Poirierite, a dense metastable polymorph of magnesium iron silicate in shocked meteorites

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A dense magnesium iron silicate polymorph with a structure intermediate between olivine, ringwoodite, and wadsleyite was theoretically predicted about four decades ago. As this group of minerals constitute the major component of shocked meteorites, constraining their transitional forms and behaviour is of potential importance for understanding impact events on their parent bodies. Here we use high-resolution transmission electron microscopy techniques and single-crystal X-ray diffraction analyses to identify naturally occurring examples of this mineral – recently named poirierite – in shocked chondritic meteorites. We observe nanoscale lamellar poirierite topotactically intergrown within wadsleyite, and additionally within ringwoodite as recently reported. Our results confirm the intermediate structure of poirierite and suggest it might be a relay point in the shear transformations between its polymorphs. We propose that poirierite formed during rapid decompression at relatively low temperature in retrograde shock metamorphism of the meteorites.

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In this study, we report further characterisations of the natural ε phase occurrences in three chondritic meteorites (Tenham, Miami and Suizhou) and discuss its formation mechanisms in shock metamorphism based on transmission electron microscopy, single-crystal X-ray diffraction, and first-principles calculations. ε-Mg2SiO4 has been approved as a new mineral species by the Commission on New Minerals and Mineral Names, International Mineralogical Association (No. 2018-026b), and named as poirierite in honour of Jean-Paul Poirier, who greatly contributed to mineral physics, including the theoretical prediction of ε-Mg2SiO4.

Results

Transmission electron microscopy. The Tenham L6 and Miami H5 chondrites have shock veins containing host rock olivine fragments that are transformed partially or totally into its high-pressure phases (Fig. 1a). In Tenham, euhedral and subhedral ringwoodite grains with sizes of 400 ± 150 nm form polycrystalline aggregates in the shock vein (Fig. 1b). Their Fe/(Mg + Fe) ratio is 0.26 ± 0.01, which is consistent with those of ringwoodite in Tenham in previous studies [Fe/(Mg + Fe) = 0.25 – 0.26], where the chemical composition is nearly the same as the host olivine. These ringwoodite grains are randomly crystallography oriented and exhibit pervasive planar defects on six equivalent planes corresponding to the ε-phase (poirierite) with the space group $Pmna$ (Fig. 2). Moreover, the SAED patterns of ringwoodite with the poirierite lamellae showed that both phases have a totophase relationship: $b_{pol} / <110>_{Rwd}$ and $c_{pol} / c_{Rwd}$. Due to the extremely thin width (<10 nm) of the lamellae, the chemical composition of poirierite could not be obtained.

In Miami, euhedral and subhedral wadsleyite grains with 1200 ± 450 nm size replace olivine grains entrapped into the shock vein (Supplementary Fig. 1a). The wadsleyite grains are randomly crystallography oriented, which is similar to that of ringwoodite in Tenham. Many of the wadsleyite grains [Fe/(Mg + Fe) = 0.24 ± 0.01]
Domain 2 is rotated by 90° along [010]Rwd compared with the orientation of domain 1. The open circles denote diffraction spots from the poirierite caused by dynamical diffraction by the overlying host ringwoodite. From the structural refinement through single-crystal X-ray diffraction (Table 1), poirierite was discovered to have grown in a chondrite sample from Miami that was shocked to sufficient pressure to exhibit planar defects at (010) (Supplementary Fig. 1b). The parts of the wadsleyite grains with stacking faults showed weak diffraction spots corresponding to those of poirierite. The wadsleyite-poirierite intergrowth shows a topotaxy of [010] zone axis and (b) its schematic illustration. The grain contains poirierite in two different but equivalent orientations (domain 1: Poi1, domain 2: Poi2). Domain 2 is rotated by 90° along [010]Rwd compared with the orientation of domain 1. The open circles denote diffraction spots from the poirierite caused by dynamical diffraction by the overlying host ringwoodite. Domain 1 is shown in Supplementary Table 1.

Select-area electron diffraction (SAED) pattern of a ringwoodite grain along the [010] zone axis and (b) its schematic illustration. The grain contains poirierite in two different but equivalent orientations (domain 1: Poi1, domain 2: Poi2). Domain 2 is rotated by 90° along [010]Rwd compared with the orientation of domain 1. The open circles denote diffraction spots from the poirierite caused by dynamical diffraction by the overlying host ringwoodite. a High-resolution transmission electron micrograph showing 0.8 nm fringes corresponding to d_{Po001}.
the ability of poirierite to display a thermodynamically stable phase under high pressures and temperatures. In addition, the DFT calculations results indicate that the structure does not have any phonon frequencies with complex numbers (Supplementary Fig. 5), which suggests that the poirierite is at least dynamically stable. In summary, poirierite can form universally in natural and synthetic samples as a metastable phase.

Polymorphic phase transformations in silicates have nucleation and growth mechanism and shear mechanism. In the former process, the product phase is nucleated mainly at the grain boundaries of the parental phase, and tends to have a granular morphology with random crystallographic orientations. In the latter process, the product phase forms inside the parental grains, and tends to have lamellar or lens shapes. This mechanism involves the spontaneous shearing of the oxygen sublattice associated with slight cation displacements in the parental structure and forces the host and product phases to have topotaxial relationships where their lattices coherently contact (low lattice misfits). Due to the absence of long-range atomic diffusion, the shear mechanism prefers low-temperature conditions. In addition, shear stress can promote the transformation process.

As mentioned previously, ringwoodite, wadsleyite and poirierite are similar because their crystal structures consist of basic structural modules (Supplementary Fig. 4), which can be distinguished by the periodic orientational arrangements of the modules; The ringwoodite and wadsleyite structures have translational periodicity represented by \( \uparrow \downarrow \uparrow \) and \( \uparrow \uparrow \downarrow \), respectively. The poirierite structure consists of a single orientation of the basic structural unit denoted by \( \uparrow \uparrow \uparrow \). Therefore, inter-transformations among these structures are highly likely to occur via the shear mechanism (Fig. 6). Evidence for this mechanism in a ringwoodite-to-wadsleyite transition has been found within a topotaxial lamellar intergrowth in a shocked chondrite. This was further confirmed experimentally via high-pressure experiments with Mg₂SiO₄. Similar processes were also proposed experimentally and

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**Table 1** Refined structure parameters of poirierite in the Suizhou chondrite from single-crystal X-ray diffraction.

| Space group | Pmma |
|-------------|------|
| Lattice parameters | a 5.802(11) Å, b 2.905(9) Å, c 8.411(16) Å |
| Atoms (Wyckoff positions) | Fractional coordinates |
| M1 (2d) (Mg₁.₀₀) | x 0 \( \frac{1}{2} \), y \( \frac{1}{2} \), z 0.0087(5) |
| M2 (2e) (Mg₀.₉₆Fe₀.₀₄) | \( \frac{1}{4} \) 0 0.2175(2), 0.0071(5) |
| T (2f) (Si₁.₀₀) | \( \frac{1}{4} \) \( \frac{1}{2} \), 0.8642(2), 0.0051(3) |
| O₁ (2e) | \( \frac{1}{4} \) 0 0.4693(5), 0.0080(8) |
| O₂ (2e) | \( \frac{1}{4} \) 0 0.9628(5), 0.0056(7) |
| O₃ (4j) | 0.0091(3), \( \frac{1}{2} \), 0.7583(3), 0.0071(6) |
| M₁-O₁ (×4) | 2.069(4) |
| M₁-O₃ (×2) | 2.173(5) |
| mean | 2.104 |
| \( \sigma^2 \) | 28.06 |
| \( \lambda_\text{iso} \) | 1.0089 |
| M₂-O₃ (×4) | 2.100(4) |
| M₂-O₁ | 2.118(6) |
| M₂-O₂ | 2.142(6) |
| mean | 2.110 |
| \( \sigma^2 \) | 23.98 |
| \( \lambda_\text{iso} \) | 1.0068 |
| T-O₃ (×2) | 1.657(3) |
| T-O₂ (×2) | 1.673(4) |
| mean | 1.665 |
| \( \sigma^2 \) | 43.53 |
| \( \lambda_\text{iso} \) | 1.0117 |

\( U_{\text{iso}} \): isotropic atomic displacement parameter, \( \sigma^2 \): bond angle variance, \( \lambda \): quadratic elongation.

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**Fig. 3** Wadsleyite with poirierite lamellae in the Miami chondrite.

- a Bright-field transmission electron microscope (TEM) image of a wadsleyite grain with (010) stacking faults.
- b and c Selected-area electron diffraction patterns obtained from portions (b and c) in (a). Asterisks show direct spots. Weak diffraction spots appear only within the portion with stacking faults. Spots in the dotted circles are from poirierite caused by dynamical diffraction.
- d Bright-field TEM image of a wadsleyite grain, and (e) its selected-area electron diffraction pattern showing topotaxy with poirierite: \( a_{\text{Wds}}/a_{\text{Poi}}, b_{\text{Wds}}/b_{\text{Poi}}, c_{\text{Wds}}/c_{\text{Poi}} \).

**Fig. 4** Relative enthalpies of the Mg₂SiO₄ polymorphs at 0 K as a function of pressure up to 20 GPa. The enthalpies are expressed in rydberg (Ry) units for the Mg₂SiO₄ component.

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![Table 1](https://www.nature.com/commsenv)
those of wadsleyite and ringwoodite were of poirierite were previous single-crystal X-ray diffraction studies. This study revealed that poirierite has a nanoscale melting (Fig. 7). According to thermal conductivity calculations, formed into stable high-pressure phases by the nucleation and occurrences suggest that the olivine grains were initially trans-aggregates with randomly oriented granular grains. These veins in the Tenham and Miami chondrites show polycrystalline supercooled mainly through thermal conduction on the order of the sub-millimetre-width shock veins in the chondrites are showed poirierite has the highest enthalpy among the Mg2SiO4 olivine. This is supported by the enthalpy calculations results that condition, that is within or approximate to the stability field of

![Raman spectra of high-pressure polymorphs of Mg2SiO4 at O K simulated by the first-principles calculations](https://example.com/raman_spectra)

**Fig. 5** Raman spectra of high-pressure polymorphs of Mg2SiO4 at 0 K simulated by the first-principles calculations. The structural parameters of poirierite were fixed at those DFT-optimized in the present study, while those of wadsleyite and ringwoodite were fixed at those determined by previous single-crystal X-ray diffraction studies.

Theoretically in the olivine-ringwoodite transformation and microstructural evidence has been found within a shocked chondrite. This study revealed that poirierite has a nanoscale lamellar morphology and a topotaxial relationship with the hosts ringwoodite and wadsleyite. From these occurrences, the poirierite also appears to have formed from the host phases by the shear mechanisms in shock metamorphism (Fig. 6).

Ringwoodite and wadsleyite in mineral fragments in shock veins in the Tenham and Miami chondrites show polycrystalline aggregates with randomly oriented granular grains. These occurrences suggest that the olivine grains were initially transformed into stable high-pressure phases by the nucleation and growth mechanism in prograde shock metamorphism without melting (Fig. 7). According to thermal conductivity calculations, the sub-millimetre-width shock veins in the chondrites are supercooled mainly through thermal conduction on the order of 10^3 °C/s before the shock pressure release. The lowered shock-vein temperature potentially hinders the back transformations from ringwoodite/wadsleyite to olivine during the retrograde shock metamorphism.

A possible result of the ringwoodite and wadsleyite grains during decompression is their partial transformation into lamellar poirierite via shear mechanisms (Fig. 7). The closer density of poirierite (3.326 g cm\(^{-3}\)) to olivine (3.254 g cm\(^{-3}\)) than wadsleyite (3.501 g cm\(^{-3}\)) and ringwoodite (3.592 g cm\(^{-3}\)) estimated assuming the same iron content [Fe/(Mg+Fe) = 0.02], suggests that poirierite forms at a relatively lower high-pressure condition, that is within or approximate to the stability field of olivine. This is supported by the enthalpy calculations results that showed poirierite has the highest enthalpy among the Mg2SiO4 polymorphs and its value approaches those of ringwoodite and wadsleyite when pressure decreases (Fig. 4).

Recently, in situ X-ray diffraction experiments under laser-shock compression clarified that olivine transforms into a dense structure within nanoseconds. This transformation strongly suggests that the shear mechanism is highly effective at promoting extremely rapid phase transformations, even in low-temperature conditions. Therefore, metastable poirierite would be rapidly formed in the ringwoodite/wadsleyite aggregates by the shear mechanism during decompression (Fig. 7). Vacancy-rich tetragonal silicate spinelloids were recently reported in the Tenham and Suizhou chondrites and the Tissint Martian meteorite. These tetragonal spinelloids occur as submicron-sized granular particles coexisting with (Mg,Fe)SiO\(_3\)-clinopyroxene or -glass in the matrices of the shock veins in Tenham and Suizhou, and in the polymorphs of olivine, pyroxene, and chromite in the melt pockets in Tissint. In Tenham and Suizhou, the occurrences of the tetragonal spineloid indicate that the mineral was crystallised from the shock-induced melt with an approximately bulk meteorite composition. This process would prevent the formation of stable majorite-magnesiowüstite assemblages due to the highly rapid cooling mentioned above. Poirierite formed in solid-state transformation mechanisms from the ringwoodite/wadsleyite aggregates entrapped in the shock-induced melts; therefore, the cooling rates of the aggregates and their surrounding melts would be comparable. However, differences in their chemistries and formation mechanisms resulted in different crystal structures.

X-ray elemental mapping and crystal structure refinement revealed that poirierite in Tenham and Suizhou is depleted in Fe compared to that in the host ringwoodite. This suggests that a nanometre-scale Mg–Fe interdiffusion occurred subsequently after the shear transformation from ringwoodite to poirierite, which is consistent with Fe being more partitioned in the spinel structure (ringwoodite) than in the spinelloid structure (wadsleyite) in high-pressure experiments and shocked chondrites. Poirierite with a spinelloid structures would also prefer the Mg-rich composition over the spinel structure.

The discovery of poirierite further elucidates the new shear-transformation paths in the polymorphic phase transition in olivine (Fig. 6c). The poirierite structure has a similar cation arrangement in each interstice of the close-packed oxygen layers as that within the olivine structure, although olivine and poirierite are composed of hexagonal- and cubic-close-packed oxygen ions, respectively. This structural similarity increases the possibility of a shear mechanism from olivine to poirierite via oxygen layer sliding along the [010] direction on the [001] direction. If this assumption is correct, the olivine-wadsleyite transformation could be enhanced via the poirierite structure by the shear mechanism at low temperature and/or high-stress conditions, such as in shocked meteorites and the Earth’s oceanic slabs subducting into the deep mantle. To test this hypothesis, experimental and theoretical studies and investigations on the presence of poirierite in the olivine in shocked meteorites are currently being performed.

This study confirms the natural occurrences of poirierite and highlights two new pathways for shear transformations associated with nanoscale Fe–Mg interdiffusion among the olivine polymorphs. Further studies of the formation conditions (temperature, pressure, and differential stress) of poirierite will lead to more detailed insights into the shock metamorphism of planetary materials and potentially also into the dynamics of the deep earth. Unusually, a smaller density of poirierite than wadsleyite and ringwoodite is also a key parameter for its formation process.
Methods

Materials. In this study, we examined three chondritic meteorites (Tenham, Miami and Suizhou) via transmission electron microscopy and single-crystal X-ray diffraction.

Tenham: A polished thin section (catalogue number: NSM-MF15737) has been deposited at the Department of Geology and Paleontology, National Museum of Nature and Science, Japan. Tenham is classified as an L6 ordinary chondrite and mainly consists of olivine, low-Ca pyroxene, high-Ca pyroxene, plagioclase, kamacite and troilite. It is highly shocked and comprised of shock veins <1 mm thick. This meteorite contains various types of high-pressure silicate minerals within and in the vicinity of the shock veins: ringwoodite, wadsleyite, majorite, majorite-pyrope garnet, tetragonal majorite, akimotoite, bridgmanite and lingunite.

Miami: This meteorite is classified as an H5 ordinary chondrite and consists mainly of olivine, low-Ca pyroxene, high-Ca pyroxene, plagioclase, kamacite and troilite. A polished thin section includes thin shock veins <200 µm thick. The shock veins in Miami contain abundant high-pressure minerals including wadsleyite and tuite.

Suizhou: A polished thin section of the Suizhou meteorite (catalogue number: 3238/I) has been deposited in the collections of the Museo di Storia Naturale, Università degli Studi di Firenze, Italy. Suizhou is classified as an L6 ordinary chondrite and mainly consists of olivine, low-Ca pyroxene, plagioclase, kamacite and troilite with thin shock veins of <300 µm in thickness. The shock veins in Suizhou contain abundant high-pressure minerals including ringwoodite, majorite, majorite-pyrope garnet, akimotoite, bridgmanite, tuite, schieleite, hemleyite, asimowite and hiroseite.

Electron microscopies. The polished thin sections of the Tenham, Miami and Suizhou chondrites were initially examined with scanning electron microscopes (Hitachi SU1510 at the Kochi Institute for Core Sample Research (KOCHI), Japan Agency for Marine-Earth Science and Technology; JEOL JSM-7100F at the National Institute of Polar Research (NIPR); Zeiss Evo MA15 at the MEMA laboratory of the Università degli Studi di Firenze) to observe the shock veins and fragments of host rocks therein. Portions of ringwoodite and wadsleyite from Tenham and Miami were processed into ultrathin foils ~150 nm thick using a Ga ion beam after the deposition of carbon protection layers in a focused ion beam (FIB) apparatus (Hitachi SMI-4050 at KOCHI). The ultrathin foils were mounted on Cu grids using a micromanipulator equipped with the FIB and studied using a TEM (JEOL JEM-ARM200F at KOCHI) operated at an accelerating voltage of 200 kV. Phase identification of the olivine polymorphs was performed using SAED and the chemical compositions of the samples were obtained using energy-dispersive X-ray spectrometry (EDS) with a 100 mm² silicon drift detector. The Fe/Mg ratios of ringwoodite and wadsleyite were determined using experimental thickness-corrected k-factors obtained from the San Carlos olivine standard. The intensities of the characteristic X-rays of each element were measured using a fixed acquisition time of 30 s, beam spot size of ~100 nm, and beam current of 200 pA. Crystal structure diagnosis was performed via single-crystal electron diffraction considering the d-spacings and the interangles of the reciprocal lattice vectors of the respective unit cells. The reflection conditions based on the symmetry of each crystal were evaluated by considering their dynamical effect on electron diffraction. The details are described in a previous paper.

Fig. 6 Shear mechanisms in polymorphic transformations in (Mg,Fe)_2SiO_4. a and b Simplified polyhedral representations of the ringwoodite (Rwd), wadsleyite (Wds), and poirierite (Poi) structures as viewed along the [1 1 0]_Rwd, [1 0 0]_Wds, and [1 0 0]_Poi [Modified after Madon and Poirier (1983)]. c Shear mechanisms and their representative crystallographic relationships. Two-direction arrows represent the shear transformation mechanisms between the phases. The arrows denote shear mechanisms previously observed in shocked chondrites and high-pressure experiments (blue), Tomioka and Okuchi (2017) and this study (green), and the theoretical model (red), respectively.
Single-crystal X-ray diffraction. Multiphase structure refinement was performed using single-crystal X-ray diffraction data collected on a poirierite fragment intergrown with ringwoodite from the Suizhou chondrite. A small crystal (19 × 22 × 26 μm), hand-picked under a reflected light microscope from a thick section of the Suizhou chondrite, was examined with a Bruker D8 Venture Photon 100 CMOS equipped with graphite-monochromatized MoKα radiation at the CRIST, Università degli Studi di Firenze. The crystal was composed of ringwoodite and poirierite in a proportion (vol.%) roughly estimable as 81(2)/19, respectively. The lattice parameters for the ringwoodite are

\[ a = 8.085(8) \text{ Å}, \quad V = 528.3(8) \text{ Å}^3, \]

and for the poirierite are

\[ a = 5.802(11), \quad b = 2.905(9) \text{ Å}, \quad c = 8.411(16) \text{ Å}, \quad V = 141.8(6) \text{ Å}^3. \]

Intensity integration, standard Lorentz-polarisation, and absorption corrections were performed using the software package APEX3 (Bruker AXS Inc.). Close attention was devoted to the data reduction of the reflections of the two phases given the topotaxial relationship of the minerals as well as Tenham, i.e. \( a_{\text{Poi}} = \frac{1}{2} a_{\text{Rwd}} \) and \( c_{\text{Poi}} = \frac{1}{2} c_{\text{Rwd}} \).

The number of extracted and independent reflections was sufficient for identifying the Fe-Mg space group of ringwoodite and refining its structure—carried out with the program SHELXL-9749 using the atomic coordinates given previously50—and to begin the structure solution of the poirierite. In detail, the observed conditions (λ = 0.71073 Å) for the reflections belonging to the poirierite structure, together with the statistical tests on the distribution of |F| values that strongly indicated the presence of an inversion centre \([I^2 = 1 - 0.965]\), pointed to the space group \( Pnma \) (Supplementary Table 1). The structure solution was then initiated in this space group. The positions of most of the atoms (all the cation positions and most of the O atoms) were determined through direct methods56. A least-squares refinement on \( F^2 \) using these positions and isotropic temperature factors produced an R factor of 0.085. Three-dimensional difference Fourier synthesis yielded the position of the remaining oxygen atoms. The program SHELXL-9749 was used for the refinement of the poirierite structure. Site-scattering values for two phases were refined using scattering curves for neutral species59 as follows: Mg vs. Fe at the Mg sites, Si vs. O (vacancy) at the tetrahedral sites and O vs. Si at the anion sites. For both phases, the O sites were fully occupied, and the occupancy factors were then fixed to 1.00. An isotropic model for both phases led to \( R_1 = 0.024 \) for 62 observed reflections \( |F_o| > 4|\sigma(F_o)| \) and \( R_1 = 0.029 \) for 117 observed reflections \( |F_o| > 4|\sigma(F_o)| \) for poirierite and ringwoodite, respectively. The detailed results of the crystal structure refinement are presented in the supplementary information as a Crystallographic Information File (CIF) (Supplementary Data 1).

First-principles calculations. The first-principles calculations based on the density functional theory (DFT) on poirierite and the known Mg2SiO4 polymorphs were performed using the Quantum Espresso code37. The crystal structure of poirierite at 0 K was optimised using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation density functional and norm-conserving pseudopotentials43 with an energy cutoff of 120.0 Ry with 12 × 20 × 8 k-point grids where space group is \( Pmna \). The parameters (lattice parameters and atomic positions) of the poirierite structure model, which were proposed in a previous topological study71,72, were used as initial parameters for the DFT calculations. Relative enthalpies of the Mg2SiO4 polymorphs were calculated using the PBE exchange-correlation density functional. Projector augmented wave method with an energy cutoff of 100.0 Ry and \( 2 \times 4 \times 2, 2 \times 2 \times 4, 2 \times 4 \times 2, 3 \times 3 \times 2 \) k-point grids were adopted for poirierite (2 × 2 × 1 super cell), forsterite, wadsleyite and ringwoodite, respectively.

Phonon dispersions of poirierite were calculated using the PBE exchange-correlation density functional. Norm-conserving pseudopotentials with an energy cutoff of 120.0 Ry with 12 × 20 × 8 k-point grids. Raman spectrum calculations of poirierite, wadsleyite and ringwoodite were performed with the local density approximation for exchange-correlation due to the ability of the Quantum Espresso code in the calculations. Norm-conserving pseudopotentials with an energy cutoff of 120.0 Ry with 12 × 20 × 8, 12 × 12 × 12, and 20 × 20 × 20 k-point grids were adopted for poirierite, wadsleyite and ringwoodite, respectively. The structural parameters of poirierite were fixed at those DFT-optimised in the present study, while those of wadsleyite and ringwoodite were fixed at those determined by previous single-crystal X-ray diffraction studies35,51.

Data availability

SEI and TEM micrographs and DFT calculation results in this paper are available at https://zenodo.org/record/4284231. The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 2049451. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

1. Ito, E. & Katsura, T. A temperature profile of the mantle transition zone. Geophys. Res. Lett. 16, 425–428 (1989).
2. Pearson, D. G. et al. Hydrous mantle transition zone indicated by ringwoodite included within diamond. Nature 507, 221–224 (2014).
3. Tomioka, N. & Miyahara, M. High-pressure minerals in shocked meteorites. Meteorit. Planet. Sci. 52, 2017–2039 (2017).
4. Bruns, R. A., Davis, R. J. & Reed, S. J. B. Ringwoodite, natural (Mg, Fe)2SiO4, spinel in the Tenham meteorite. Nature 221, 943–944 (1969).
5. Price, G. D., Putnis, A., Agrell, S. O. & Smith, D. G. W. Wadsleyite, natural β-(Mg,Fe)2SiO4 from the Peace River meteorite. Canad. Mineral. 21, 29–53 (1983).
6. Ma, C. et al. Ahrenhite, γ-Fe2SiO4, a new shock-metamorphic mineral from the Tissint meteorite: Implications for the Tissint shock event on Mars. Geochim. Cosmochim. Acta 184, 240–256 (2016).
7. Bindi, L. et al. Discovery of asimowite, the Fe-analog of wadsleyite, in shock-melted silicate droplets of the Suizhou L6 and the Quebrada Chimborazo 001 CB3.0 chondrites. Amer. Mineral. 104, 775–778 (2019).
8. Xie, Z. & Sharp, T. G. Host rock solid-state transformation in a shock-induced melt vein of Tenham L6 chondrite. Earth Planet. Sci. Lett. 254, 433–445 (2007).
9. Miyahara, M. et al. Evidence for fractional crystallization of wadsleyite and ringwoodite from olivine melts in chondrules entrained in shock-melt veins. Proc. Natl. Acad. Sci. USA 105, 8542–8547 (2008).
10. Feng, L., Lin, Y., Hu, S., Xu, L. & Miao, B. Estimating compositions of natural ringwoodite in the heavily shocked Grove Mountains 052049 meteorite from Raman spectra. Amer. Mineral. 96, 1480–1489 (2011).
11. Xie, Z., Li, X., Sharp, T. G. & De Carli, P. S. Shock-induced ringwoodite rims around olivine fragments in melt vein of Antarctic chondrite GRV022321: transformation mechanism. In 43rd Lunar and Planetary Science Conf. (2012).
12. Pettarello, L. et al. From olivine to ringwoodite: a TEM study of a complex deformation mechanism in the mantle transition zone. In 43rd Lunar and Planetary Science Conf. (2012).
13. Xie, Z., Sharp, T. G. & De Carli, P. Estimating shock pressures based on high-pressure minerals in shock-induced melt veins of L chondrites. Meteorit. Planet. Sci. 41, 1883–1898 (2006).
14. Ohtani, E. et al. Formation of high-pressure minerals in shocked L6 chondrite Yamato 791384: constraints on shock conditions and parent body size. Earth Planet. Sci. Lett. 227, 505–515 (2004).
15. Miyahara, M. et al. Coherent and subsequent incoherent ringwoodite growth in olivine of shocked L6 chondrites. Earth Planet. Sci. Lett. 295, 321–327 (2010).
16. Madon, M. & Poirier, J. P. Dislocations in spinel and garnet high-pressure polymorphs of olivine and pyroxene: implications for mantle rheology. Science 207, 66–68 (1980).
17. Madon, M. & Poirier, J. P. Transmission electron microscope observation of α, β and (Mg,Fe)2SiO4 in shocked meteorites: planar defects and polymorphic transitions. Phys. Earth Planet. Inter. 33, 31–44 (1983).
18. Price, G. D. The nature and significance of stacking faults in wadsleyite, natural (Mg,Fe),SiO3 from the Peace River meteorite. Phys. Earth Planet. Inter. 33, 127–137 (1983).

19. Tomioka, N. & Okuchi, T. A new high-pressure form of Mg,SiO3 highlighting diffusionless phase transitions of olivine. Sci. Rep. 7, 17351 (2017).

20. Langenhorst, F., Joreau, P. & Doukhan, J. C. Thermal and shock metamorphism of the Tenham chondrite: a TEM examination. Geochim. Cosmochim. Acta 72, 1835–1845 (1995).

21. Xie, Z., Sharp, T. G. & DeCarli, P. S. High-pressure phases in a shock-induced melt vein of the Tenham L6 chondrite: Constraints on shock pressure and duration. Geochim. Cosmochim. Acta 70, 504–515 (2006).

22. Hyde, B. G., White, T. J., O’Keefe, M. & Johnson, A. W. Structures related to those of spinel and the β-phase, and a possible mechanism for the transformation olivine ↔ spinel. Z. Kristallogr. 160, 53–62 (1982).

23. Robinson, K., Gibbs, G. V. & Ribbe, P. H. Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. Science 172, 567–570 (1971).

24. Burnley, P. C. The fate of olivine in subducting slabs: a reconnaissance study. Amer. Miner. 80, 1295–1301 (1995).

25. Price, G. D., Putnis, A. & Smith, D. G. W. A spinel to β-phase transformation mechanism in (Mg,Fe)2SiO4. Nature 296, 729–731 (1982).

26. Beareley, A. J., Rubie, D. C. & Ito, E. Mechanisms of the transformations between the β and γ polytypes of Mg,Fe2SiO4 at 15 GPa. Phys. Chem. Miner. 18, 343–358 (1992).

27. Beland, J. N. & Liu, L. G. Olivine to spinel transformation in Mg,Fe2SiO4 via faulted structures. Nature 303, 233–235 (1983).

28. Burnley, P. C. & Green II, H. W. Stress dependence of the mechanism of the olivine–spinel transformation. Nature 338, 753–756 (1989).

29. Kerschhofer, L., Sharp, T. G. & Rubie, D. C. Intracrystalline transformation of olivine to wadsleyite and ringwoodite under subduction zone conditions. Science 271, 79–81 (1996).

30. Kerschhofer, L. et al. Polymorphic transformations between olivine, wadsleyite and ringwoodite: mechanisms of intracrystalline nucleation and the role of elastic strain. Mineral. Mag. 62, 617–638 (1998).

31. Poirier, J. P. Martensitic olivine-spinel transformation and plasticity of the mantle transition zone. In Anelasticity in the Earth, Vol. 4 (eds Stacey, F. D., Paterson, M. S. & Nicholas, A. J.) 113–117 (American Geophysical Union, Washington, D.C., 1981).

32. Tomioka, N., Miyahara, M. & Ito, M. Discovery of natural Mg,Fe2SiO4 tetragonal garnet in a shocked chondritic meteorite. Sci. Adv. 2, e1610251 (2016).

33. Fujino, K., Sasaki, S., Takeuchi, Y. & Sadanaga, R. X-ray determination of electron distributions in forsterite, fayalite and tephroite. Acta Crystallogr. B37, 513–518 (1981).

34. Finger, L. W., Hazen, R. M., Zhang, J., Ko, J. & Navrotsky, A. The effect of Fe on the crystal structure of wadsleyite β-(Mg2,Fe4)SiO6. 0.00 ≪ c ≪ 0.40. Phys. Chem. Miner. 19, 361–368 (1993).

35. Sasaki, S., Prewitt, C. T., Sato, Y. & Ito, E. Single-crystal X ray study of γ Mg2SiO4. J. Geophys. Res. 87, 7829–7832 (1982).

36. Yagi, T., Marumo, F. & Akimoto, S. Crystal structures of spinel polymorphs of olivine and spinel. Phys. Chem. Miner. 94, 1563–1569 (1989).

37. Tomioka, N. & Fujino, K. Natural (Mg,Fe),SiO3-ilmenite and -perovskite in the Tenham meteorite. Science 277, 1084–1086 (1997).

38. Tomioka, N., Mori, H. & Fujino, K. Shock-induced transition of NaAlSiO4 feldspar into a hollandite structure in a L6 chondrite. Geophys. Res. Lett. 27, 3997–4000 (2000).

39. Tomioka, N. & Kimura, M. The breakdown of diopside to Ca-rich majorite and glass in a shocked H chondrite. Earth Planet. Sci. Lett. 208, 271–278 (2003).

40. Chen, M., Shu, J. & Mao, H.-K. Xie, a new mineral of high-pressure FeCr2O4 polymorph. Chin. Sci. Bull. 53, 3341–3345 (2008).

41. Putnis, A. & Price, G. High-pressure (Mg,Fe)2SiO4 phases in the Tenham meteorite. Amer. Miner. 78, 1320–1323 (1993).

42. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett., 77, 3865–3868 (1996).

43. Horiiuchi, H. & Sawamoto, H. β-Mg2SiO4 Single-crystal X ray diffraction study. Amer. Miner. 66, 568–575 (1981).

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Author contributions

N.T. organised the research project. N.T., M.M., I.T., X.T., R.T., and Y.K. conducted SEM observations, and N.T., R.T., and Y.K. prepared ultrathin foil specimens using FIB. N.T. and M.M. conducted the TEM observations. N.T., T.O., and N.P. conducted electron diffraction analysis and crystal structure modelling. L.B. conducted single crystal X-ray diffraction analysis and crystal structure refinements. T.I., Z.L., and T.K., conducted the first-principles calculations. N.T. wrote the paper and all the authors discussed the results and commented on the paper.

Competing interests

The authors declare that they have no competing interests.

Additional information

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