LETTERS
PUBLISHED ONLINE: 31 MARCH 2013 | DOI: 10.1038/NGEO1772
nature geoscience

Stagnation of subducting slabs in the transition zone due to slow diffusion in majoritic garnet

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Oceanic lithosphere sinks into Earth's mantle at subduction zones. However, seismic tomography shows that the sinking slabs of lithosphere often stagnate in the lower part of the mantle transition zone[1], at depths less than 660 km, where rocks undergo pressure-induced phase transitions and become denser. Greater pressures are required to induce phase transitions in cold slabs compared with the hotter ambient mantle at the 660 km discontinuity, and so, at the boundary between the transition zone and the lower mantle, the slabs are buoyant[2]. The slabs may also contain low-density minerals that could contribute to their buoyancy[3]. Here we use laboratory experiments to analyse the rate of dissolution of the common slab mineral pyroxene into garnet, at pressures and temperatures representative of the lower part of the mantle transition zone. We find that the majorite component in garnet—a product of the transition from pyroxene into garnet—is one of the slowest-diffusing components in Earth's mantle. At the relatively low temperatures of the slab, this slow diffusion inhibits the dissolution of pyroxene into garnet, so that the slab remains buoyant relative to the ambient mantle and stagnates. However, at the base of the mantle transition zone, pyroxene undergoes another phase transformation to the mineral akimotoite, which causes a sudden increase in slab density. We conclude that the slab is likely to penetrate into the lower mantle eventually.

In the upper mantle, garnets are dominated by the pyrope endmember (that is, $Mg_3Al_2Si_3O_{12}$). However, at conditions of Earth's mantle transition zone (410–660 km depth) garnets should contain large proportions of the majorite component, which has the stoichiometry of pyroxene (that is, $Mg_4Si_4O_{12}$), and arises from the coupled substitution of Mg and Si into the octahedrally coordinated Al site in garnet. Under equilibrium conditions majoritic garnet makes up 40–60 volume% of Earth's transition zone[4,5], whereas subducted oceanic crust under the same conditions would consist of up to 80 volume % majoritic garnet[6]. Mantle garnets become progressively majoritic at pressures above 6 GPa at the expense of ortho and clinopyroxene, with the result that the transition zone is considered to be free of pyroxene at pressures above ~18 GPa (refs 5–7). Thus, under equilibrium conditions, the pyroxene to garnet reaction occurs over a wide pressure range. However, the kinetics of this reaction must be controlled by the rate of diffusion of the majorite component in garnet. So far only qualitative reports have been published through which to assess this diffusion rate[8,9].

We performed diffusion experiments on majorite–natural pyrope diffusion couples in a multianvil apparatus at mantle transition zone conditions. The submicrometre diffusion profiles were measured by transmission electron microscopy (TEM) and subsequently compositionally independent diffusion coefficients for each component were fitted to the profiles (see Methods). Typical diffusion profiles, expressed in terms of the conventional garnet components, are shown in Fig. 1 for a pyrope–majorite experiment performed at 1,800 °C for 2 h. From the profiles, the

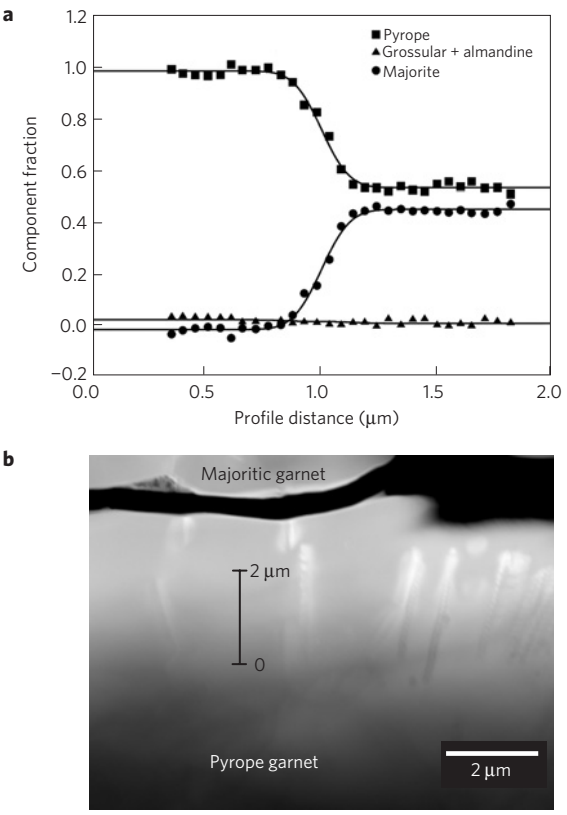

Figure 1 | Diffusion profiles obtained from a pyrope–majorite diffusion couple H3050. a, The concentration profiles expressed in garnet endmember fractions. The negligible almandine and grossular components have been summed up as one virtual component. The symbols denote quantitative EDX–TEM data and the lines show fitted diffusion profiles. **b**, The location (solid black line) of the diffusion profile in **a**. The original boundary between the diffusion couple halves migrated into the majoritic garnet and is at the position of the black crack near the top of the figure. See Supplementary Notes for a more detailed discussion.

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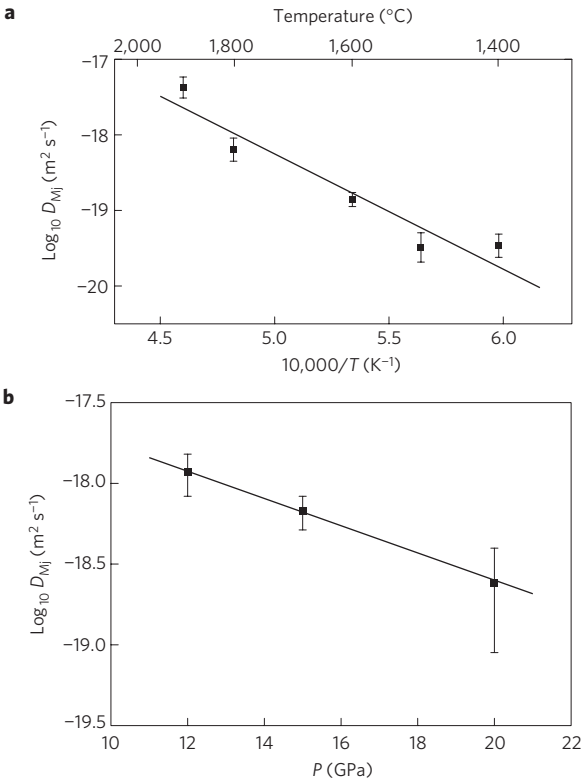

Figure 2 | Diffusion coefficients for majorite diffusion in garnet as a function of temperature and pressure. a, Results of diffusion experiments performed between 1,400 and 1,900 °C at 15 GPa. **b**, Results of diffusion experiments performed between 12 and 20 GPa at 1,800 °C. Error bars indicate uncertainties obtained from the fitting of the diffusion coefficients to the measured profiles at the 90% confidence interval.

effective binary diffusion coefficients[10] for the pyrope and majorite components were determined to be $D_{Py} = 6(2) \times 10^{-19}$ m^2 s^{-1} and $D_{Mj} = 7(1) \times 10^{-19}$ m^2 s^{-1}, respectively.

Garnet diffusion coefficients determined from pyrope–majorite experiments at 15 GPa are shown in Fig. 2a as a function of inverse temperature. The activation enthalpy for diffusion of the majorite component in garnet, obtained by fitting the measured binary diffusion coefficient to an Arrhenius equation, is 291 ± 51 kJ mol^{-1} with the pre-exponential factor being 2.3×10^{-11} m^2 s^{-1}(the confidence interval lies between the two limiting values 9.4×10^{-14} and 5.4×10^{-10} m^2 s^{-1}, all reported errors are at the 68% confidence level unless stated otherwise). For the pyrope component the values are within error the same. The effect of pressure on the diffusivity was determined from experiments performed at 1,800 °C and 12, 15 and 20 GPa, using the same pyrope–majorite garnet diffusion couples as in the experiments described above. The results of the three

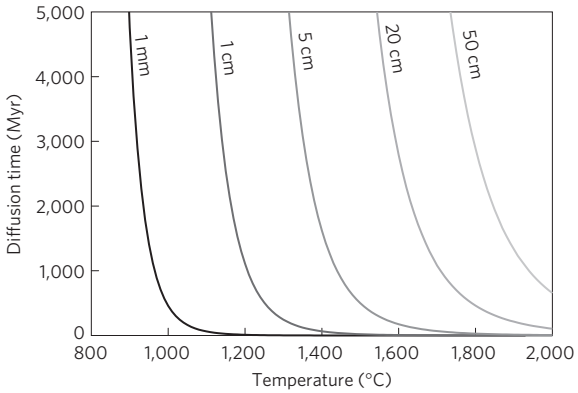

Figure 3 | Diffusion distance for the majorite component in garnet at 18 GPa. The diffusion distance has been calculated as a function of diffusion time and temperature. The main mechanism of mass transport is assumed to be volume diffusion.

diffusion experiments are shown in Fig. 2b and listed in Table 1. The diffusivity of the majorite component in garnet decreases from $1.2(2) \times 10^{-18}$ m^2 s^{-1} at 12 GPa to $2.4(8) \times 10^{-19}$ m^2 s^{-1} at 20 GPa and the resulting activation volume for diffusion of the majorite component in garnet was determined to be 3.3(1) cm^3 mol^{-1}. Combining this with the previously determined activation enthalpy at 15 GPa, we derive an activation energy for diffusion of the majorite component in garnet of 241 ± 54 kJ mol^{-1} and a pre-exponential factor of 1.4×10^{-11} m^2 s^{-1} (the confidence interval lies between the two limiting values 5.6×10^{-13} and 3.5×10^{-10} m^{2}s^{-1}).

Wadsleyite and ringwoodite are the most abundant mineral phases that coexist with majoritic garnet in the mantle transition zone. A comparison of the results of this study with other diffusion studies shows that at 1,500 °C diffusion of the majorite component in garnet is about 7 orders of magnitude slower than Fe–Mg interdiffusion in wadsleyite at 15 GPa (refs 11,12) and similar to the rates of silicon diffusion in wadsleyite and ringwoodite at the conditions at which these phases are stable[12,13]. Extrapolation of the data to pressures of the top of the lower mantle shows that at 1,700 °C diffusion of the majorite component in garnet is even slower than both the diffusion of silicon and Fe–Mg interdiffusion in silicate perovskite (at an oxygen fugacity near or above the iron–wüstite buffer)[14]. It is, therefore, one of the slowest-diffusing chemical components in Earth's mantle.

Our diffusion data can be used to estimate equilibration times and distances over which chemical heterogeneities, characterized by lithologies with different garnet compositions and proportions, can be homogenized in Earth's transition zone. Through the subduction of oceanic lithosphere, large-scale chemical heterogeneities are introduced into the mantle at rates of several centimetres per year but in many instances subducting slabs stagnate at the base of the transition zone[2]. The major mantle lithologies in the transition

Table 1 | Run conditions of the experiments.

Run number	Pressure	Temperature	Run duration	D_{Py} (m^{2}s^{-1})	D_{Mj} (m^{2}s^{-1})
H3257	15 GPa	1,400 °C	24 h	$2.5(8) \times 10^{-20}$	$3.4(8) \times 10^{-20}$
H3076	15 GPa	1,500 °C	24 h	$4(2) \times 10^{-20}$	$3(1) \times 10^{-20}$
H2986	15 GPa	1,600 °C	4 h	$1.4(2) \times 10^{-19}$	$1.4(2) \times 10^{-19}$
H3050	15 GPa	1,800 °C	2 h	$6(2) \times 10^{-19}$	$7(1) \times 10^{-19}$
H3106	15 GPa	1,900 °C	2 h	$3.7(7) \times 10^{-18}$	$4(1) \times 10^{-18}$
H3084	20 GPa	1,800 °C	20 h	$2.2(7) \times 10^{-19}$	$2(1) \times 10^{-19}$
H3201	12 GPa	1,800 °C	4 h	$9(5) \times 10^{-19}$	$1.2(3) \times 10^{-18}$

Reported errors are at the 90% confidence level.

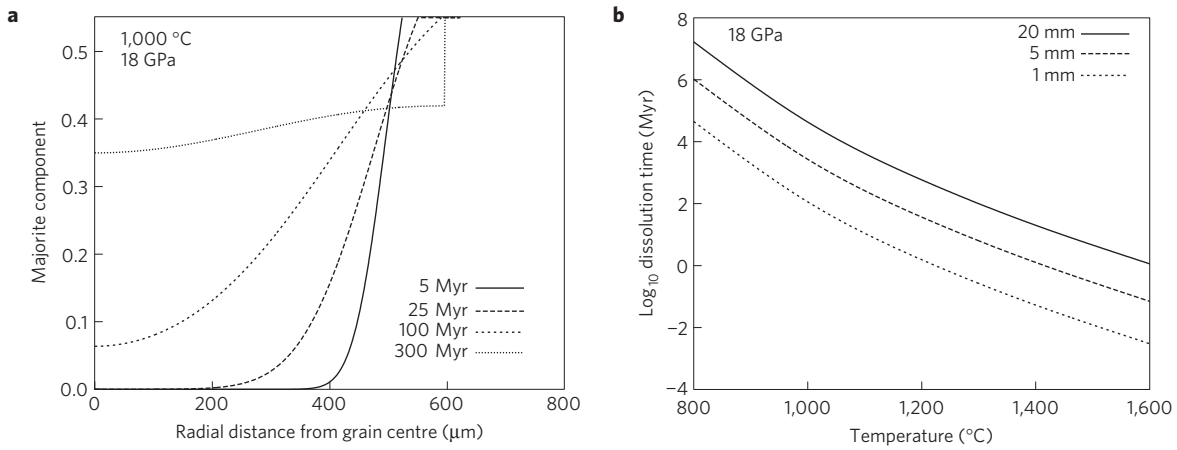

Figure 4 | Timescales for the dissolution of pyroxene into garnet during subduction. a, Concentration profiles at different times for diffusion-controlled growth of a spherical garnet grain surrounded by pyroxene that acts as the majorite source. Initial grain diameter is 1 mm; final grain diameter is 1.18 mm. After ~100 Myr all pyroxene is dissolved into garnet, with homogenization after 300 Myr. **b**, Dissolution timescales for different grain sizes representative of the bulk mantle. The exact dependence on temperature is nonlinear because the equilibrium garnet composition at the interface also depends on temperature. The composition of the interface was taken from the literature[23,29].

zone, that is, subducted oceanic crust, subducted suboceanic mantle and fertile mantle peridotite, have chemical differences that are expressed mainly in terms of differences in the contents and composition of majoritic garnet. A fundamental question concerns the spatial extent over which solid-state diffusion of the majorite component can homogenize such large-scale heterogeneities, or more realistically, the length scale to which such heterogeneities would have to be stretched or thinned by mantle convection before chemical homogenization could occur in the transition zone. To answer this question, we calculated the distance that the majorite component can diffuse as a function of temperature and time. Volume diffusion was chosen as the main mode of mass transport. The length scale of heterogeneities that can be homogenized can be approximated by $x = 2\sqrt{(D_{vol} \times t)}$, where D_{vol} is the volume diffusion coefficient and t is the diffusion time, after equation 4.17 and Fig. 4.1 in ref. 15. The temperatures for the ambient transition zone, that is, far away from any subducting slab, have been estimated from thermal models of the mantle[16–18], and span 1,450 to 1,800 °C, depending on the exact depth and the distance from subduction zones. Figure 3 shows that the maximum distance the majorite component is able to diffuse in the transition zone is 5–50 cm over a timescale of the age of the Earth. The temperatures in the cold interior of a subducted slab are commonly assumed to be well below 1,000 °C. At such low temperatures diffusion is possible only over distances of less than a millimetre. Although the mantle is polycrystalline, grain boundary diffusion is not expected to enhance the diffusion distance by more than a factor 50 for reasonable transition zone grain size estimates and grain boundary diffusivities (see Supplementary Notes). Solid-state diffusion cannot, therefore, homogenize subducted oceanic crust over more than 25 m within the bulk of the mantle. Hence, subducted lithospheric material will persist as chemical heterogeneities in the convecting mantle throughout the evolution of the Earth, unless intense deformation and/or fluid influx strongly catalyses the rate of equilibration reactions.

Majoritic garnet can crystallize within a few hours in high-pressure phase equilibrium experiments that are performed on glass or fine-grained (for example <2 μm) crushed powdered starting materials at relatively high temperatures[19]. Owing to the highly reactive nature of the starting materials, such experiments do not provide information about kinetics in Earth's mantle where rocks are well sintered with grain sizes of the order of millimetres[20]. However, our new diffusion data can be used to assess the extent to which chemical equilibrium is maintained between crystals of garnet and pyroxene as they react in the various lithologies of subducting slabs. To model the effect of diffusion on the kinetics of the pyroxene to garnet reaction, we have modelled spherically symmetric diffusion of the enstatite component into a spherical grain of initially pure pyrope combined with the diffusion-controlled growth of this grain (see Supplementary Methods).

First we consider the case for the oceanic crust component of subducting lithosphere. The initial grain size is taken as 1 mm, which is a typical minimum grain size for eclogites[21]. Representative pressure–temperature conditions for the oceanic crust in the transition zone are taken to be 1,000 °C and 18 GPa (ref. 22). The composition of the rim of the garnet grain was fixed at $Py_{45}Mj_{55}$, which is the equilibrium composition at the above conditions[23]. As the bulk system is undersaturated in pyroxene[6], a maximum influx of majorite was chosen such that the final garnet composition after complete equilibration is $Py_{60}Mj_{40}$, after which dissolution of pyroxene into garnet is stopped. The resulting concentration profiles in the spherical garnet grain after four different times at 1,000 °C and 18 GPa are shown in Fig. 4. The results show that it takes ~100 Myr to fully dissolve the pyroxene component into the garnet. The subducting slab needs about 10–15 Myr to pass through the transition zone, assuming an average subduction rate of 20 mm yr^{-1}. After 12.5 Myr only about 35% of the pyroxene has dissolved into garnet. It is thus unlikely that subducted oceanic crust can reach a state of thermodynamic equilibrium and a metastable mineral assemblage consisting of pyroxene and pyrope-rich garnet is thus expected to be present in subducted oceanic crust. To reach thermodynamic equilibrium the oceanic crust needs to heat up, which requires that the slab remains for a prolonged period in the transition zone.

Second we consider the case for subducting peridotitic mantle, which would experience temperatures that range from below that of the oceanic crust (<1,000 °C), up to the ambient mantle temperature (1,600 °C; refs 22,24). Peridotites typically have grain sizes larger than 1 mm (ref. 25). Dissolution timescales for grain sizes from 1 to 20 mm are plotted in Fig. 4b. This shows that dissolution of pyroxene into garnet would take several billion years at 1,000 °C. Only when the temperature of the subducted slab has increased to at least 1,400 °C would chemical equilibration occur on a geologically reasonable timescale of a few million years. Therefore, most of the subducted lithospheric mantle is also not expected to thermodynamically equilibrate during

subduction and will transport metastable mineral assemblages into the transition zone.

The metastable persistence of pyroxene in both the oceanic crust and peridotitic components of a subducting slab has two important implications for mantle dynamics. First, the density of the down-going slab will initially remain low during subduction (we estimate a 1–2% reduction in density), contributing to slab deceleration and possibly transient stagnation in the transition zone. Second, as the slab enters the deeper transition zone, it is likely that metastable pyroxene will undergo phase transformations directly to higher-pressure polymorphs[26], resulting, in turn, in a large density increase. Subducted lithospheric mantle, particularly the harzburgitic layer, contains up to 40 vol% enstatitic pyroxene that could transform directly into metastable akimotoite when the pressure reaches ~19 GPa (ref. 26), corresponding to a depth of 550 km, with a huge density increase of ~16%. The existence of such metastable akimotoite-bearing slab regions in the Tonga slab has recently been proposed on the basis of seismic anisotropy[27]. Such a large increase in density would cause the remobilization of a stagnant slab and catalyse its descent into the lower mantle. Thus, slab dynamics in the mantle transition zone are likely to be controlled to a large extent by metastability and the kinetics of pyroxene-breakdown reactions.

Methods

Diffusion experiments with polycrystalline majoritic garnet–natural pyrope diffusion couples have been conducted in a 1,200 ton multianvil apparatus between 1,400 °C and 1,900 °C and from 12 GPa to 20 GPa. After recovery, the samples were prepared for TEM investigation by mechanical polishing followed either by argon-milling or focused ion beam preparation. The diffusion profiles have been measured in scanning transmission electron microscope mode using a Philips CM20 TEM at 200 kV equipped with an energy-dispersive X-ray (EDX) detector. To obtain the diffusion coefficients from the measured profiles, the profiles have been fitted by a numerical finite-difference model with a constant (that is, compositionally independent) diffusion coefficient for each component. Note that rather than characterizing diffusion in terms of individual elements[28], we can describe diffusion in terms of garnet components because the diffusion of the individual elements (for example, Mg and Si) must be coupled to preserve charge balance. Furthermore, within error, the diffusion coefficients for both the components in the majorite–pyrope diffusion experiments are identical. This is to be expected because the concentrations of the grossular and almandine components are very low such that the experiments basically involve binary diffusion between the pyrope and majorite components, which can be characterized by a single diffusion coefficient.

In the Supplementary Information a more detailed description of the experimental, analytical and computational methods used in this study is given.

Received 4 October 2012; accepted 14 February 2013; published online 31 March 2013

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Acknowledgements

Funding of this project is provided by the European Commission through the Marie Curie Research Training Network 'c2c' (Contract No. MRTN-CT-2,006-035957) and the Leibniz programme of the Deutsche Forschungsgemeinschaft (LA 830/14-1).

Author contributions

All authors contributed in writing the paper. F.L. and W.L.v.M. conceived the idea for the experiments. F.L. supervised the project. D.J.F. and D.C.R. provided further advice for developing the experimental strategy. W.L.v.M. performed the experiments, conducted the TEM measurements and carried out the data reduction. Numerical modelling was performed by W.L.v.M.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to W.L.v.M.

Competing financial interests

The authors declare no competing financial interests.

nature geoscience

SUPPLEMENTARY INFORMATION

DOI: 10.1038/NGEO1772

Stagnation of subducting slabs in the transition zone due to slow diffusion in majoritic garnet

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Supplementary information: Methods

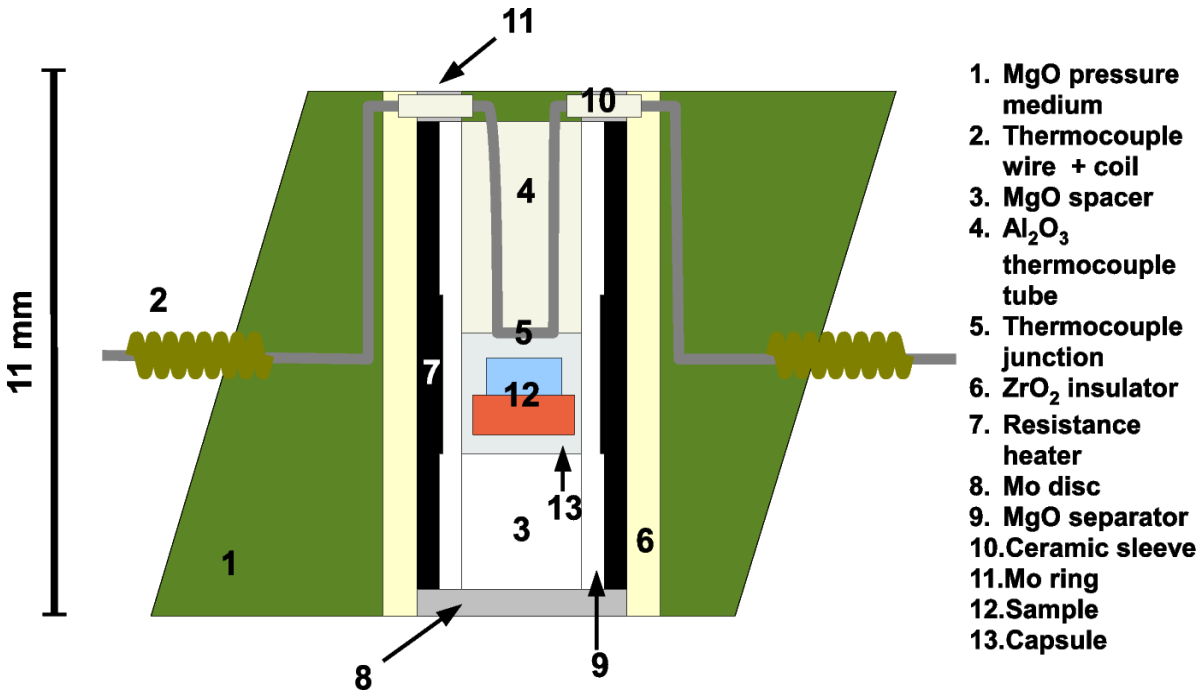
Starting Materials and High-Pressure Experiments

Diffusion experiments were conducted using the diffusion couple method, i.e. two cylinders of garnet with their faces mirror polished were placed together in a capsule and then annealed at high pressure. The garnet cylinders consisted of polished cylinders of polycrystalline synthetic majoritic garnet (composition $Py_{55}Mj_{45}$) and natural pyrope garnet ($Py_{93}Alm_5Gr_2$) single crystal from the Dora Maira Massif in Italy[1] to determine pyrope – majorite interdiffusivity. The compositions of the starting materials are listed in Supplementary Table 1. Furthermore, FTIR spectra were measured to determine the water contents in garnets using the calibration of Bell[2]. The measurements reveal very low water contents, the highest concentration of 58(6) ppm wt H_2O was determined for pyrope and showed no change during the experiment. For majorite the water content was only determined after the experiment and was about 37(4) ppm wt H_2O.

Since majoritic garnet is not commonly found in nature, it was synthesized using the multi-anvil technique. First, reagent grade MgO, Al_2O_3 and SiO_2 oxide powders were ground and mixed under ethanol. The resulting powders were then fused in a furnace at 1650 °C and quenched to a glass. To thoroughly homogenize the starting material, the glass was crushed, ground and fused a second time. The final glass was crushed to a powder that was then loaded into a Pt capsule (inner diameter 0.8 mm, outer diameter 1.2 mm, length 2.2 mm) for synthesizing majoritic garnet. Just before the synthesis experiments, the loaded capsule was heated for 5 minutes at 1000 °C to dry the powder, after which it was sealed mechanically. Majoritic garnet was then synthesized in a multi-anvil apparatus using a 10/5 assembly

(numbers denote octahedron edge length and WC cube truncation edge length in mm, respectively) at 1800 °C and 16 GPa for 8 hours. After recovery the platinum capsule was cut into discs of 0.5 mm thickness and one side was polished, where the final polishing was performed using a 0.25 μm diamond polishing paste. The final surface topography was measured using a confocal microscope and for the single crystal pyrope was determined to be ~ 3 nm over a lateral length of ~ 25 μm and for the polycrystalline majoritic garnet cylinders ~ 20 nm over a lateral length of ~ 25 μm. The average grain size of the synthetic majoritic garnet was 5 – 10 μm.

Before the diffusion experiments, the samples were dried in a vacuum oven at 175 °C for 24 hours, after which the capsules were mechanically sealed as fast as possible in a bench vice. The diffusion experiments were carried out in a 1000 ton multi-anvil apparatus at the Bayerisches Geoinstitut. Each diffusion couple was contained within a platinum capsule. A W 3% Re - W 25% Re thermocouple was used to measure the temperature. To prevent the thermocouple from reacting with the capsule, it was separated from the capsule with a 25 μm thick Re disk. After the pressure cell was loaded in the multi-anvil apparatus the sample was compressed to the desired pressure and then the temperature was increased at a rate of 100 °C / minute, with the final 200 °C being achieved in one minute. Quenching was performed by cutting the electrical power, which results in the sample temperature decreasing to 100 °C in ~10 seconds.



Supplementary Figure 1: Sketch of the pressure cell used in the diffusion anneals.

Analytical methods

After recovery of the sample, the capsule was cut perpendicular to the interface between the two halves of the diffusion couple and was prepared as a 30 µm thick thin section. These thin sections were subsequently analysed by a JEOL JXA-8200 electron microprobe to determine the length of the diffusion profiles. Since in all cases the diffusion profiles were too short to be measured by electron microprobe, the samples were further prepared for TEM by ion milling with a conventional Gatan DUOMILL and a FEI Quanta 3D FEG dual beam device (FIB/SEM). TEM foils were analyzed in a Philips CM20 FEG TEM operating at 200 kV and being equipped with an ThermoNoran EDS system. To ensure that the beam direction, and thus excitation volume for EDS analysis, was perpendicular to the diffusion gradient, the TEM foil was oriented in such a way that one of rotation axes of the specimen holder was parallel to the diffusion interface and the other one was perpendicular to it.

Diffusion profiles were measured in STEM mode with a slightly-defocused beam to avoid beam damage. The scanning pattern size of a single analysis is ~ 40 nm. In the case that beam

damage was still observed, a time series was measured to quantify the beam damage and correct for it. Analyses were quantified using a method similar to that proposed in Van Cappellen and Doukhan[3].

The garnet component mole fractions are calculated from the elemental compositions using a least squares technique. Since Fe has a strong prevalence for the dodecahedral site[4] it is assumed that the Fe-majorite component ($FeSiO_3$) is negligible in the majorite garnet. For the pyrope – majorite garnet analyses, the grossular and almandine components have been taken together as one virtual component $(Ca+Fe)_3Al_2Si_3O_{12}$, leading to the following components to be calculated from the elemental compositions:

$Mg_w(Ca+Fe)_xAl_ySi_zO12 = a\ Mg_3Al_2Si_3O_{12} + b\ (Ca+Fe)_3Al_2Si_3O_{12} + c\ Mg_4Si_4O_{12}$

for which the following matrix equation can be written and solved:

$$\begin{bmatrix} 3 & 0 & 4 \\ 0 & 3 & 0 \\ 2 & 2 & 0 \\ 3 & 3 & 4 \end{bmatrix} \cdot \begin{bmatrix} a \\ b \\ c \end{bmatrix} = \begin{bmatrix} w \\ x \\ y \\ z \end{bmatrix} \qquad (1)$$

$$A \cdot c_{comp} = c_{element}$$

The errors on the component compositions are calculated using the following formula, which can be obtained from the propagation of errors:

$$M^{comp} = A^{+} \cdot M^{element} \cdot (A^{+})^{T} \qquad (2)$$

where $M^{element}$ is the covariance matrix of the elemental concentrations and where the diagonal elements (variances) are the squared errors of the elemental concentrations, which were estimated from the relative errors of the counting statistics. The off-diagonal elements were set to zero (zero covariance between elements). A^{+} denotes the Moore – Penrose pseudoinverse of A, and the superscript T denotes the transpose.

Numerical modeling of diffusion profiles

Because the shape of the diffusion profiles did not give any indications for a composition dependent diffusion coefficient, the diffusion profiles have been modeled using the following equation:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} \qquad (3)$$

where C_i , t, x, and D_i are the concentration of component i, time, spatial coordinate and the diffusion coefficient for component i, respectively. D_i has been assumed to be composition independent in this study, because using compositionally-dependent diffusion coefficients did not significantly improve the fits. The modeling and fitting of diffusion profiles was done by two programs (mcdiff and mcfitter), which solve equation (3) using a finite difference approach. The Levenberg-Marquardt algorithm has been employed for the fitting of calculated diffusion profiles to the measured ones. The confidence intervals of the diffusion coefficients have been determined using the bootstrap method with resampling of residuals[5]. In addition to determining the diffusion coefficients, this study includes also the determination of temperature and pressure dependence of the diffusivity of the majorite component in garnet. The dependence on these variables has been expressed by an Arrhenius relation:

$$\ln D_i^0(T) = \ln D_i'^0 - \frac{\Delta H}{RT} \qquad (4)$$

where the activation enthalpy is expressed as $\Delta H = \Delta E + P\Delta V$. Here P, T, R, ΔE, and ΔV are pressure, temperature, the gas constant, and the activation energy and activation volume for diffusion of the majorite component in garnet, respectively. The values and error bounds of activation enthalpy, activation energy, activation volume and the pre-exponential factors were

111 determined using the weighted least squares method (weights inverse proportional to the
112 variances), though using the normal least squares method did not give significant different
113 results.
114
115
116 *Modeling of pyroxene dissolution in garnet*
117 To model diffusion in a grain together with diffusion-controlled growth a finite difference
118 model was used. The basic equation that governs diffusion in a spherically symmetric
119 geometry assuming a constant diffusion coefficient D is given by[6]:
120

121 $$\frac{\partial C}{\partial t} = D\left(\frac{2}{r}\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2}\right) \qquad (5)$$

122 where C is the concentration, r the radial distance from the centre, t time and D the diffusion
123 coefficient,. Equation 5 has been discretized using a fully implicit scheme[7]:
124

125 $$C_i^k = -\alpha\left(\frac{1}{\Delta r} + \frac{1}{r_i}\right)C_{i+1}^{k+1} + \left(1 + \frac{2\alpha}{\Delta r}\right)C_i^{k+1} - \alpha\left(\frac{1}{\Delta r} - \frac{1}{r_i}\right)C_{i-1}^{k+1} \qquad (6)$$
$$\text{with } \alpha = \frac{D\Delta t}{\Delta r}$$

126
127 where k is the time index, i the spatial index, Δr the distance between two nodes, and Δt the
128 time step for temporal discretization. Equation 6 leads to a system of linear equations that
129 may be represented in a matrix form involving a tridiagonal matrix that can be solved using
130 standard methods included in the LAPACK software[8]. The code has been tested against a
131 steady state analytical solution for a hollow sphere.

Because the solubility of aluminium in pyroxene at the conditions of the transition zone is very low[9] and thus there cannot be a direct transformation of pyroxene into garnet, dissolution of pyroxene in garnet will not occur by a simple exchange mechanism. Therefore the garnet grain needs to grow during dissolution of pyroxene into garnet. Grain growth (or shrinkage) was modeled by dividing the domain into three parts; the internal part, the boundary and the external part. The internal part corresponds to the grain and for this part equation 6 is solved for every time step. The boundary has a constant concentration, that corresponds to the equilibrium concentration of the grain in contact with the external phase, and its position determines the size of the external and internal part. The external part is a volume reservoir to allow for grain growth or shrinkage and has a constant concentration, not necessarily equal to the boundary concentration. If the boundary concentration is different from the concentration of the internal part, material will flow in or out of the grain. The total flux of material that has diffused into or out of the grain is determined after every time step by integration of the concentration profile over the complete grain, taking into account the proper geometry. The boundary position is then updated for the next time step based on the total mass of material that has moved in/out of the grain (M_{int}) and the concentration or density of material in the external part:

$$\Delta V_{grain} = \frac{M_{\text{int}} - M_0}{C_{ext}} \qquad (7)$$

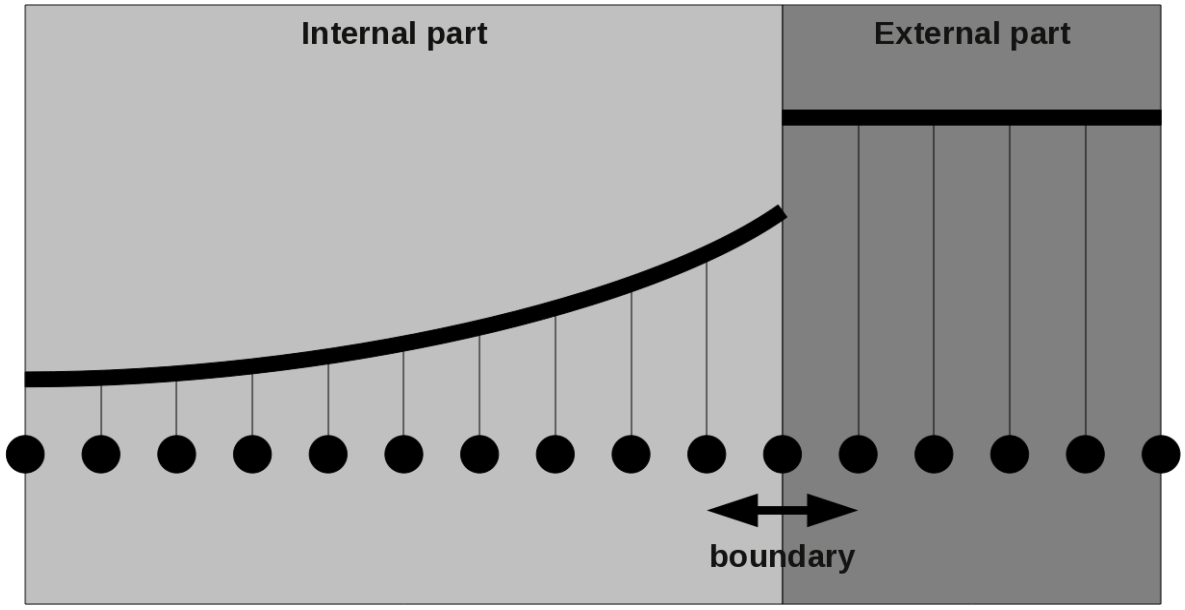
M_0 is the starting concentration of material in the grain and C_{ext} the concentration in the external part. ΔV_{grain} is the change in volume of the grain. In the case of grain growth, the composition of the new nodal points in the internal part is set to the boundary composition (Supplementary fig. 2).

The growth of the grain can be stopped after a certain amount of material has diffused into the grain. The boundary position is kept constant after this point has reached. To stop material

from flowing in or out of the grain, the boundary flux is forced to be zero using a Neumann boundary condition:

$$C_b^{k+1} - C_{b-1}^{k+1} = 0 \qquad (8)$$

where b is the boundary node. In the case that the internal part contains the first node, also a Neumann type boundary condition was used for the first node. In this study diffusion of the majorite component into the garnet grain has been stopped at the point where the mean concentration is $Py_{60}Mj_{40}$, i.e. after complete homogenization the grain would have this composition. This garnet equilibrium composition corresponds to experiments conducted on refractory MORB material after partial melting and transformation to an eclogite assemblage, representative of the subducted oceanic crust[9].



Supplementary Figure 2: Sketch of the discretization model used in the numerical model for the calculation of the dissolution of pyroxene into garnet.

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Supplementary tables

Supplementary Table 1: Electron microprobe analyses of the starting materials in wt. % and cations per 12 oxygens.

Oxide	**Dora Maira pyrope**	**Majorite garnet**
MgO	27.49	34.37
SiO_2	44.13	51.57
CaO	0.61	0.00
MnO	0.05	0.00
FeO	2.51	0.02
Al_2O_3	24.84	12.59
TiO2	0.02	0.00
Total wt. %	***99.65***	***98.55***
Mg^{2+}	2.79	3.48
Ca^{2+}	0.05	0.00
Fe^{2+}	0.14	0.00
Fe^{3+}	0.00	0.00
Al^{3+}	2.00	1.01
Ti^{4+}	0.00	0.00
Si^{4+}	3.01	3.50

Stagnation of subducting slabs in the transition zone due to slow diffusion in majoritic garnet

Authors: W.L. van Mierlo, F. Langenhorst, D.J. Frost, D.C. Rubie

Supplementary Notes

Note on the effective diffusivity of a polycrystalline aggregate

The effective diffusion coefficient can be expressed as $D_{eff} = f D_{gb} + (1 - f)D_{vol}$, where f is the grain boundary volume fraction and D_{gb} the grain boundary diffusivity[1]. Assuming that the grain boundary width is 1 nm, diffusion distance enhancement factors range from 1 to 50 for a 100 µm grain for grain boundary diffusion rates from $10^3 \times D_{vol}$ to $10^8 \times D_{vol}$. For 1 mm grains the enhancement factors range from 1 to 17.

Note on the migration of the interfacial grain boundary in the diffusion couples

All majoritic garnet – pyrope garnet diffusion couples showed that after the diffusion anneals the grain boundary that formed the interface between both diffusion couples migrated into the majoritic garnet half of the diffusion couple. We believe that this is caused by a process similar to Oswald ripening, i.e. the smaller grains (majoritic aggregate) are consumed by the larger grains (pyrope crystal) and thereby reducing the total surface energy. There is virtually no strain at the diffusion interface after grain boundary migration occurred, because of great similarity between the lattice parameters of majoritic garnet and pyrope[2]. Therefore from the point of view of grain boundary migration the whole diffusion couples acted as a single phase aggregate. The orientation of the interface was determined in the experiments by measuring several diffusion profiles and in this way the position of the interface at several locations was determined. We don't believe that this process influenced the determined diffusion coefficients, because the width of dry grain boundaries is not more than a few nanometer at most and the region of influence is confined to this range. If it would have influenced the

experiment at all, it would have brought it closer to a true bulk diffusivity measurement, removing the influence of nearby grain boundaries.

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on the circumpolar westerlies, rather than stratospheric ozone depletion.

Steig and colleagues[9] find a more subtle change hidden in the oxygen isotopic composition of ice cores spanning West Antarctica. The oxygen isotope signature of ice is typically interpreted as a proxy for temperature. However, it also responds to wider circulation anomalies that have influenced the region, including changes in sea ice and wind-driven ocean changes. Steig *et al.* interpreted the isotope values in terms of these broader trends. They used an ice core from the West Antarctic Ice Sheet Divide that spanned 2,000 years, in conjunction with an array of shorter cores, to document unusually high oxygen isotope ratios in the 1990s. Comparable events occurred in just 1% of the time series studied. The trend in oxygen isotopes over the past 50 years at the divide is also unusual, with comparable trends present in just 2% of the records.

Building on previous work that identified tropical influences on West Antarctic climate, they link the isotopic anomalies to changes in atmospheric convection over the tropical Pacific Ocean, propagated to the high latitudes through atmospheric waves. An isotope-equipped climate model, fed with tropical Pacific sea surface temperatures, reproduces the prominent isotope anomaly in the 1990s that is recorded in the West Antarctic ice cores. Interestingly, the authors note that the Pacific variability associated with this 1990s anomaly was not outside the natural range of variability observed over past centuries.

Although the tropical drivers of the West Antarctic isotopic anomalies may not be unprecedented, the very existence of a link adds to concerns about future change in the region. A strong influence of tropical processes on the climate of West Antarctica adds an extra source of uncertainty in estimates of the manifestation of greenhouse-gas-induced climate change. Steig and colleagues also suggest that the decadal-scale variability in the tropics has masked the local Antarctic response to anthropogenic forcing.

These studies remind us that we should not expect Antarctic climate change to be uniform in time or space. The climate response is mediated by multiple processes, each having varied seasonal and geographical expressions, linked by hemispheric and global scale connections, and subject to decadal-scale variability that can confound detection of the forced signal. Improvements in capturing these processes in models and testing with improved data, both observational and palaeoclimatic, are the keys to predicting the patterns and rates of change.

Individually, the ice core records presented by Abram *et al.*[8] and Steig *et al.*[9] add to the evidence that changes currently seen in Antarctica are unusual relative to the past 2,000 years. Taken together, alongside other indicators of change, the message is becoming clearer: Antarctica is very likely to be showing a response to the warming climate of the planet. ❐

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MINERALOGY

Garnet goes hungry

Sinking slabs of oceanic lithosphere often stagnate in Earth's mantle. Experiments show that common slab minerals transform to their high-pressure, high-density counterparts at very slow rates, thus keeping the slabs buoyant and impeding subduction.

Craig R. Bina

Students in the petrology lab learn quickly that the mineral garnet — an abundant component of the Earth's mantle — 'eats' everything. Indeed, this mineral's complex crystalline structure can accommodate a bewildering variety of cations. Writing in *Nature Geoscience*, van Mierlo *et al.*[1] use high-pressure and high-temperature experiments to show that garnet dines rather slowly, at least under conditions prevailing in subduction zones, with important implications for subduction dynamics and mantle chemistry.

Slabs of oceanic lithosphere contain abundant amounts of the minerals garnet and pyroxene. As the slabs sink into the mantle, the pyroxene is thought to dissolve into the denser garnet, where it forms a component known as majorite[2]. The rate at which such dissolution occurs, however, is controlled by how fast majorite can diffuse through the garnet structure. High pressures within the mantle should cause the remaining components of the subducting oceanic slab — dominated by the mineral olivine — to also undergo phase transitions, thus increasing the slab's density as it sinks deeper into the Earth. Yet in seismic images of Earth's interior, the slabs often seem to stall near the base of the mantle transition zone, which is a region located between 410 and 660 km depth. This stalled subduction may be linked to these complex mineral transformations that occur within the slab.

Our understanding of how pyroxene in an oceanic slab dissolves into garnet is based on laboratory experiments. In an attempt to simulate these transformations, which occur over long geological timescales and at hundreds of kilometres depth in the mantle, the samples are usually ground into fine powders that are squeezed and heated. Yet, in real subduction zones, grain sizes within subducting slabs are large and the temperatures in the slab are low compared with the warm surrounding mantle.

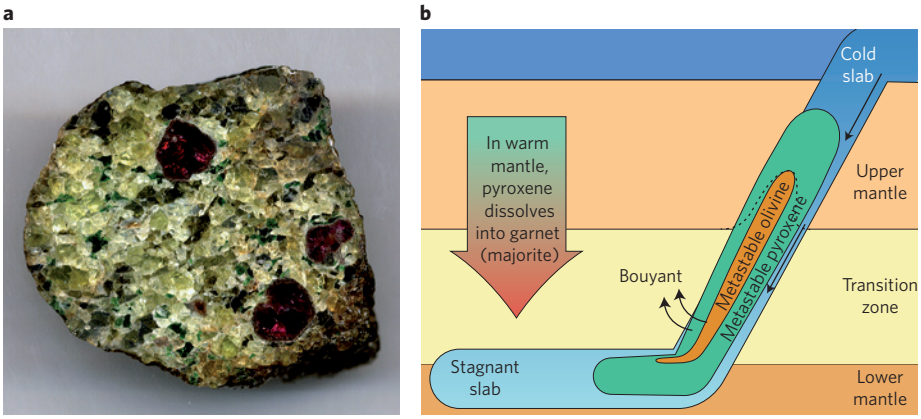

Figure 1 | Subduction of oceanic lithosphere in the mantle transition zone. **a**, Slabs of oceanic lithosphere contain a variety of minerals including olivine (pale green), pyroxene (dark green) and garnet (red). **b**, As the slab subducts into the mantle, it encounters higher temperatures and pressures that cause the minerals to undergo phase transformations. The common slab mineral pyroxene dissolves into garnet, forming the component majorite within the garnet. Similarly, the olivine transforms to denser phases. Van Mierlo and colleagues[1] use laboratory experiments to show that majorite is one of the slowest diffusing components of the mantle. Further dissolution of pyroxene is therefore inhibited and the pyroxene persists in a metastable, buoyant state that can potentially slow and deflect subduction.

A first step towards improved understanding of these transitions was to carry out experiments and modelling to explore reaction kinetics at the relatively low slab temperatures. The results suggested that, although olivine and pyroxene were expected to become unstable under the high-pressure conditions of Earth's mantle, they might instead remain in a metastable (and thus buoyant) state[3–5]. Pyroxene was kinetically inhibited from dissolving into garnet[6], but the relevant diffusion rates remained unknown.

Now van Mierlo *et al.*[1] have taken the next step. They use laboratory experiments to measure precisely (at the micrometre scale) the rate at which the majorite component — formed by the dissolution of pyroxene into garnet — diffuses through the garnet structure, over a range of high pressures and temperatures. The results are extrapolated to the conditions of the mantle transition zone, and they are striking. It turns out that garnet is a very slow eater. Even at high temperatures and pressures of 1,800 °C and 15 GPa — warmer than the corresponding depth in the mantle transition zone — the rate of majorite diffusion is extremely low, with a diffusion coefficient below 10^{-18} m^2 s^{-1}. This rate of diffusion is comparable to the diffusion of magnesium in garnet at much lower temperatures and pressures, below 1,000 °C at 1 GPa (ref. 7). Majorite therefore seems to be one of the most slowly diffusing components in the mantle.

The slow diffusion of majorite has two important implications for mantle chemistry and geodynamics. First, majorite components formed in the mantle may persist over very long timescales. Van Mierlo and colleagues extrapolate the diffusion data to realistic grain sizes for oceanic slabs (on the order of millimetres) and show that majorite-bearing heterogeneities formed in the mantle transition zone would be homogenized at length-scales of, at most, tens of metres over timescales comparable to the age of the planet. Yet subducted slabs are typically thousands of metres thick, meaning that the majorite components will not fully homogenize and may remain as chemical anomalies in the transition zone for billions of years. This finding supports suggestions that the mantle transition zone may be a mechanical mixture of different components, rather than a homogenized unit[8].

Second, there is the prospect of metastable pyroxene persisting to depths at which it should have been devoured by garnet. Entry of pyroxene into the garnet structure as majorite is controlled by the rate of majorite diffusion. Thus, the slow diffusion of majorite prevents pyroxene being dissolved into the garnet, and the garnet goes hungry. Pyroxene is less dense than garnet, and its persistence will impart positive buoyancy to the slab, thereby impeding subduction (Fig. 1). Similar buoyancy perturbations have been posited for other slab minerals, such as metastable olivine, at temperatures below about 700 °C in the coldest core of the slab[4]. However, the new diffusion data imply that pyroxene can remain metastable and buoyant to temperatures as high as 1,400 °C, extending the potential for metastability over a much larger area of the slab and thereby amplifying the buoyancy effect.

The slow diffusion of majorite can therefore help explain the stagnation of subducting slabs in the mantle transition zone. The metastable pyroxene may remain undigested for some time, and the positive buoyancy would then generate slower slab descent rates and cause the wholesale flexure of the slab into a sub-horizontal stagnant posture in the transition zone. Such slab stagnation may persist until thermal assimilation warms the slab sufficiently to allow consumption or further reaction (perhaps to metastable akimotoite) of the buoyant metastable material.

The experiments illuminate the metastability of magnesium-rich pyroxene. However, complex natural pyroxenes may be more reactive than the magnesium-rich variety[9]. The behaviour of multi-component mineral assemblages with, for example, differing iron or hydrogen concentrations have yet to be fully investigated. Buoyancy relations are further complicated by the fact that, although metastable pyroxene may persist over a larger extent of the slab than metastable olivine, the latter is more buoyant than the former.

Van Mierlo *et al.*[1] demonstrate that garnet dines rather slowly, at least under conditions prevailing in subduction zones. Slow diffusion of majorite can inhibit the dissolution of pyroxene into garnet in subducting slabs, giving the slabs added buoyancy and causing them to stagnate in their descent through the mantle. Those investigating the chemistry, seismology and geodynamics of deep subduction will need to reflect on the dining habits of garnet. ❐

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