

Seismic velocities of CaSiO_3 perovskite can explain LLSVPs in Earth's lower mantle

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Seismology records the presence of various heterogeneities throughout the lower mantle^{1,2}, but the origins of these signals—whether thermal or chemical—remain uncertain, and therefore much of the information that they hold about the nature of the deep Earth is obscured. Accurate interpretation of observed seismic velocities requires knowledge of the seismic properties of all of Earth's possible mineral components. Calcium silicate (CaSiO_3) perovskite is believed to be the third most abundant mineral throughout the lower mantle. Here we simultaneously measure the crystal structure and the shear-wave and compressional-wave velocities of samples of CaSiO_3 perovskite, and provide direct constraints on the adiabatic bulk and shear moduli of this material. We observe that incorporation of titanium into CaSiO_3 perovskite stabilizes the tetragonal structure at higher temperatures, and that the material's shear modulus is substantially lower than is predicted by computations^{3–5} or thermodynamic datasets⁶. When combined with literature data and extrapolated, our results suggest that subducted oceanic crust will be visible as low-seismic-velocity anomalies throughout the lower mantle. In particular, we show that large low-shear-velocity provinces (LLSVPs) are consistent with moderate enrichment of recycled oceanic crust, and mid-mantle discontinuities can be explained by a tetragonal–cubic phase transition in Ti-bearing CaSiO_3 perovskite.

The lower mantle is vast, extending from the seismic discontinuity observed at approximately 660 km depth to the core–mantle boundary (CMB) at a depth of about 2,890 km. Tomographic images demonstrate that despite a smooth variation of compressional-wave velocity, shear-wave velocity and density (respectively v_p , v_s and ρ) in 1D velocity models, the lower mantle is heterogeneous and regularly refertilized by subducting slabs^{7,8}. Sluggish diffusive re-equilibration and incomplete mechanical mixing⁹ mean that large-scale patterns of mantle convection may be directly observed via tomographic velocity anomalies and/or the distribution of seismic scatterers. Identifying the causes of heterogeneities requires accurate mineralogical models of Earth's mantle to facilitate comparisons between geophysical observations and predicted seismic velocities. However, a major uncertainty in many models^{10,11} has been the influence of CaSiO_3 perovskite (Ca-Pv, here corresponding to $\text{Ca}[\text{Si}_x\text{Ti}_{1-x}]\text{O}_3$) on velocity, despite the widespread expectation that it is the lower mantle's third most abundant phase, comprising 5–10 vol.% and 24–29 vol.% of peridotitic¹² and basaltic¹³ assemblages, respectively.

Uncertainties stem from a sparsity of reliable measurements of Ca-Pv's physical properties, which are technically challenging because CaSiO_3 is unrecoverable¹⁴, undergoing spontaneous amorphization at room temperature during decompression. The widely used thermodynamic model of Stixrude et al.⁶ predicts that the seismic velocity of Ca-Pv is substantially higher than in average one-dimensional profiles such as the Preliminary Reference Earth Model (PREM)¹⁵, and therefore low-velocity anomalies are difficult to explain using recycled crustal material. Although this is the widely adopted view, there is

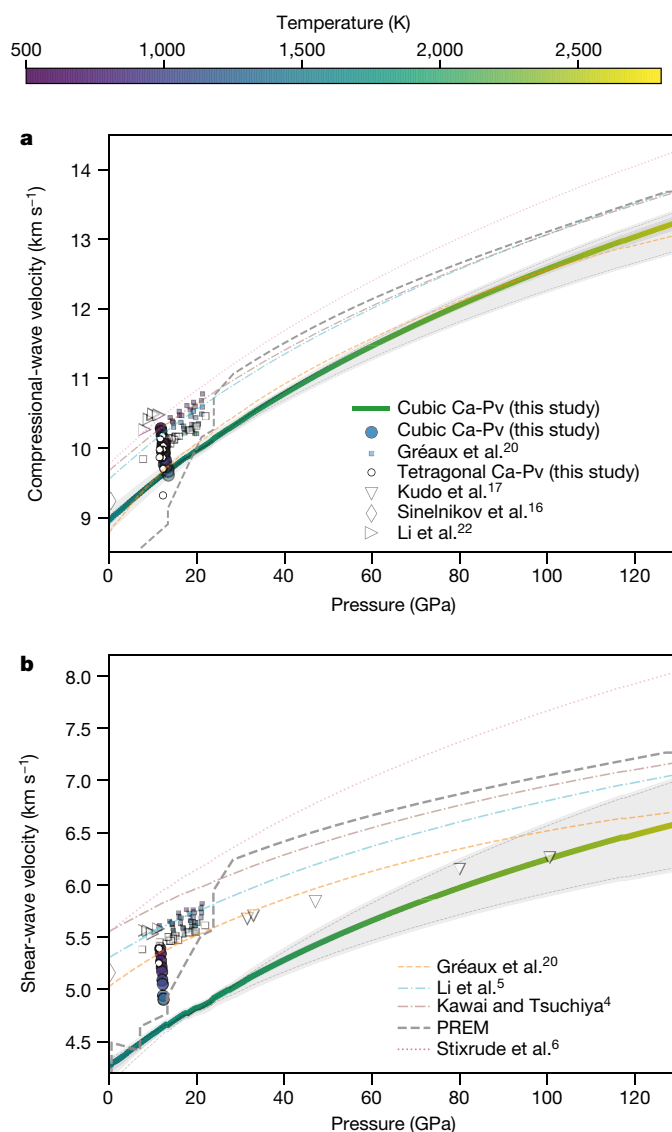
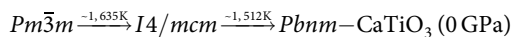
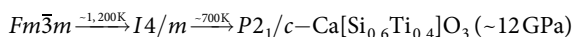
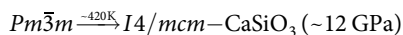


Fig. 1 | Compressional- and shear-wave velocities of cubic CaSiO_3 perovskite from this and previous studies. **a**, Compressional-wave velocity and **b**, shear-wave velocity of CaSiO_3 perovskite predicted in this and previous^{4–6,16,17,20,22} studies throughout the mantle. Individual experimental measurements are shown with symbols, coloured by temperature (key at top; white symbols are data collected at 300 K). All velocity curves are extracted along a 1,500 K mantle adiabat. Thick coloured curve (and 95% confidence interval in grey) represents the velocity of cubic Ca-Pv based on finite-strain modelling (this study). Bold dashed line is the PREM velocity profile.

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currently no consensus on the seismic properties of Ca-Pv. Existing high-temperature calculations^{3–5} suggest that the velocity of Ca-Pv might be either slightly lower or much higher than in PREM¹⁵ (Fig. 1). By contrast, room-temperature experiments^{16,17} have measured a shear velocity of Ca-Pv that is at least 7% lower than the lowest computational estimates; however, there is difficulty extrapolating these to high-temperature conditions due to intervening phase transformations of the Ca-Pv structure^{3,18,19}. Very recently, high-temperature experimental velocity measurements that are also lower than all computational values have been reported²⁰, although this study did not consider extrapolations of Ca-Pv's velocity throughout the deep mantle, leaving Ca-Pv's contribution in generating lower-mantle signatures unresolved. Here we report synchrotron-based high-pressure (P), high-temperature (T), experiments that simultaneously measure the crystal structure and seismic velocities (v_p and v_s) of $\text{Ca}[\text{Si}_x\text{Ti}_{1-x}]\text{O}_3$ compositions ($x = 0.6$ and 1) that bracket the range of inclusions found in natural superdeep diamonds and are expected in lower-mantle assemblages²¹. Combining our new data with ab initio calculations and literature data, we directly address the influence of crystallographic phase transitions on the velocity of Ca-Pv and apply our results to provide a new understanding of Ca-Pv's geophysical signature throughout the lower mantle (see Methods)^{16,17,22}.

In line with expectations from previous experiments¹⁸, in situ diffraction confirms that Ca-Pv is cubic at high temperature, and undergoes one or more structural distortions upon cooling to room temperature (Fig. 2a). Refinement and indexing of diffraction patterns reveals that endmember CaSiO_3 transforms on cooling from cubic ($Pm\bar{3}m$) at high temperatures into tetragonal ($I4/mcm$) perovskite between 380 K and 420 K at about 12 GPa (Fig. 2c). This phase transition is identified by the nonlinear splitting upon cooling (observed as broadening) of all diffraction peaks, except for those with indices hhh (that is, 111 and 222), from the cubic aristotype unit cell ($a \approx 3.5$ Å, Fig. 2b and Extended Data Fig. 1e). Additionally, weak superlattice reflections at d -spacings (in Å) of approximately 2.11, 1.61, 1.07 and 0.98 (Extended Data Fig. 2), which uniquely identify the $I4/mcm$ structure, were observed below about 420 K. Titanium incorporation (similarly to aluminium²³) increases the upper stability limit of tetragonal Ca-Pv considerably, here by nearly 800 K. We find that $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ takes the $Fm\bar{3}m$ space group at high temperature (Extended Data Figs. 1, 3, 4), possessing a double perovskite unit cell, with partial Si:Ti cation ordering that is apparently maintained throughout cooling. The cubic–tetragonal ($Fm\bar{3}m$ – $I4/m$) transition in $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ is observed at approximately 1,200 K (Extended Data Fig. 1). Upon further cooling, a subsequent symmetry distortion, thought to be to $P2_1/c$, is observed at about 700 K. These observations provide very strong evidence that Ca-Pv follows the same structural transitions on cooling as CaTiO_3 (see equations below²⁴), with the apparent reductions in symmetry from $I4/mcm$ and $Pbnm$ to their $I4/m$ and $P2_1/c$ subgroups being a consequence of cation ordering:



Acoustic velocities, determined simultaneously with synchrotron X-ray diffraction using pulse-echo ultrasonic interferometry, demonstrate that the observed phase transitions of Ca-Pv are associated with large elastic anomalies. CaSiO_3 and $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ samples undergo v_p and v_s reductions of 4–14% and 8–20%, respectively, owing to their cubic–tetragonal transitions (Fig. 3). Continued cooling of $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ into its presumed monoclinic structure sees the velocities increase near ambient temperature. The acoustic ‘shear-strengthening’ with temperature that we observe in tetragonal Ca-Pv is also reported for polycrystalline BaTiO_3 samples²⁵. Such behaviour is thought to result from a temperature-activated twin-domain-wall process that also causes high

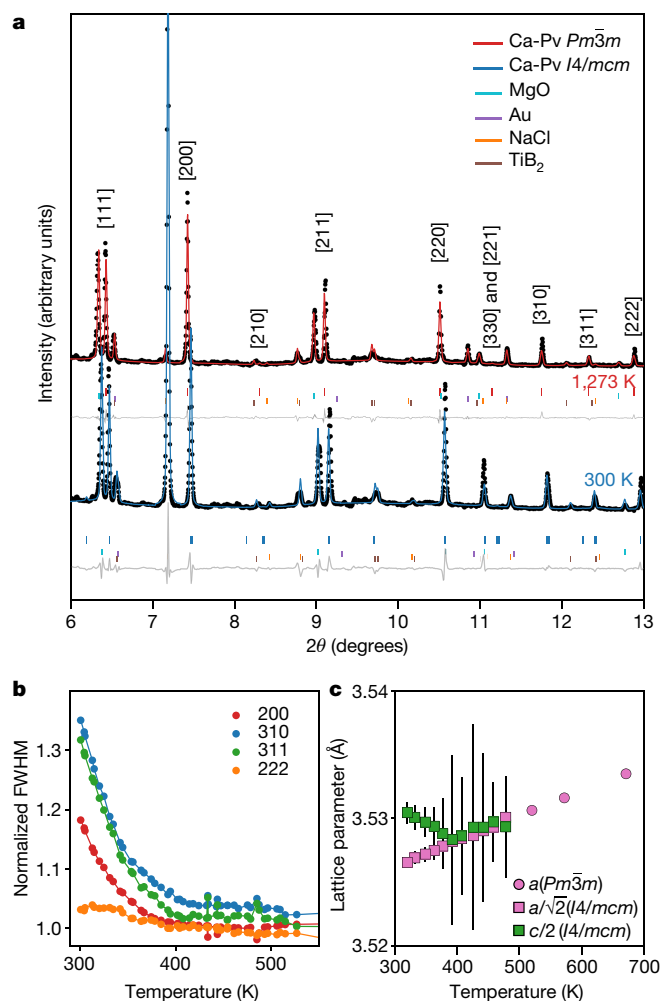


Fig. 2 | X-ray diffraction patterns demonstrating the cubic–tetragonal phase transition in CaSiO_3 perovskite. **a**, Rietveld refined X-ray diffraction patterns collected at about 12 GPa and 1,273 K (red, cubic) or 300 K (blue, tetragonal), with cubic CaSiO_3 peaks labelled by $[hkl]$ and tick marks for other cell components. **b**, Normalized full-width at half-maximum (FWHM) of selected diffraction peaks (see key) of CaSiO_3 perovskite as a function of temperature. **c**, Refined lattice parameters of CaSiO_3 perovskite sample as a function of experimental temperature with 2σ uncertainties.

acoustic attenuation²⁶. Although we cannot rigorously measure acoustic attenuation, we do observe a diminution in the intensity of reflected acoustic waves when samples are tetragonal. Experiments on endmember CaSiO_3 demonstrate a modest reduction in v_p and v_s across the cubic–tetragonal transition at $T < 450$ K; however, the relatively small decrease observed is likely to continue at sub-ambient temperatures that could not be examined in this study. We suggest that CaSiO_3 , if cooled further, probably undergoes similar magnitudes of velocity reduction to those observed for $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$. Absolute acoustic velocities measured for CaSiO_3 are lower than computational predictions, but v_p and v_s in this study agree extremely well with previous experimental measurements made at room temperature^{16,17,20}. It is only with increasing temperature that our results diverge from previous experimental data²⁰. The excellent room-temperature agreement leads us to conclude that previous calculations must have overestimated the velocities, specifically the shear modulus (G), of Ca-Pv (as discussed below). We also observe that the temperature dependences of velocities ($\frac{1}{v} \frac{dv}{dT}$) in cubic Ca-Pv are 1.5–3 times larger than those experimentally observed for other mantle silicates²⁷. However, the temperature dependence of the elastic moduli in our experiments (dK/dT and dG/dT are both about -0.027 to -0.03 GPa K^{-1}) match those observed for cubic $[\text{Ca},\text{Sr}]\text{TiO}_3$

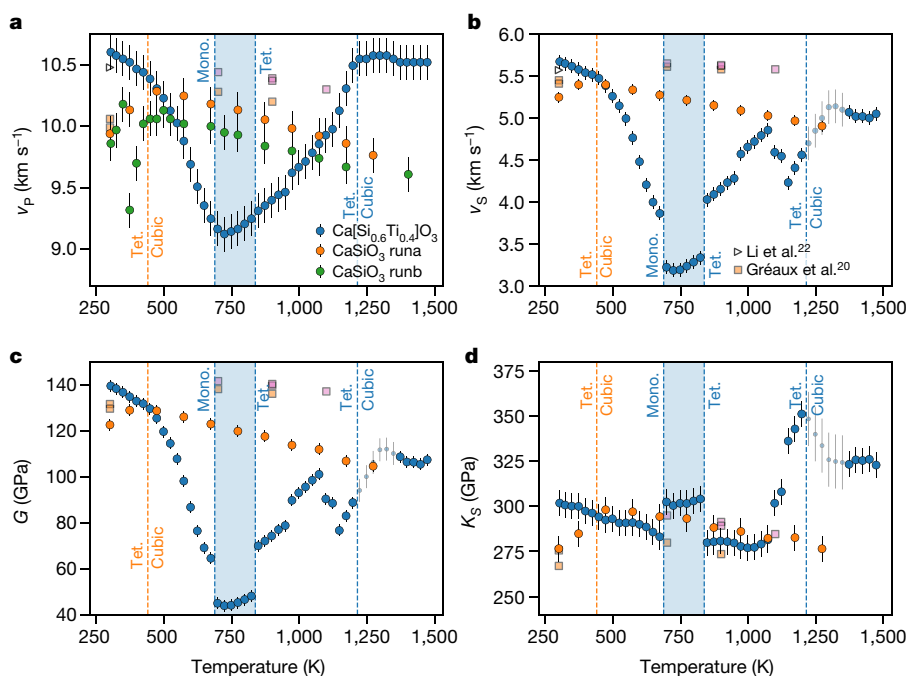


Fig. 3 | Acoustic velocities of Ca-Pv samples at high-PT conditions. **a–d**, Compressional-wave (v_P ; **a**) and shear-wave (v_S ; **b**) velocities, with derived shear modulus (G ; **c**) and bulk modulus (K_S ; **d**) of Ca-Pv samples measured as a function of temperature at constant pressure (about 12 GPa), for $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ (blue circles) and CaSiO_3 samples (orange and green circles). Data from “runa” and “runb” are results from two separate experiments on CaSiO_3 at slightly different pressure. Uncertainties are all 2σ . Small blue circles are data with a low signal-to-noise ratio, due to

low amplitude of the buffer rod reflection, and have larger uncertainties. Experimental velocity measurements from previous studies are plotted as triangles²² (about 12 GPa) and squares²⁰ (orange, 12 ± 1 GPa; purple, 15 ± 1 GPa). Dashed vertical lines indicate the temperatures of observed phase transitions for CaSiO_3 (orange) and $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ (blue) to/from cubic (Cub.), tetragonal (Tet.) and/or monoclinic (Mono.) structure. The blue temperature interval represents the extent of the first-order $I4/m$ to $P2_1/c$ transition in $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$.

perovskites (-0.024 to -0.03 GPa K^{-1})²⁶ and the bulk (K_S), but not the shear, modulus in previous experiments on CaSiO_3 ($dK_S/dT \approx -0.036$ and $dG/dT \approx -0.015$ GPa K^{-1})²⁰.

Using ab initio molecular dynamics, we have calculated the PT slope of the $I4/mcm \rightarrow Pm\bar{3}m$ phase transition in CaSiO_3 perovskite (Methods, Extended Data Fig. 5) in order to apply our results to Earth's deep mantle. The calculated slope, approximately 15 K GPa^{-1} , is similar to results from previous calculations (about 10 K GPa^{-1})³ and experiments on the $I4/mcm \rightarrow Pm\bar{3}m$ transition in SrTiO_3 (approximately 18.5 K GPa^{-1})²⁸. However, it is much larger than, but still within uncertainty of, experimental estimates (≤ 2 K GPa^{-1})^{18,23} for CaSiO_3 . Assuming our PT slope is only shifted in temperature by Ti-incorporation, average mid-ocean-ridge basalt (MORB) Ca-Pv ($\sim \text{Ca}[\text{Si}_{0.9}\text{Ti}_{0.1}]\text{O}_3$, ignoring other chemical components)¹³, should undergo a cubic $\rightarrow$ tetragonal transformation at mid-mantle depths. In addition, Ca-Pv subducted within slab assemblages, particularly for Ti-rich Ca-Pv compositions, may in fact retain the tetragonal structure throughout the entire mantle at average temperatures (Extended Data Fig. 5). Pure CaSiO_3 , which is similar to the composition stable in peridotitic and harzburgitic assemblages, is unlikely to become tetragonal in the ambient mantle, but could undergo a cubic–tetragonal transition in cold slab assemblages reaching pressures greater than about 90 GPa.

To evaluate our experimental results in the context of Earth's lower mantle, we have fitted finite-strain equations of state (EoS) for cubic and tetragonal CaSiO_3 perovskite, using the thermodynamically self-consistent Mie–Debye–Grüneisen–Birch–Murnaghan formalism²⁹ commonly adopted in mineralogical models⁶. The narrow pressure range of our experiments means additional constraints from literature data are required for extrapolations where velocities remain experimentally unconstrained. All available literature data judged to reliably constrain Ca-Pv volume and/or acoustic velocities at high- PT conditions (Supplementary Table 1) were collated and converted to a common pressure scale for joint inversion with new data from this study

(see Methods for full fitting procedure). We note that data from recent high- PT experiments²⁰ are not included, owing to inconsistencies within this dataset (Methods). Recovered EoS parameters (see Methods for nomenclature) for tetragonal Ca-Pv at 300 K are $V_0 = 46.10(6)$ $\text{\AA}^3$ per formula unit, $K_0 = 224(4)$ GPa, $K'_0 = 4$ (fixed), $G_0 = 107(6)$ GPa and $G'_0 = 1.4(1)$ (Extended Data Fig. 6a). The EoS for cubic Ca-Pv, fitted using high-temperature data lying above the phase transition calculated by ab initio methods in this study (Fig. 1, Extended Data Fig. 6b, Supplementary Table 2) has the parameters: $V_0 = 45.57(2)$ $\text{\AA}^3$, $K_0 = 248(3)$ GPa, $K'_0 = 3.6(1)$, $G_0 = 107(1)$ GPa, $G'_0 = 1.66$ (fixed, but manually varied by ± 0.22), $q_0 = 1.1(2)$, $\gamma_0 = 1.67(4)$, $\theta_0 = 771(90)$ K and $\eta_{s0} = 3.3$ (fixed to approximately $2\gamma_0$). Incorporation of our newly collected data, compared with only fitting literature data, improves estimations of G_0 , γ_0 , q_0 and α , owing to the high temperature resolution provided by this study, whereas the dominant constraints on K_0 and K'_0 come from the highest-pressure literature data. The narrow pressure range of our velocity measurements mean they mainly constrain the shear modulus, but not its pressure derivative G'_0 . However, literature values of G_0 from calculations and experiments^{4,5,20} are highly consistent and it can be fixed with some confidence, although we have also varied it manually to assess its effect on extrapolations. Our approach relies on high-precision data from four previous diffraction studies on Ca-Pv at high- PT conditions and results in a single EoS that explains all data with no outliers at the 3σ level. This provides the best option to date to investigate Ca-Pv's velocity at deep mantle conditions and offers self-consistent EoS values without apparent reduction in predictive capacity throughout the pressures and temperatures relevant to Earth's mantle.

Our results imply that cubic Ca-Pv's compressional- and shear-velocity profiles are substantially lower than PREM¹⁵ (see Fig. 1), whereas its bulk sound velocity is virtually indistinguishable from PREM¹⁵ (Extended Data Fig. 7a). We observe Ca-Pv's velocities, especially v_S , to be much lower than those predicted from thermodynamic

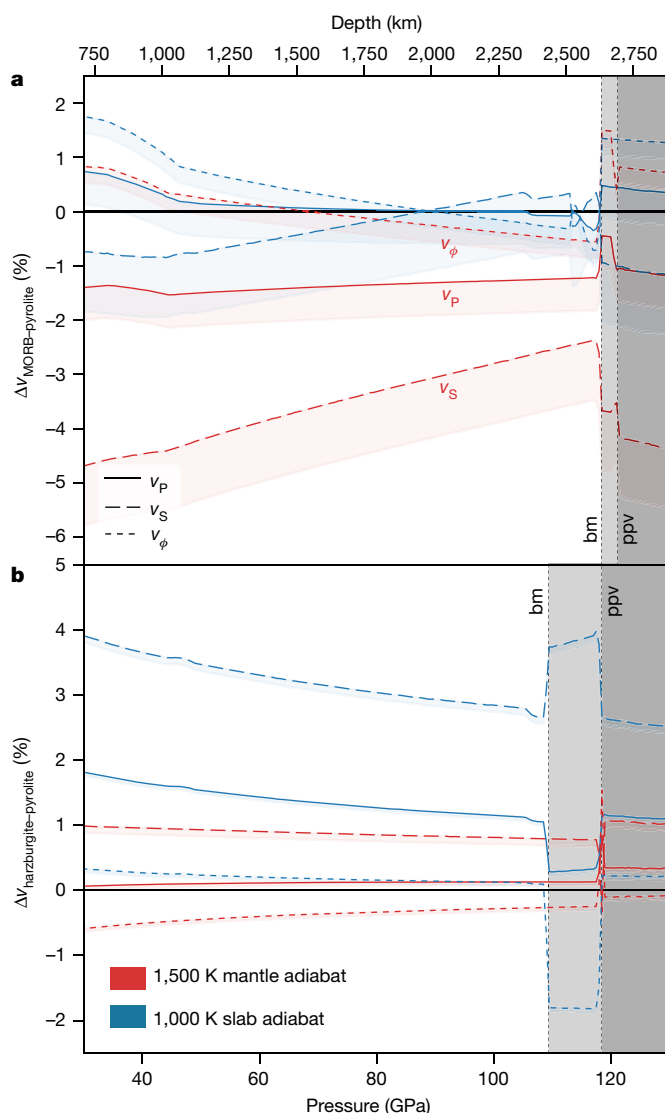


Fig. 4 | Modelled velocity profiles of lower-mantle phase assemblages incorporating Ca-Pv based on this study. **a, b,** Models of MORB (**a**) and harzburgite (**b**) phase assemblages relative to pyrolite throughout the lower mantle. Shown are profiles of compressional velocities, v_P (solid curves), shear velocities, v_S (long dashed curves) and bulk sound velocities, v_ϕ (short-dashed curves); red curves are calculated velocity profiles along a self-consistent 1,500 K adiabat, blue curves are calculated along a 1,000 K adiabat. The coloured lines are the velocity when Ca-Pv is cubic, whereas the lower bound of the coloured shading is indicative of the velocity expected if Ca-Pv forms a tetragonal structure. The vertical dashed lines, and corresponding grey shading, mark the depth of the bridgmanite (bm) to post-perovskite (ppv) transition in each assemblage.

datasets⁶, by previous high-temperature calculations^{3–5}, or high-*PT* experiments²⁰. In all cases the discrepancy is almost entirely due to the much lower shear modulus observed in this study. Indeed, it is evident that the shear modulus of Ca-Pv is one of the most critical parameters for accurately modelling the velocity of basaltic assemblages throughout the lower mantle. A full comparison with results from previous studies is provided in Methods. Although titanium-bearing Ca-Pv has not been included in finite-strain modelling, our experimental data demonstrate that titanium-incorporation will increase Ca-Pv's velocity by $<1 \text{ km s}^{-1}$ for v_P and $<0.5 \text{ km s}^{-1}$ for v_S for $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$. As MORB-derived Ca-Pv has¹³ an approximate composition of $\text{Ca}[\text{Si}_{0.9}\text{Ti}_{0.1}]\text{O}_3$, the effect of this titanium content on mantle velocities is expected to be smaller.

Understanding the cause of the LLSVPs remains one of the most prominent questions currently pursued by the deep Earth research

community³⁰. Identifying whether they are purely thermal anomalies or are thermo-chemical piles of recycled or primordial material could have profound consequences for our understanding of mantle convection. In order to address the question of LLSVP composition, we have incorporated our new cubic Ca-Pv EoS in thermodynamic models (Methods, Fig. 4), extracting the acoustic velocities of recycled basalt and harzburgite assemblages, relative to pyrolite, throughout lower-mantle conditions (we are assuming pyrolite is representative of average lower-mantle composition). Along a 1,500 K mantle adiabat, recycled MORB is predicted to have distinctly lower compressional and shear velocities than pyrolite. This result is in stark contrast with published thermodynamic datasets, in which predicted MORB assemblages have a velocity 1%–2% higher than the average deep mantle⁶. Thus, despite geochemical observations implying a long-lived reservoir of recycled crust in the deep Earth³¹ and the high density of MORB³² favouring its accumulation in the LLSVPs⁷, this was previously considered incompatible with observed low velocities unless temperatures were extremely hot³³. However, our new results now imply LLSVPs are well explained by modest enrichments in recycled oceanic crust, without requiring excess temperature anomalies. Compared to the bulk mantle composition, which is assumed to be a mixture of approximately 80:20 harzburgite:MORB, the v_S anomalies of -1.5% and the v_S/v_P anomaly ratio >2 observed in LLSVPs³⁰ can be reproduced by a bimodal mixture of MORB + harzburgite consisting 64% MORB at about 100 GPa ($v_P = -0.77\%$) or 48% MORB at about 125 GPa ($v_P = -0.36\%$) if Ca-Pv is cubic. If the LLSVPs are hotter, or if Ca-Pv is tetragonal near the CMB, the proportion of basalt required to explain the LLSVPs would reduce. Our modelling further implies that the above-average velocities that surround the LLSVPs, lying beneath palaeo-subduction zones that are often considered to be slab graveyards³⁰, could potentially represent depleted assemblages. MORB-enriched LLSVPs, surrounded by depleted material, also provide an explanation for the anti- or non-correlation of v_S and v_ϕ (bulk sound velocity) just above the CMB if post-perovskite is stable³⁰. Taken at face value, the predicted properties of CaSiO_3 suggest that pyrolite assemblages may be slightly slower than PREM¹⁵. However, although we are confident that our work robustly demonstrates that subducted MORB assemblages are slow, the amount of Ca-Pv in pyrolite is smaller and so further investigations on the effects of titanium and/or aluminium³² in Ca-Pv are required to determine whether or not the average velocity of the lower mantle remains compatible with a pyrolitic bulk composition.

The properties of Ca-Pv also provide an explanation for observed seismic reflectors throughout the mid-mantle². In very cold slabs following a 1,000 K adiabat, subducted basalts (if Ca-Pv is cubic) are predicted to have very similar velocities to pyrolitic assemblages on a 1,500 K adiabat and so may be seismically invisible. However, if stranded fragments are thermally equilibrated with surrounding depleted materials, impedance contrasts with magnitudes of up to about $\pm 2.8\%$ will be created, making them seismically visible as reflectors or as slow regions. Alternatively, if Ca-Pv undergoes the cubic–tetragonal phase transition, this may also generate mid-mantle anomalies (Extended Data Fig. 5). Although constraining the depth and compositional dependence of this phase transition requires further studies, it is expected that cold downwelling Ca-Pv is likely to experience the cubic to tetragonal transformation somewhere beyond 1,000 km depth. Stagnant or delaminated materials in the upper–lower mantle boundary region⁸ may undergo the tetragonal–cubic transition during thermal equilibration, reducing MORB's shear velocity, which may be the origin of observed mid-mantle reflectors².

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41586-019-1483-x>.

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METHODS

Starting materials. Starting materials of CaSiO_3 and $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}\text{O}_3]$ compositions were initially prepared by grinding appropriate quantities of high purity CaCO_3 , SiO_2 and TiO_2 together in an agate mortar before decarbonation and, in the case of CaSiO_3 , sintering into crystalline wollastonite, or in the case of $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}\text{O}_3]$, fusing to a glass. All materials were analysed with scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM EDS) to check composition, and the CaSiO_3 was confirmed as pure wollastonite using X-ray powder diffraction ($\lambda = 1.7904 \text{ \AA}$). Ultrasonic experiments require fully dense cylindrical samples with parallel polished faces and an aspect ratio (length/diameter) < 2 . Thus, the $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}\text{O}_3]$ glass was hot-pressed into Ca-Pv at $\sim 14 \text{ GPa}$ and $1,400^\circ\text{C}$ using a 10/5 multi anvil assembly, and the recovered products manipulated into suitable forms for subsequent acoustic experiments. Since CaSiO_3 perovskite is unrecoverable, undergoing a decomposition to amorphous ‘glass’ with pervasive fracturing at room temperature, it is not possible to prepare a similar sample of the endmember perovskite composition. Instead samples of walsstromite were prepared, which is the highest-pressure recoverable polymorph of CaSiO_3 , by sintering at $\sim 7 \text{ GPa}$ and $1,300^\circ\text{C}$ using a 14/8 multi-anvil assembly.

Diffraction and ultrasonic experimental methods. X-ray diffraction and pulse-echo ultrasonic experiments were performed on beamline ID06-LVP of the ESRF synchrotron, where modified 10/5 multi anvil assemblies were employed to allow simultaneous measurement of sample diffraction, length and acoustic velocity. Samples were placed adjacent to a polished polycrystalline alumina buffer rod on one side that reached the cube to which the ultrasonic transducer was attached, and an $\text{MgO} + \text{NaCl}$ mixture serving as soft backing and (for the NaCl) as a pressure marker on the other. Thin Au foils were placed at each end of the sample to allow sample length to be observed with radiographic imaging, and also between the cube and buffer rod to assist with acoustic coupling. This acoustic column was encapsulated in a crushable MgO sleeve, and a Re or $\text{TiB}_2 + \text{BN}$ furnace, which was contained within ZrO_2 insulation and a Cr:MgO octahedral pressure medium. A W-Re thermocouple was used, inserted from the opposite end of the cell assembly in an MgO sleeve to monitor temperature adjacent to the sample throughout the experiments (Extended Data Fig. 8c).

Along the path of the X-ray beam, the normal ceramic materials were replaced by high transparency amorphous SiBCN(O) windows. Monochromatic synchrotron X-rays ($\lambda = 0.22542 \text{ \AA}$ or $0.2296 \text{ \AA}$) were used to collect diffraction patterns from the sample and pressure markers throughout experiments using two different detectors available at ID06. In all experiments the standard Detection Technology X-scan 1D detector³⁴, which has a fixed 10-Hz integration rate, was used to record diffraction patterns every 3.2 s (continuous, with $32 \times$ rebin) and every 32 s (on increasing and decreasing pressure). Throughout one experiment on CaSiO_3 an additional Pixirad-8 detector was employed to assist with the identification of weak superlattice reflections from the sample. X-ray sample-detector geometry was calibrated using Si and/or LaB_6 NIST standards, and the collected diffraction patterns were suitably reduced and analysed using Fit2d³⁵ software. Rietveld refinement of selected diffraction patterns was performed using the GSAS software package³⁶ (Supplementary Tables 3 and 4). Experimental unit-cell volumes were also calculated and used to determine the pressure–volume–temperature (PVT) EoS by fitting the position and width of individual diffraction lines from the Ca-Pv samples and pressure markers. In this case Ca-Pv volumes are determined using the average volume calculated from the 200, 310, 321 and 222 diffraction peaks of the sample, while the volumes of NaCl and Au were determined using their 220 and 310 peaks, respectively (Supplementary Table 5).

Samples were compressed to target load and initially heated to $T > 1,000 \text{ K}$ to remove stress in the sample that might affect acoustic measurements. In the experiments on CaSiO_3 , the starting material of walsstromite was converted into Ca-Pv by annealing at constant load (initial pressure $\sim 14 \text{ GPa}$) and $1,200$ – $1,500 \text{ K}$ for a period of 2–4 h, until all signs of walsstromite diffraction peaks were lost. Pressure throughout the experiments was determined from the unit-cell volumes of NaCl-B1 and/or Au using cross-calibrated high-temperature EoS³⁷, and the sample length was measured using the standard imaging system installed on ID06-LVP. Sample lengths determined with X-ray imaging were checked against those measured before and after (in the case of $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}\text{O}_3]$ experiments with a digital gauge ($1 \mu\text{m}$ accuracy). Uncertainties in sample lengths are estimated from images as ± 5 pixels, corresponding to $\pm 5.4 \mu\text{m}$ ($< 2\%$ overall sample length), and it is this uncertainty that produces the reported uncertainties in velocities (Supplementary Table 6 and Fig. 3). Alongside ultrasonic measurements accompanied by diffraction and imaging, the crystallographic evolution of the samples was specifically investigated using continuous diffraction collected during constant rate cooling ramps (25 – 50 K min^{-1}) for CaSiO_3 and $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}\text{O}_3]$ samples without collecting ultrasonic data.

Acoustic signals, always collected after sample annealing at high T , were transmitted into and received from the sample assembly using a 10° Y-cut dual mode LiNbO_3 piezoelectric transducer that was fixed to the corner of the ‘acoustic cube’

opposite to the sample using Epo-tek 353ND epoxy. A signal generator (Tektronix AFG3101C or Keysight 33622A) was used to create acoustic pulses composed of three consecutive periods of sine waves with 30–60 MHz frequency and 2.5 or 5 V peak-to-peak amplitude, which were passed to the transducer and oscilloscope. The resonant frequencies of ν_p and ν_s from the transducer crystal were $\sim 50 \text{ MHz}$ and $\sim 30 \text{ MHz}$, respectively. Received echoes were measured using the same oscilloscope (Tektronix DPO5140 or Keysight DSOS104A) to record the delay between arrival times of compressional- and shear-wave signals at a rate of either 2.5×10^9 or 5×10^9 samples per s. In later experiments, a directional bridge (Keysight 86205A), preamplifier (LA020-OS) on the return signal, and external trigger (trigger rate 2 kHz) were variously used, as the system was continuously developed throughout this study. Collection times of individual acoustic spectra ranged from 5 s to 300 s with the various systems employed throughout this study. Two-way travel times of ultrasonic arrivals were converted into sample velocities using the ‘pulse-echo overlap method’ (for reflections from the near and far ends of the sample), which was implemented by maximizing absolute values of signal cross-correlation and sample lengths measured with X-ray imaging. Predicted reflection coefficients for both interfaces (based on $R = (Z_2 - Z_1)/(Z_1 + Z_2)$, with $Z_i = \rho_i v_i$) are both negative (approximately -0.025 and -0.25 for Al_2O_3 –Ca-Pv and Ca-Pv–NaCl+MgO respectively) at the PT conditions of the experiments, suggesting that no phase shift is expected in the acoustic signals. The lack of observed phase shifts and measured pulse/echo amplitude ratios were found to be consistent with these expectations, which provides assurance that the phase of acoustic arrivals has been correctly identified. Measured velocities are reported in Supplementary Table 6. It should be noted that two independent experiments were performed to measure the velocity of CaSiO_3 samples (which agree within uncertainty for ν_p) during separate visits to the ESRF, one employing a Re and the other a TiB_2 –BN furnace. In the second of these experiments on CaSiO_3 , the shear-wave signal from the sample was not observable above noise levels and thus the shear-wave velocity was not determined. These are labelled ‘runa’ and ‘runb’ in Fig. 3. Additionally, the ultrasonic data reported for $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}\text{O}_3]$ above 975 K were collected on heating after annealing, while data below 975 K were subsequently collected upon cooling the sample. This results in a small pressure difference between the two sets of measurements and explains the discontinuity in Fig. 3.

Structure determination. Refined diffraction data from experiments on CaSiO_3 are consistent with a cubic crystal structure for Ca-Pv at high temperatures. All observed diffraction peaks have approximately constant widths at half maximum intensity, in line with expectations from the diffractometer geometry, and all observed diffraction peaks could be attributed to diffraction from the sample (in space group $Pm\bar{3}m$) or other cell components (MgO , Au, NaCl, TiB_2 , Al_2O_3). Upon cooling, the diffraction peaks from the sample undergo substantial nonlinear hkl -dependent broadening below $\sim 420 \text{ K}$ (Fig. 2 and Extended Data Fig. 1e). Similarly to previous studies^{18,23}, we interpret this observation as the result of a cubic–tetragonal transition in CaSiO_3 . Close inspection of diffraction data from the Pixirad-8 detector, which was employed during one experiment, reveals that weak superlattice peaks from CaSiO_3 (otherwise unexplained by other cell components) appear in data collected at 373 K and 300 K (Extended Data Fig. 2). The strongest of these is observed at $2\theta \approx 6.1^\circ$ (indexed as $3/2 \ 1/2 \ 1/2$ on the cubic sublattice) but additional peaks can also be observed at 2θ values of 8.05° ($3/2 \ 3/2 \ 1/2$), 12.1° ($5/2 \ 3/2 \ 3/2$) and 13.2° ($5/2 \ 5/2 \ 1/2$) (d -spacings of about 2.11, 1.61, 1.07 and 0.98 $\text{\AA}$, respectively). Assuming that CaSiO_3 ’s initial distortion upon cooling is to a tetragonal phase, there are three likely candidate structures, with space groups $I4/mcm$, $P4/mbm$ and $I4/mmm$. The predicted superlattice peak positions for the structure with $I4/mcm$ symmetry exactly match the observed superlattice peak positions, explaining all four observed peaks, while CaSiO_3 structures with space groups $P4/mbm$ or $I4/mmm$ cannot account for the observations (Extended Data Fig. 2) as these should both produce many additional superlattice peaks (for example, those indexed as $1/2 \ 0 \ 3/2$, $3/2 \ 1/2 \ 1$, $1/2 \ 0 \ 5/2$, $5/2 \ 1 \ 1/2$ and so on, on the basis of the cubic subcell) that are not observed. Given that there are no additional unexplained diffraction peaks, the knowledge that the most obvious superlattice peak at $2\theta \approx 6.1^\circ$ should indeed be the strongest in $I4/mcm$ and that the same transition ($Pm\bar{3}m$ to $I4/mcm$) occurs²⁴ in CaTiO_3 , we see no reason to doubt that the structure of CaSiO_3 at room temperature and at about 12 GPa is tetragonal with space group $I4/mcm$.

The observed behaviour of $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}\text{O}_3]$ is similar to that of CaSiO_3 , but the intensities of the superlattice peaks are much greater and the material is recoverable to ambient conditions. Diffraction patterns collected from the starting material $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}\text{O}_3]$ (measured alongside LaB_6 as a calibrant at 300 K, Extended Data Fig. 3a) allow identification of superlattice peaks with odd and even Miller indices, which requires positive and negative octahedral tilts³⁸. Thus, the highest possible symmetry of $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}\text{O}_3]$ at ambient conditions is orthorhombic. Refining the diffraction data in three likely space groups ($Pbnm$, $Cmcm$ and $P4_2/nmc$) demonstrates that both $Pbnm$ and $Cmcm$ can explain the patterns equally well, and so it is concluded that ambient $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}\text{O}_3]$ is orthorhombic (actually monoclinic

when B-cation ordered, see below). We choose to assume the space group is *Pbnm*, as this is the known²⁴ structure of CaTiO_3 . Since no phase transition is observed during decompression, the room-temperature structure at high pressure is also assumed to be *Pbnm*, or its B-cation ordered equivalent ($P2_1/c$). At high-*PT* conditions, $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ is observed to undergo two structural phase transitions (Extended Data Fig. 4). At the highest temperatures, the diffraction pattern is well explained if the sample takes a cubic *Fm3m* structure. With respect to the cubic form of CaSiO_3 , this has a double unit-cell edge length and partial B-cation ordering (assumed to follow a 1:1 B-site scheme³⁹) of Si and Ti, a common ordering scheme in perovskites. On cooling, the $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ first distorts to a tetragonal structure marked by the appearance of the same set of superlattice peaks that were observed for CaSiO_3 . Since the cubic Ti-bearing Ca-Pv is B-cation ordered, it is assumed the tetragonal phase maintains this B-cation ordering, making the space group of the tetragonal phase *I4/m*. Continued cooling sees distortion into the room-temperature phase, which is assigned to be monoclinic $P2_1/c$ (the B-cation ordered variant of *Pbnm*). Between the tetragonal and monoclinic structures there is a temperature interval where the diffraction pattern cannot be indexed using a single structure model, and it is observed that this temperature interval corresponds to very low acoustic velocities. This may be indicative of a first-order phase transition, which further implies a preference for *Pbnm* or $P2_1/c$ over *Cmcm* or *C2/c*, based on the analysis of Glazer³⁸. Alternative explanations for this behaviour are a temperature interval of phase coexistence, an additional perovskite structure or some other unexplained phenomena. Similar observations have been made for CaTiO_3 (ref. 40), where there is a small temperature interval between the *I4/mcm* and *Pbnm* structures where the behaviour is attributed to an interval of phase coexistence caused by the kinetic energy barrier of the first-order phase transition. A more detailed discussion of the crystallographic behaviour of Ca-Pv samples lies beyond the scope of the current study.

Ab initio calculations and the slope of the Ca-Pv tetragonal–cubic transition.

Ab initio calculations were performed to constrain the conditions of the tetragonal–cubic transition of Ca-Pv throughout the Earth's mantle. All simulations were carried out with the density-functional-theory (DFT) code VASP⁴¹ using the projector-augmented-wave (PAW) method⁴² and the PBE formulation of the generalized gradient approximation⁴³. Molecular dynamics (MD) calculations used the Nosé thermostat and were run at the gamma point with a cut-off of 600 eV and relaxed to within 10^{-5} eV and all forces to below $0.03 \text{ eV } \text{\AA}^{-1}$. All computational runs were at least 20 ps in duration, although all measured properties were observed to be fully converged by 12 ps. Phonon calculations for calculating the force-constant matrix used an energy cut-off of 850 eV, $4 \times 4 \times 4$ K points and were relaxed to 10^{-8} eV with forces below $0.01 \text{ eV } \text{\AA}^{-1}$. The finite difference method was used and processing was done with the phonopy code⁴⁴. Ca atom semicore 3s and 3p states were treated as valence states. All static and molecular dynamics runs were spin-polarized and CaSiO_3 was always simulated with an 80-atom simulation box, based on a $2 \times 2 \times 4$ assemblage of the perovskite cubic aristotype cell containing 5 atoms. For cubic perovskite calculations, the subcells from which the simulation box was constructed were fixed to have a geometry of $a = b = c$, whereas for tetragonal CaSiO_3 the simulation geometry for was fixed such that $a = b \neq c$. Details of simulation cell volumes are provided in Supplementary Table 7. In each case the final stress on the crystal was correct to within 0.04 GPa for static calculations and to within 0.1 GPa (on average) for MD calculations. After the geometries were imposed at each *PT* condition the atoms were allowed to relax (within constraints maintaining cubic or tetragonal structure), before the simulations used to obtain free energies.

Free energy differences were calculated at 25, 75 and 125 GPa and at 0, 1,000, 2,000 and 3,000 K. To calculate the free energy of each state, we used an approximation of the thermodynamic integration represented by equation (1):

$$F - F_0 \cong \langle U - U_0 \rangle_0 + \frac{1}{2k_B T} \langle [U - U_0 - \langle U - U_0 \rangle_0]^2 \rangle_0 \quad (1)$$

where subscript 0 represents the reference state and other terms the state of interest. For a reference state we used a harmonic oscillator with free energy defined by equation (2):

$$U_0 = U + \sum_i \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{ij} u_i \Phi_{ij} u_j \quad (2)$$

where u_x is a displacement vector and Φ_{ij} is the force constant matrix. As cubic CaSiO_3 is unstable at low temperatures it has negative frequencies in its phonon spectrum, and the free energy cannot be calculated directly from its force constant matrix. Thus, we applied a small correction to eliminate these imaginary frequencies and allow free energy calculations. The correction matrix (Φ_{ij}^c) is formed by multiplying the onsite terms in the force constant matrix by kI (where I is the identity matrix and k is the smallest constant that eliminates all imaginary

frequencies). The correction procedure then subtracts the correction matrix from the true force constant matrix ($\Phi_{ij} - \Phi_{ij}^c$) to produce a modified force constant matrix Φ_{ij}^* , which is used in equation (2). While this procedure cannot predict the correct absolute free energies, it should accurately calculate the free energy difference relative to a reference state that has had the same correction procedure applied. This procedure is repeated for both cubic (cub) and tetragonal (tet) CaSiO_3 structures at each *PT* condition, and finally the free energy difference between these states is determined using equation (3):

$$\Delta G_{\text{cub-tet}} = \Delta G_{\text{final-ref}}^{\text{cub}} + G_{\text{ref}}^{\text{cub}} - (\Delta G_{\text{final-ref}}^{\text{tet}} + G_{\text{ref}}^{\text{tet}}) \quad (3)$$

The final calculated free energy differences between cubic and tetragonal states are reported in Supplementary Table 7. All free energy differences are subject to uncertainties, which are assumed to be 1 meV per formula unit (f.u.) at 0 K, and calculated to be <10 meV per f.u. at high temperatures, from the statistical uncertainty in the simulation energies. These uncertainties were incorporated in the weighted least-squares regression used to determine the conditions and uncertainty of the tetragonal–cubic transformation at each pressure (25, 75 and 125 GPa), as plotted in Extended Data Fig. 5.

Calcium perovskite EoS. PVT-velocity data from experiments in this, and literature, studies were combined to allow fitting of an EoS for both tetragonal and cubic CaSiO_3 perovskite. The pressures of all reported literature data were converted to a single pressure scale, which was used for pressure measurement in this study³⁷. This ensures consistency of the pressure scale used throughout the dataset. The fitted EoS for tetragonal Ca-Pv uses only room-temperature data and all literature data collected on samples compressed in diamond anvil cells without use of a pressure-transmitting medium were discarded (small symbols in Extended Data Fig. 6a). The remaining PV data^{19,45}, including one-twentieth of the data collected during room-temperature decompression in this study before amorphization, were fitted to a second-order Birch–Murnaghan EoS for V_0 (volume at ambient conditions) and K_{T0} (isothermal bulk modulus at ambient conditions) using the BurnMan software package¹¹ (Supplementary Table 2). Only one-twentieth of the current data were used, to ensure that the final fitted model was not overly biased to the data collected in this study. Subsequently, room-temperature velocity measurements from this study were combined with literature data^{17,20} to fit the shear modulus (G_0) and its pressure derivative (G_0') within the SLB2005²⁹ formalism, as provided in BurnMan. As the EoS is only calibrated at room temperature, estimates of velocity reductions for tetragonal Ca-Pv in Fig. 4 are qualitatively based on the magnitude of reductions observed in measurements from $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$, taken ~ 100 K below the phase transition, in this study, and are not calculated by using the tetragonal Ca-Pv EoS.

The EoS for cubic Ca-Pv (Supplementary Table 2) also fits data from this study and the literature^{45–48} using the SLB2005²⁹ Mie–Grüneisen–Debye Birch–Murnaghan formalism implemented in BurnMan¹¹. Only data falling above the calculated *P–T* curve of the tetragonal–cubic phase transition (Extended Data Fig. 5) were used, to ensure that no data from tetragonal-structured Ca-Pv were included (Extended Data Fig. 6b). PVT data were first used to fit V_0 , K_0 , K_0' (pressure derivative of the bulk modulus) and γ_0 (Grüneisen parameter). Subsequently, the complete PVT-velocity dataset was re-fitted for G_0 , γ_0 , q_0 (temperature dependence of the bulk moduli) and θ (Debye temperature) (V_0 , K_{T0} , K_0' were unchanged) assuming $G_0' = 1.66$. G_0' was fixed to literature values^{45,20} due to the small pressure range of velocity measurements in this study, a value consistent with literature scaling rules²⁹. η_{s0} (temperature dependence of the shear moduli) was fixed at 3.3, based on the scaling rules ($\eta_{s0}/\gamma_0 \approx 2$) from Stixrude²⁹. Alternatively, η_{s0} can also be a fitted parameter (Supplementary Table 2). However, since this second fit (with variable η_{s0}) results in slightly lower extrapolated velocities without drastically altering subsequent interpretation, fixing η_{s0} was viewed as a more conservative way to evaluate the influence of Ca-Pv. It is noted that the uncertainty bounds plotted in Fig. 1 account for variation of G_0' from 1.44 to 1.88 and Ca-Pv remains slower than PREM and ab initio estimates throughout this entire range. We recognize that, without using literature data, extrapolation throughout the mantle pressure range would be completely unrealistic—and are beholden to accepting the reliability of literature data; however we note that four previous studies on Ca-Pv at high-*PT* conditions, after conversion to a common pressure scale, can be combined and fitted to a single EoS without any outliers at the 3σ level. Readers are referred to Stixrude²⁹ for details of the SLB2005 formalism.

Thermodynamic modelling. The acoustic properties of MORB, peridotitic and harzburgitic assemblages have been calculated using the MMA-EoS software package⁴⁹. Simplified bulk compositions for MORB (NCFMAS) and pyrolyte/harzburgite (CFMAS) from the software's library were employed as typical of these assemblages throughout the lower mantle. Equilibrium phase assemblages were calculated across a 0.5 GPa by 25 K grid throughout the mantle for each system, and the elastic properties of each assemblage extracted along self-consistent adiabatic temperature profiles beginning at 1,000 K (representing slabs) and 1,500 K (average

mantle), which are plotted relative to one another in Fig. 4. The latter temperature profile is very similar to the geotherm of Brown and Shankland⁵⁰. Thermoelastic data from Stixrude⁶ were used for all phases except for the MgSiO₃ bridgmanite endmember (which used updated properties from Zhang⁵¹) and calcium perovskite which is defined in this study. We note that this database provides a somewhat simplified view of lower-mantle materials, as it does not include the effects of iron spin-transitions in ferropericlase or bridgmanite^{52,53} or the ferroelastic phase transitions of stishovite⁵⁴. We also highlight that the modelling in this study inherently assumes that the database from Stixrude et al.⁶ accurately describes the elastic properties of all other lower-mantle phases.

Comparison with previous studies. As noted in the main text, the acoustic velocities of CaSiO₃ observed in this study are observed to be substantially slower than predicted in computational studies^{3–5} and mineralogical databases⁶. Additionally, they are also observed to be slower than those found in previous high-*PT* experiments²⁰. Although we cannot fully explain the reasons for all disagreements, we discuss some observations that may partially explain the mismatches. Database elastic properties⁶ predict the fastest Ca-Pv velocities plotted in Fig. 1, and it is these that the Earth science community currently uses when interpreting seismic observations. Results from the two *ab initio* molecular dynamics (AIMD) computational studies^{4,5} and experiments²⁰ all predict that Ca-Pv should be equal to (v_P) or slower (v_S) than PREM. If any of these results were adopted in mineralogical databases, slow velocity anomalies in the lower mantle could be interpreted as they are in this study, an indicator of MORB enrichment, although not to the extent implied here. We note that the other pseudo-high-temperature calculations³ do not provide enough information in the paper to calculate acoustic properties at elevated temperatures, since the temperature effect on density is unquantified in the original publication.

Comparing our work in detail, first with previous experimental results, it is observed that the room-temperature velocities measured in this study are in excellent agreement with those of Gréaux et al.²⁰, Kudo et al.¹⁷ and extrapolated estimates from Sinelnikov et al.¹⁶. Room-temperature velocities measured by Li et al.²² are somewhat faster, but given the lack of details provided in that paper, which is a technical review, they are not considered further. It is observed that our reported velocities disagree with previous experimental data only at high temperature²⁰, appearing to diverge as the reported temperature increases. Given the similarities in methodology, it is most likely that temperature uncertainties are responsible for the differences. Based on published details, we believe Gréaux et al.²⁰ employed samples of 0.93–1.3 mm length (Fig. 2 and Extended Data Fig. 3 of Gréaux et al.²⁰) and 2 mm diameter, with the thermocouple inserted radially (through the furnace) adjacent to the far end of the pressure marker that in their experiments is initially ~1 mm in length. This arrangement is substantially larger than the samples used in this study, which were 0.4–0.6 mm in length and 1.5 mm diameter, with the thermocouple inserted axially to the end of the pressure marker that had a maximum length of 0.5 mm. Thus, the maximum distance between the thermocouple and far end of the sample in our study is 1.1 mm, probably 0.75 mm at high pressure, approximately half of the equivalent distance in Gréaux et al.²⁰ (probably ≥ 1.5 mm at pressure). Additionally, by inserting the thermocouple axially we ensure the sample is centred in the cell at high pressure, whereas it is unclear whether or not this would be the case with a radial thermocouple, which could also have been affected by contacting the metal furnace. Given that, at 12–22 GPa, the sample column is likely to be 4–5 mm in length, the differences in geometry might have a very large influence on the temperature conditions experienced by samples. Thermal modelling using finite element code⁵⁵ suggests that the thermal gradient across samples at a measured temperature of 1,200 °C in our set-up should be <50–60 °C, with the measured temperature likely to be lower than peak conditions. By contrast, assuming the thermocouple is centred (as drawn by Gréaux et al.²⁰) and measuring 1,200 °C, the range of temperatures experienced by a sample of 1 mm length $\times$ 2 mm diameter could very conceivably be 250–300 °C lower than that measured by the thermocouple. This implies that the apparent effect of temperature on velocities should be smaller using the geometry of Gréaux et al.²⁰, since portions of samples would be colder than believed. This is consistent with the observed differences in velocities between Gréaux et al.²⁰ and the present study, where the offset in reported velocities increases at higher temperatures. Additional evidence that the high-temperature velocities reported by Gréaux et al.²⁰ might be less reliable is demonstrated by comparing the independent estimates of bulk sound velocity (v_ϕ) expected for Ca-Pv from *PT*-volume systematics and acoustic measurements ($v_\phi = \sqrt{v_P^2 - \frac{4}{3}v_S^2} = \sqrt{K_S/\rho}$, where K_S is a function of K_{0T} , K' , γ and α).

We observe that the bulk sound velocity extracted from ultrasonic measurements in Gréaux et al.²⁰ are inconsistent with velocity extracted via a *PVT* EoS using their diffraction data (Extended Data Fig. 9). Ultrasonic v_ϕ values from Gréaux et al.²⁰ are offset to slower values and have a much larger reduction at high temperature than those predicted via an EoS fitted using density from their or compiled literature data^{45–48}. In contrast, bulk sound velocities from data in this study are

consistent with literature *PVT* EoS fitting. This inconsistency suggests that velocities reported in Gréaux et al.²⁰ might be affected by large temperature gradients.

Considering calculated properties of Ca-Pv, we observe that the database values³ best reproduce the adiabatic bulk moduli of Ca-Pv (compared with that from the global experimental dataset, Extended Data Fig. 7b), while the two AIMD studies^{4,5} predict a larger pressure effect on K_S than is observed in the experimental data. Other calculations employing mean-field and Landau theory³ suggest that shear softening should be associated with the cubic–tetragonal transition, while AIMD approaches do not include this behaviour^{4,5}. However, it has been proposed⁴ that the choice of cubic unit cell employed by Stixrude et al.³ prevented rotations of the SiO₆ octahedra, leading to an anomalously large shear modulus and explaining the high velocities. The AIMD results of Kawai and Tsuchiya⁴ should be preferred to those from Li et al.⁵, as the latter may not have fully converged and insufficiently sampled the Brillouin zone⁴ to accurately predict crystal structure. Despite differences, all three computational studies predict a larger shear modulus than required by experimental data (from both this and previous studies^{16,17}). It is possible that this discrepancy results from the strong anharmonicity of Ca-Pv, implying that extremely expensive calculations may be required to accurately describe Ca-Pv's elasticity using computational methods. Indeed, common first-principles methods inaccurately predict the elasticity or phonon temperature dependence of other anharmonic cubic perovskites (SrTiO₃, BaTiO₃ and PbTiO₃)^{56–58}. DFT calculations that under/overestimate the cubic lattice parameter consistently over/underestimate the shear modulus in the opposite sense^{56–58}. The local-density approximation, used by Kawai and Tsuchiya⁴, has been observed to overestimate the shear modulus (c_{44}) of SrTiO₃, BaTiO₃ and PbTiO₃ by 8–18% for ~1% underestimate of unit cell volume⁵⁶. Since we observe a similar mismatch between the volume of cubic CaSiO₃ at adiabatic conditions based on our fit to experimental data and the results of Kawai and Tsuchiya⁴, which are ~1% too small, we expect that Ca-Pv's velocities predicted by Kawai and Tsuchiya⁴ will be somewhat overestimated. However, it is unlikely this effect can explain the entirety of the disagreement between previous calculations and our experimental results. A second contributor to the mismatch could be the presence of crystallographic preferred orientation (CPO) within experimental samples, especially if the alignment of an acoustically slow direction coincided with the ultrasonic path. However, since refinement of X-ray diffraction patterns did not require CPO in the cubic CaSiO₃ field to fit the data, this seems unlikely. Additionally, the way crystal symmetry is stipulated and the lack of grain boundaries/defects in calculations may frustrate some phonon modes, further explaining the offset from experimental values. Finally, we re-iterate that the finite-strain model we report in this paper is subject to very large extrapolation from the experimental *PT* conditions (~12 GPa, 300–1,500 K) to those of the mantle (<130 GPa, 1,500–3,000 K) and we acknowledge additional experiments are now required to investigate in better detail the changes of Ca-Pv velocity at more extreme conditions.

Data availability

Raw data were collected at the European Synchrotron Radiation Facility in Grenoble and are available from <https://doi.org/10.5285/6db95d87-365f-4018-abec-00e96e8fc8d>. Derived data from this study, which includes source data for Figs. 2 and 3 and Extended Data Figs. 1 and 5, are provided in the Supplementary Tables.

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Author contributions A.R.T. designed, performed and analysed the experiments, gathered data from the literature and wrote the manuscript. W.A.C. designed and developed the experimental procedure at ID06 of the ESRF. I.G.W. assisted with interpretation and refinement of diffraction data. J.P.B., D.P.D., W.A.C. and N.C.S. helped perform experiments over two sessions at the ESRF. J.M.R.M. performed the computational simulations. S.A.H. assisted with data analysis. All authors contributed to the scientific discussion and preparation of the manuscript.

Competing interests The authors declare no competing interests.

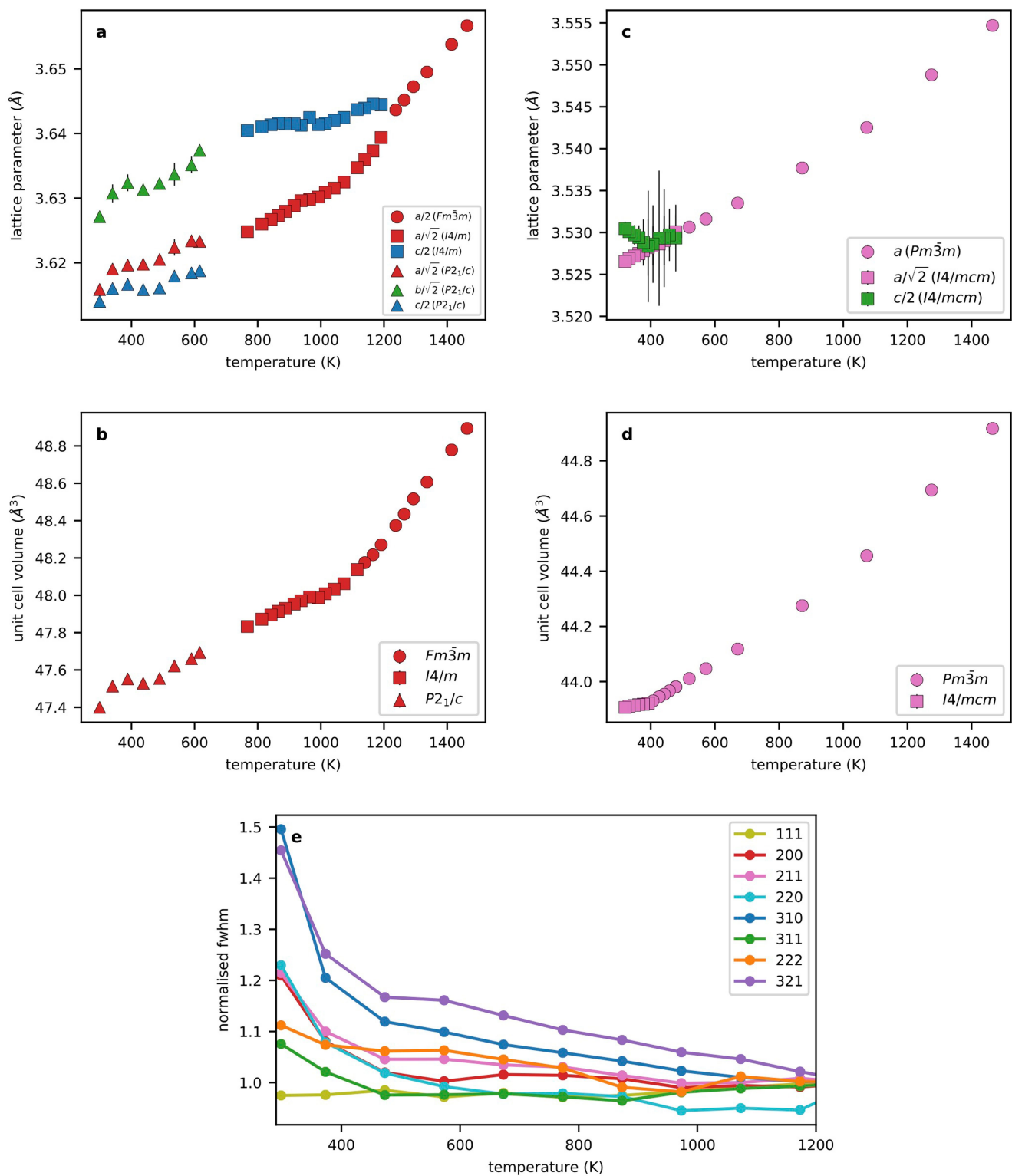
Additional information

Supplementary information is available for this paper at <https://doi.org/10.1038/s41586-019-1483-x>.

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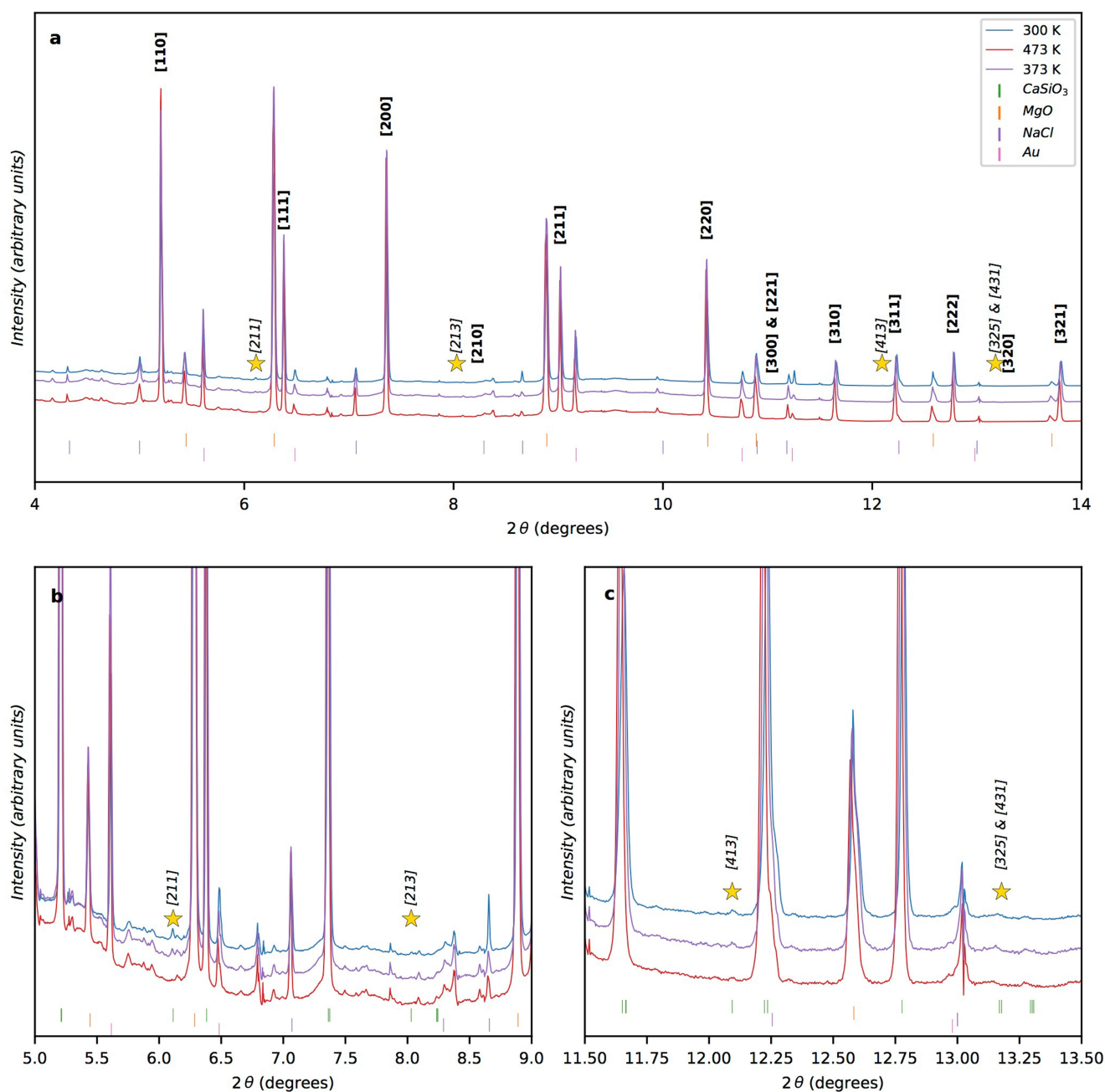
Peer review information *Nature* thanks Ian Jackson and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

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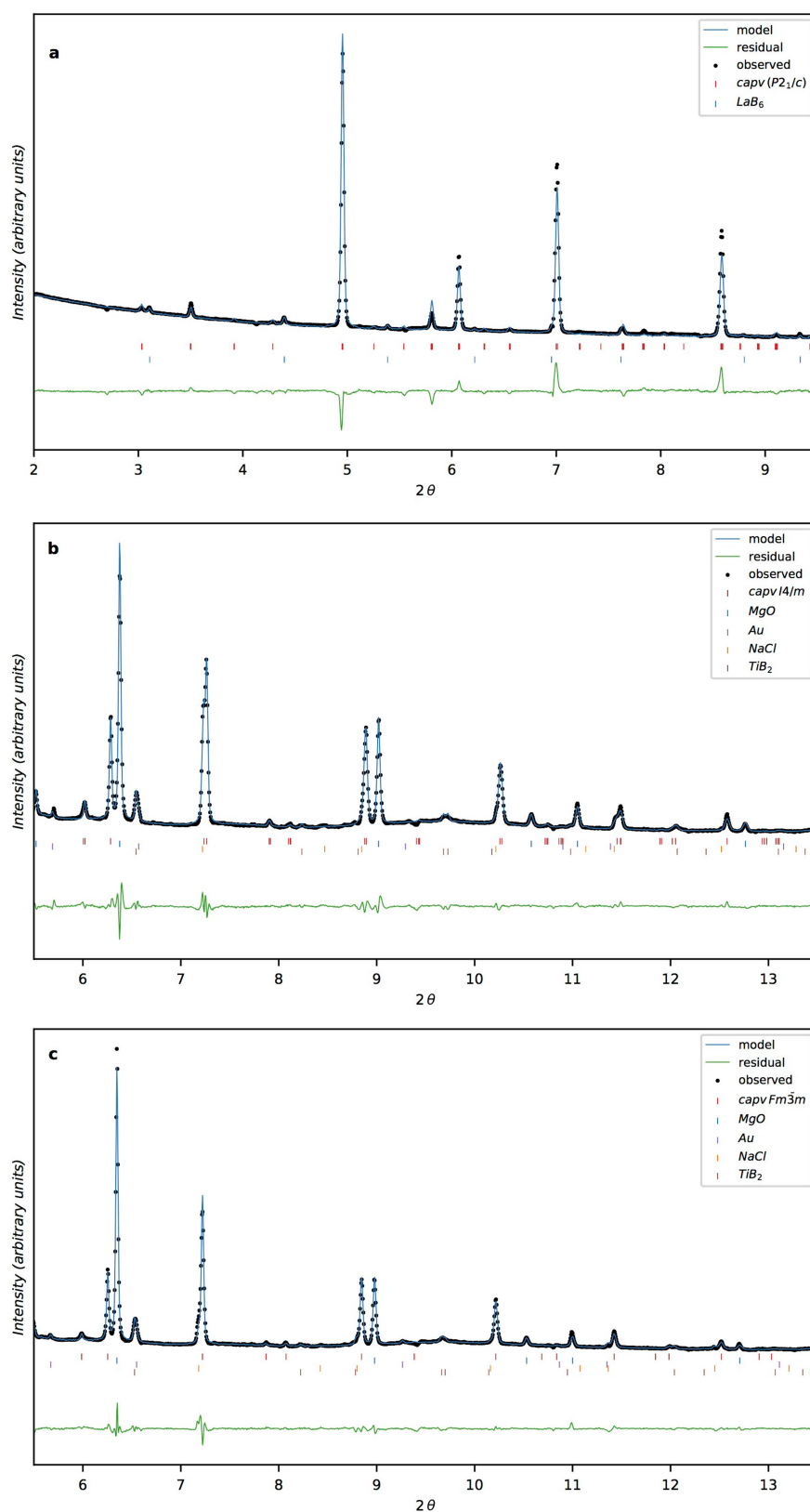
Extended Data Fig. 1 | Lattice and diffraction peak parameters for CaSiO_3 and $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ perovskite. a–d, Refined lattice parameters and pseudo-cubic unit cell volumes from $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ (a, c) and CaSiO_3 (b, d) plotted as a function of experimental temperature with 2σ

uncertainties. e, Full-width at half-maximum (FWHM) of diffraction peaks (see key) of the CaSiO_3 perovskite sample, normalized to the FWHM at high temperature, measured at 100 K intervals in a separate experiment to that in Fig. 2.



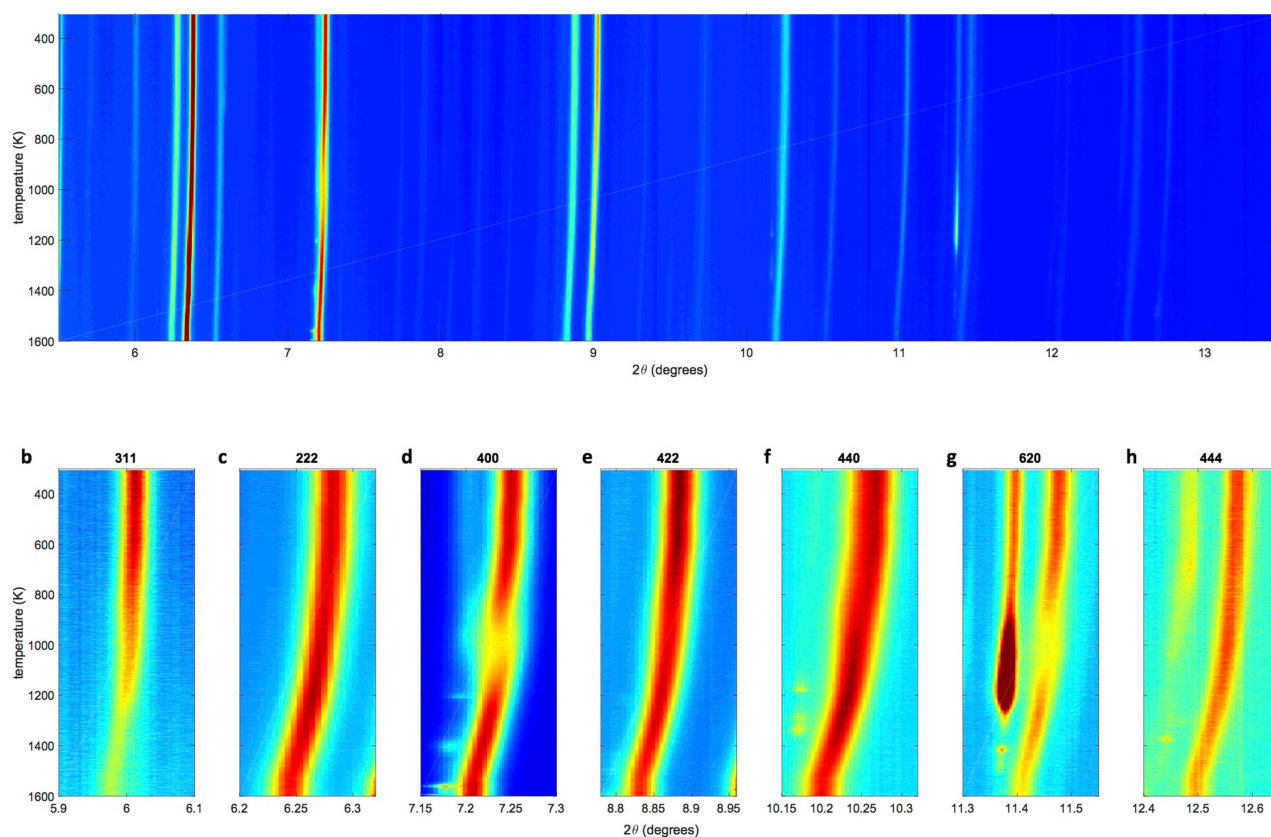
Extended Data Fig. 2 | X-ray diffraction patterns from CaSiO_3 perovskite. Shown are stacked diffraction patterns of CaSiO_3 perovskite; each panel shows data at 300 K, 373 K and 473 K (see key in **a**). **a**, Full patterns; **b**, **c**, patterns limited in the 2θ range to allow indication of weak superlattice peaks. The positions of the diffraction peaks from the Ca-Pv sample, MgO, NaCl and Au are indicated by markers—other small peaks are from boron epoxy and/or furnace components. Cubic Ca-Pv peaks

are labelled with indices, hkl , in bold. The diffraction patterns reveal the appearance of small superlattice reflections at $T = 373$ K and 300 K at 2θ values of about 6.1° , 8.05° , 12.1° and 13.2° (we note there is believed to be an additional superlattice reflection obscured at $2\theta = 10.5^\circ$) labelled with hkl indexed on the tetragonal ($I4/mcm$) unit cell and marked with gold stars.



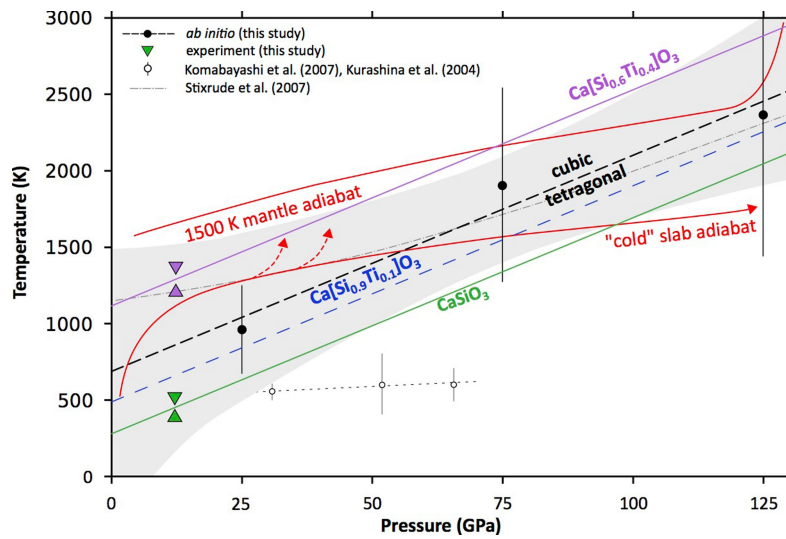
Extended Data Fig. 3 | Refined X-ray diffraction patterns from $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ perovskite. a–c, Rietveld refinements of $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ samples: a, in $P2_1/c$ with LaB_6 calibrant, at 300 K and ambient pressure; b, in the tetragonal $I4/m$ structure (with other cell components) at 890 K and high pressure (about 12 GPa); and c, in $Fm\bar{3}m$ at 1,336 K and high

pressure (12 GPa). In each panel, the black dots are the collected data, the blue curve the model pattern and the green curve the residual. The coloured tick-marks indicate the positions of diffraction peaks of each phase.



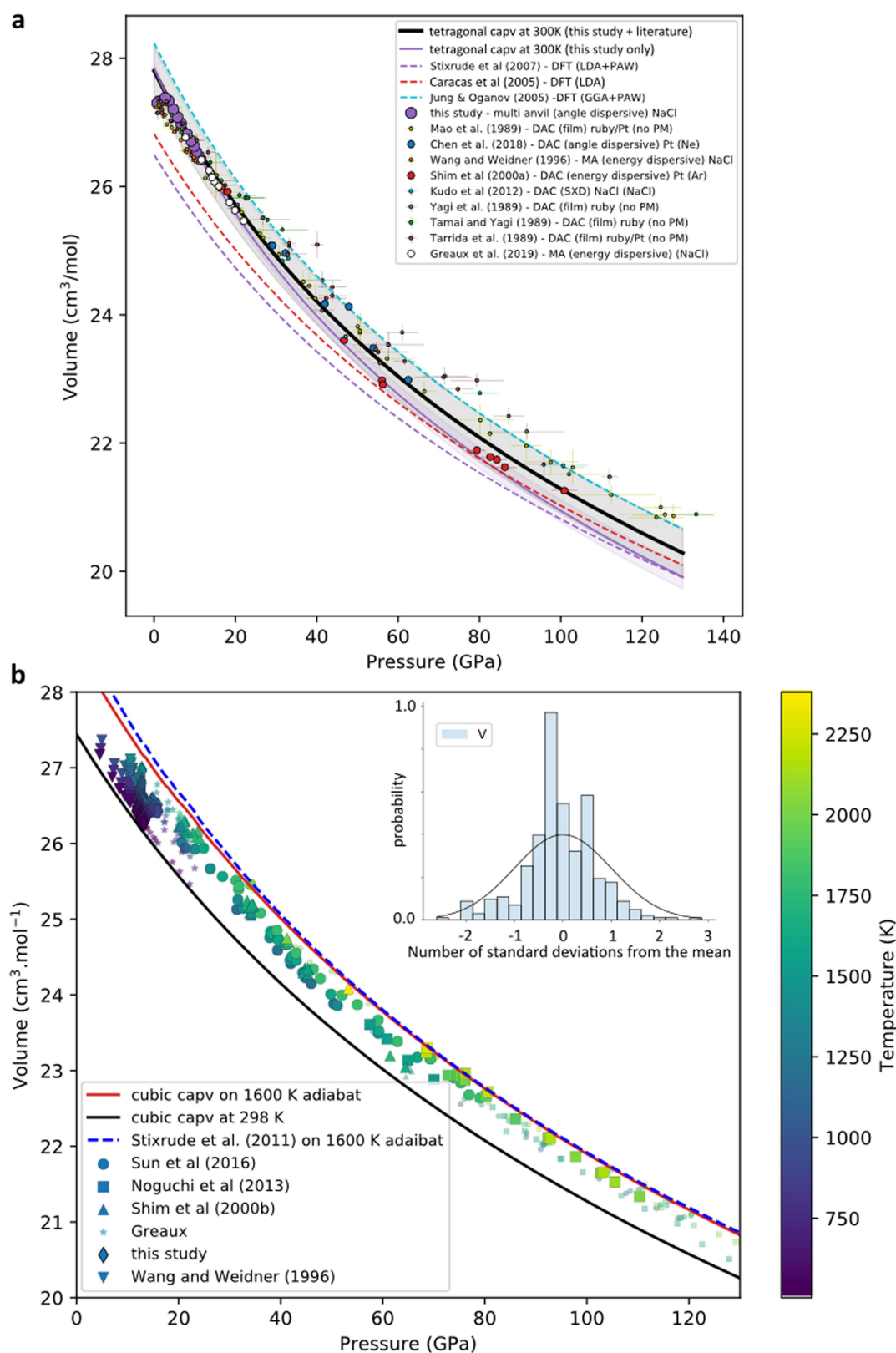
Extended Data Fig. 4 | X-ray diffraction patterns from $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ perovskite. **a**, Complete diffraction pattern of the $\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ sample as a function of temperature at about 12 GPa, with diffraction intensity indicated by colour scaling. **b–h**, Magnified panels from **a** focusing on the temperature evolution of the 311, 222, 400, 422, 440,

620 and 444 diffraction peaks (**b–h**, respectively; indexed using a cubic lattice with $a \approx 7.3 \text{ \AA}$), demonstrating the change in thermal expansivity between cubic and tetragonal/monoclinic structures, and allowing visual identification of the observed phase transitions.



Extended Data Fig. 5 | Phase diagram of calcium perovskite throughout the mantle from ab initio simulations and experiments. Shown is the cubic-tetragonal transition extrapolated throughout the mantle based on ab initio (solid circles) and experimental (triangles) constraints from this study. Vertical error bars (1σ) and the grey envelope (80% confidence interval) represent the uncertainty in computational results from this

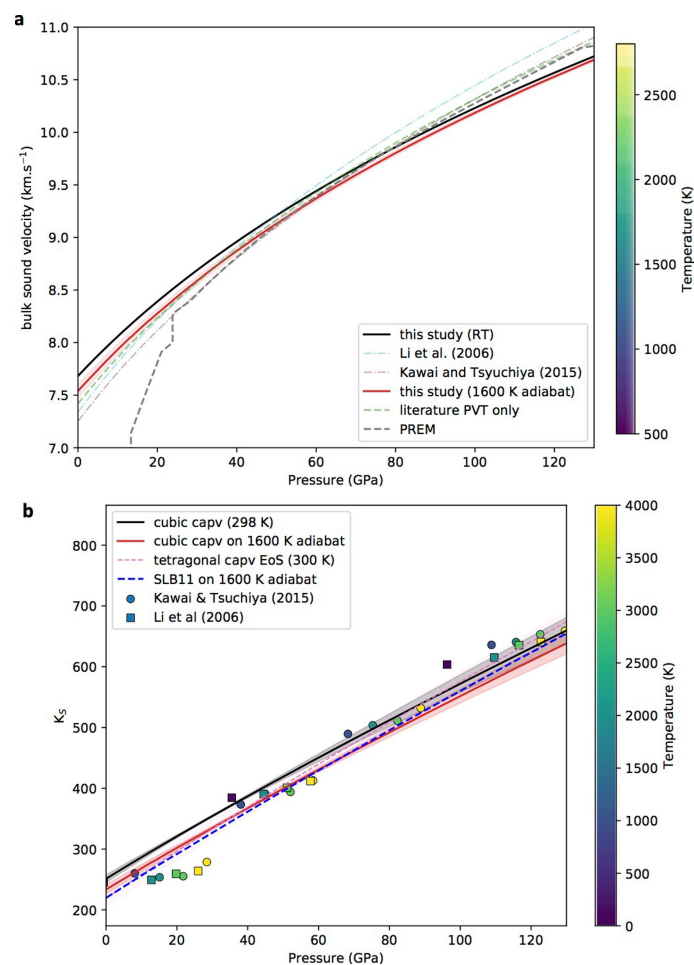
study. A 1,500 K mantle adiabat and cold slab temperature profile are plotted as red curves, with dashed red arrows indicating the warming occurring during slab stagnation at 700–1,000 km depth. Results from previous experimental^{18,23} and computational³ studies are plotted as open symbols and grey curves, respectively.



Extended Data Fig. 6 | Equations of state for CaSiO_3 perovskite.

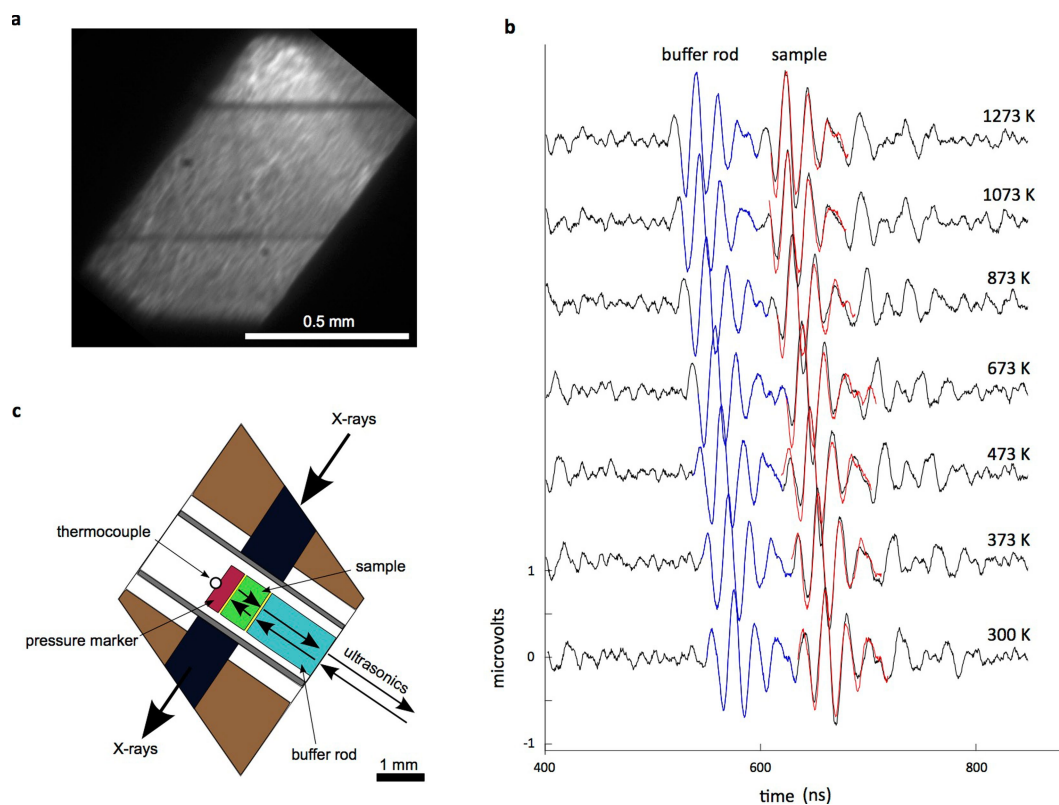
a, PV EoS for tetragonal CaSiO_3 at 300 K, fitted to data from this study only (purple line) and combined with data from previous studies (thick black curve). Only data with large symbols, those that used pressure transmitting media, have been included in fitting the EoS. All small symbols are from experiments that did not employ a pressure-transmitting medium so have been excluded as volumes are expected to be affected by residual sample stress. Additionally, data from Wang et al.⁴⁷ were excluded as they used energy dispersive diffraction in the large volume press, which can be subject to larger uncertainties in volume. Error bars

represent pressure and volume uncertainties as reported in previous studies. Computational EoS for tetragonal Ca-Pv are plotted as dashed curves for comparison^{3,17,19,45,47,59–64}. **b**, PVT EoS for cubic CaSiO_3 perovskite at 298 K and along a 1,600 K adiabat fitted to data from this and previous studies. Small, partially transparent symbols are literature data that were not included in the fitting, either due to falling below the calculated slope of the cubic–tetragonal transition (Methods) or due to concerns about data accuracy. The inset histogram shows the, approximately normal, distribution for the residuals for the fitted data compared with the best-fit model, demonstrating the lack of outliers^{45–48}.



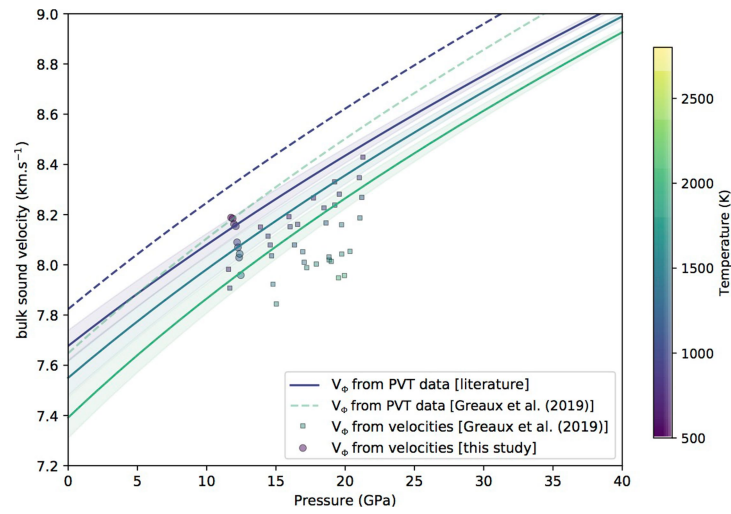
Extended Data Fig. 7 | Bulk sound velocity and bulk modulus of CaSiO₃ perovskite. **a**, Bulk sound velocity of Ca-Pv predicted from the EoS in this study along a 1,600 K mantle adiabat and at 300 K, compared with results from previous computational studies on a 1,600 K adiabat⁴⁻⁶, a fit to previously published *PVT* diffraction data, and PREM¹⁵. **b**, The

adiabatic bulk modulus of CaSiO₃ perovskite calculated at 300 K and along a 1,600 K mantle adiabat using the finite strain model from this study, compared with thermodynamic results in Stixrude et al.⁶ and previous high-temperature computational studies^{4,5}.



Extended Data Fig. 8 | Exemplar radiographic image, ultrasonic data and schematic of the experimental cell design. a, Example of synchrotron radiographic image in plan view used to measure sample length in a

$\text{Ca}[\text{Si}_{0.6}\text{Ti}_{0.4}]\text{O}_3$ sample. **b**, Ultrasonic signals from the 'runa' experiment on a CaSiO_3 sample. **c**, Cross-section of the experimental assembly (to scale) used in ultrasonic experiments throughout this study.



Extended Data Fig. 9 | Comparison of bulk sound velocity from diffraction and ultrasonic measurements. Shown is a comparison of bulk sound velocity calculated from *PVT* EoSs, fitted to literature diffraction data (solid curves) with 2σ uncertainties shown by shaded regions, and only to that reported by Gréaux et al.²⁰ (dashed curves),

with bulk sound velocities calculated from ultrasonic measurements via $v_{\text{bulk}} = (v_p^2 - 4/3 v_s^2)^{0.5}$ for data from Gréaux et al.²⁰ (squares) and this study (circles). All curves and symbols are coloured for temperature (colour scale at right).