that anomalous diffusion can displace the sulphuric acid spikes that are used as stratigraphic markers to correlate timescales between different ice cores and the tephra deposits contained in other sedimentary records \(^2\). Our model explains how diffusion preserves the amplitudes of anomalies in the \(c_0\) record, but the anomalies themselves are translated relative to the surrounding ice. Efforts should be made to account for this behaviour when analysing data from the older portions of ice cores by increasing spatial resolution. This could be particularly important when the relative timing of concentration peaks is needed to test theories for the causal links between the various climate proxies.

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**The post-spinel transformation in Mg$_2$SiO$_4$ and its relation to the 660-km seismic discontinuity**

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The 660-km seismic discontinuity in the Earth’s mantle has long been identified with the transformation of (Mg,Fe)$_2$SiO$_4$ from γ-spinel (ringwoodite) to (Mg,Fe)$_2$SiO$_4$-perovskite and (Mg,Fe)O-magnesiowüstite. This has been based on experimental studies of materials quenched from high pressure and temperature$^\ddagger$, which have shown that the transformation is consistent with the seismically observed sharpness and the depth of the discontinuity at expected mantle temperatures. But the first in situ examination of this phase transformation in Mg$_2$SiO$_4$ using a multi-anvil press$^\ddagger$ indicated that the transformation occurs at a pressure about 2 GPa lower than previously thought (equivalent to ~600 km depth) and hence that it may not be associated with the 660-km discontinuity. Here we report the results of an in situ study of Mg$_2$SiO$_4$ at pressures of 20–36 GPa using a combination of double-sided laser-heating and synchrotron X-ray diffraction in a diamond-anvil cell. The phase transformation from γ-Mg$_2$SiO$_4$ to Mg$_2$SiO$_4$-perovskite and MgO (periclase) is readily observed in both the forward and reverse directions. In contrast to the in situ multi-

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**Figure 1 a–e. Representative X-ray diffraction patterns at the indicated P–T conditions. Peak identifications are: Rw, ringwoodite; Pv, perovskite; Pc, periclase; Pt, platinum; Ar, argon; asterisk, platinum fluorescence; e, detector escape peak.**
anvil-press study, we find that the pressure and temperature of the post-spinel transformation in Mg$_2$SiO$_4$ is consistent with seismic observations for the 660-km discontinuity.

Pure synthetic forsterite was mixed with 10 wt% platinum which serves as an internal pressure scale and laser absorber. A 15-µm-thick foil of the sample mixture was loaded in a 100-µm hole in a steel gasket and compressed by 300-µm diamond anvils. Argon served as a pressure transmitting and insulation medium. Ruby chips were also loaded in an unheated area.

The laser-heating system at the GSECARS sector of the Advanced Photon Source provides a radially homogeneous temperature profile over 20–30 µm by using a TEM$_{00}$ Nd:YLF laser mode, and reduces the axial thermal gradient by heating from both sides. Temperature profiles were measured using imaging spectrometers on each side. Temperature was determined by fitting the radiation spectra, corrected for system response, to Planck’s equation. A three-dimensional averaging technique was used to calculate the mean temperature over the volume exposed to X-rays. Including radial and axial gradients, temperature fluctuations during X-ray exposure, and the fitting residual, the temperature uncertainty (1σ) was ±50–150 K in these experiments.

Energy dispersive X-ray diffraction measurements were performed using a small (5 µm × 7 µm) horizontally focused X-ray beam and a solid-state detector (Fig. 1). We oscillated the diamond cell (±20°) about its loading axis to minimize the effect of preferred orientation. The primary pressure scale used here is the pressure–volume–temperature (P–V–T) equation of state (EOS) of platinum. Pressure was also measured using the ruby scale before and after heating.

Below 20 GPa, we performed two heating runs to synthesize ringwoodite. The pressure was then increased to 20.4 GPa and a third run was performed. We observed an increase of 2–4 GPa during heating due to the thermal pressure (Fig. 1). After 20 minutes of heating, the pericline (200) peak appeared and co-existed with ringwoodite diffraction lines. By increasing the temperature from 1,672(50) K to 1942(75) K (numbers in parentheses are 1σ uncertainties), we observed a pressure decrease from 24.6(4) GPa to 22.3(6) GPa as a result of thermal relaxation (P–V–T path for run 3 in Fig. 2). At this point, the pericline (200) line disappeared, owing to back transformation to the lower-pressure phase. In the fourth run, we increased pressure to 23.1 GPa (Fig. 1a). After eight minutes of heating, diagnostic perovskite lines, (002)+(110) and (004)+(220) doublets, appeared (Fig. 1b). The pericline (200) line was also observed in other patterns during this run. We performed two more runs at 25–29 GPa (run 5 in Fig. 2) and 30–35 GPa, where we observed complete transformation from ringwoodite to perovskite+pericline (Fig. 1c). To observe the transformation from perovskite+pericline to ringwoodite, we decreased pressure and performed three heating runs at 27–30, 25–26 and 21–25 GPa. For the last run, ringwoodite appeared after 6 minutes of heating and the transformation was complete after 24 minutes (Fig. 1d, e). Additional details regarding the P–T paths are provided in the Supplementary Information.

We observe that the low- and high-pressure phase assemblages coexist within a range of about 2 GPa (Fig. 2). This scatter is due to both temperature uncertainty and kinetic effects. The temperature uncertainty is 50–150 K, and this propagates to a pressure uncertainty of 0.3–0.9 GPa. Kinetics and the P–T path may also be important. For example, as shown above in the P–T path for run 3 (Fig. 2), we observed that the high-pressure assemblage synthesized above the phase boundary can survive at slightly below the phase boundary for 5 minutes before complete back transformation.

Using data points for which we observed a mixture of low- and high-pressure phases, we obtained the phase boundary. We fixed the slope of the phase boundary to the average from two multi-anvil studies (–2.75 MPa K$^{-1}$), because our data scatter precludes constraining the slope reliably. A weight was assigned to each data point using its pressure and temperature uncertainties. The transformation pressure was found to be 23.7 ± 1.1 GPa at 1,800 K. However, the boundary obtained in ref. 5 is 2.6 GPa lower than this, which is a statistically significant difference at the 2σ level (Fig. 2).

In order to examine this result, we investigated several error sources. In the laser-heated diamond cell, the greatest error source is the temperature uncertainty. The error in temperature propagates to pressure through the thermal-pressure term. The sensitivity of pressure for temperature, (δP/δT)$_p$, is calculated for platinum using its P–V–T EOS. To have a 2.6-GPa error, the temperature must be overestimated by 380 K. However, including all random error sources, our temperature uncertainty is less than 150 K. Systematic error sources have also been examined, and are estimated to be less than 100 K for this heating system. Using lattice strain theory, we...
differential stresses were also investigated and found to be negligible at high temperature.

We also compared pressures obtained from different materials in our sample, such as periclase and ringwoodite. On average, the platinum pressure scale overestimates pressure by 0.2 GPa compared to periclase and by 2.0 GPa compared to ringwoodite. We also examined the difference between platinum and ruby pressures before and after heating. On average, platinum yields a larger pressure by ~1.2 GPa. However, the ruby chips were located at the edge of the sample chamber where the pressure should be lower, owing to the radial gradient. Thus, except for ringwoodite, all pressures are internally consistent within 1.2 GPa.

One possibility for the discrepancy between our result and those of Izumi et al. is the inconsistency of the equations of state of platinum and gold. Izumi et al. justifi ed the use of the gold pressure scale of ref. 18 on the basis of an earlier study that found good agreement between the gold EOS of Anderson et al. and the periclase EOS by Jamieson et al. In our study, we observed that the platinum pressure scale by Holmes et al. shows good agreement with the periclase pressure scale by Speziale et al. Thus by comparing the periclase EOS values, we can obtain an intercomparison of gold and platinum. Figure 3 shows the difference between the periclase EOS of Jamieson et al. and Speziale et al.

We observe a maximum difference of 2.1 GPa between the two periclase pressure calculations at P–T conditions of the post-spinel transformation. This means that the gold EOS yields ~2 GPa lower pressure than the platinum EOS. We also observed a 2 GPa underestimation of pressure by the ringwoodite EOS, which was also obtained using the gold pressure scale of ref. 18.

The discrepancy between the two periclase scales is mainly caused by the use of different Grüneisen parameters. As shown in Fig. 3, the discrepancy decreases drastically just by changing the Grüneisen parameter used by Speziale et al. (1.52 ± 0.05) to the value used by Jamieson et al. (1.32). The former workers obtained the Grüneisen parameter using a thermodynamic relationship, γ = αKs/ρCp (α is the thermal expansivity, Ks is the adiabatic bulk modulus, ρ is the density and Cp is the isobaric heat capacity), and accurately determined thermodynamic parameters, whereas the value used by the latter workers was based on low-accuracy estimates from porous shock wave data. In addition, the EOS of Speziale et al. satisfies a wide range of high P–T data including static compression and shock wave data.

A recent study by Ng et al. that intercompared pressure standards suggested that the gold and platinum pressure scales are consistent. However, this study also found that various different standards yield pressures that differ by ~2 GPa at 24 GPa. We also note that Anderson later concluded that the gold EOS may not be reliable. These results emphasize the need for further studies of pressure standards. Other possible sources of systematic errors—such as the effect of pressure on the thermocouple e.m.f. in multi-anvil studies, temperature gradients, deviatoric stress, and stress inhomogeneity—also need to be investigated.

Phase boundaries for mantle minerals determined using in situ techniques at pressures near 660-km depth are shown in Fig. 4. Apart from this work, all determinations were performed in the multi-anvil press using the gold scale of Anderson et al. The post-spinel and post-ilmenite boundaries yield low temperatures (< 900 K) at 660-km depth. However, a variety of geophysical constraints including xenoliths, basalt melting temperatures, and in situ data for the α–β transformation in Mg2SiO4 suggest that transition zone temperatures are ~1,600–1,900 K (refs 27–29). At these temperatures, the post-spinel boundary would occur at ~610-km depth. Because no discontinuity is observed near here, this would place severe limits on the olivine abundance of the transition zone and further require that the 660-km discontinuity be associated with a chemical change or the garnet–perovskite transformation. However, seismological data suggest the 660-km discontinuity does not prevent the penetration of subducting slabs. Furthermore, to associate the post-garnet boundary with the 660-km discontinuity, aluminium enrichment relative to pyrolite is required. Although the thickness and depth of this boundary will be affected by bulk composition, the slope of the post-garnet boundary conflicts with the seismically observed negative Clapeyron slope of the 660-km discontinuity. In contrast, our observations of the post-spinel transformation are fully consistent with geophysical data for the 660-km discontinuity.

We have thus shown that the laser-heated diamond-anvil cell can accurately determine phase boundaries of mantle constituents. We find that the post-spinel phase boundary lies within a plausible mantle temperature range at 660 km depth, and thus this transformation remains the best candidate to explain this seismic discontinuity.

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Figure 4 Seismic velocity profiles and phase boundaries of mantle constituents near the 660-km discontinuity. Top, P-wave and S-wave velocities as a function of depth in the Earth. Data from earth model AK135 (ref. 6). Bottom, phase boundaries of mantle constituents (solid lines, dashed where extrapolated). The post-ilmenite (II–Pv, where II indicates ilmenite and Pv indicates perovskite) boundary is from ref. 31. The post-garnet (Gt–Pv) transformation with 6 mol% Al2O3 (from ref. 24) is plotted as a shaded area where majorite garnet (Gt) and perovskite coexist. The post-spinel (Rw–Pv+Pc, where Rw indicates ringwoodite and Pc indicates periclase) boundaries are from ref. 5 and this study.
High-pressure polymorphs of olivine and the 660-km seismic discontinuity

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It had long been accepted that the 400-km seismic discontinuity in the Earth’s mantle results from the phase transition of (Mg,Fe)$_2$SiO$_4$-olivine to its high-pressure polymorph β-spinel (wadsleyite), and that the 660-km discontinuity results from the breakdown of the higher-pressure polymorph γ-spinel (ringwoodite) to MgSiO$_3$-perovskite and (Mg,Fe)O-magnesiowüstite$^{–4}$. An in situ multi-anvil-press X-ray study$^{2}$ indicated, however, that the phase boundary of the latter transition occurs at pressures 2 GPa lower than had been found in earlier studies using multi-anvil

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**Supplementary information** is available on Nature’s World-Wide Web site (http://www.nature.com) or as paper copy from the London editorial office of Nature.

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**Figure 1** Diamond-cell arrangements used in this study to heat samples of Mg$_2$SiO$_3$-forsterite. a, Schematic cross-section. Samples were polished disks of pure, synthetic Mg$_2$SiO$_3$-forsterite, 10–15 μm thick and with diameters of 20 to 100 μm, thermally insulated from the bottom diamond by grains of forsterite. Argon or CaCl$_2$ were used as pressure media. The pressure chambers were typically 170–180 μm in diameter and 45–55 μm in thickness. The samples were either heated directly with a 150 W CO$_2$ laser (λ = 10.6 μm), or were sputtered with films of Mo, Re or Cr (<1 μm thick) and then heated with a 50 W YLF (yttrium-lithium-fluoride) laser (λ = 1.05 μm)—and in some experiments with the combined beams of an additional 20 W YLF laser. b, Molybdenum-sputtered forsterite sample after heating. The heated portion showed full conversion to γ-Mg$_2$SiO$_3$. Thermal pressure increase was measured from two adjacent grains of ruby and strontium borate excited with an argon laser. c, Small crystal (15–20 μm in size) inside a Re microfurnace with outer diameter 80 μm, inner diameter 20 μm, and a thickness of 30 μm. This furnace was uniformly heated with the YLF laser in an argon pressure medium. This heating method essentially eliminated temperature gradients in the sample.
Mantle cookbook calibration
Craig R. Bina

Doubts about a fundamental model of the chemistry of Earth’s deep interior have now been transmuted into doubts about a standard used to calibrate these studies — gold’s equation of state.

The properties of the Earth’s mantle change abruptly 660 km below the surface, with sharp rises in both density and the transmission speed of seismic waves created by earthquakes. But in 1998 it was announced that highly sophisticated laboratory experiments had failed to confirm this 660 km transition — instead, seeming to place the mineral transformation concerned at 600 km. Elsewhere in this issue, Chudinovskikh and Boehler, and Shim et al., describe how they have revisited the question. The news they report is both reassuring and disturbing.

For decades, the global 660-km seismic discontinuity has been thought to coincide with the chemical reaction γ+pv + mw, in which the mineral γ-(Mg,Fe)2SiO4 (also called ringwoodite or silicate spinel) breaks down to a mixture of pv-(Mg,Fe)2SiO4 (silicate perovskite) and mw-(Mg,Fe)O (magnesiowüstite, also called ferropericlase) at high pressures. This view was supported by experiments in which the reaction occurred at pressures and temperatures believed to be appropriate to 660 km depth. In these experiments, samples were subjected to high pressures and temperatures inside diamond-anvil and multi-anvil devices, and were then cooled quickly and removed for analysis — a bit like looking at one’s baking after removing it from the oven and allowing it to cool.

In 1998 Irifune et al. used synchrotron X-rays to peer through the oven door and observe the baking in situ. But consternation greeted their report that the γ+pv + mw transition took place at pressures about 2 gigapascals (GPa) lower than expected, equivalent to a depth of 600 km rather than 660 km. Irifune et al. gave two possible explanations for this result: either their state-of-the-art pressure measurements were in error, or the common model of Earth’s deep chemistry was wrong.

The two new papers describe experiments aimed at resolving the equilibrium pressure of the γ+pv + mw reaction. Using diamond-anvil devices, Chudinovskikh and Boehler (page 574) subjected samples of Mg,SiO2 to high pressures and temperatures, swiftly cooled them to room temperature, and examined them using Raman spectroscopy while still at high pressures. Shim et al. (page 571) do precisely what Chudinovskikh and Boehler suggest in their closing sentence: they examined such samples in situ, at high pressures and temperatures, using synchrotron X-rays. The two groups used different methods of pressure calibration,
but both conclude that the $\gamma \rightarrow $pv + mw transition occurs at pressures and temperatures (about 24 GPa and 1,800–1,900 K) appropriate to 660 km depth. This points to problems in experimental pressure calibration, rather than to a fundamental misunderstanding of the chemistry of Earth's interior. More specifically, it seems that the source of the 2-GPa discrepancy may lie largely in the equation of state (EOS) of gold.

Our estimates of pressures and temperatures inside the Earth are indirect. They come from a variety of sources, and the consistency between them gives us confidence in their validity. But reproducing and measuring these conditions inside a device such as a diamond anvil is no easy matter. In multi-anvil devices, temperatures are measured using thermocouples, and pressures are calibrated by extrapolation from reactions at lower pressures. Irifune et al.'s great advance was to peer through the multi-anvil oven door using intense X-rays, allowing not only observation of the sample in situ, but also direct measurement of pressure by comparing the in situ specific volume of a standard material (gold) to an EOS that specifies its volume as a function of pressure and temperature. In diamond-anvil devices, temperatures are measured from radiation spectra, and pressures are determined from shifts in the fluorescence spectrum of ruby. An in situ approach using intense X-rays allows pressure to be calibrated from the EOS of a standard material — such as gold, or platinum.

Problems arise in choosing an EOS for pressure calibration. As Chudnovskikh and Boehler point out, there are discrepancies between various reference EOS for gold. Indeed, experiments on the ilm $\rightarrow $pv transition on a cousin of the $\gamma \rightarrow $pv + mw transition but occurring in MgSiO$_3$, silicate ilmenite) confirmed that one such EOS (also used by Irifune et al. for their pressure standard) places the transition at pressures 2–3 GPa lower than does another EOS for gold. The platinum pressure standard used by Shim et al., perhaps chosen to avoid the ambiguities of gold, is consistent with this second gold EOS, hence their higher pressures. In other experiments there has been agreement between the gold- and platinum-based pressure scales, but the group concerned appear to have used a different platinum EOS to that used by Shim et al.

The results of all these studies suggest that there are two distinct classes of EOS for pressure calibration — as if there were two different brands of oven thermometers (or rather barometers). One class of EOS yields pressures that place the $\gamma \rightarrow $pv + mw transition at 660 km, whereas the other yields pressures about 2 GPa lower, placing the transition at 600 km. Furthermore, in a sort of EOS contagion, the low transition pressure for the $\gamma \rightarrow $pv + mw reaction reported by Irifune et al. has already been used to calibrate pressures in a study of the ilm $\rightarrow $pv transition. Unsurprisingly, this yields transition pressures about 2 GPa lower than in other studies.

So the controversial 2-GPa (60-km) apparent shift of the $\gamma \rightarrow $pv + mw transition appears to signal disagreements about high-pressure EOS of standard reference materials, rather than a misunderstanding of Earth's internal chemistry. This is both reassuring and disturbing.

It is reassuring because continued study of the transition reveals behaviour that provides a remarkably good match with the observed properties (depth, magnitude, sharpness, fine structure and topographic undulations) of the 660-km discontinuity. If the $\gamma \rightarrow $pv + mw transition occurs instead at 600 km, why is there no seismic discontinuity observed there, and what causes the observed 660-km discontinuity? Such paradoxes would require a radical change in mantle chemistry somewhere between 410 and 600 km deep, which is not observed geophysically.

The disturbing aspect is that, even with the remarkable ability to look inside the oven while it is baking, there is still confusion about the relative calibrations of different pressure scales. Further interlaboratory comparisons are needed, along with assessments of the EOS from other techniques such as calorimetry, spectroscopy and ab initio simulations of material properties.

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