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Lessing, S, Dobson, DP, Rost, S orcid.org/0000-0003-0218-247X et al. (2 more authors) (2022) Kinetic effects on the 660 km-phase transition in mantle upstreams and seismological implications. Geophysical Journal International. ISSN 0956-540X

https://doi.org/10.1093/gji/ggac196

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Kinetic effects on the 660 km-phase transition in mantle upstreams and seismological implications.

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Accepted *May 19, 2022*. Received *May 16, 2022.* In original form *February 5, 2022.*

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Abstract

The effects of reaction kinetics of bridgmanite and ferropericlase transforming to ringwoodite on elastic properties in upwelling mantle are investigated using data of kinetic experiments and internally self-consistent thermodynamic modelling of density and seismic velocities. The kinetic experiments show inhibited grain growth of ringwoodite. At the initiation of ringwoodite growth, bridgmanite completely transforms to a metastable pyrope-bearing garnet. Ringwoodite then gradually grows from the metastable assemblage of ferropericlase and garnet. The changes in mineralogy result in a low-velocity zone directly above the 660 km seismic discontinuity due to the lower seismic velocities and densities of ferropericlase and garnet compared to ringwoodite and bridgmanite. The modelling of the effects of reaction kinetics and its effect on seismic structure at ~660 km depth shows more sensitivity to grain size than to temperature and upwelling rate. Modelling 1-D synthetic seismograms of PP (SS) underside reflections off the kinetically inhibited backward reaction to ringwoodite shows advanced travel times of underside reflections off ~660 km depth of 0.2 - 0.8 s (1.2 - 1.6 s) for upwelling rates of 50 cm/yr and initial grain sizes between 5 and 20 cm due to the low-velocity zone above the 660 km discontinuity. The finite width of the low-velocity layer results in frequency-dependent behaviour of PP and SS underside reflection amplitudes, with higher amplitudes towards shorter periods. The effect on the travel times of P-to-s conversions used for receiver function is small (< 0.7 s) but the inhibited backward reaction leads to strong amplitude changes and significant waveform variations. The effects of reaction kinetics in mantle upwellings might serve as an additional means to map regions of large-scale upwellings and to constrain grain size in the lower mantle.

Key words: Phase transitions, Composition and structure of the mantle, High-pressure behaviour, Body waves

1 Introduction

The seismic structure of the Earth's mantle transition zone between upper and lower mantle is dominated by two seismic discontinuities at which the seismic velocities and density increase over short depth intervals. These discontinuities are found in most spherically averaged 1-D Earth reference models, e.g., ak135 (Kennett et al., 1995), and are considered as the seismic expressions of solid-solid phase transitions and mineral reactions (both hereafter called phase transformations) of the olivine system (e.g., Ringwood, 1969; Helffrich, 2000; Shearer, 2000; Weidner & Wang, 2000; Deuss, 2015). Thermodynamic calculations of mantle mineral phase relations are frequently used to interpret observations of seismic velocities and seismic discontinuity structure and help to identify and quantify their thermal and compositional origins (e.g., Cobden et al., 2008; Ritsema et al., 2009; Saki et al., 2019; Vilella et al., 2021; Waszek et al., 2021).

For thermodynamic modelling of phase equilibria and their seismic properties, the Earth's mantle is usually assumed as vigorously convecting, homogeneous and well mixed. However, geodynamic studies have demonstrated the long-term existence of thermal and compositional heterogeneities throughout the mantle (e.g., Allègre & Turcotte, 1986; Kellogg et al., 2002; Tackley et al., 2005; Ballmer et al., 2017). Small diffusivities of the solid mantle (e.g., Hofmann & Hart, 1978; Farber et al., 1994) lead to the question: to what degree have the mineral assemblages reached thermodynamic equilibrium and mineral transformations been completed? The mechanisms of mineral transformations, i.e., their reaction kinetics, might therefore affect the dynamics and seismic structure of the Earth's mantle (e.g., Kubo et al., 2002; Kubo et al., 2008). Therefore, taking the reaction kinetics into account might be essential for our interpretation of the seismic signals in terms of mantle composition and temperature.

The influence of reaction kinetics on mineral transformations was first investigated in detail when seismologists looked for mechanisms of deep earthquakes in subducting slabs (e.g., Sung & Burns, 1976; see Kirby, 1996, for a review). Motivated by observations of apparently stagnant slabs at ~660 km depth in seismic tomography models (e.g., van der Hilst, 1991; Fukao et al., 2001; Fukao et al., 2009), Kubo et al. (2002) and Kubo et al. (2008) investigated the reaction kinetics of phase transformations of ringwoodite to ferropericlase and bridgmanite and of garnet to bridgmanite at ~660 km depth and temperature conditions typical for subducting slabs. The kinetic experiments by Kubo et al. (2002) and Kubo et al. (2008) show that low temperatures within the slab decrease the mobility of atoms in the crystal lattice and hence could reduce reaction rates of mineral transformations. The kinetic inhibition of the phase transformations of ringwoodite to ferropericlase and bridgmanite and of garnet to bridgmanite result in neutral to positive buoyancy which may lead to stagnant slabs. Recently it has also been shown that kinetics of the bridgmanite to post-perovskite phase transition can affect visibility of the D" reflector (Langrand et al., 2019).

Reaction mechanisms of mineral transformations can also change for higher temperatures. Studies by Gasparik (1996a), Gasparik (1996b), Weidner & Wang (1998), Irifune et al. (1998) and Hirose (2002) show that the reaction mechanism of ringwoodite to ferropericlase and bridgmanite changes for mantle temperatures larger than 2100 K. This temperature is considered as a reasonable estimate for the centre of hot mantle upwellings (e.g., Sleep, 1990; Schilling, 1991; Weidner & Wang, 1998). For aluminium contents of approximately 5 wt% and temperatures of at least 2100 K, ringwoodite transforms to bridgmanite and ferropericlase via the dissociation of ringwoodite to ferropericlase and majorite garnet, and finally to ferropericlase and bridgmanite (Gasparik, 1996a; Gasparik, 1996b; Weidner & Wang, 1998; Irifune et al., 1998; Hirose, 2002).

Kinetic studies by Shimojuku et al. (2014) and Dobson & Mariani (2014) have investigated the reaction kinetics for the reverse reaction of bridgmanite and ferropericlase to ringwoodite in upwelling mantle. The kinetic experiments show that the growth of ringwoodite is kinetically inhibited, and that bridgmanite transforms to pyrope-bearing garnet. The reverse reaction from bridgmanite and ferropericlase to ringwoodite and garnet (in mantle upwellings) requires diffusion on a much larger length-scale than the forward reaction because macroscopic grains of bridgmanite and ferropericlase must recombine to form ringwoodite (Dobson & Mariani, 2014). In the case of aluminous garnets, the interface between ringwoodite and garnet develops a fingering instability resulting in a complex intergrowth (Figure 1). Garnet incorporates the aluminium oxide of the bridgmanite into its crystal lattice and has the same bulk chemistry as the bridgmanite before the transformation, and hence this isochemical transformation is fast compared to the diffusion-controlled reaction between bridgmanite and ferropericlase. Over time, this chemically metastable garnet reacts with ferropericlase, and the stable phase, ringwoodite, starts to nucleate and grow at the interface between ferropericlase and garnet.

The growth of ringwoodite on the ferropericlase grains is most likely controlled by the slow diffusion of SiO_2 from garnet across the reaction layer into the grains of ferropericlase. The ringwoodite growth rate is sensitive to the initial grain size of lower mantle minerals (Dobson

& Mariani, 2014). The initial ferropericlase grain size is the typical length scale of diffusion. The amount of ringwoodite formed depends on bulk composition and ambient temperature. The bulk composition affects the individual molar amounts of the mineral solid solutions. The ambient mantle temperature influences the equilibrium phase relations and mobility of atoms, determining the diffusion rate of atoms across interfaces and grain boundaries (e.g., Putnis, 1992). The initial grain size controls the relative proportions of reactants and products for a given amount of diffusion across the reacting interface.

Our study investigates the effects of reaction kinetics for the recombination of bridgmanite and ferropericlase to ringwoodite in mantle upwellings on density and seismic wave velocities to assess the possibility to observe the effects of the kinematically inhibited back reaction seismically. The kinetically inhibited growth of ringwoodite is determined for a range of mantle temperatures at 660 km depth, varying grain sizes and mantle upwelling rates. The changed volume fractions of the minerals as a function of pressure are used to calculate profiles of density, P- and S-wave velocities for kinetically inhibited and equilibrated phase assemblages using internally self-consistent thermodynamic modelling. These models are used to compute 1-D synthetic seismograms for PP and SS underside reflections off the resulting discontinuity and for P-to-s conversions at the discontinuity (known as P receiver functions), two probes often used to study upper mantle discontinuities, to assess the effects on travel times and waveforms. Our aim is not to carry out a seismic study at this point to search for such effects in observed seismic data. This work presents a previously unstudied effect of mantle phase transitions on seismic data that should be kept in mind in future seismic studies.

2 Methods

The kinetically inhibited growth of ringwoodite and its effects on phase assemblages and seismic properties are computed in five steps:

1. calculation of phase equilibria,
2. calculation of the thickness of the ringwoodite layer produced for a given temperature, grain size and mantle upwelling rate,
3. mass balancing consumption of metastable ferropericlase and garnet,
4. calculation of density and seismic wave velocities.
5. computation of 1-D synthetic seismograms

2.1 Calculation of phase equilibria

Phase equilibria for the CFMAS (calcium oxide, iron(II) oxide, magnesium oxide, aluminium oxide and silica) system are calculated for a pyrolitic mantle composition (Table 1) with the Perple_X program package (Connolly, 2005) that utilises the free-energy minimization algorithm by Ita & Stixrude (1992) and Stixrude & Lithgow-Bertelloni (2005), and the elastic and thermodynamic properties and the solid solution model of Stixrude & Lithgow-Bertelloni (2011). From the calculated phase equilibria, profiles of P-wave velocity, S-wave velocity and density are extracted along adiabatic mantle geotherms (e.g., Cobden et al., 2008). The values of P-wave velocity, S-wave velocity, and density of the phase assemblage at a specific P-T-point are calculated as the Hill average of Voigt and Reuss bounds of the constituent minerals (Voigt, 1928; Reuss, 1929; Hill, 1965).

2.2 Kinetically inhibited growth of ringwoodite and mineral reactions

The seismic structures of the kinetically inhibited phase assemblages are calculated from the grain growth of ringwoodite for fixed temperature, grain size and upwelling rate (Figure 2). Before we describe the calculations of kinetically inhibited growth of ringwoodite and its impact on seismic properties, we compare the mineral reactions at thermodynamic equilibrium with those observed by Dobson & Mariani (2014).

The recombination reaction at thermodynamic equilibrium is described as

$$MgO + MgSiO_3 \leftrightarrow Mg_2SiO_4 \tag{1}$$
$$\text{ferropericlase + bridgmanite} \leftrightarrow \text{ringwoodite}$$

Dobson & Mariani (2014) observe in the kinetic experiments that bridgmanite entirely transforms to garnet, where the aluminium-bearing bridgmanite transform to pyrope garnet:

$$3.75\ MgSiO_3 \cdot 0.25\ Al_2O_3 \leftrightarrow 0.75\ Mg_4Si_4O_{12} + 0.25\ Mg_3Al_2Si_3O_{12} \tag{2}$$
$$\text{aluminous bridgmanite} \leftrightarrow \text{majorite garnet + pyrope garnet}$$

The consumption of bridgmanite to ringwoodite comprises of several reactions. At the onset of ringwoodite growth, the entire amount of bridgmanite transforms to garnet,

$$MgSiO_3 \rightarrow 0.25\ Mg_4Si_4O_{12}, \quad (3)$$

bridgmanite → majorite garnet

creating an excess of garnet compared to conditions at thermodynamic equilibrium. The difference between the decrease of ferropericlase with kinetic inhibition effects and the phase fraction of ferropericlase is later used to infer the decrease of garnet which recombines with ferropericlase to give ringwoodite via the reaction

$$MgO + 0.25\ Mg_4Si_4O_{12} \leftrightarrow Mg_2SiO_4 \quad (4)$$

ferropericlase + majorite garnet ↔ ringwoodite

The kinetically inhibited growth of ringwoodite and the dependent mineral transformations of bridgmanite and garnet are assumed to leave calcium-bearing garnets and the exsolution of calcium perovskite unaffected. Therefore, amounts of calcium-bearing garnets and calcium perovskite are extracted from the thermodynamic calculations.

We now derive how we calculate the growth kinetics of ringwoodite and account for the mineral reactions mentioned above. The growth kinetics of ringwoodite are controlled by two parameters which are determined in experiments: its enthalpy ΔH_a and its reaction rate constant k_0 which is closely linked to the reaction entropy ΔS_a.

For a mineral transformation from mineral assemblages A and B to a mineral assemblage C, the reaction rate is proportional to the molar concentrations of mineral phases A and B, C_A and C_B (Putnis, 1992):

$$\text{Reaction rate} \propto K^*\ C_A\ C_B \quad (5)$$

In our case, C_A and C_B are the concentration of ferropericlase and majorite garnet. The equilibrium constant of the reaction K^* is a function of the change of reaction Gibbs free energy, ΔG_a,

$$K^* = exp(-\Delta G_a/(R\ T)\ ) = exp(\Delta S_a/R)\ exp(-\Delta H_a/(R\ T)\ ) \quad (6)$$

using the definition of the reaction Gibbs free energy $\Delta G_a = \Delta H_a - T\Delta S_a$ with the enthalpy of the reaction ΔH_a and the entropy of the reaction ΔS_a. R denotes the gas constant and T is temperature. The reaction rate can be rewritten as

$$\text{Reaction rate} = c\ exp(\Delta S_a/R)\ exp(-\Delta H_a/(R\ T))\ C_A\ C_B \tag{7}$$

where c is a constant. As the concentration of the reactants changes during the reaction, the reaction rate will change accordingly. The reaction rate thus becomes a function of the phase fraction C

$$\text{Reaction rate} = k\ f(C) \tag{8}$$

where the reaction rate parameter k describes how the reaction rate depends on the concentration of the reactants. Therefore, the rate constant is

$$k = k(T) = c\ exp(\Delta S_a/R)\ exp(-\Delta H_a/(R\ T)\ ) = k_0\ exp(-\Delta H_a/(R\ T)\ ) \tag{9}$$

with the reaction rate constant $k_0 = c\ exp(\Delta S_a/R)$ where c is an experimentally determined factor.

Dobson & Mariani (2014) show that the growth kinetics of ringwoodite are controlled by diffusion kinetics. In this case, the rate of growth of the interface is linear with the square-root of time and the thickness of reaction rims measured at each temperature can be converted into apparent rate constants (Watson & Price, 2002). Following Tammann (1920) and Watson & Price (2002), the temperature dependent rate constant $k(T)$ is given by

$$k(T) = \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}x^2 \tag{10}$$

where x is the thickness of the growing interface and t is time. Integration of (10) gives the interface thickness evolution as a function of time and temperature:

$$x(t, T) = ((2\ k(T)\ t)^{1/2}). \tag{11}$$

To model the kinetic inhibition of ringwoodite growth, the interface grows until reaching the assumed initial grain size d. In this study, radially isotropic growth of the ringwoodite interface is assumed. We therefore normalise the ringwoodite interface thickness evolution (11) with half of the desired grain size (d) which results in a relative grain size: :

$$x_{\mathrm{rel}}(t, T) = ((2\, k(T)\, t)^{1/2})/(0.5\, d). \tag{12}$$

Since temperatures are approximately constant along the chosen adiabats, we assume a constant temperature T_0 during the reaction:

$$x_{\mathrm{rel}}(t) = ((2\, k(T_0)\, t)^{1/2})/(0.5\, d). \tag{13}$$

Due to its inverse dependency on grain size d, eq. (13) indicates that growth of ringwoodite takes more time in case of large grain size.

Assuming an upwelling rate v and utilizing the depth-to-pressure scale used by Cobden et al. (2008), the time of grain growth is converted to a grain growth curve as a function of pressure, $x_{\mathrm{rel}}(P)$. In our calculations, upwelling rates in the mantle are estimated to range between 1 and 100 cm/yr considering current heat flux estimates in upwelling mantle (e.g., Sleep, 1990; Courtillot et al., 2003) and geodynamic modelling experiments (Farnetani & Hofmann, 2010). The average grain size in the lower mantle is estimated to range between 1 µm (Yamazaki et al., 1996) and 10 cm (Solomatov, 1996; Korenaga, 2005) based on varying estimates of grain growth kinetics of mineral transformations in downwelling, or primordial, mantle. In the interior of a subducting slab, Yamazaki et al. (1996) and Yamazaki et al. (2005) find very slow grain growth rates for ferropericlase and bridgmanite, with grain sizes ranging between 10 µm to 100 µm for temperatures typical for subduction zones and for 10 million years after grain nucleation, but Fei et al. (2021) find a much smaller grain size exponent compared to Yamazaki et al. (1996). Their estimate for grain size in subducted slabs is on the order of 30-45 µm. Solomatov et al. (2002) question estimates of grain size for the bulk mantle as they cannot be reconciled with viscosity models or laboratory data for other materials. Solomatov et al. (2002) argue that the experiments have not been run sufficiently long to evaluate grain growth kinetics beyond transient effects. Solomatov (1996) and Korenaga (2005) have additionally suggested that deep-mantle plumes might have a significantly larger grain size than the ambient lower mantle due to (i) the temperature of the source region of the mantle upwelling, (ii) the kinetics of grain growth from an early magma ocean, and (iii) seismic tomographic imaging of wide slow structures which have been interpreted as wide plume roots (French & Romanowicz, 2015).

2.3 Mass balancing consumption of metastable ferropericlase and garnet

We follow the workflow in Figure 2 to calculate volume fractions of the mineral phases affected by the kinetically inhibited growth of ringwoodite for given grain size d, upwelling rate v and constant temperature T_0. Ringwoodite starts to grow at pressure P_{Start} where the molar amount of ringwoodite is non-zero in the equilibrium phase assemblage. The kinetically inhibited growth of ringwoodite is calculated as the convolution of the grain growth curve and the derivative of the molar amounts of ringwoodite at thermodynamic equilibrium as a function of depth. The growth curve x_{rel} is truncated where the relative growth of ringwoodite equals 1. At this pressure, hereafter called P_{end}, the molar amount of ringwoodite with kinetically inhibited growth conditions is considered to be equal to the amount of ringwoodite at thermodynamic equilibrium. Using the molar amount of ringwoodite at P_{end}, $n_{\mathrm{Rw,end}}$, we convert the grain growth curve (12) into molar amount of ringwoodite:

$$n_{\mathrm{Rw}}(P) = n_{\mathrm{Rw,end}}\, x_{\mathrm{rel}}(P) \tag{13}$$

We calculate the mass balances of ferropericlase, majorite garnet and pyrope garnet, following the mineral reactions in (2) – (4). Using molar volumes of the individual mineral phases from our thermodynamic calculations in section 2.1, we convert molar amounts to volume fractions within the pressure interval from P_{end} to P_{start}.

2.4 Calculation of density and seismic wave velocities

Utilizing their volume fractions calculated as described in section 2.3, we calculate the seismic properties of the kinetically inhibited phase assemblages, for the Hill average of Voigt and Reuss bounds of the constituent minerals (Voigt, 1928; Reuss, 1929; Hill, 1965). For each mineral, the density and seismic velocity are determined at the given pressure and temperature. The seismic properties of the kinetically inhibited phase assemblages are fit to the seismic profiles of phase assemblages at thermodynamic equilibrium for the corresponding adiabatic mantle geotherm.

2.5 Computation of 1-D synthetic seismograms

The mineral physical results can be used to test if the effects of the kinetically inhibited transformation of bridgmanite and ferropericlase to ringwoodite can be observed in seismological data. We focus on effects of PP and SS underside reflections and P-to-s conversions as they are commonly used probes to study upper mantle discontinuities. For this, the computed profiles of density, P wave and S wave velocity for equilibrated and kinetically inhibited phase assemblages are used to calculate 1-D reflectivity synthetic seismograms (Fuchs & Müller, 1971; Müller, 1985) for a range of dominant periods. Attenuation values are taken from PREM (Dziewonski & Anderson, 1981). For comparison, 1-D reflectivity synthetic seismograms using the 1-D velocity model ak135 (Kennett et al., 1995) and attenuation of PREM (Dziewonski & Anderson, 1981) are computed. Dominant periods of PP underside reflections are 1, 3, 5, 8 and 10 s. A source at 50 km depth is chosen and the data are analysed on the vertical component. For SS underside reflections, dominant periods are 5, 8, 10, 15 and 20 s. The source is at 50 km depth and the data are analysed on the transverse component. 21 receivers are distributed as a linear array around 120° epicentral distance with an aperture of 5°. An epicentral distance of 120° is within typical distances used for PP and SS precursor studies (e.g., Shearer, 1991; Thomas & Billen, 2009; Deuss, 2009). The seismograms are aligned on the PP/SS arrival and are normalised to unit amplitude.

For the P-to-s conversions we use dominant periods of 0.5 s, 1 s and 2 s with a source depth of 2 km to avoid interference of the P660s (and P410s for reference) arrivals with depth phases. We use a linear array with 1° receiver spacing between 40° and 80°. We calculate three-component seismograms (Z, R, T) but only analyse the radial component. Due to the simple source time function and the consistent waveforms, we abstain from deconvolving the vertical component P-wave and interpret the relevant waveform variation in the Results section.

3 Results

3.1 Effects of kinetic inhibition on seismic fine structure

The effects of kinetic inhibition on phase assemblages are compared with phase assemblages at thermodynamic equilibrium with regard to the mineral proportions and seismic properties. The kinetically inhibited growth of ringwoodite and the metastable assemblage of ferropericlase and pyrope-bearing garnet change the phase proportions above the onset depth of the phase transformation (Figure 3). For equilibrated phase assemblages at a temperature of ~1850 K (following the adiabat with 1300°C potential surface temperature, abbreviated hereafter as "1300°C adiabat"; please see Table 2 and Cobden et al., 2008 for details), ringwoodite dissociates to ferropericlase and bridgmanite within a pressure interval of ~0.1-0.2 GPa (i.e., ~2 km) at ~23.4 GPa (i.e., at ~659 km depth) (Figure 3a). The amount of garnet decreases due to the exsolution of bridgmanite, starting at ~22.7 GPa (~642 km).

The thickness of inhibited growth of ringwoodite is sensitive to temperature, grain size and mantle upwelling rate. For 5 cm grain size and 50 cm/yr upwelling rate, the kinetic inhibition leads to a growth of ringwoodite over a pressure interval of 1 GPa (~25 km) (Figure 3b). The gradual growth of ringwoodite results in a gradual consumption of ferropericlase. At the pressure where ringwoodite starts to grow, the entire amount of bridgmanite reacts to garnet, thus its volume fraction increases to 70%. The recombination reaction of garnet and ferropericlase to ringwoodite gradually decreases the amount of garnet towards lower pressures.

The excess of garnet changes the seismic structure around 660 km depth (Figure 3c). Since garnet has lower P- and S-wave velocities (garnet: $v_p \approx 9.8$ km/s, $v_s \approx 5.2$ km/s at 23.4 GPa and 1850 K) than ringwoodite and bridgmanite (ringwoodite: $v_p \approx 10.2$ km/s, $v_s \approx 5.6$ km/s; bridgmanite: $v_p \approx 11.2$ km/s, $v_s \approx 6.3$ km/s at 23.4 GPa and 1850 K), the kinetically inhibited growth of ringwoodite and the abundance of garnet results in a low-velocity layer above the 660 km discontinuity of $\Delta v_p \approx -5\%$, $\Delta v_s \approx -7\%$ (Figure 45). The low-velocity layer above the lower boundary of the ringwoodite-forming reaction thus increases the P- and S-wave impedance contrast. When the growth of ringwoodite has reached equilibrium conditions, the profiles of density and seismic wave speeds intersect the profiles of the phase assemblages at thermodynamic equilibrium.

The effects of initial grain size d and mantle upwelling rate v can be described by a kinetic parameter D which is proportional to the upwelling rate and the squared grain size (Dobson & Mariani, 2014):

$$D \sim v\, d^2.$$

Scenarios of kinetic inhibition with different initial grain sizes and upwelling rates give the same results if they can be described by the same kinetic parameter. Therefore, the kinetic parameter is an appropriate entity to compare scenarios of kinetically inhibited phase assemblages. Since the kinetic parameter scales with the square of initial grain size d, the kinetic inhibition of ringwoodite is more sensitive to grain size than to upwelling rate. In this study, we set the proportional factor to unity and use

$$D = v\, d^2.$$

in order to compare scenarios of initial grain size *d* and mantle upwelling rate *v.*

The thickness of the low-velocity layer, i.e., the depth interval between the onset and the completion of ringwoodite growth, increases exponentially with increasing kinetic parameter of the kinetic parameter (Figure 5). The exponential behaviour can be explained by the grain growth equation which includes the Arrhenius relation for the reaction rate parameter $k(T)$ (cf. Eq. (9)). For kinetic parameters D between 10 and 100 cm^3/yr, kinetic inhibition occurs over a pressure interval of ~0.1 GPa which is as narrow as the transformation pressure interval of the recombination of ringwoodite from ferropericlase and bridgmanite. A transformation pressure interval of ~0.1 GPa is equivalent to a low-velocity layer of thickness ~2 km which is likely below the resolution threshold even of short period PP waves and at the resolution level for receiver function (Ps). Seismic waves therefore sample the reflector and low-velocity layer above in the same way as the reflector for phase assemblages at thermodynamic equilibrium. The onset of seismically detectable kinetic inhibition in terms of the kinetic parameter D is $D > 100$ cm^3/yr for 1850 K, $D > 1000$ cm^3/yr for 1960 K and $D > 2500$ cm^3/yr for 2050 K. The temperature dependence can be explained by the increased diffusion of ions at higher temperatures.

3.2 Synthetic seismograms

We have calculated 1-D synthetic seismograms from the synthetic velocity and density profiles using the reflectivity methods (Fuchs & Müller, 1971; Müller, 1985) as described in section 2.4. Here we discuss the effects of the kinematically inhibited velocity structures on PP/SS underside reflections and P-to-s conversions, two probes regularly used for the study of upper mantle discontinuities.

3.2.1 PP and SS Precursors

The seismograms calculated for the velocity models with kinetically inhibited recombination reaction of ringwoodite from bridgmanite and ferropericlase are compared to seismograms for velocity models with equilibrated phase assemblages. Using linear vespagrams (Davies et al., 1971; Muirhead et al., 1976), PP/SS and P660P/S660S waveforms are extracted for travel times predicted by ak135 (Kennett et al., 1995) (Figure 6).

For velocity models where the kinetic inhibition of the ringwoodite growth results in a thicker low-velocity layer of the order of ~25 km, the PP/SS precursors off the reflector caused by kinetically inhibited recombination of ringwoodite are noticeably advanced for reaction intervals wider than 25 km compared to PP/SS precursors reflected off discontinuities of equilibrated phase transformations (Figure 3b). The travel time advances also affect secondary phases of the underside reflections such as depth phases, e.g., pP660P (Figure 6). For the kinetic parameters tested here, the maximum travel time advances for PP underside reflections are ~0.8 s, whereas maximum travel time advances for SS underside reflections are ~1.3 s (Figure 7). These travel time residuals correspond to apparent maximum shifts of the discontinuity depth on the order of 5 km.

Amplitudes for PP precursors with a dominant period of 1 s reflected off the kinetically inhibited formation of ringwoodite vary between 120% and 160% relative to the equilibrium model at 1850 K. For the same temperature, amplitudes of SS precursors with a dominant period of 5 s range between 120% and 160% relative to the equilibrium model. The precursor amplitudes for the kinetically inhibited phase assemblages decrease with increasing periods (Figure 8). The transition from enhanced to apparently unaltered precursor amplitudes is at a dominant period of 5 s for PP and 10 s for SS. Moreover, the PP and SS precursor amplitudes increase with increasing kinetic parameters and increasing thickness of the low-velocity layer. The PP/SS precursors off the lower boundary of the phase transformation are less affected by interference with PP/SS precursors off the gradient above the low-velocity layer.

While it appears that underside reflections of PP waves at the ringwoodite to bridgmanite plus ferropericlase transition are more difficult to detect than the corresponding SS underside reflection (Estabrook & Kind, 1996), there is evidence for P660P waves in some regional studies (e.g., Deuss et al., 2006; Thomas & Billen, 2009; Schmerr & Thomas, 2011, Saki et al., 2014) and usually the amplitudes of observed P660P waves are smaller than predicted by PREM or a pyrolytic mantle. There is also a noted discrepancy between the detection of P660P and its equivalent underside reflection of PKPPKP (P’660P’) (Day & Deuss, 2013). The scarcity of P660P detections in recorded data can likely be explained by compositional and thermal effects that are not captured in our modelling and the assumed pyrolytic starting model (Lessing et al., 2015; Guo & Zhou et al.,2020; Waszek er al., 2021).

Underside reflection of PP from the 660 km phase transition are rarely detected in recorded data although such detections exist (Deuss et al., 2006; Day & Deuss, 2013).

The finite width of the low-velocity layer (Figure 3a) and the vertical resolution of the seismic waves lead to a frequency-dependent behaviour of P660P/S660S precursor amplitudes (Figure 9). PP waves with 1 s dominant period appear to resolve the increased P wave impedance contrast off the reflector caused by the kinetically inhibited recombination of ringwoodite. The increased P wave impedance contrast results in increased PP precursor amplitudes compared to the reflections for equilibrated phase assemblages. If the dominant period is increased, PP precursor amplitudes off the reflector with kinetic inhibition decrease and have similar PP precursor amplitudes off the reflector as those without kinetic inhibition.

3.2.2 P-to-s conversions (P receiver functions)

Examples of the synthetic waveforms for the kinetically inhibited models and pyrolitic models at equilibrium conditions are shown in Figure 10. For varying temperatures at equilibrium, we observe strong conversions from the 660 km discontinuity and other discontinuities (e.g., 410-km as well as shallower) with minor waveform and amplitude variations. We calculated synthetics for dominant periods of 0.5 s, 1 s, and 2 s and observe very minor variability of the results. While absolute travel times for P- and P-coda arrivals vary, differential travel time variations are minor, with 0.2 s and 0.6 s for the 1960 K and 2050 K simulations, respectively, compared to the 1850 K simulations. Waveform variations are limited to larger moveout for a deeper transition, arriving 5.1 to 8.9 s after P660s.

For the kinetically inhibited transformations we observe strong waveform variations with temperature, where the waveforms of the high temperature models show a dominant precursor about 7 s preceding the arrival from P660s (Figure 10b and c). The precursor due to the low velocity zone will lead to a likely detectable negative polarity precursor in P-wave receiver functions (see Figure S1 for an additional velocity profile at 2050 K). Those detectable negative polarity precursors have been reported in some up-flowing regions of the mantle (e.g., Negi et al., 2022). We observe amplitude variations dependent on grain size, upwelling rate, and temperature (Figure 10d). Amplitudes vary between 52% and 122% relative to the equilibrium model at 1960 K with the smallest amplitudes observed for the highest temperatures. Interference effects lead to apparent inverted waveforms for the P-to-s conversion relative to P. Both amplitude and waveform variations for these models would be large enough to be observed in receiver function analyses.

Travel times relative to P vary slightly for the different models. We observe travel time variations of ±0.3 s relative to the equilibrium model at 1960 K. While detectable, these might be difficult to detect for recorded data due to the 3-D velocity variations known to exist in upper mantle.

4 Discussion

4.1 Estimates of uncertainties

The effects of initial grain size and upwelling rate on the seismic properties of kinetically inhibited phase assemblages have been investigated in section 3.1. Among the kinetic input parameters, i.e., kinetic rate parameter k_0, reaction enthalpy ΔH_a and temperature T), uncertainties of the reaction enthalpy predominantly affect the seismic properties of kinetically inhibited phase assemblages (Figure 11a and b). Dobson & Mariani (2014) measure the enthalpy of the reaction with an uncertainty of ±40 kJ mol^{-1} for the ringwoodite layer (Table 1). Varying the enthalpy of the reaction with this value while keeping remaining parameters constant in eq. (9) results in variations of the growth time of ringwoodite until equilibrium conditions by one order of magnitude (Figure 11b).

Converting growth time into the thickness of the reaction interval using the upwelling rate gives uncertainties of the reaction interval of one order of magnitude. Given the uncertainty of the enthalpy of the reaction for the ringwoodite layer, the reaction interval could therefore range from 1 km to ~250 km for kinetic parameters ranging from 1 to 10.000 cm^3/yr. On the one hand, reaction intervals with a width of 1-10 km are close to the vertical resolution of PP and SS precursors (e.g., Thomas & Billen, 2009; Schmerr & Thomas, 2011) and it might be challenging to discriminate kinetic effects from other influences on reaction intervals. On the other hand, reaction intervals with widths of 100-200 km would give increased PP and SS precursor amplitudes due to the increased P wave and S wave impedance contrast and due to the more gradual change of seismic properties from the low-velocity region relative to seismic properties at thermodynamic equilibrium. P-to-s conversions at the discontinuities beneath the receiver typically show higher resolution and are likely able to detect even the thinner layers inferred for the smaller kinetic parameters. Thicker reaction intervals would result in strongly reduced amplitudes of Ps. Reaction intervals of 100-200 km would also affect phase transformations at smaller pressures/shallower depths, e.g., the wadsleyite to ringwoodite transition, as well as the phase transformations from pyroxene to garnet and from garnet to calcium silicate perovskite. The kinetics of the olivine to wadsleyite phase transition (Poirier, 1982; Brearley et al., 1992; Kirby et al., 1996) and of pyroxene to garnet (Hogrefe et al., 1994) have been studied for harzburgitic mantle composition so far. However, kinetic data of other phase transformations in the transition zone are necessary to allow for consistent treatment of kinetic effects on seismic properties within and above the transition zone.

The reaction rate constant k_0 has a minor effect on the seismic properties of the kinetically inhibited phase assemblage (Figure 11c). P- and S-wave velocity vary by ±0.05 km/s, and density is changed by ±0.02 g cm^{-3} for varying k_0 to its lower and upper bounds. The thickness of the low-velocity layer above the 660 km discontinuity shifts by ±4 km.

4.2 Seismological and geodynamic implications

Patterns of mantle flow and dynamics have been investigated using seismic wave speed anomalies in seismic tomography models (e.g., Li et al., 2008; Ritsema et al., 2011) and seismic waves sampling the upper mantle and mantle transition zone discontinuities using receiver functions (e.g., Vinnik, 1977; Farra & Vinnik, 2000; Rondenay, 2009), short period P'P' reflections (e.g., Niazi & Anderson, 1965; Vidale & Benz, 1993; Day & Deuss, 2013), and PP and SS precursors (e.g., Shearer, 1991; Deuss, 2009). Since the upper mantle and mantle transition zone discontinuities are sensitive to thermal variations due to their Clapeyron slopes (Bina & Helffrich, 1994; Helffrich, 2000; Weidner & Wang, 2000), variations of discontinuity depth and of transition zone thickness (i.e., the depth between the 410 and 660 km discontinuity) and constraints from mineral physics, are frequently used to infer thermal variations in the mantle (e.g., Shearer, 2000, Ritsema et al. 2009).

The investigation of reaction kinetics of the reaction from ferropericlase and bridgmanite to ringwoodite can add further constraints on mantle temperature and flow patterns. The effect of kinetic inhibition can be compared to seismic data using a two-step approach. In a first step, through forward modelling of synthetic seismograms for a range of temperatures, upwelling rates, and grain sizes. Relevant temperatures can be determined from adiabatic mantle geotherms (Brown & Shankland, 1981; Spiliopoulos, 1984; Ita & Stixrude, 1992; Cobden et al., 2008) to estimate excess temperatures (e.g., Sleep, 1990; Schilling, 1991; Herzberg et al., 2007). Heat flux estimates (e.g., Sleep, 1990; Courtillot et al., 2003) can be converted into estimates for upwelling rates using convection models for vertical upwellings. A steady-state axisymmetric plume with temperature-dependent viscosity might serve as a starting point for estimates of upwelling rates as a function of heat flux and excess temperatures (Loper & Stacey, 1983; Schubert et al., 2001). In a second step, the seismic recordings can be compared to the set of synthetic seismograms and those models are taken which give the best match with regard to frequency dependent travel time residuals and amplitude ratios. The set of matching models gives the range of corresponding grain sizes and upwelling rates.

Considering the effects of reaction kinetics of ferropericlase and bridgmanite to ringwoodite on the amplitudes and travel times may offer additional constraints on mapping mantle flow using P-to-s receiver functions. P-to-s conversions typically have higher frequencies (Li et al., 2000; Wölbern et al., 2006). Several studies (van der Meijde et al., 2003; Schmandt, 2012; Huckfeldt et al., 2013) show frequency dependent behaviour of P-to-s conversions at mantle transition zone discontinuities. We see little frequency dependence of P-to-s conversion in our synthetic models within the range typically used for receiver functions, but observe strong waveform variations that are likely to be observable in recorded data as well as strong amplitude variations and small travel time variations that might add additional constraints for detecting regions with mantle upstreams.

The analysis of PP and SS precursors might have some resolution limitations with respect to the scale of the mantle upwellings which might hamper the detection of the predicted waveforms. Geodynamic modelling indicates that deep thermal mantle plumes have typical diameters of ~200 km (e.g., Sleep, 1990; Schubert et al., 2001; Steinberger & Antretter, 2006) whereas thermochemical plumes might have larger diameters ranging from 600 to 800 km (Farnetani, 2005; Farnetani & Hofmann, 2010; Stockmann et al., 2019). Lessing et al. (2015) use the 2.5-D axisymmetric finite difference technique PSVaxi (Jahnke, 2008; Thorne et al., 2013) to examine the effects of topography of the upper mantle discontinuities imaged by PP underside reflections with dominant periods of 2 s. Their models show that the PP wavefield reflected off a locally elevated 660 km with a diameter of 200 to 400 km does not differ significantly from the PP wavefield reflected off a flat reflector at 660 km depth. The size of the detailed topography of the perturbed reflector is smaller than the PP Fresnel zone at 660 km depth and thus might not be resolved. The detection of effects of the kinetically inhibited reaction from ferropericlase and bridgmanite to ringwoodite might therefore be challenging in narrow mantle upwellings. Although conduction might lead to thermal halos around narrow mantle plumes the effect might be small (Sleep, 2004) and might not influence the detectability of the plume using underside reflection. Nonetheless, recent tomographic images show that plumes might be broad upstreams (French and Romanowicz, 2015), very different to early numerical and laboratory plume experiments which might make the upstream detectable seismically. The pooling of plume material beneath the 660 km discontinuity due to the endothermic phase transition might lead to larger scale temperature anomalies in the region of plume-like mantle upstreams (Tackley et al., 1994, Schubert et al, 1995, Stockmann et al., 2019).Possible candidates for upwellings with large, detectable lateral dimensions are large transient domes near the mantle transition zone (Courtillot et al., 2003, Davaille et al., 2005, Kumagai et al., 2007; Kumagai et al., 2008). The transient domes are characterised by upwelling rates slower than deep mantle plumes due to their small buoyancy ratio (ratio of chemically driven buoyancy to thermally driven buoyancy). Nonetheless, the transient domes could have excess temperatures up to 300 K in their centre and form a thermal boundary layer with the ambient mantle (Davaille et al., 2005). Upwelling mantle material might pond beneath the 660 km discontinuity when encountering the phase transformation from bridgmanite and ferropericlase to ringwoodite (e.g., Schubert & Turcotte, 1975; Schubert & Tackley, 1995; Tackley, 1995; Steinbach & Yuen, 1997; Brunet & Yuen, 2000; Davaille et al., 2005, Farnetani & Samuel, 2005). Due to the negative Clapeyron slope, the transformation pressure of the warmer material is shifted towards lower pressure, resulting in a negative buoyancy force which delays further upwelling. The material starts to pond beneath the phase transformation (Davaille et al., 2005) and spreads laterally, growing with dimensions broader than plume conduits (e.g., Steinbach & Yuen, 1997; Davaille et al., 2005, Stockmann et al., 2019).

Furthermore, the viscosity contrast across the 660 km discontinuity (e.g., Mitrovica & Forte, 2004) might support lateral mantle flow beneath the discontinuity. The geodynamic models of Tosi & Yuen (2013) show additional evidence for horizontal flow whose scale is governed by the viscosity contrast due to temperature variations. For small values of the viscosity contrast, broad and highly viscous plumes are generated that tend to pass through the transition zone relatively unperturbed. For higher values of the viscosity contrast ($10^2 \leq \Delta\eta_T \leq 10^3$), the geodynamic simulations show horizontal channel flows beneath the 660 km discontinuity which might extend up to 1500 km horizontally before tilting to more vertical flow. Therefore, lateral mantle flow could change the fine-scale seismic structure at ~660 km depth in a way that could allow for the detection of the effects of kinetically inhibited growth with seismic methods sensitive to upper mantle discontinuity structure.

This study has predicted effects of kinetically inhibited growth of ringwoodite in mantle upstreams and the expected effect on seismic probes for discontinuity structure. We find that the effect on PP/SS underside reflection travel times is small; amplitudes, although harder to assess in recorded data, might show a larger response to the altered discontinuity structure. For P-to-s conversions travel time effects are minor but waveforms and amplitudes of conversions are noticeably affected. Potentially P-to-s receiver function could be a suitable probe to detect kinetic effects in the phase transitions and to map out mantle flow.

5 Conclusions

The effects of reaction kinetics of bridgmanite and ferropericlase to ringwoodite in upwelling mantle on elastic properties were investigated using data of kinetic experiments and internally self-consistent thermodynamic modelling. As the kinetic experiments show, growth of ringwoodite is initiated at ferropericlase grain boundaries and is kinetically inhibited due to the necessary diffusion of chemical components. At the initiation of ringwoodite growth, bridgmanite transforms into metastable garnet. Ringwoodite grows from the metastable assemblage of ferropericlase and pyrope-bearing garnet.

The results of the analysis of kinetically inhibited transformation at ~660 km depth predict possible effects of kinetically inhibited growth of ringwoodite on seismic data which can be summarized as follows:

1. The increased amount of ferropericlase and garnet results in a localized low velocity zone of $\Delta v_P \sim -5\%$, $\Delta v_S \sim -7\%$ directly above the 660 km seismic discontinuity due to the lower seismic velocities and density of ferropericlase and garnet compared to ringwoodite and bridgmanite. The impedance contrasts for P and S waves are thus increased compared with seismic velocity profiles of an equilibrated pyrolite mineral assemblage.
2. The effects of reaction kinetics on the seismic fine structure at ~660 km depth depend on the product of the squared grain size and upwelling rate. The change of seismic properties correlates with the product of squared grain size and upwelling rate. Modelling 1-D synthetic seismograms using the seismic profiles of kinetically inhibited phase assemblages show travel time delays of 0.4-0.8 s for PP precursors and delays of 1.2-1.6 s for SS precursors for kinetic inhibition of the ringwoodite-forming reaction. The finite width of the low-velocity layer above the seismic discontinuity results in frequency dependent behaviour of PP and SS underside reflection amplitudes, with higher amplitudes for 1-3 s PP waves and 5-8 s SS waves. However, high-frequency PP

and SS waves are rarely observed, and the predicted travel time differences are of similar magnitude as typical picking uncertainties. Hence, it might be challenging to utilize PP and SS underside reflections in order to observe kinetic effects.

3. Synthetic seismograms for P-to-s converted waves for velocity models for kinetically inhibited transformations predict strong waveform variations for higher temperature models and amplitude variations dependent on temperature, grain size and upwelling rate. Travel time variations are maximum ±0.3 s relative to models at equilibrium for temperature of 1960 K. Receiver functions therefore might be a suitable seismic probe to look for kinetic effects on the seismic structure of the 660 km discontinuity in mantle upwellings. A future re-evaluation of P-to-s receiver functions at mantle upwellings would be necessary to study the predicted effects described in this paper.
4. Possible candidates for mantle upwellings where reaction kinetics may become important are transient domes with low buoyancy ratios and large lateral dimensions, or broader scale plume upwellings. Material stalling at the phase transformation of bridgmanite and ferropericlase to ringwoodite might generate structure in the resolution range of P-to-s converted waves.

Data Availability

The resulting data of this work and sources code developed during this work are not publicly available. Except the results from kinetic experiments by Dobson & Mariani (2014), data are based on tools available in the public domain:

1. Perple_X program package (Connolly, 2005), utilising the elastic and thermodynamic properties and the solid solution model of Stixrude & Lithgow-Bertelloni (2011)
2. 1-D synthetic seismic modelling using the reflectivity method (Fuchs & Müller, 1971)
3. and data processing with seismic waveform analysis tool SeismicHandler (Stammler, 1993).

If you are interested in detailed data, please contact the corresponding author.

Acknowledgements

We are grateful for the constructive reviews by the editor Ian Bastow and two anonymous reviewers that helped to greatly improve the quality of the manuscript. We thank Jamie Connolly for assistance with the Perple_X program package (Connolly, 2005). Data analyses were carried out with SeismicHandler (Stammler, 1993). Figures were produced with Generic

Mapping Tools (GMT) (Wessel & Smith, 1995). S. Lessing was supported under grant DFG TH1530/2–1. The high-pressure kinetic experiments were largely performed at the Bayerisches Geoinstitut under the aegis of an EU large-scale facility grant to D. Rubie and an Alexander von Humboldt fellowship to D. Dobson. The Al- free experiment was performed at the ETH Zurich during a visiting professorship by D. Dobson. We acknowledge funding from NERC (grants NE/L006898 and NE/L007363). L. Cobden was supported under grant DFG TH1530/5–1.

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Figures

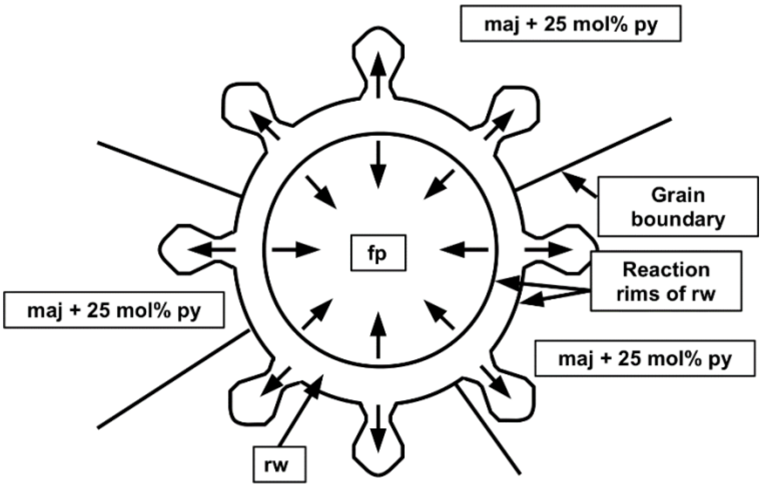

Figure 1: Sketch of the reaction mechanism for the recombination of bridgmanite and ferropericlase (fp) to ringwoodite (rw). The ringwoodite layer nucleates on the fp grain surface and grows into majorite garnet (maj) which contains 25 mol% Al-bearing pyrope (py) in a fingering instability. After Dobson & Mariani (2014).

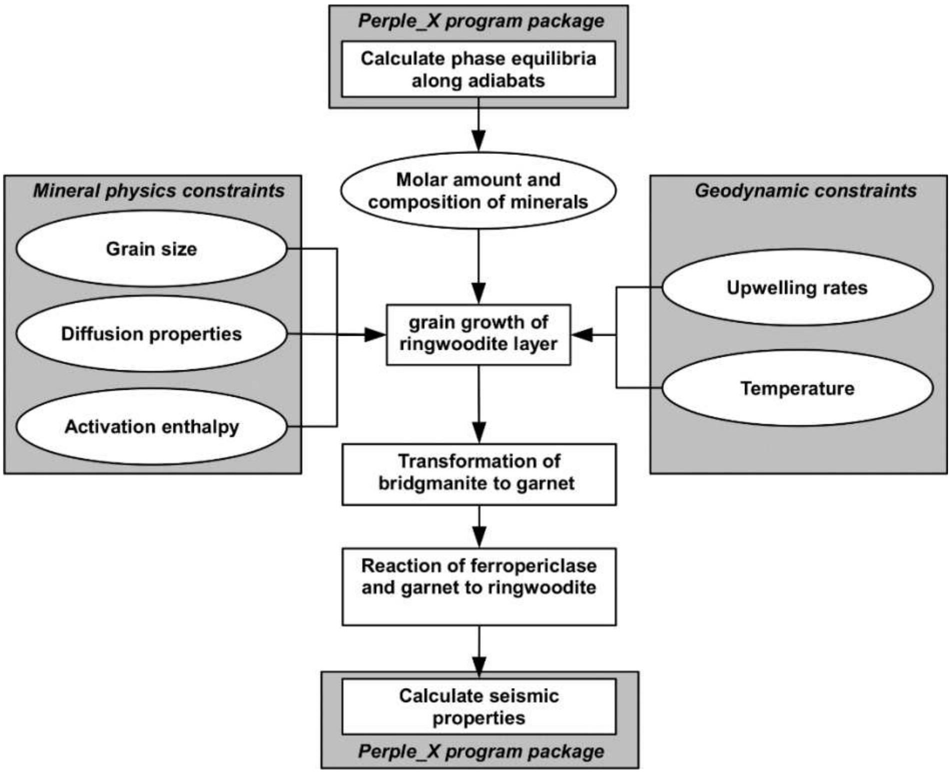

Figure 2: Forward modelling of seismic properties for kinetically inhibited growth of ringwoodite and corresponding mineral reactions for ferropericlase, bridgmanite and garnet.

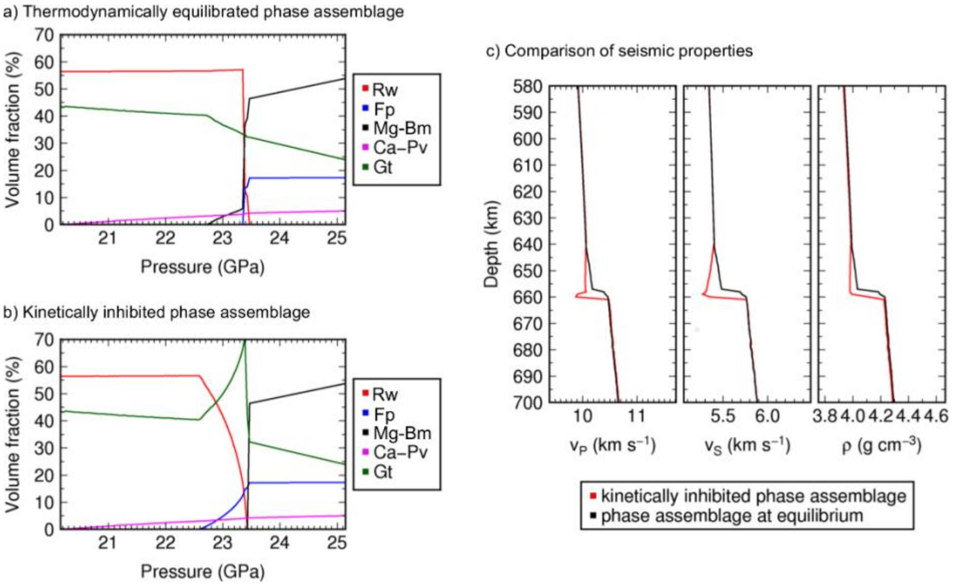

Figure 3: Example for effects of kinetic inhibition of ringwoodite growth on volume fractions of minerals and on seismic properties of phase assemblages for temperature of 1850 K (following the 1300°C adiabat), 5 cm initial grain size and 50 cm/yr upwelling rate. a) Volume fractions of equilibrated phase assemblages as a function of pressure for pyrolite composition along the 1300°C adiabat. Mineral phases are abbreviated as follows: Rw: ringwoodite, Fp: ferropericlase, Mg-Bm: magnesium bridgmanite, Ca-Pv: calcium perovskite, Gt: garnet. b) Volume fractions of kinetically inhibited phase assemblages as a function of pressure for pyrolite composition along the 1300°C adiabat. c) Comparison of seismic velocities and density between equilibrated and kinetically inhibited phase assemblages.

d

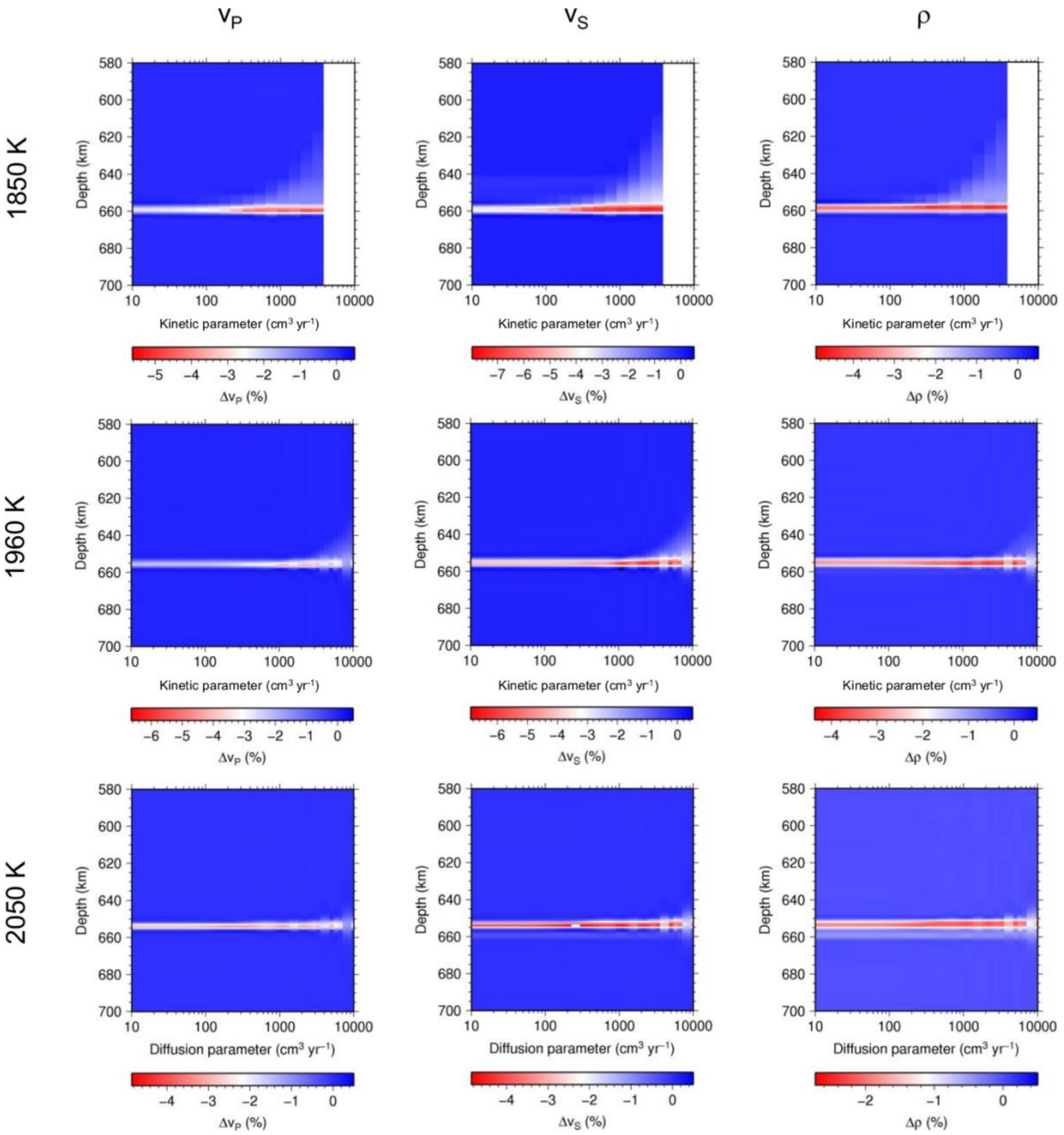

Figure 4: Relative differences of P wave velocity, S wave velocity and density due to the kinetically inhibited growth of ringwoodite and the presence of metastable ferropericlase and garnet for temperatures of 1850 K, 1960 K and 2050 K. No data are available for kinetic parameters > 4000 cm^3 yr^{-1} because the ringwoodite growth interferes with the ringwoodite-to-wadsleyite transition. To date, no studies with kinetic data for the ringwoodite-to-wadsleyite transition in mantle upstreams are known to the authors.

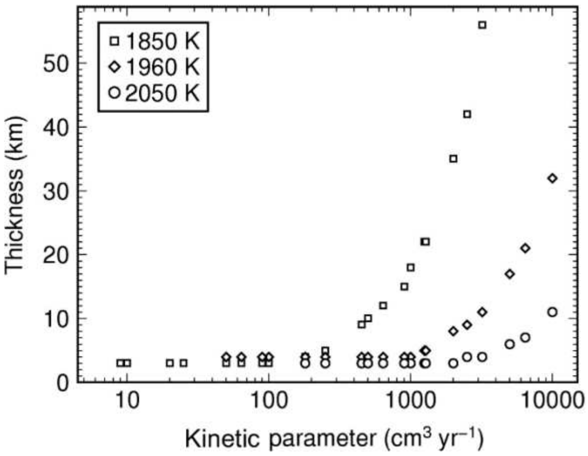

Figure 5: Thickness of the reaction interval where ringwoodite grows from the recombination of ferropericlase and garnet as function of the kinetic parameter *D*. The kinetic parameter *D* is proportional to the upwelling rate *v* and the square of grain size *d*, for simplicity we set the proportion factor to unity so that $D = v\ d^2$. Scenarios which have different grain size and upwelling rates, but have the same kinetic parameter, show the same kinetic inhibition.

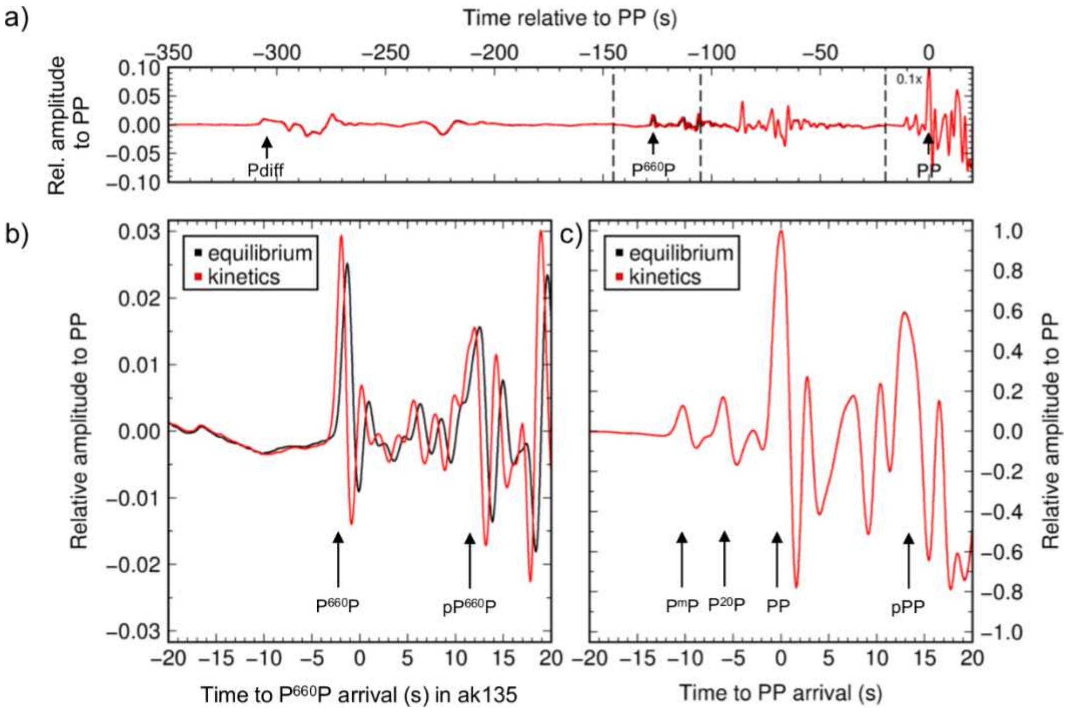

Figure 6: Synthetic seismograms of PP precursors with a dominant period of 3 s from seismic models of equilibrated and kinetically inhibited phase assemblages at an array with reference epicentral distance of 120 deg, a temperature of 1850 K, grain size of 5 cm and a vertical upwelling rate of 50 cm/yr. a) shows the linearly stacked traces of all calculated seismograms for equilibrated pyrolite phase assemblages (black) and kinetically inhibited phase assemblages (red) aligned with slowness for PP from ak135 (Kennett et al., 1995). Time windows around the predicted arrivals of P660P and PP from ak135 shown b) and c) and are marked by vertical lines and the phase names. Arrows indicate the arrivals of P660P and pP660P in zoomed diagram b) and the arrivals of PP and pPP in zoomed diagram c).

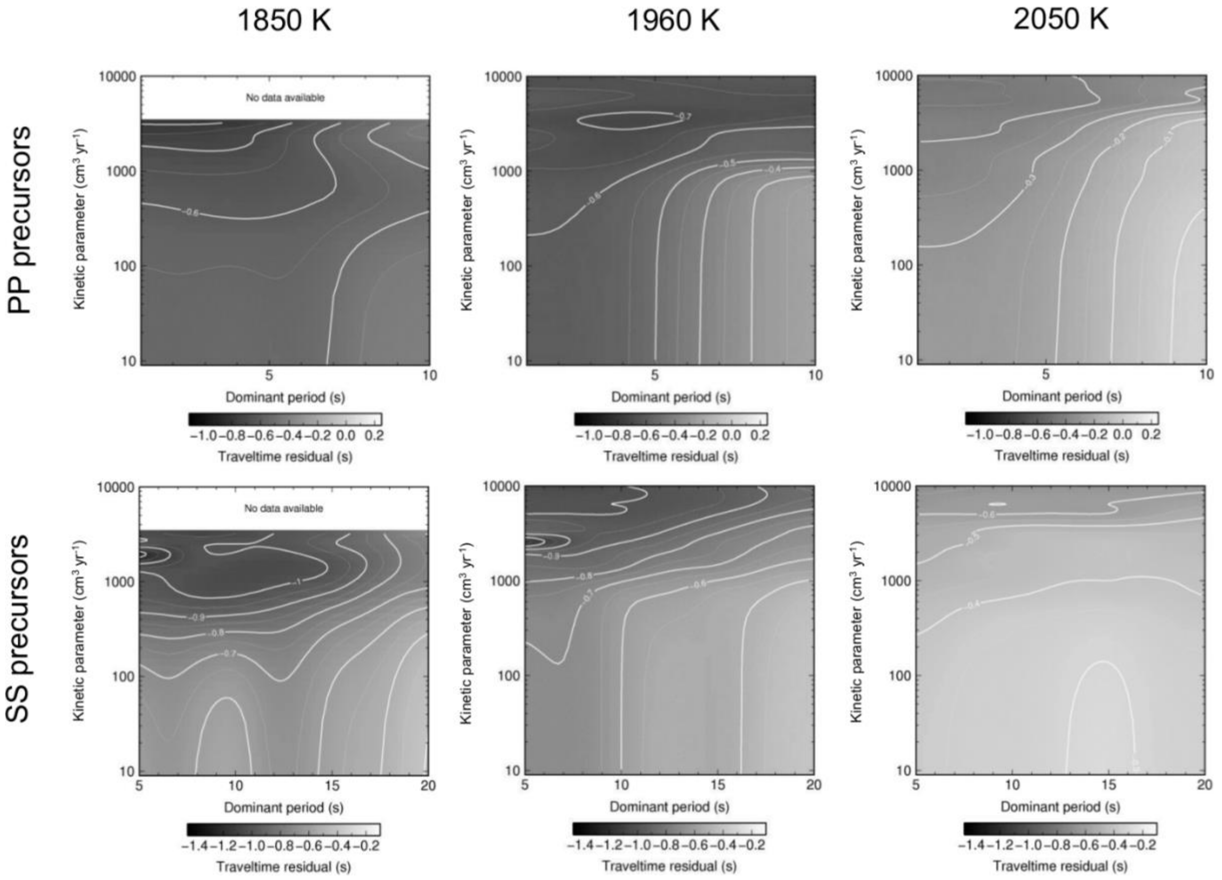

Figure 7: Travel time residuals of stacked PP and SS precursors between kinetically inhibited and equilibrated backward reaction to ringwoodite as a function of temperature and kinetic parameter for varying dominant periods at an epicentral distance of 120°C. Bold lines denote changes of travel time residuals by 0.1, thin lines denotes changes of travel time residuals by 0.05. Data are not available at temperature pf 1850 K and kinetic parameters > 4000 cm^3 yr^{-1} (cf. Figure 4).

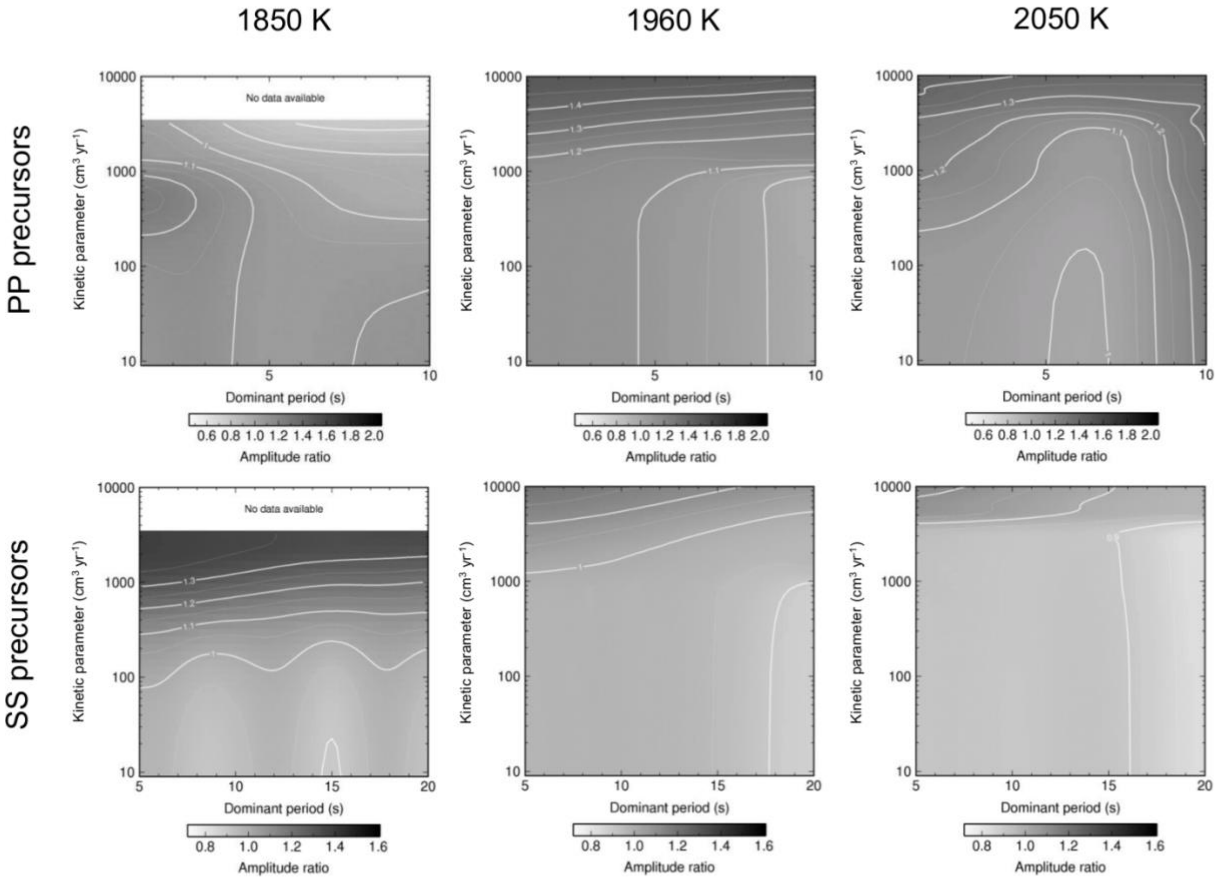

Figure 8: PP and SS precursor amplitude ratios of reflections off the kinetically inhibited reaction vs. off the equilibrated reaction to ringwoodite as a function of temperature and kinetic parameter for varying dominant periods at an epicentral distance of 120°. Bold lines denote changes of amplitude ratios by 0.1, thin lines denote changes of amplitude ratios by 0.05. Data are not available at temperature pf 1850 K and kinetic parameters > 4000 cm^3 yr^{-1} (cf. Figure 4).

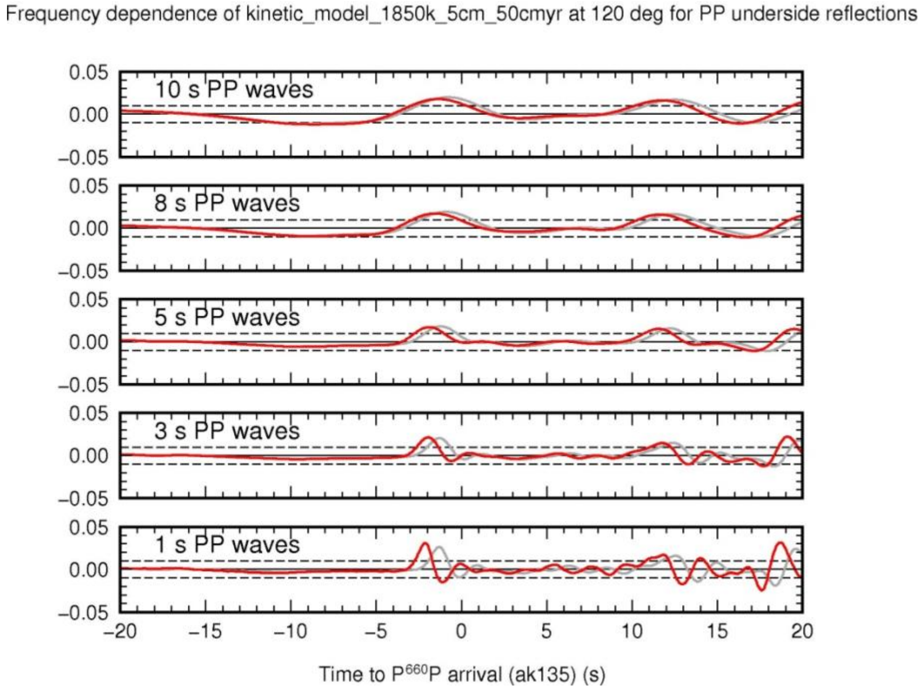

Figure 9: Frequency dependence of $P^{660}P$ underside reflections for equilibrated and kinetically inhibited phase assemblages at 1850 K, for 5 cm grain size and 50 cm/yr upwelling rate for dominant periods of 1 to 10 s. Waveforms of reflections off the kinetically inhibited backward reaction to ringwoodite are depicted in red, whereas waveforms of reflections off the equilibrated backward reaction to ringwoodite are depicted in black.

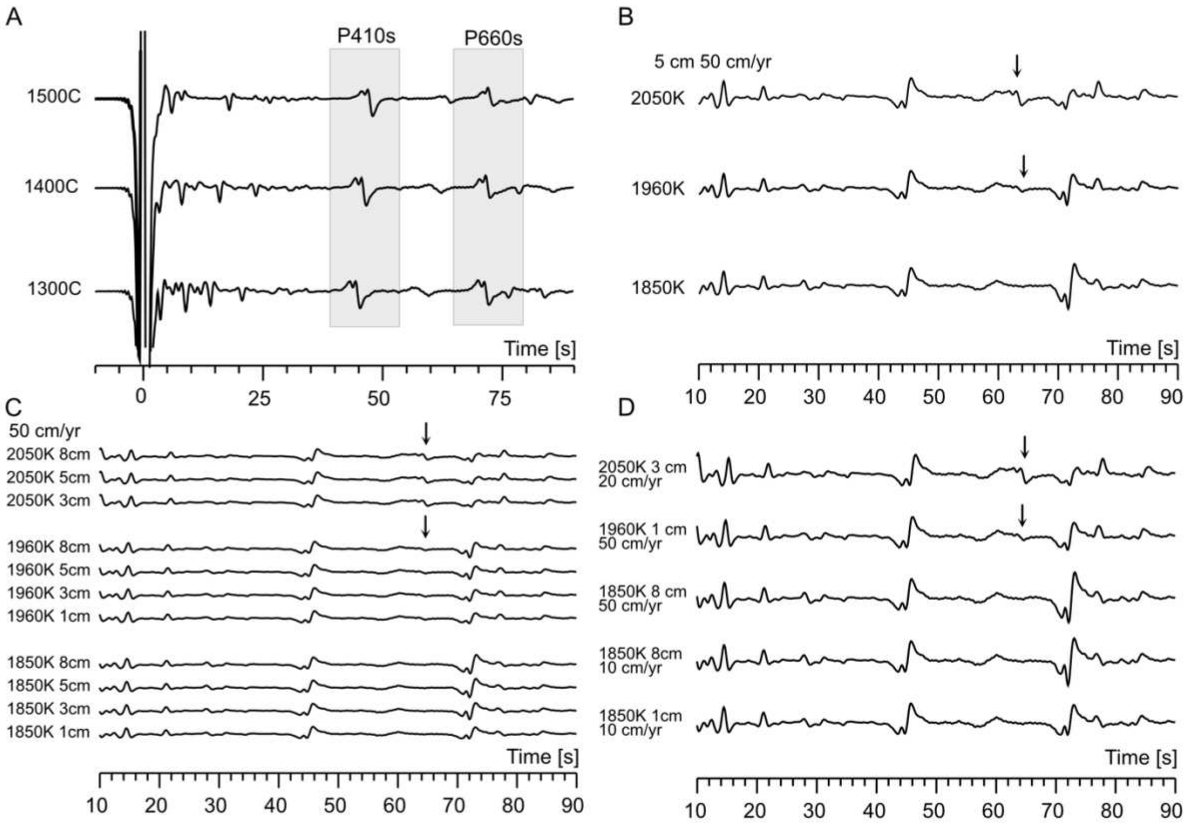

Figure 10: Synthetic waveforms for P-to-S conversions arriving in the P-wave coda with dominant period of 1 s. All traces are recorded at 43 deg epicentral distance and aligned on the theoretical P-wave arrival. All times are given relative to P-wave arrival time. A) Waveforms for pyrolytic models at equilibrium conditions for mantle adiabats with surface potential temperatures ranging from 1300 to 1500 °C. P-to-s conversions from the 410-km discontinuity and the 660 km discontinuity are highlighted. B) Waveforms for kinetically inhibited transformation for models with 5 cm grain sizes and an upwelling rate of 50 cm/yr for geotherms at 1850 K, 1960 K and 2050 K. Amplitudes are normalized on the P-wave amplitude. Arrows indicate detectable precursors to P660s. C) Waveforms for kinetically inhibited transformation for 50 cm/yr upwelling rate and varying temperatures and grain sizes. Amplitudes are normalized on the P-wave amplitude. Arrows indicate detectable precursors to P600s. D) Waveforms for kinetically inhibited transformation for varying temperatures, upwelling rates and grain sizes. Amplitudes have not been normalized and the amplitude variations of the P-to-S conversion from the ferropericlase and bridgmanite to ringwoodite are observable. Arrows indicate detectable precursors to P660s.

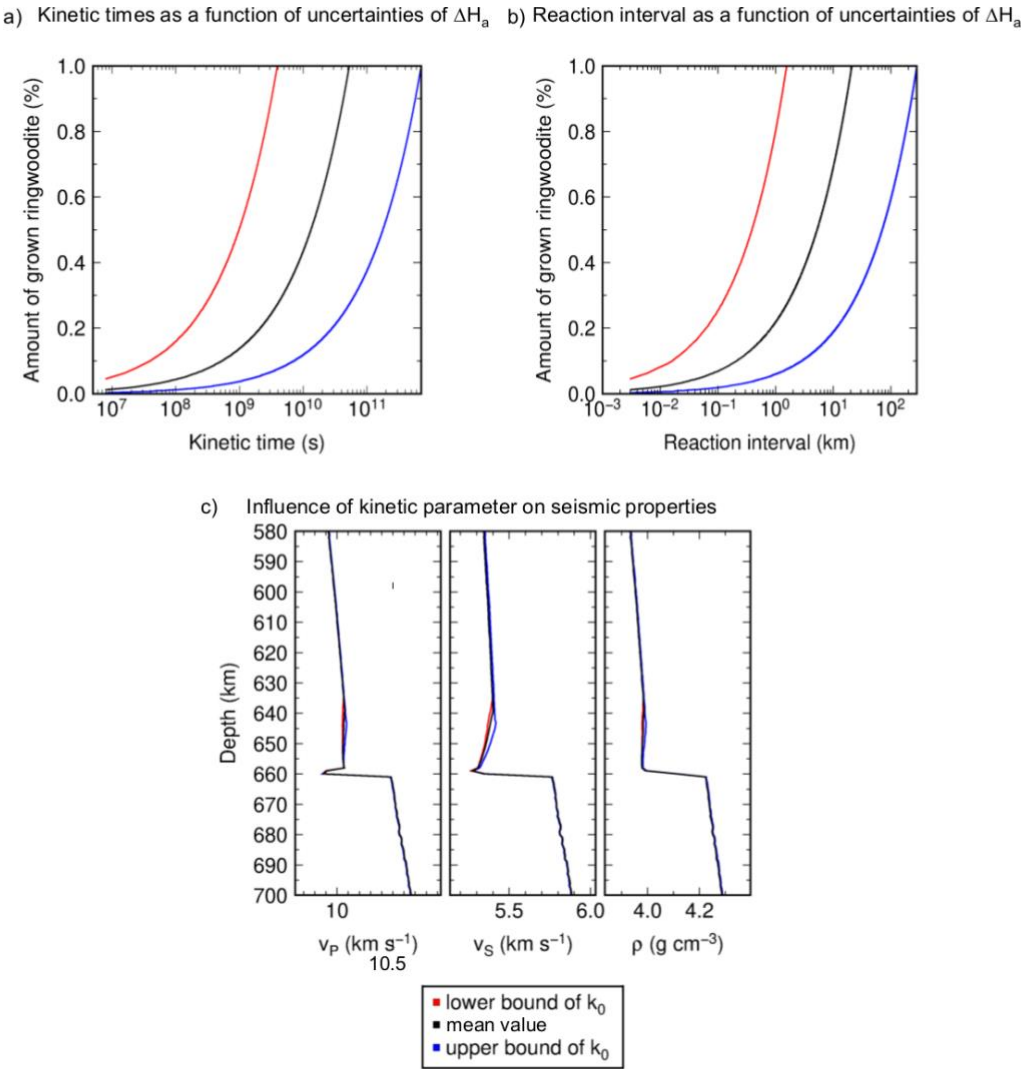

Figure 11: Effects of uncertainties of kinetic parameters on seismic properties of kinetically inhibited phase assemblages and thickness of the low-velocity layer above the onset of ringwoodite growth. The effects have been calculated for an ambient mantle temperature of 1850 K, an initial grain size of 5 cm and an upwelling rate of 50 cm/yr. a) Effects of uncertainties of the enthalpy ΔH_a on the growth time of ringwoodite. The red curve denotes the calculation for the lower bound of ΔH_a from Table 3 whereas the blue curve the upper bound of ΔH_a. b) Effects of uncertainties of the enthalpy ΔH_a on the width of inhibited ringwoodite. c) Effects of uncertainties of the diffusion coefficient k_0 on the seismic wave speeds and density. The lower and upper bound of k_0 correspond to the uncertainties in Table 3.

Tables:

Table 1: Pyrolite composition by Sun et al. (1982) used in this study. The oxides of the CFMAS system are given as molar percentages.

SiO_2	MgO	Al_2O_3	FeO	CaO
38.61	49.13	2.77	6.24	3.25

Table 2: Relationship between surface potential temperature of a mantle adiabat and their ambient temperatures at ~23.4 GPa, i.e., at ~660 km depth. Surface potential temperature are often given in °C (e.g., Cammarano et al., 2005; Cobden et al., 2008) whereas ambient temperatures are usually given in K.

Potential temperature (°C)	1300	1400	1500
Ambient temperature (K)	1850	1960	2050

Table 3: Parameter range for calculating the seismic properties of kinetically inhibited phase assemblages.

Parameter	Value(s)
From the kinetic experiments by Dobson & Mariani (2014):	
Enthalpy of the reaction ΔH_a (kJ mol^{-1})	456±40
Diffusion coefficient $\ln(k_0)$ (m^2/s)	-6.36±0.25
For modelling seismic properties:	
Temperatures (K)	1850, 1960, 2050
Grain size (cm)	1, 5, 10, 20
Upwelling rate (cm/yr)	1, 5, 10, 50, 100