models suggest different characteristics in the lower mantle[21–23], despite similar P- and S-wave coverage and thus similar resolution within the mid-lower mantle[24,25]. Thus, we focus on characteristics within fast and slow velocity regions in P-wave and S-wave models, both via individual tomography models and combined through tomographic vote maps.

2 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[26–28]. Here we use 4 P-wave models (DETOX-P01[29], GAP-P4[30,31], HMSL-P06[32], MITP-2011[33]), and 4 S-wave models (HMSL-S06[32], S40RTS[34], savani[35], SEMUCB-WM1[36]) 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 exceed one standard deviation (σ) from the mode 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, $\leq$-1σ 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 more variability between the P-wave models than between the S-wave models, as also noted in [37]. 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.

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 [38] (Fig. 3a-c, see Methods). The highest count (Fig. 1b-c; 4 votes) indicates regions where all four models (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 Ocean[38]. Likewise, the cluster analysis-based vote map technique [37,39] 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 tomography models; it rather highlights the features that are common to multiple models. For example, when analysing global, whole mantle models, it is difficult to know if any given patch of anomalously fast or slow velocity is due to imperfect input data, inversion artefacts, or is a genuine signal present in the lower mantle. Each tomography model utilizes different types of input data, parameterization, regularization, and other subjective choices in their construction (e.g. see model compilations[28,38,40,41]). Therefore, we expect that features introduced into individual tomography models due to unique tomographic data and/or modeling approaches will not have a strong influence in the highest count of the vote maps (e.g.[39]). Furthermore, our contour analysis 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.

Vote maps - fast: 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 composition, Fig. 1a. The decorrelation of anomalous P-wave and S-wave abundances is a robust signal 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 also demonstrated in an earlier vote map paper [38] which used an expanded set of 14 tomography models and contoured by the mean of the positive values rather than standard deviation. Furthermore, in Supplementary Fig. 7 we compare the depth-dependent signal when using 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.

Vote maps - slow: To further test the hypothesis that the decoupling of the fast velocity signals in P-wave and S-wave models reflects a spin crossover in Fp, we examine seismically slow, and presumably warm, portions of tomographic models. The surface area of slow velocity regions in the vote maps (Fig. 1c) reveals that the onset of divergence shifts to greater depths (i.e. below $\sim$1,800 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), leading to a more diffuse seismic signal. The divergence in slow velocity regions between P- and 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 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).

Figs. 5-6 show horizontal and vertical cross-sections, respectively, through vote maps of fast and slow velocity regions. All vote values are shown in these images (i.e. 0-4 votes). We can qualitatively observe a divergence in the agreement among P-wave models compared to S-wave models in the mid mantle for both fast and slow anomalies. For example, fast anomalies attributed to subducted slabs under North America and SE-Asia appear contiguous through the mid-mantle in S-wave vote maps. However, the P-wave vote maps show a weakening of the fast seismic signal in the mid mantle (coherent subducted lithosphere at the top and bottom of the lower mantle is still observed). Likewise, the slow mantle domain under Africa and the Afar hotpot region is more readily apparent in S-wave than in P-wave vote maps towards the lowermost mantle. This observed interference is what is predicted for the spin crossover in Fp[12]. The disruption of slab and plume images in the mid-mantle has also been noted in other studies [22,42–46]. Fig. 7 shows difference maps, highlighting the spatial and depth-dependent differences between the P- and S-wave vote maps. There is a dominance of S-wave votes over P-wave votes in the lowermost mantle, especially for the fast anomalies in regions of long-lived subduction (Figs. 5 and 6), and in the slow anomalies for regions corresponding to the LLSVP domains.

We note that the abundance of fast velocity regions in both P-wave and S-wave models (Fig. 1b, 4) increases below $\sim$2,500 km depth, with the area of fast S-wave anomalies increasing rapidly toward the base of the mantle. This relative difference between fast S- and P-wave anomalies near the core-mantle boundary is likely caused by the appearance of post-perovskite in cold mantle, which is expected to increase S-wave velocity by $\sim$1-2% but has notably smaller effect on P-waves[47–49]. The difference maps between P-wave and S-wave votes at 2,800 km depth, shown in Fig. 7, reveal regions of potential post-perovskite (dark purple regions indicating higher S-wave votes than P-wave votes). The antipodal LLSVPs, beneath the Pacific and Africa, are areas where the S-wave velocity is greatly reduced relative to the P-velocity at the base of the mantle ($\sim$2,700 km). The divergence between S- and P-wave behaviours within the LLSVPs has been used to argue for the presence of dense chemically distinct piles in these regions[50].

Effect of iron partitioning: The spin crossover is expected to influence the iron partitioning (K_D) between bridgmanite (Bm), (Mg,Fe,Al,Si)O_3, and Fp[1,51] by increasing the mole% of FeO in Fp, thus decreasing K_D[51]. Since the spin crossover may shift to higher pressures as K_D decreases[6], 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[51] 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 content below $\sim$20 mole% (e.g.[52,53]). 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 for Fp-rich compositions, Supplementary Fig. 1.

Implications for lower mantle composition: A reduction in the 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. Due to uncertainties in the average mantle geotherm[16] we compare our predicted P- and S-wave velocities to the Preliminary Reference Earth Model (PREM)[54] radial P-wave profile using a temperature profile that aligns the predicted S-wave velocity to PREM, Fig. 1d. These predictions for a pyrolite composition demonstrate that the spin crossover signal could be present in 1-D seismic profiles if the lower mantle had an adiabatic temperature profile and Fp-bearing composition. However, the intensity of the P-wave velocity reduction depends on the Fp abundance and the abundance of iron in the Fp which could be different than our model composition. Since Bm has a similar spin crossover for ferric iron (Fe^{3+}) located in the octahedral B-site[55], the lack of a distinct iron crossover in the lower mantle [56] suggests that aluminium displaces Fe^{3+} from the B-site[57]. While there are still uncertainties on the spin crossover pressure range and magnitude of the seismic signal at the highest mantle temperatures, the general agreement between theoretical predictions[5] and experimental measurements[11] at room temperature compels us to consider how to reconcile the patterns observed here, in both the fast and slow regions, with those from the 1-D average profiles.

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 mantle regions expected to have peridotitic-to-pyrolitic compositions. Variable composition, such as regions with less Fp than pyrolite or less iron in the Fp, could disrupt and reduce the spin crossover signal [10,16]. Lateral temperature variations introduce a depth dependence to the P-wave seismic velocity inflection, which could reduce the globally averaged signal. Geodynamically, the lack of a ubiquitous signal of the iron spin crossover in the lower mantle may indicate that sluggish mantle mixing has yet to erase large-scale heterogeneities. The concentration of Fp in the fastest and slowest regions of the lower mantle is complementary to high viscosity thus likely Fp-poor regions occupying large domains of the lower mantle [20,58]. In addition, 1-D seismic models using low-order polynomial parameterizations of radial velocities may have smoothed the seismic signal of the iron spin crossover which becomes more subdued as the shape and distribution of thermo-chemical provinces becomes more varied. High resolution regional 1-D profiles are challenging to construct but would reveal the presence or absence of Fp outside of regions with large lateral temperature variations such as those identified in this study. Further analysis is needed to more fully address the range of scales and compositions that could jointly satisfy mineral physics and seismic constraints.

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 subtle 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. Uniquely identifying 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 temperature and composition variations in the lower mantle.

3 Methods

Predictions of the Spin Crossover in Fp. Fig. 1a was calculated for $Mg_{1-x}Fe_xO$ with x=18.75% using published models[5,12]. The low spin fraction is calculated as:

$$n(P,T) = \frac{1}{1 + m(2S+1)\exp\left[\frac{\Delta G^{\text{st+vib}}_{\text{HS-LS}}}{X_{\text{Fe}} k_B T}\right]} \quad (1)$$

where m = 3 for the three possible orientations of minority electron d orbital (xy, yz, or zx) and S = 2. $\Delta G^{\text{st+vib}}_{\text{HS-LS}}$ includes only static and vibrational energy, without electronic entropy. Our elastic moduli and densities are also taken from published models[5,13,59,60]. These calculations used the rotationally invariant local density approximation LDA+U_{SC} method calculated with a self-consistent Hubbard U[61]. Results for Fp were obtained using a 64-atom supercell with an iron concentration of x=18.75% (24 Mg, 32 O, and 6 Fe maximally separated from each other). Thermoelastic properties were then obtained for other concentrations by linearly interpolating between x=0 and x=18.75%. The vibrational density of states (VDOS) was computed using the vibrational virtual-crystal model[9], 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 measurements[11]. Thermoelastic properties from[59,60] are used for Fe^{2+}-, Fe^{3+}- and Al-bearing bridgmanite.

The mantle is thought to be a lithological mix of depleted peridotite and separate slivers and

	SiO_2	MgO	FeO	CaO	Al_2O_3
Harzburgite	43.52 (36.07)	45.73 (56.51)	8.76 (6.07)	0.91 (0.81)	1.09 (0.53)
Peridotite	44.48 (38.50)	39.22 (50.61)	8.1 (5.86)	3.44 (3.19)	3.59 (1.83)
Pyrolite	45.00 (39.37)	37.80 (49.30)	8.05 (5.89)	3.55 (3.33)	4.09 (2.11)
Fp-free model	54.79 (48.91)	30.11 (40.06)	7.85 (5.86)	3.11 (2.97)	4.14 (2.18)

Table 1: Compositions used in this study and in [13] in wt.% (mole %). The velocities, elastic moduli, and self consistent thermal profiles (isentrope) for harzburgite[62], pyrolite[63,64], peridotite[65], and an Fe-free model composition[64] are derived from recent *ab initio* calculations[13] which incorporate the effects of the iron spin crossover in Fp. The signature of the spin crossover in peridotite occurs at a similar pressure and temperature range as for pyrolite for the same geotherm.

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 Archean (e.g. [66]). Although a depleted peridotite has higher Fp-content with higher Fe/Mg ratio than a fertile (pyrolitic) peridotite [51], presumably resulting in 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 pyrolite[63] 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 oxide components (Table 1) are 45 wt.% SiO_2, 38 wt.% MgO, 8 wt.% FeO, 4 wt.% CaO, and 4 wt.% Al_2O_3, and the rock mineralogy is 76 mole% bridgmanite, 17 mole% ferropericlase, and 7 wt.% calcium perovskite. The calculations for peridotite (Table 1) are the same, but with 6 mole% CaO. Ferropericlase, $(Mg_{0.85},Fe_{0.15})O$, hosts 15 mol% FeO[13]. 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 mantle[67]. Here the P-wave velocity in Fig. 1d is calculated using temperatures that align pyrolite S-wave velocity to PREM[54] 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 averaged 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.[34,39,42]. 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 influences[22]. 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 models[41], 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 procedure [41] 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 Figs. 10, 11). If the 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 to be defined as "fast" or "slow" anomalies from the determination of what constitutes fast or slow velocities;

only the dominant modal variation of relatively modest velocity variations is used to obtain σ for each model. Supplementary Fig. 10 shows the mid-mantle reference distributions for all of the models used in this study, along with the Gaussian fits we obtain in the -1< σ <1 intervals. Supplementary Fig. 11 shows that the gaussian fitting procedure does not affect the relative variation of seismic velocities in the models, it only serves to bring them into alignment and enables their core velocity variations to exhibit similar amplitudes.

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.[39] and Cottaar and Lekic[37] developed a k-means cluster analysis-style vote map for the lower mantle. This was expanded in Shephard et al.[38], 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.[28]).

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-P01[29], GAP-P4[30,31], HMSL-P06[32], MITP-2011[33], and the 4 S-wave models are HMSL-S06[32], S40RTS[34], savani[35], SEMUCB-WM1[36]. We refer to the original vote maps paper[38] which applied a similar process but to an expanded set of 7 P-wave and 7 S-wave models, and contoured by the mean of the positive values. The original models are not filtered to exclude any spherical harmonic degrees, and can be accessed via the SubMachine website[28] http://submachine.earth.ox.ac.uk/.

As outlined in the original vote map methodology adapted here[38], 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 5.3.1[68]). The vote map methodology uses sigma values (standard deviation) as the contour metric for each tomography model at each depth (i.e.[41]). Each model contributes one vote at each grid cell according 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 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 maximum agreement) for alternative sigma thresholds for the individual seismic tomography models are shown Supplementary Figs. 2-3. Two additional tomography models TX2019[69] and SP12RTS[70] which show higher variability than the models chosen in our analysis, are included for comparison (Supplementary Fig. 12). They were constructed with different data and with different purposes, to image the core-mantle boundary for SP12RTS and to test the influence on subducting slabs for TX2019, which may not make them ideal for our focus on the mid-mantle. Scientific, perceptually uniform colour maps [71,72] were used in all figures.

Data Availability The datasets generated and/or analysed during the current study are available at Zenodo [will be updated upon acceptance], temporary file link:

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

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.

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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[13] profile of P-wave velocities for pyrolite using temperatures that fit S-wave velocities to PREM[54] reveals a significant departure suggesting that the signature of the spin crossover is not a globally-averaged feature. See Methods. Colour maps from[71].

Figure 2 Depth dependence of elastic moduli and seismic velocities for pyrolite[63] containing 17 wt.% Fp with 16 mol% of FeO, 76 wt.% bridgmanite, and 7 wt.% calcium perovskite[13]. (a) Shear and bulk moduli. The anomalous behaviour of the bulk modulus, K,[9] ($K = -V(dP/dV)$, where V is volume and P is pressure) is due to the iron octahedron volume collapse during the spin-state change[4] associated with the spin crossover. As previously shown[9], 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) S-wave ($V_s = \sqrt{G/\rho}$) and (c) P-wave ($V_p = \sqrt{(K + 4/3G)/\rho}$) velocity for pyrolite at different temperatures. The average mantle temperature profile (black) is calculated by setting the starting temperature to 1873 K at 660 km, and integrating the adiabatic temperature gradient[13] through the lower mantle. The blue/magenta curves were calculated using the same technique, but decreasing/increasing the temperature at 1873 km by $\pm$500 K. In the mixed-spin region, the softening of K[9] causes a reduction in P-wave velocity sensitivity to isobaric temperature variations[12], while the S-wave velocity remains sensitive to such temperature variations. Consequently, the expected seismic signal of 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[10,12]. Alternative compositions shown in Supplementary Fig. 1

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 ($>$+1σ from the mean), and slow ($<$-1σ 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.

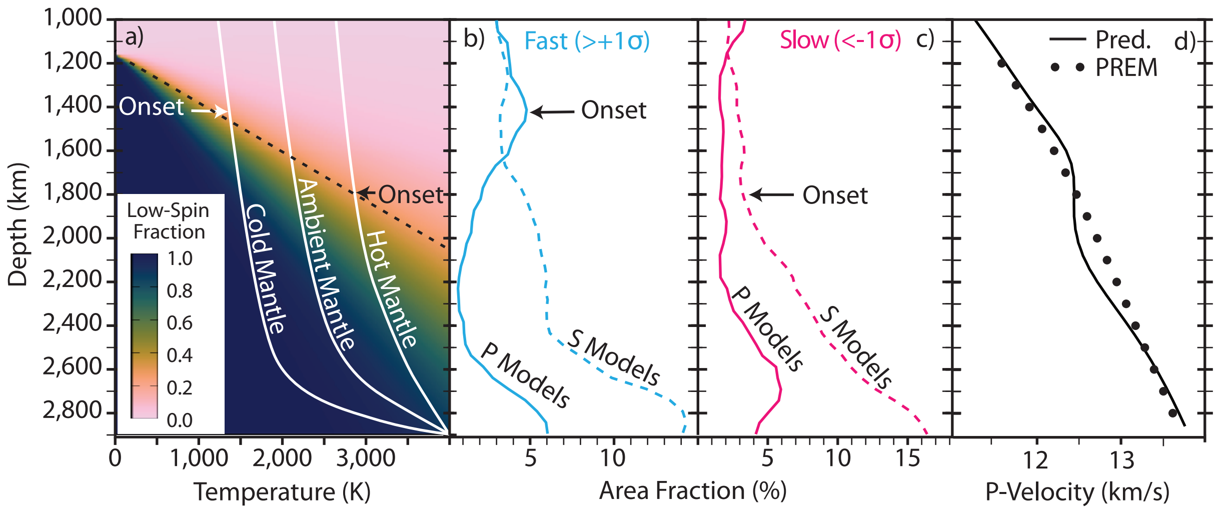
Figure 4 The depth-dependent changes in surface area for the (a) fast ($>$+1σ from the mean), and (b) slow ($<$-1σ from the mean) regions, as applied individually to each of the the 4 P-wave, and 4 S-wave tomography models. The individual model names and details are shown in Supplementary Figs. 1,2. The dark 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 and c, but without any vote map analysis.

Figure 5 Vote maps of mantle tomography models. Variable depth vote maps for fast ($>$+1σ from the mean), and slow ($<$-1σ from the mean) mantle for all (a) 4 S-wave and (b) 4 P-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 maps from[71].

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 reconstruction[73]. 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 depths at the base of the mantle where the seismic signal is dominated by the LLSVPs, and also occurs over a broader depth range.

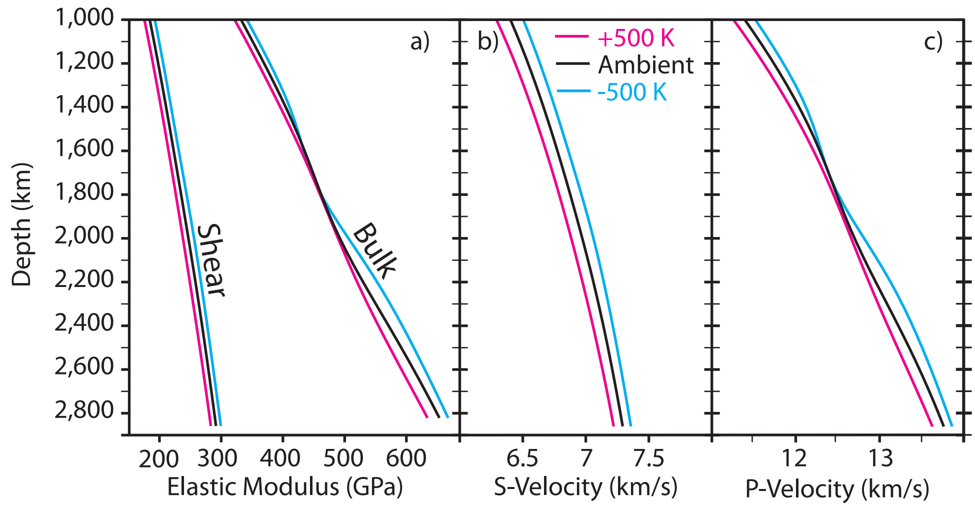
Figure 7 Difference maps between P-wave and S-wave models. Difference maps for the fast (left panels) and slow (right panels) vote maps constructed by subtracting the S-wave model votes (constructed with 4 models) from P-wave model votes (constructed with 4 models). Yellow areas indicate high votes (i.e. 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



a)
b)
c)
d)
Depth (km)
1,000
1,200
1,400
1,600
1,800
2,000
2,200
2,400
2,600
2,800
Onset
Onset
Low-Spin Fraction
1.0
0.8
0.6
0.4
0.2
0.0
Cold Mantle
Ambient Mantle
Hot Mantle
0
1,000
2,000
3,000
Temperature (K)
Fast (>+1σ)
Onset
P Models
S Models
Slow (<-1σ)
Onset
P Models
S Models
5
10
5
10
15
Area Fraction (%)
Pred.
PREM
12
13
P-Velocity (km/s)

Figure 2



1,000
1,200
1,400
1,600
1,800
2,000
2,200
2,400
2,600
2,800
Depth (km)
a)
Shear
Bulk
200
300
400
500
600
Elastic Modulus (GPa)
b)
+500 K
Ambient
-500 K
6.5
7
7.5
S-Velocity (km/s)
c)
12
13
P-Velocity (km/s)

Figure 3

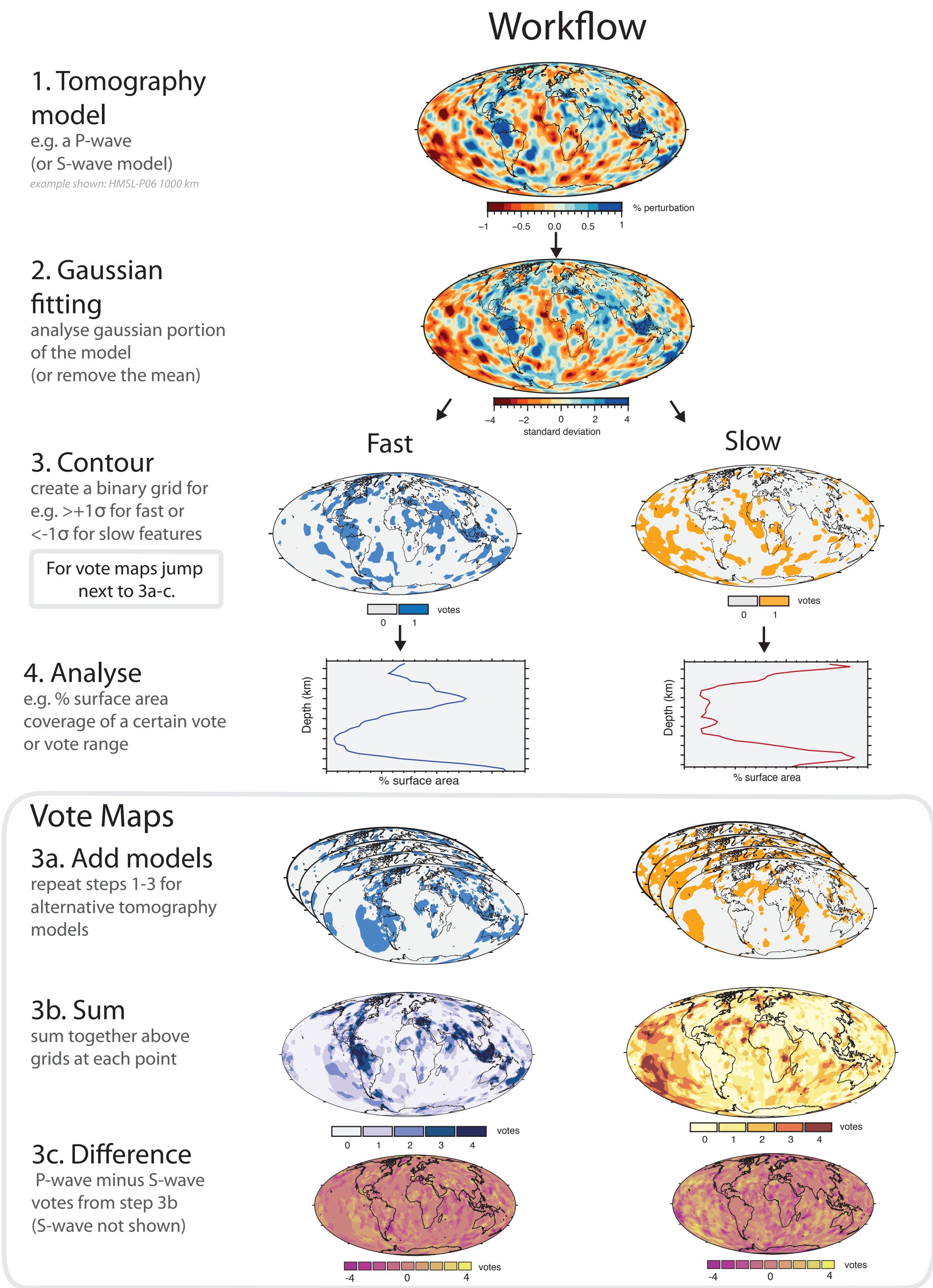

Workflow
1. Tomography model
e.g. a P-wave
(or S-wave model)
example shown: HMSL-P06 1000 km
% perturbation
−1 −0.5 0.0 0.5 1
2. Gaussian fitting
analyse gaussian portion
of the model
(or remove the mean)
standard deviation
−4 −2 0 2 4
Fast
Slow
3. Contour
create a binary grid for
e.g. >+1σ for fast or
<-1σ for slow features
For vote maps jump
next to 3a-c.
votes
0 1
4. Analyse
e.g. % surface area
coverage of a certain vote
or vote range
Depth (km)
% surface area
Vote Maps
3a. Add models
repeat steps 1-3 for
alternative tomography
models
3b. Sum
sum together above
grids at each point
votes
0 1 2 3 4
3c. Difference
P-wave minus S-wave
votes from step 3b
(S-wave not shown)
votes
-4 0 4

Figure 4

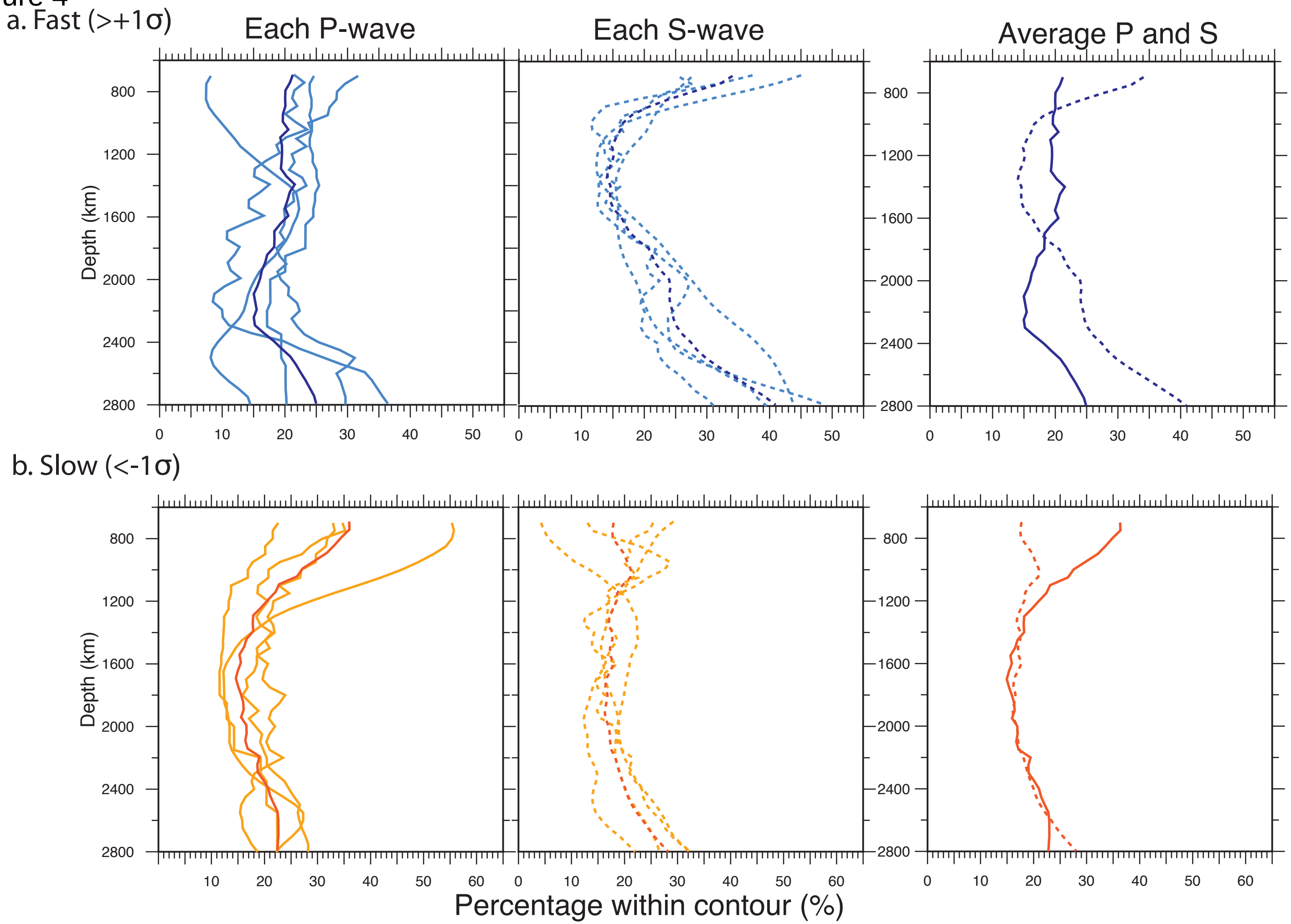
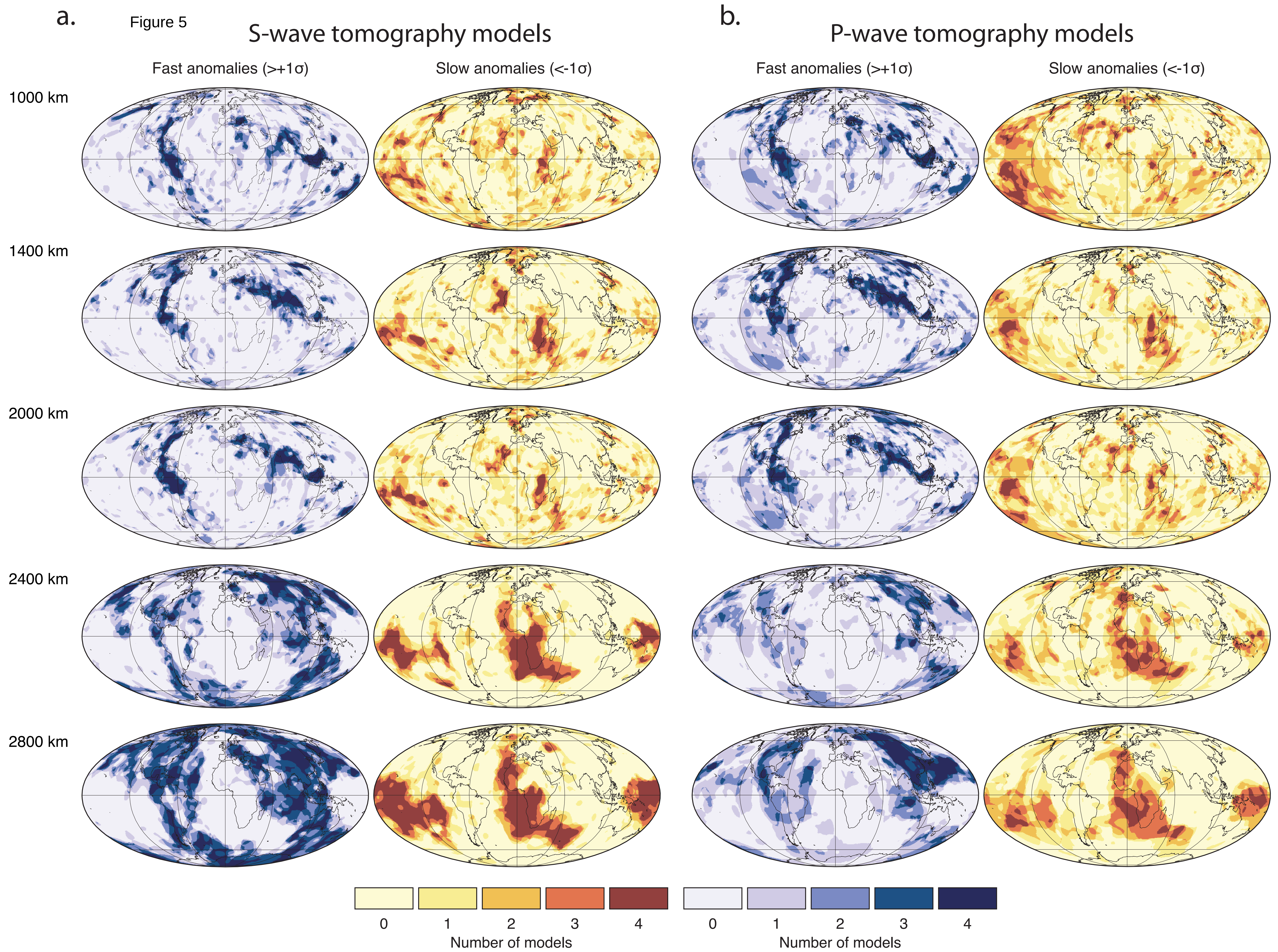

a. Fast (>+1σ)
Each P-wave
Each S-wave
Average P and S
b. Slow (<-1σ)
Depth (km)
800
1200
1600
2000
2400
2800
0
10
20
30
40
50
60
Percentage within contour (%)

Figure 5



a.
S-wave tomography models
Fast anomalies (>+1σ)
Slow anomalies (<-1σ)
b.
P-wave tomography models
Fast anomalies (>+1σ)
Slow anomalies (<-1σ)
1000 km
1400 km
2000 km
2400 km
2800 km
0
1
2
3
4
Number of models
0
1
2
3
4
Number of models

Figure 6

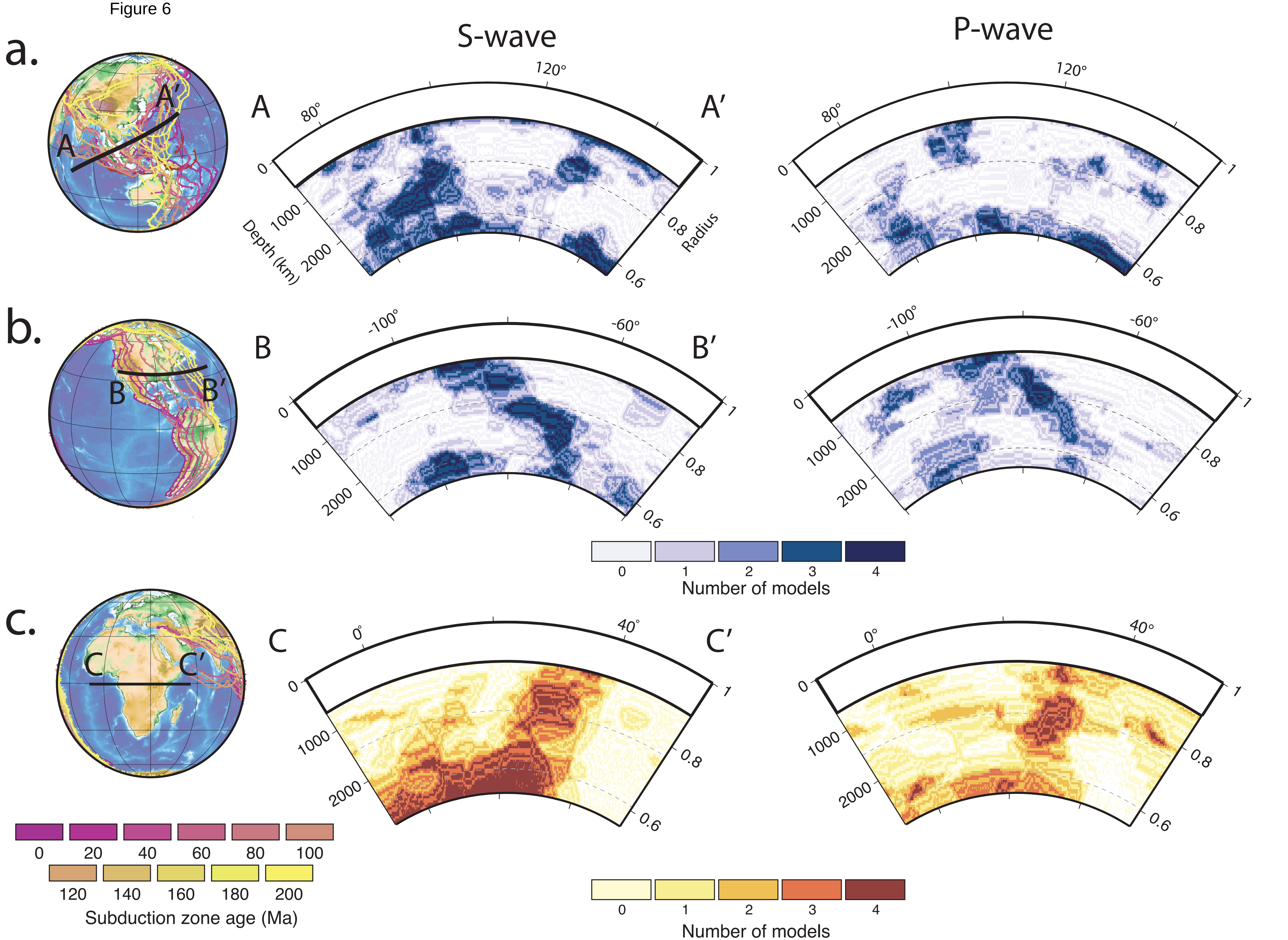
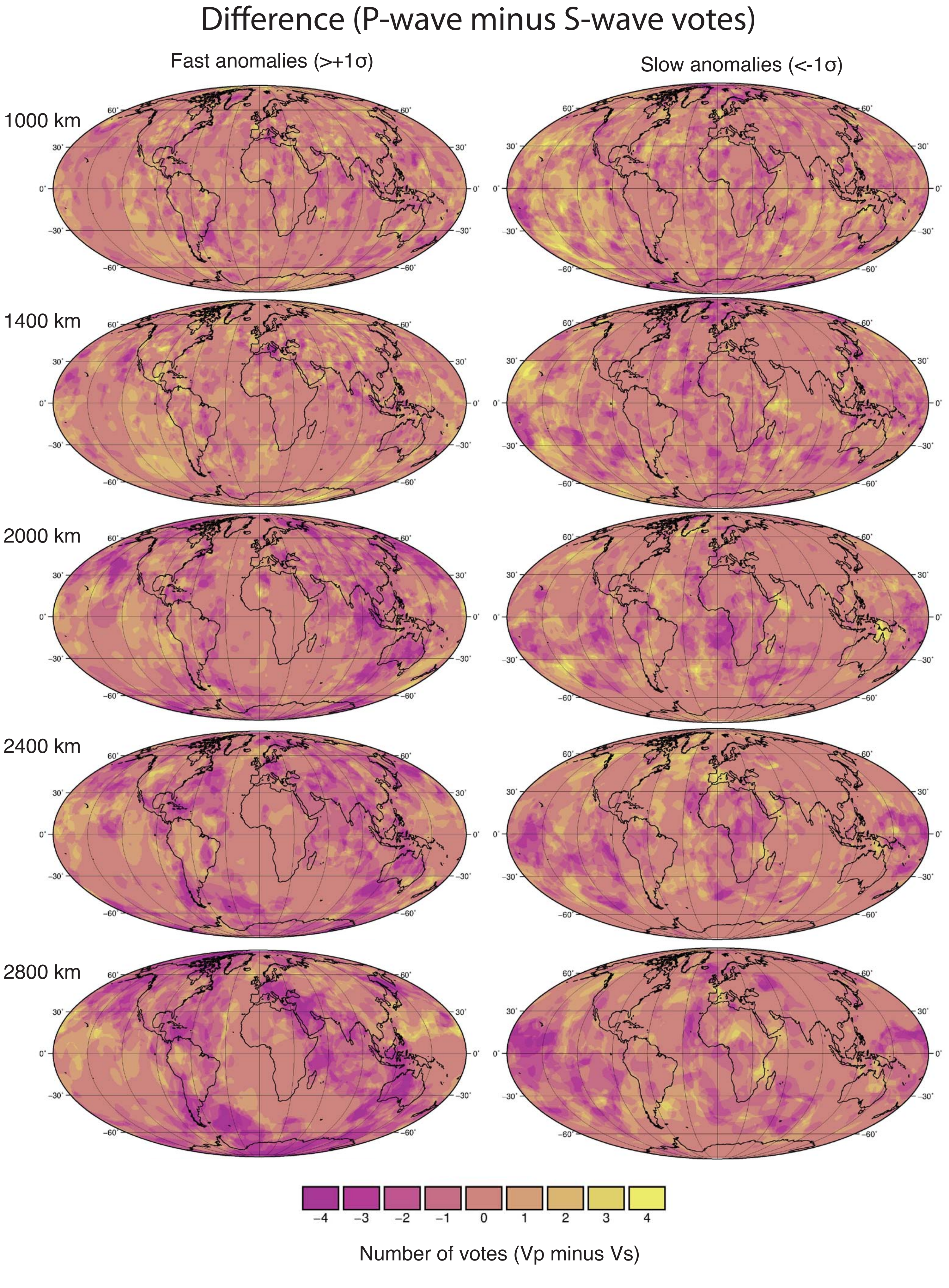

a.
b.
c.
S-wave
P-wave
A
A′
B
B′
C
C′
80°
120°
-100°
-60°
0°
40°
0
1000
2000
Depth (km)
1
0.8
0.6
Radius
0
1
2
3
4
Number of models
0
20
40
60
80
100
120
140
160
180
200
Subduction zone age (Ma)

Figure 7



Difference (P-wave minus S-wave votes)
Fast anomalies (>+1σ)
Slow anomalies (<-1σ)
1000 km
1400 km
2000 km
2400 km
2800 km
60°
30°
0°
−30°
−60°
−4
−3
−2
−1
0
1
2
3
4
Number of votes (Vp minus Vs)

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

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Supplementary Figures

Supplementary Figure 1 Calculated shear and compressional velocities using the *ab initio* technique described in Methods section for harzburgite (top) and an Fp-free model composition with 94 and 6 mol% of Bm and Ca-perovskite, respectively (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 75 wt.% bridgmanite, 23 wt.% ferropericlase, and 2 wt.% calcium perovskitite.

Supplementary Figure 2 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 HMSL[3]), 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.

Supplementary Figure 3 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.

Supplementary Figure 4 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 Figures 10 and 11 for details). 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 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.

Supplementary Figure 6 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.

Supplementary Figure 7 Comparison of depth-dependent changes in surface area for alternative vote combinations, Vp (solid) and Vs (dashed). In Figure 1, only the maximum vote of 4 was shown. The vote counts are listed in the inset panel. Fast velocities are shown in the top panels (a) and slow velocities in the lower panels (b). 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) for further details). Nonetheless, the robustness of the signal suggests that the effects of the iron spin cross-over can be observed.

Supplementary Figure 8 The change in the seismic velocities using constant versus depth-dependent partitioning of iron between Br and Fp, K_D. Panel (a): Depth-dependent K_D[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 K_D[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 K_D) may increase the crossover pressure[6]. We find that Fe in ferropericlase remains below the 25% threshold for observing substantial increases in the crossover transition pressure[7] for the depth-dependent K_D case. Thus, depth-dependent K_D 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.

Supplementary Figure 9 The self-consistent geotherms for pyrolite. These are calculated by setting the starting temperature of the calculation 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) for the elastic moduli and velocity profiles plotted in Figure 2.

Supplementary Figure 10 Analysis of velocity-frequency distributions of a variety of tomographic models reveals that they exhibit significant differences that may confound inter-model comparisons (Hernlund and Houser, 2008). These differences can be categorized via scale/amplitude (caused by variability in tomographic model data and construction), shift/alignment (caused by reference to different 1D seismic velocity models) and the shape of the distributions (related to variations in the distribution that remain even after accounting for relative shifting of the reference baseline and scaling of amplitudes. There is a large difference in the models between the depth range of 1000-2200 km (see also Hernlund and Houser, 2008). In order to account for this we analyse the Gaussian portion of the models at each depth, derived from this depth range and applied to all mantle depths. See also Supplementary Figure 11.).

Supplementary Figure 11 Panels a and b reveal the depth-dependent mean and standard deviation for each of the 8 individual models used in this study, respectively, before any gaussian fitting is applied. The recalculated standard deviations after the fitting (see Extended Figure 10) are shown in panels c, the black lines are the average of the 4 models and are used in panel d. Panel d shows the ratio of the (averaged) standard deviation of the S wave models (from panel c) as compared to the P wave models. There is an increase in the ration of RS/P between the depths of 1200-2000 km depth. In summary, the gaussian fitting procedure does not affect the relative variation of seismic velocities in the models, it only serves to bring them into alignment and forces their core velocity variations to exhibit similar amplitudes.

Supplementary Figure 12 In addition to the eight models used in the paper, depth-dependent change in surface areas for the joint tomography models of SP12RTS[8] and TX2019[9] 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 HMSL, Supplementary Figure 5) but do hint at a mid-mantle decorrelation related to the spin crossover.

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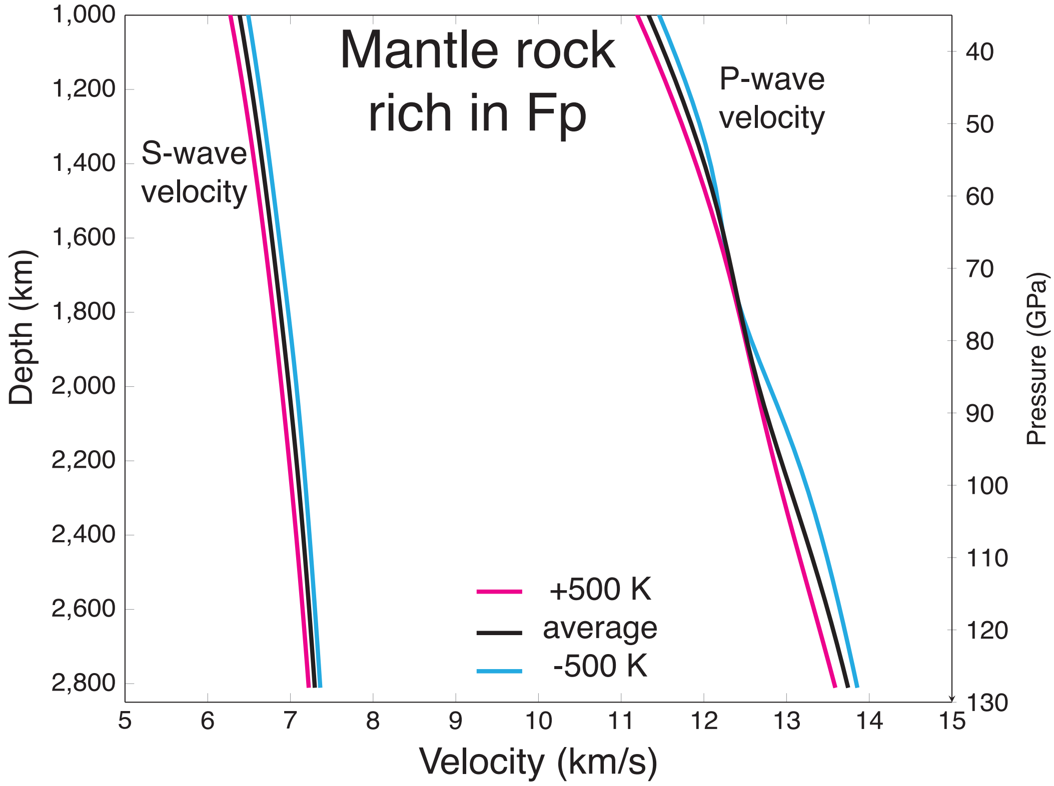
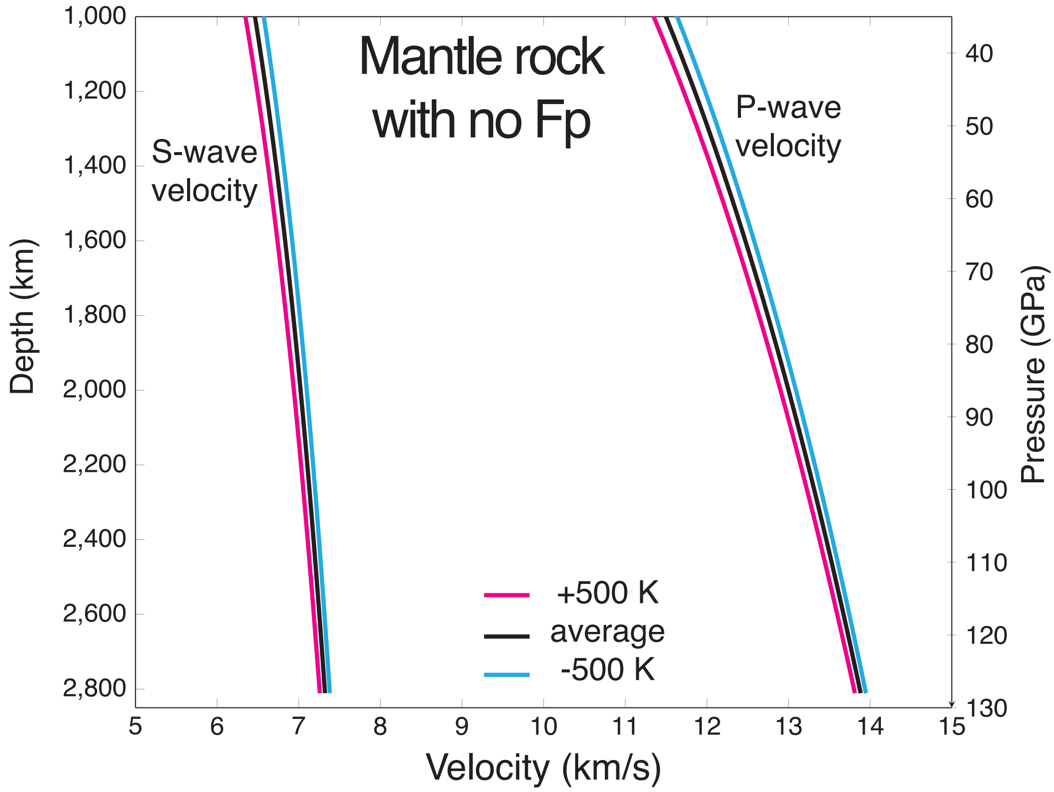
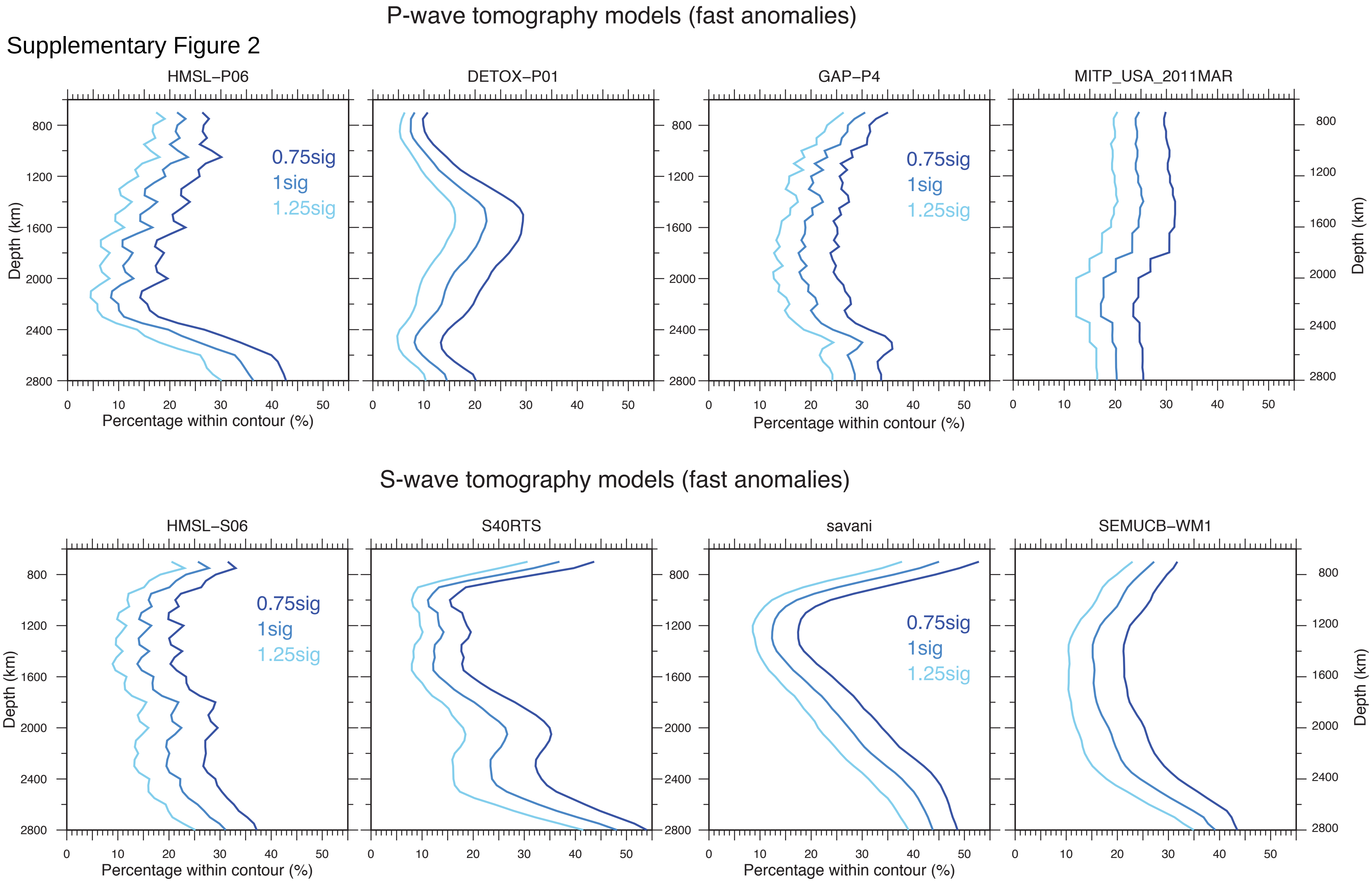
Supplementary Figure 1



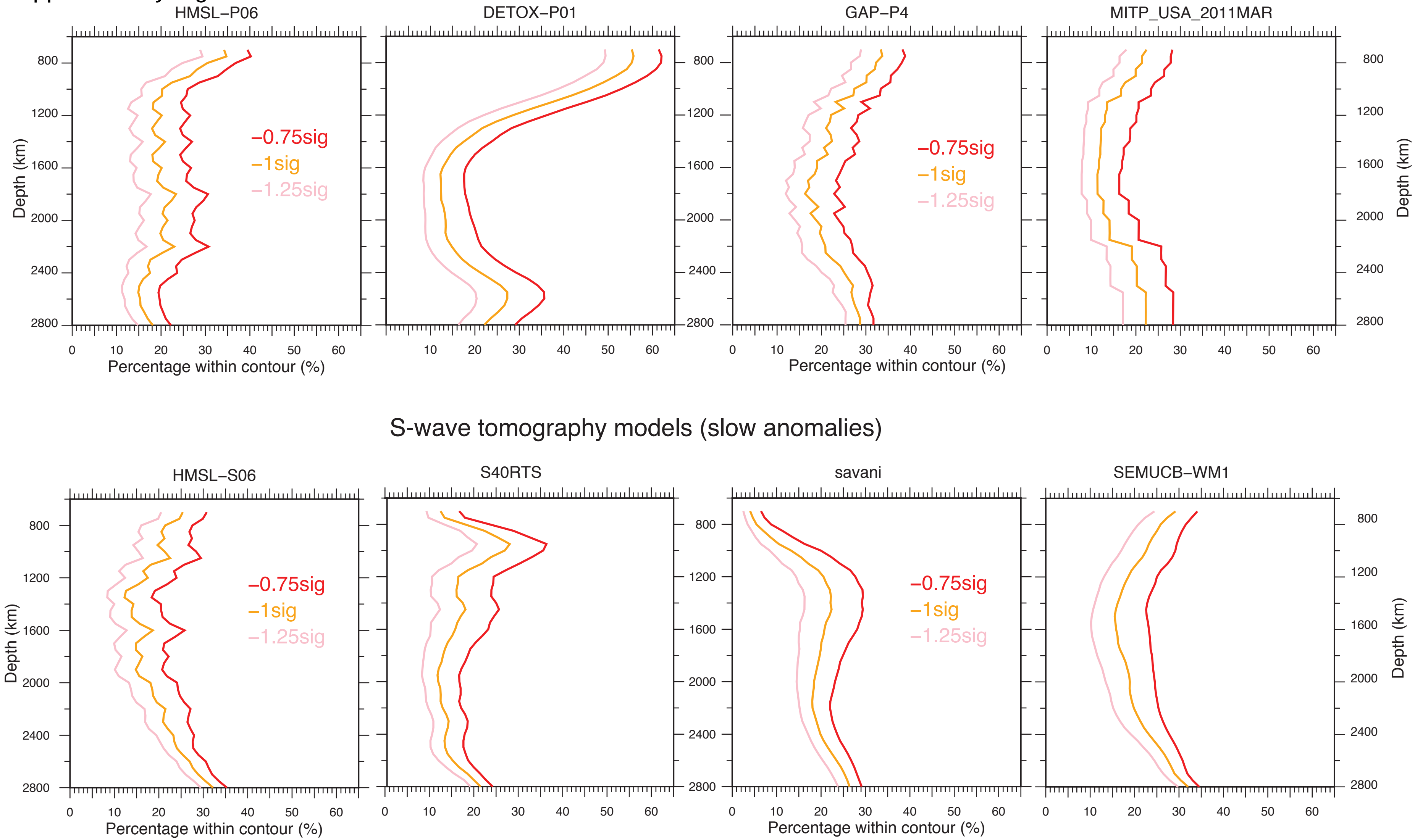


Supplementary Figure 2

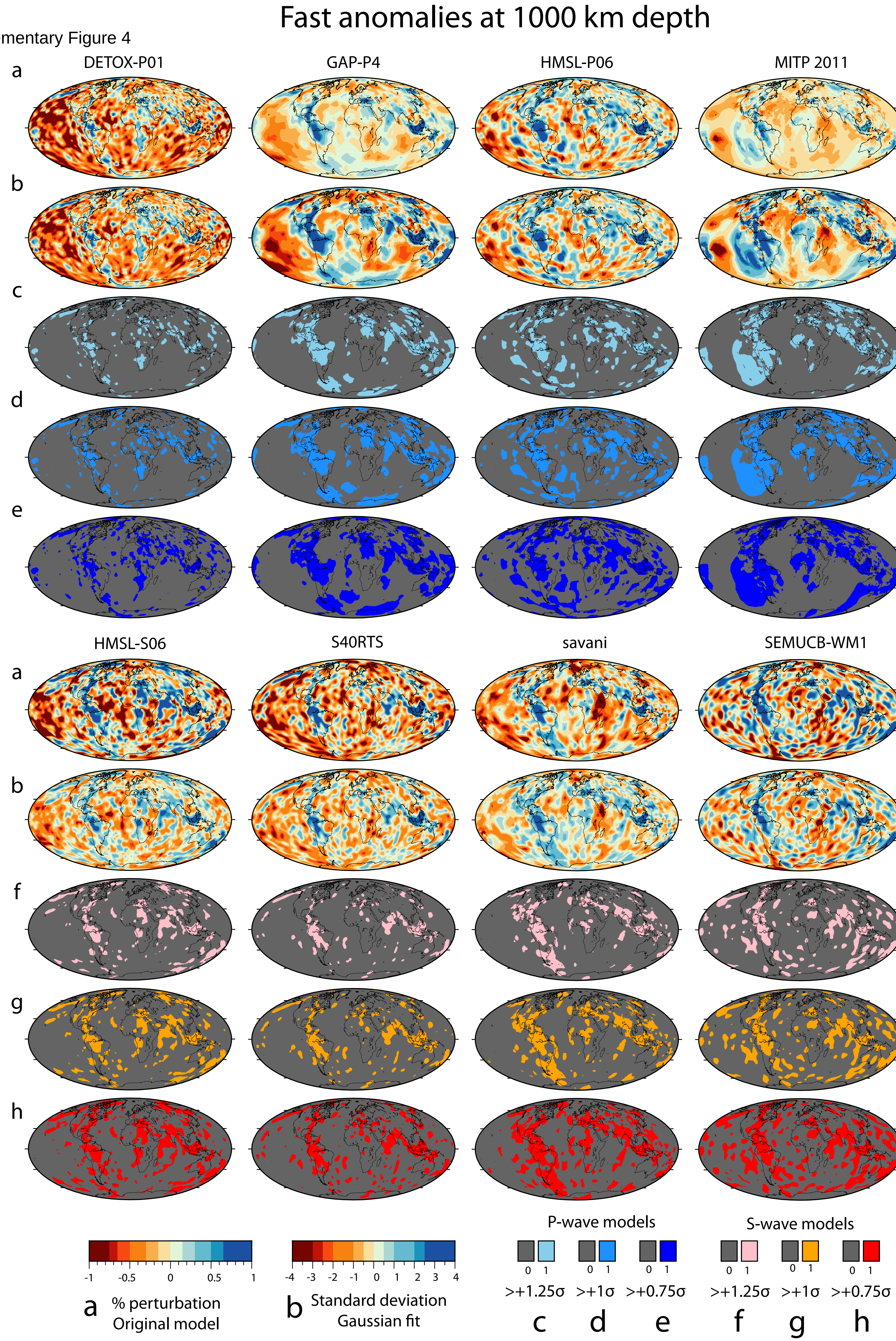


Supplementary Figure 3

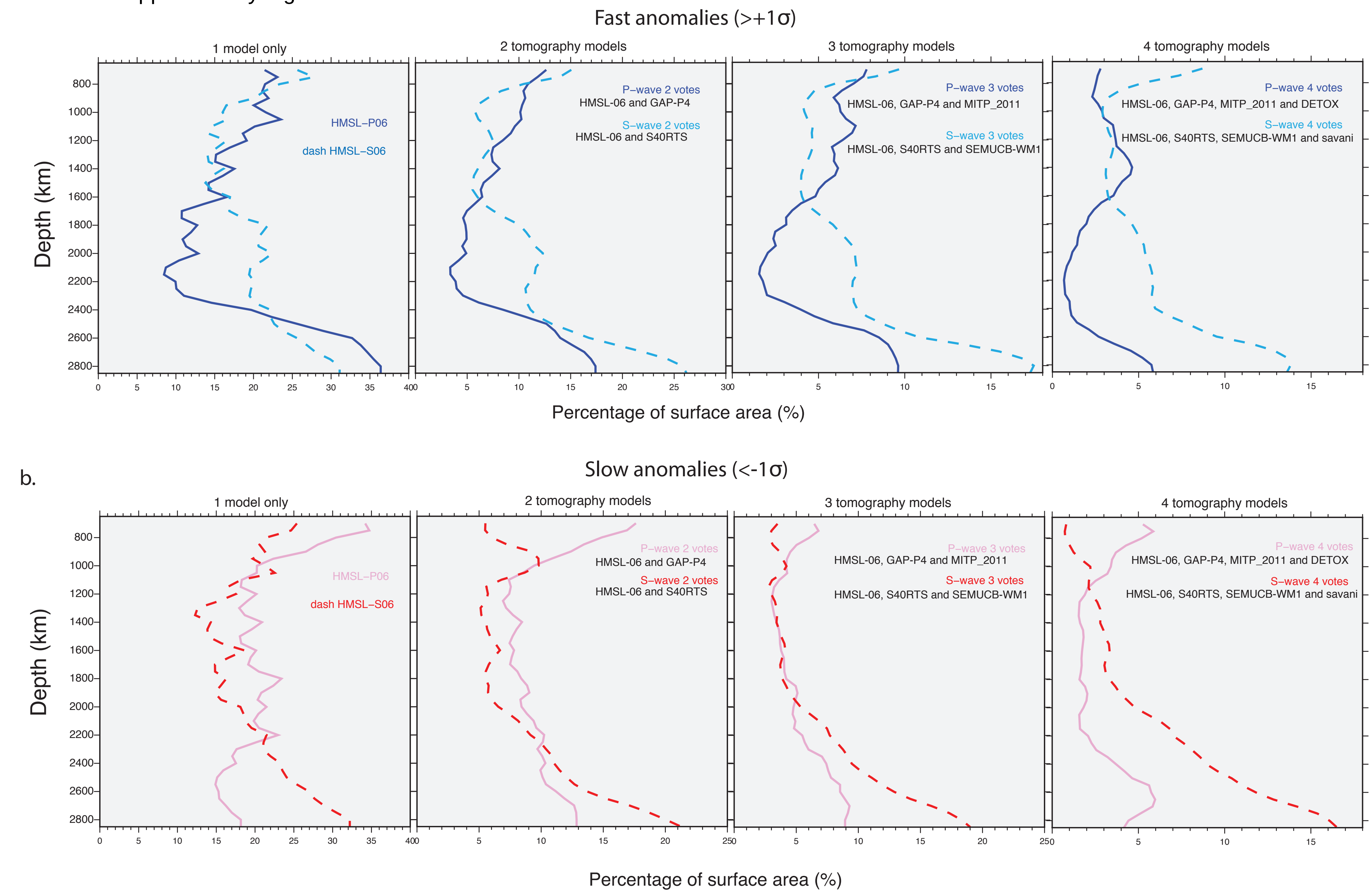
P-wave tomography models (slow anomalies)



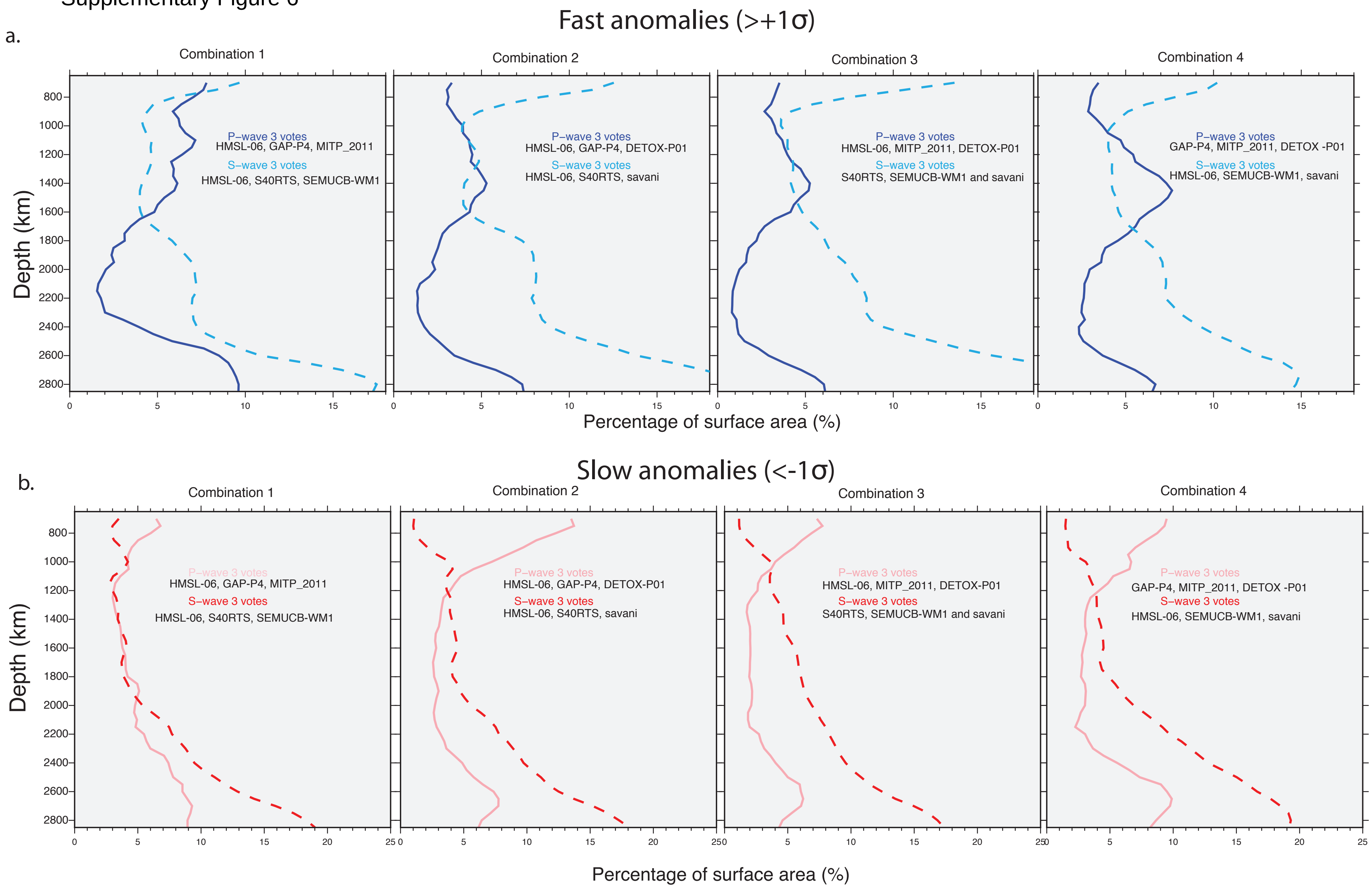
Supplementary Figure 4



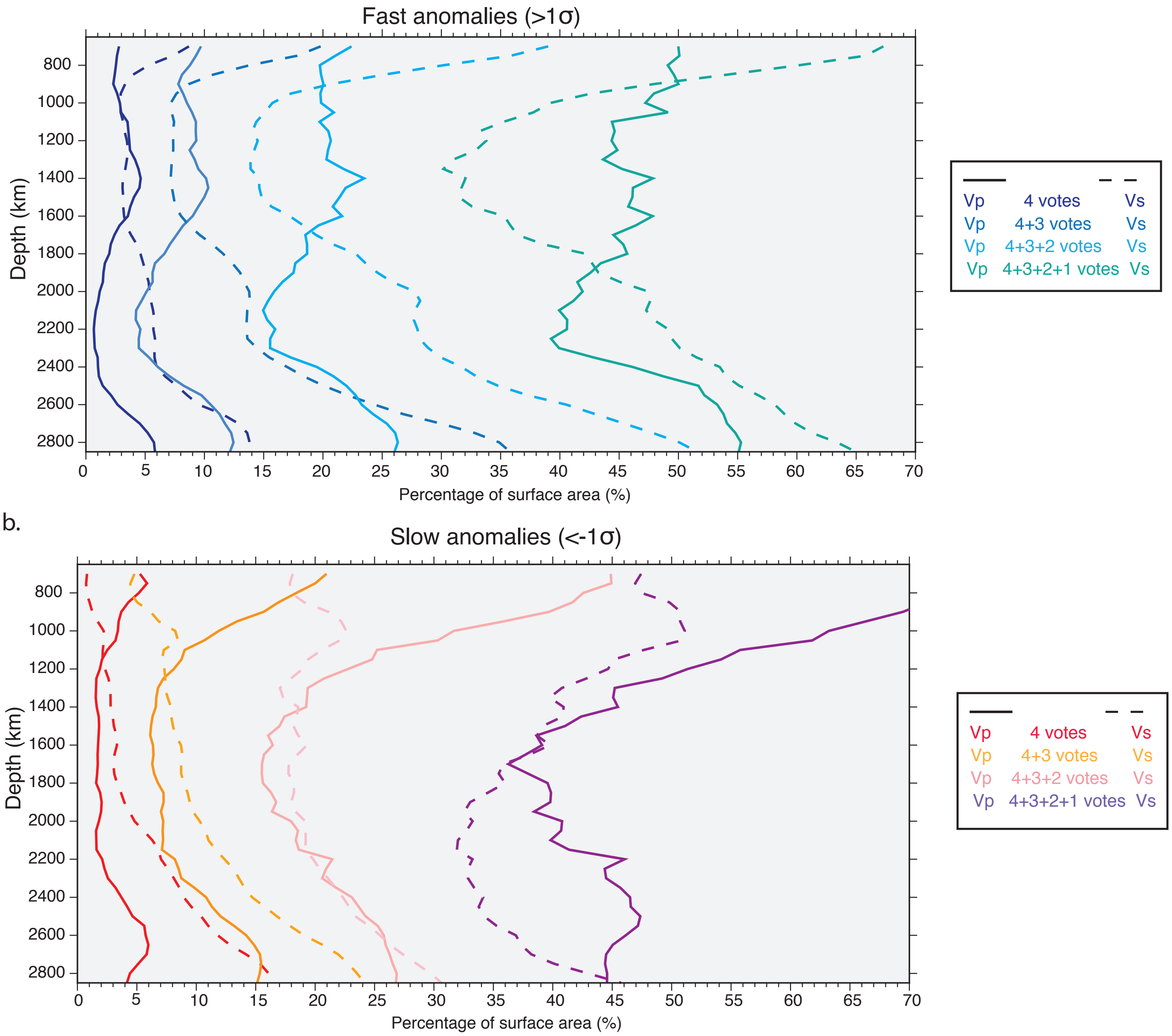
Supplementary Figure 5



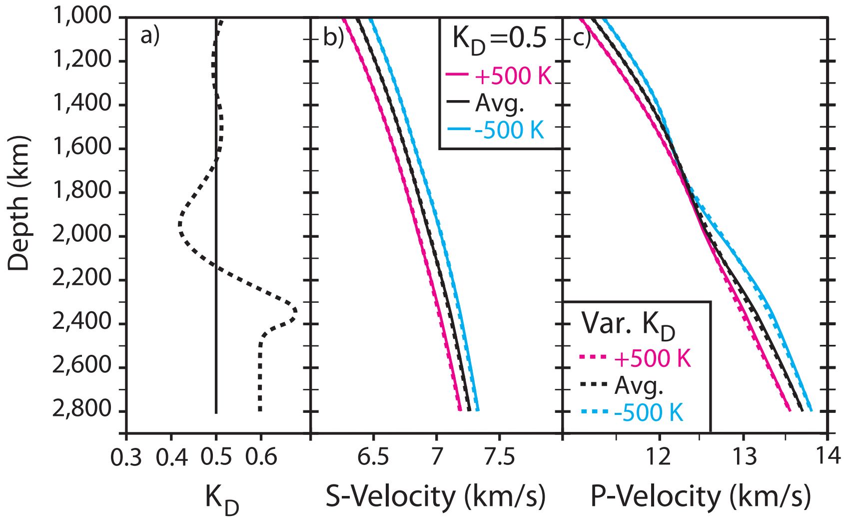
Supplementary Figure 6



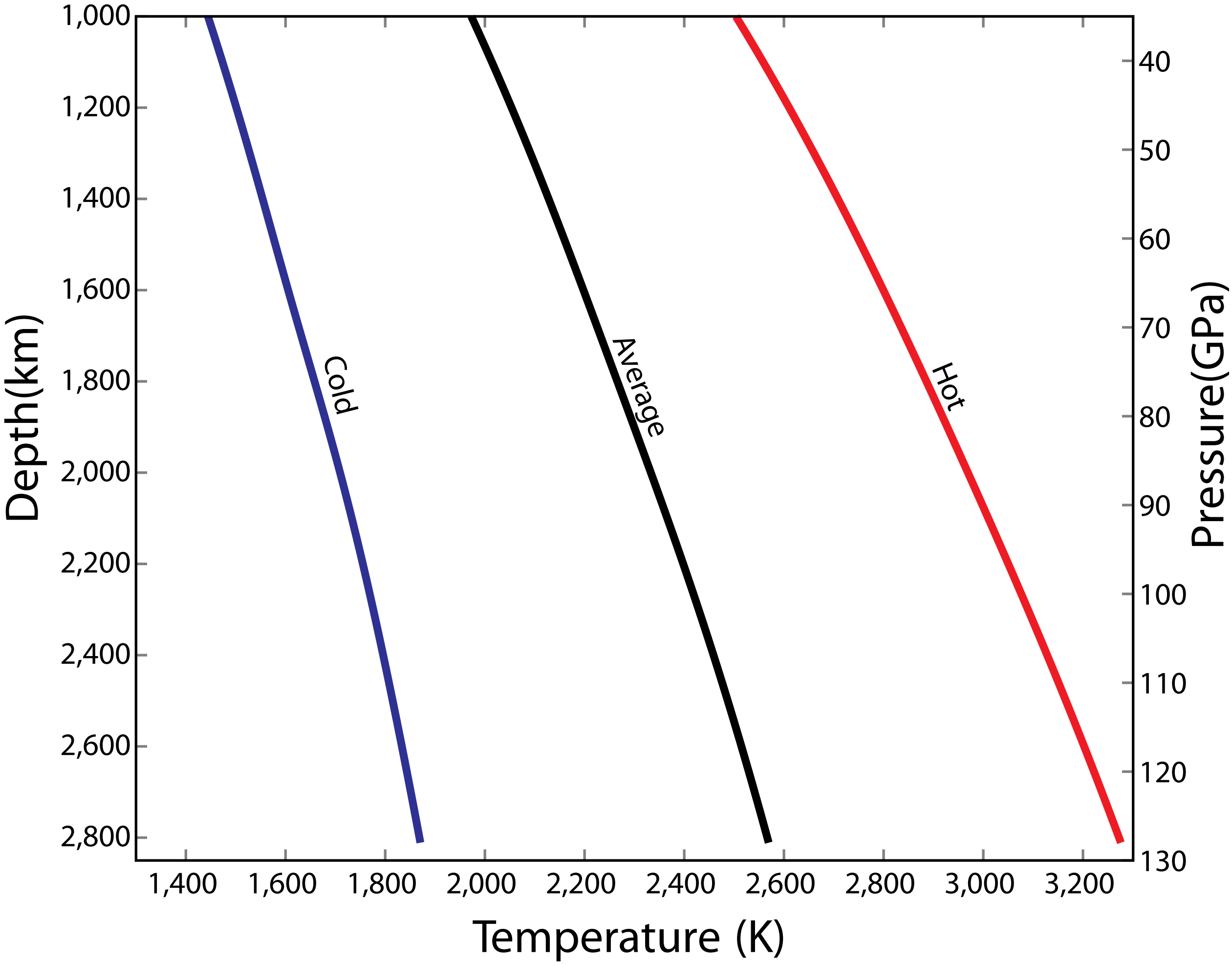
a. Supplementary Figure 7



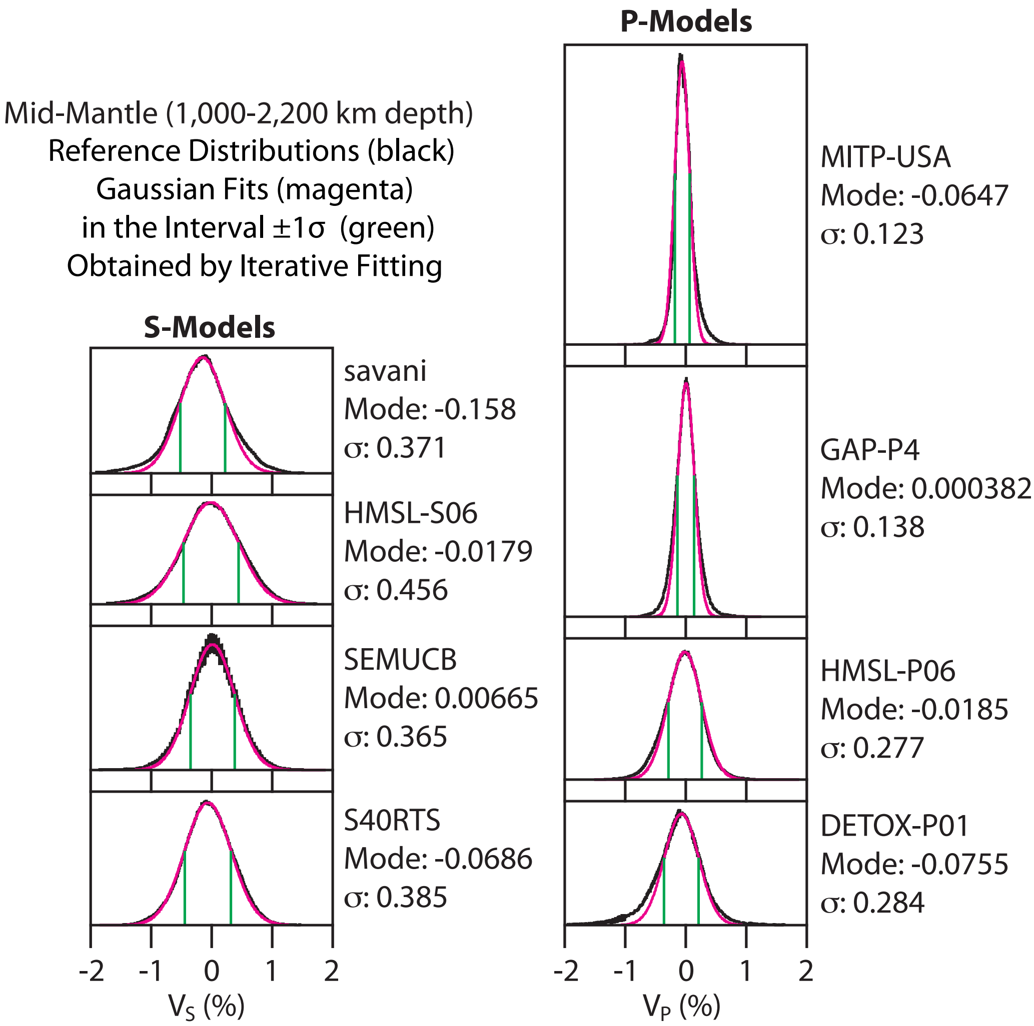
Supplementary Figure 8



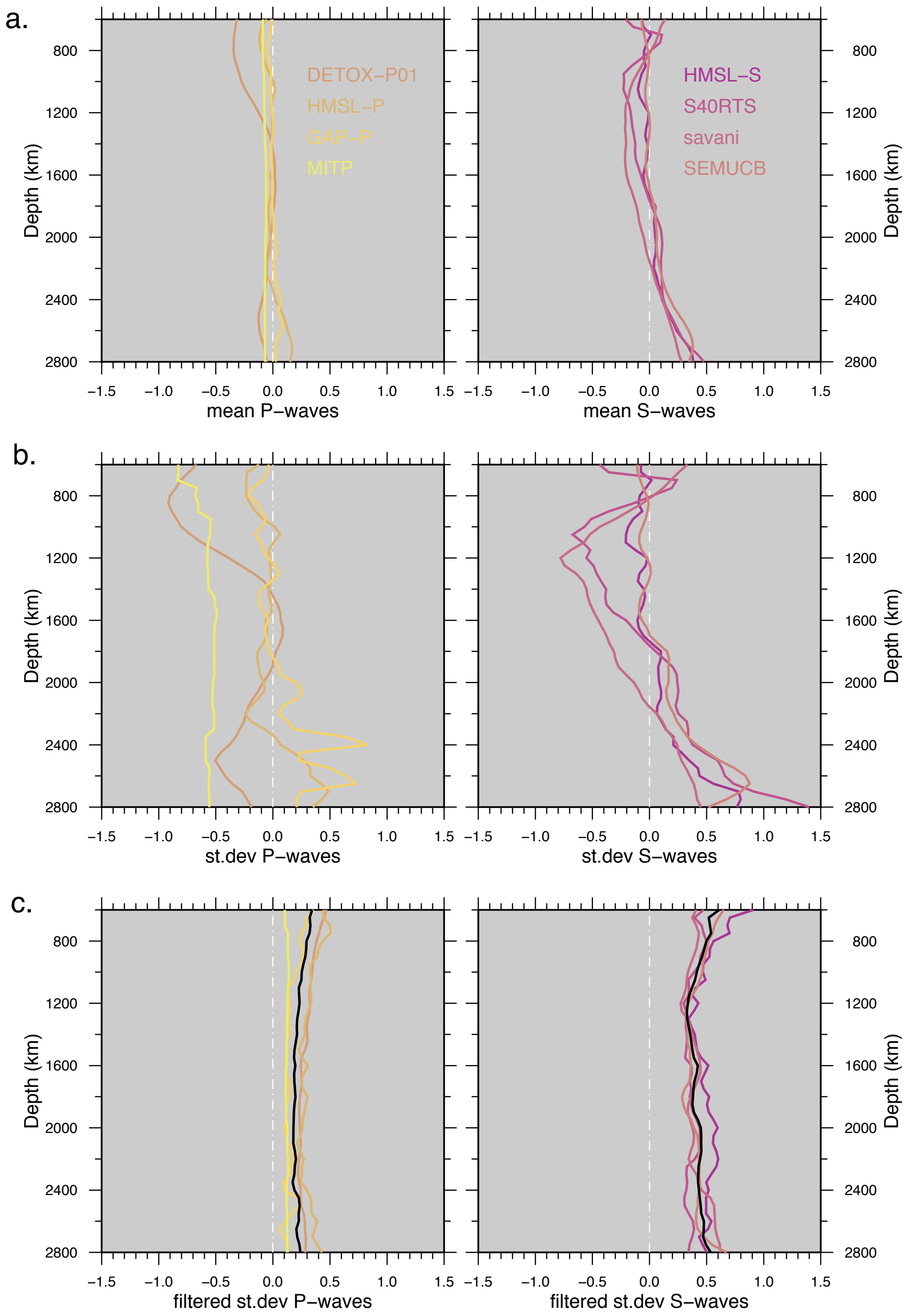
Supplementary Figure 9

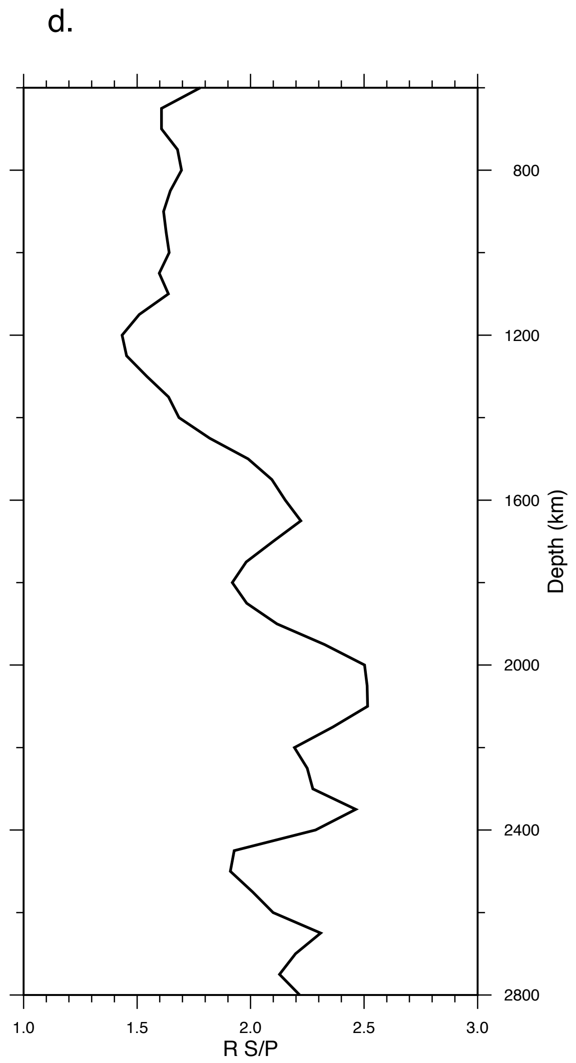


Supplementary Figure 10



Supplementary Figure 11





Supplementary Figure 12