Prediction of a hexagonal SiO₂ phase affecting stabilities of MgSiO₃ and CaSiO₃ at multimegabar pressures

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Results and Discussion

Calculated static (0 K) enthalpies (Fig. 1A and SI Text) indicate that seven phases including α-PbO₂, pyrite, orthorhombic-I, baddeleyite (α-ZrO₂), cotunnite, Fe₂P, and P1 structures are grouped to have relatively lower enthalpies than the other eight phases. The α-PbO₂ phase is the most stable under low pressure and is found to transform to the pyrite phase at about 0.2 TPa, being consistent with previous studies (9, 11). However, our calculations clearly indicate that after the pyrite phase stability a previously uncharacterized phase change occurs at 0.69 TPa to an unexpected Fe₂P-type structure, not to cotunnite, which has been thought to be the final high-pressure phase in several dioxides (11–16). Although the enthalpies of these two structures are in the same level because of a similarity in local environment around Si explained in detail below, the Fe₂P phase has a lower enthalpy than cotunnite above 0.64 TPa and entirely eclipses the cotunnite stability at the static condition. No other stable structure was derived even after further structure searches by metadynamics simulations. As demonstrated in the Inset of Fig. 1A, calculations within GGA also yield the same trend on the static phase relations but with a pyrite-Fe₂P transition pressure of ~30 GPa higher.

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Exploration of new high-pressure phases of silica has always attracted substantial interests in geophysics, materials science, and condensed matter physics because of its broad fundamental applicability (1–10). Low-pressure polymorphs of silica such as quartz have Si tetrahedrally coordinated by O, whereas in stishovite- (a rutile-type SiO₂ phase), CaCl₂-, α-PbO₂-, and pyrite (FeS₂-) type phases, which form subsequently from ~10 to ~250 GPa, the coordination number (CoN) of Si increases to 6. Recent ab initio theoretical calculations have predicted a phase transition from the pyrite- to the cotunnite (α-PbCl₂)-type structure around 700 GPa accompanied with further increase in CoN to 9 (11, 12). Although these studies showed some new aspects of SiO₂ at the pressures where experiments of solid-solid phase change are nearly impossible, they adopted the cotunnite structure to SiO₂ simply based on the knowledge of high-pressure behaviors of some analog compounds (13–16) with no attention to other candidates.

Recent improvements in detection methods allow for the discovery of low-mass terrestrial exoplanets with 1–10 times Earth’s mass (Mₑ), so-called “super-Earths” (17–20). Because pressure conditions of their deep mantles, as well as those of the cores of some gas giants, are located in a sub-terapascal range (21, 22), ultrahigh-pressure and temperature stabilities of SiO₂ and some other silicates such as MgSiO₃ and CaSiO₃, major components in the Earth’s and possibly in super-Earth’s, mantle (23, 24), are also of particular astrophysical importance. Those are still highly unclear but should be clarified before developing models of their internal structures.

In this study, we first theoretically searched for a possible new high-pressure phase of SiO₂, and then investigated ultrahigh-Fe₂P type phase evolutions not only of SiO₂ but also of MgSiO₃ and CaSiO₃. The structure search for SiO₂ was performed by examining the adaptability of several dense packing structure models with AX₂ stoichiometry to SiO₂, which have various high CoNs of atom A ranging from 6 to 12 (SI Text), by means of the traditional ab initio density functional constant-pressure molecular dynamics method within the local density approximations and generalized gradient approximations (GGA), similarly to our previous studies (25). We then further applied a modern ab initio metadynamics method (26) to find out structural derivatives from all the optimized structures with more efficient exploration in free energy space. The initial structure models tested here included not only known dioxide structures but also structures for nonionic intermetallic compounds including Laves phases. For reliable calculations under strong compressions, we constructed pseudopotentials with small core radii, similarly to the previous study (12). This needed a large kinetic energy cutoff of 400 Ry for a convergence in the Fourier expansion of wave functions (SI Text).

Ultrahigh-pressure phase relationship of SiO₂ silica in multimegabar pressure condition is still quite unclear. Here, we report a theoretical prediction on a previously uncharacterized stable structure of silica with an unexpected hexagonal Fe₂P-type form. This phase, more stable than the cotunnite-type structure, a previously postulated postpyrite phase, was discovered to stabilize at 640 GPa through a careful structure search by means of ab initio density functional computations over various structure models. This is the first evidential result of the pressure-induced phase transition to the Fe₂P-type structure among all dioxide compounds. The crystal structure consists of closely packed, fairly regular SiO₉ tricapped trigonal prisms with a significantly compact lattice. Additional investigation further elucidates large effects of this phase change in SiO₂ on the stability of MgSiO₃ and CaSiO₃ at multimegabar pressures. A postperovskite phase of MgSiO₃ breaks down at ~5 TPa accompanied with further increase in CoN and is found to transform to the pyrite phase at about 0.2 TPa, being consistent with previous studies (9, 11). However, our calculations clearly indicate that after the pyrite phase stability a previously uncharacterized phase change occurs at 0.69 TPa to an unexpected Fe₂P-type structure, not to cotunnite, which has been thought to be the final high-pressure phase in several dioxides (11–16). Although the enthalpies of these two structures are in the same level because of a similarity in local environment around Si explained in detail below, the Fe₂P phase has a lower enthalpy than cotunnite above 0.64 TPa and entirely eclipses the cotunnite stability at the static condition. No other stable structure was derived even after further structure searches by metadynamics simulations. As demonstrated in the Inset of Fig. 1A, calculations within GGA also yield the same trend on the static phase relations but with a pyrite-Fe₂P transition pressure of ~30 GPa higher.

ab initio density functional simulation | multimegabar crystalline phase | silicon dioxide | super-Earth mantle

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Pressure-induced phase changes to the Fe$_2$P-type structure have never been reported or suggested in any dioxides so far. Therefore, the current results are quite surprising. The Fe$_2$P structure (Fig. 1B and C and Table 1) has a flattened hexagonal cell with the space group $P6_2m$ and $Z = 3$ (27) and specified by four structural parameters ($a$, $c$, $x_{O1}$, and $x_{O2}$), which is known to be applicable also to some other 3d transition metal phosphides, Mn$_2$P and Ni$_2$P (28). In the case of SiO$_2$, Si and O atoms sit at the P and Fe positions, respectively. This structure is composed of two different kinds of SiO$_2$ polyhedra, which form fairly regular tricapped trigonal prisms (Fig. 1B), so that their effective coordination numbers (ECoN) (29) are about 8.5, which is very close to the apparent CoN of 9. This can be considered a primary reason for the Fe$_2$P stability compared to cotunnite, which is also composed of SiO$_2$ polyhedra but with a much smaller ECoN of 7.7 because of large distortion of the polyhedra at all the pressures (Fig. 2B). Such distortion is likely acceptable to the dioxides with larger cations, but not to SiO$_2$ with more covalent bonds suggested from deformed charge densities of O ions residing between Si and O (Fig. 1C). Those polyhedra connect with each other by sharing edges along the a and b directions and by sharing faces along the c direction, making two different chains parallel to the c axis (Fig. 1B), which produces remarkable polyhedral occupancy ($\sum V_{poly}/V_{cell}$) reaching 0.8. Nevertheless, calculated Si-O distances are found ranging from 1.55 to 1.71 Å at 0.7 TPa (Fig. 1B). This is quite counterintuitive, because they are even comparable to the ambient pressure values in the low-pressure phase of silica (e.g., quartz) of $\sim$1.6 Å. These mean that the significant densification in the Fe$_2$P structure is achieved not by shrinking of nearest-neighbor Si-O distances but by increments of cation CoN and associated dense polyhedral packing.

Mechanical structural stabilities in the relevant pressure range of each stable phase were investigated by inspecting phonon properties shown in SI Text. Energetically stable phases were also found to be vibrationally stable at least at the pressure ranges investigated in this study. But imaginary phonon frequencies appeared in Fe$_2$P-SiO$_2$ below 300 GPa, indicating that this phase is unquenchable down to ambient pressure. The high ninefold coordination of Si is considered to be less adaptable at low-pressure condition. Thermodynamic properties of this phase were then determined by using these phonon spectra within the quasiharmonic approximation (QHA). This approximation is generally known to become invalid at high temperatures with approaching melting. However, the $P,T$ conditions we focus on were confirmed to sufficiently remain in its validity range (12, 30), which rapidly expands to higher temperatures with compression (SI Text). Prop-

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Fig. 1. Calculated static enthalpies of relatively stable structures and crystal structure of the Fe$_2$P phase. (A) Enthalpy differences relative to the pyrite phase (horizontal black line) plotted as a function of pressure. Those of the Fe$_2$P and pyrite phases relative to cotunnite are also shown in Inset with results by GGA (dashed lines). (B) Structural details of hexagonal Fe$_2$P with two different kinds of SiO$_2$ polyhedron distinguished by dark and light blue. Red spheres indicate O atoms, and Si atoms sit at the center of polyhedra. (C) Charge densities of Fe$_2$P on the (001) and (110) planes at 0.7 TPa. The unit cell is indicated by black lines. (D) Details of the two SiO$_2$ tricapped trigonal prisms calculated at 0.7 TPa with $V_{poly}$, ECoN (17), and Si-O distances.

Fig. 2. Compression behaviors of SiO$_2$ above 0.3 TPa. Pressure-volume relationships at several different temperatures (A). At 300 K, pyrite-type SiO$_2$ (dashed line) directly transforms to the Fe$_2$P phase (solid line) with a large volume reduction of 4.9%, whereas at higher temperatures, the pyrite phase first transforms to the cotunnite phase (dotted-dashed line) with $\sim$3−4% volume reductions, then to the Fe$_2$P phase with $\sim$0.3−0.5% volume reductions. Noticeable volume compression, reaching in total $\sim$40%, is achieved from 0.3 to 1.5 TPa. ECoNs for one and two SiO$_2$ polyhedra in the cotunnite and Fe$_2$P-type structures as a function of pressure, respectively (B). The mean value for Fe$_2$P is shown by a red dashed line, and the ideal CoN of 9 is given by a gray dashed line.
erties calculated at 0.7 TPa and selected temperatures from 0.3 to 6 kK are also listed in Table 1, showing a significant bulk modulus (B) larger than 2.5 TPa and a high Debye temperature ($\theta_D$) of almost 2.0 kK. Strong compression also suppresses the thermal expansivity ($\alpha$) to quite low values, less than $0.55 \times 10^{-5}$ K$^{-1}$, producing a small product of $\alpha \gamma T$ of about 0.02 even at 4 kK and even for the standard magnitude of the Grüneisen parameters ($\gamma$) of about 1.2. This leads to marginal differences between iso-thermal and adiabatic quantities in B or specific heat (C) at these ultrahigh pressures, which might be typical features of the dense matters.

Calculated volume compression curves of SiO$_2$, displayed in Fig. 2A at several different temperatures, indicate that the volume reductions associated with the postpyrite transitions are surprisingly large (−4 to approximately −5%) even at the strong compressions. They are clearly due to significant increase in the polyhedral occupancy associated with the increase in Si-Co-N from 6 to 9. The volume changes across the postcotunnite transition are much smaller (approximately −0.5%) but still negative at all the temperatures. Such small volume contrasts even have important contributions to stabilize the Fe$_2$P structure (SI Text).

Ultrahigh-P,T phase diagram of SiO$_2$ was determined by comparing finite-temperature Gibbs free energy of each phase, as in our previous studies (8, 17). It is shown in Fig. 3A, indicating that at low temperatures, pyrite-type SiO$_2$ directly transforms to the Fe$_2$P form as at the static condition, whereas at the temperatures higher than 700 K, the cotunnite stability appears between the pyrite and Fe$_2$P stability fields. The pyrite–cotunnite boundary has a slightly negative but less temperature sensitive Clapeyron slope ($dP_{tr}/dT$), whereas the cotunnite and Fe$_2$P boundary has strong positive temperature dependence. Therefore, the stability range of cotunnite phase increases with increasing temperature. This makes the high-T phase diagram more complicated than the static one, suggesting that the Fe$_2$P-type phase should be recognized as a postcottonite phase rather than the postpyrite phase.

Induced geotherm proposed to the super-Earths based on mass-radius distribution analyses (21) is also plotted in Fig. 3 with P,T conditions proposed for some giant planetary cores (22). Along the geotherm, the cotunnite-type phase diagrams of the MgSiO$_3$ and CaSiO$_3$ systems (Fig. 3B and C) were determined similarly to SiO$_2$. Assumed mantle adiabats indicate that in the case of MgSiO$_3$, the postperovskite (pPv) phase (SI Text) dissociates into Fe$_2$P-type SiO$_2$ and B2-type MgO at 1.04 TPa along the adiabat. Dashed boundaries indicate P,T conditions out of the QHA validity range (12, 30). Low-pressure phase boundaries of SiO$_2$ below 0.3 TPa (31) are also plotted by solid gray lines.

Figs. 3. Ultrahigh-P,T phase diagrams of SiO$_2$ (A), MgSiO$_3$ (B), and CaSiO$_3$ (C). Proposed super-Earths’ mantle adiabat (21) is also plotted by orange line with corresponding core-mantle boundary pressures for super-Earths with 5 and 8 $M_\oplus$ (vertical dashed lines). Blue and green shaded areas represent P,T conditions proposed for the cores of Uranus and Neptune and for the core of Saturn, respectively (22). Dissociation boundaries both have largely negative Clapeyron slopes of −12 MPa/K (for MgSiO$_3$) and −8.9 MPa/K (for CaSiO$_3$) along the adiabat. Dashed boundaries indicate P,T conditions out of the QHA validity range (12, 30). Low-pressure phase boundaries of SiO$_2$ below 0.3 TPa (31) are also plotted by solid gray lines.

Then, static enthalpy relations and P,T phase diagrams of the MgSiO$_3$ and CaSiO$_3$ systems (Fig. 3 B and C) were determined similarly to SiO$_2$. Assumed mantle adiabats indicate that in the case of MgSiO$_3$, the postperovskite (pPv) phase (SI Text) dissociates into Fe$_2$P-type SiO$_2$ and B2-type MgO at 1.04 TPa along the adiabat. The breakdown can therefore be expected in a massive

| Table 1. Structural and thermodynamic properties of Fe$_2$P-type SiO$_2$ at 0.7 TPa |
|----------------------------------|-----------------|
| **Space group** | 3 |
| **Cell parameters, Å** | 4.166 (a) |
| **Volume, Å$^3$/cell** | 33.931 |
| **Atomic positions** | site | x | y | z |
| S1 | 2c | 1/3 | 2/3 | 1/2 |
| S2 | 1b | 0 | 0 | 0 |
| O1 | 3f | 0.257 | 0 | 1/2 |
| O2 | 3g | 0.590 | 0 | 0 |
| **Polythermal bulk modulus, TPa** | 0.3 kK |
| **Adiabatic bulk modulus, TPa** | 2.747 |
| **Isothermal bulk modulus, TPa** | 2.694 |
| **Adiabatic bulk modulus, TPa** | 2.627 |
| ** Thermal expansivity, 10$^{-5}$ K$^{-1}$** | 0.12 |
| **Grüneisen parameter** | 1.28 |
| **Debye temperature, kK** | 1.970 |

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super-Earth with $M \geq 8M_\oplus$. Unlike a previous suggestion (12), no cotunnite-type SiO$_2$ is yielded in this dissociation reaction. On the other hand, CaSiO$_3$ shows a richer phase diagram, where the pV stability is limited at low temperatures with much higher transition pressures surpassly due to high ideality of the perovskite (Pv) structure (25), and thus the Pv phase directly dissociates first into pyrite-type SiO$_2$ + B$_2$-type CaO along the proposed adiabat. Then, SiO$_2$ subsequently transforms to cotunnite, in this case, and finally to Fe$_2$P with rising pressure. The Pv breakdown is predicted at a pressure of about 0.60 TPa along the adiabat, considerably lower than the stability limit of MgSiO$_3$. Thus, the collapse of CaSiO$_3$ is expected in a super-Earth with $M \geq 5M_\oplus$. Interestingly, this B$_2$-type CaO was found to be metallic (SI Text), whereas all the other phases remain insulating even at 2 TPa. The large negative Clapeyron slopes expected for both dissociations (Fig. 3 B and C) combining positive density jumps would have some effects on internal activity of the super-Earths' mantles (SI Text).

Also, P, T conditions corresponding to cores of some giant planets (22) are found to fall in the ranges close to the dissociation boundaries of MgSiO$_3$. Present results suggest that the cores of Uranus and Neptune are expected to consist of MgSiO$_3$ and cotunnite-type SiO$_2$ but no CaSiO$_3$, whereas the core of Saturn no longer contains MgSiO$_3$. However, these P, T conditions would also be fairly close to their melting points (31), though they are still poorly constrained. Liquid cores are also highly possible therein. Exchanging further dissociations in SiO$_2$, MgO, and CaO into elemental solids indicated no reactions at least up to 2 TPa (SI Text). Fe$_2$P-type SiO$_2$ can therefore be considered a strong candidate for dominant components in the massive super-Earths' mantles.

Computational Methods
Calculation methods are based on the density functional theory. Plane-wave basis and pseudopotentials were applied to represent electronic structures. To avoid core overlapping in calculations involving the structure search, we constructed unique pseudopotentials with sufficiently small core radii (SI Text). They guarantee no core overlapping even under the significant compression, though it is noted in the text that the interatomic distances in the stable structures such as Fe$_2$P remain surprisingly long. To search for the stable silica phase at ultrahigh pressures, we applied variable-cell-size molecular dynamics and performed structural optimizations of several initial structure models and also metadynamics simulations (26) to find out structural derivatives from all the structure models efficiently (SI Text). Finite-temperature properties were calculated based on the lattice dynamics method combined with the QHA (SI Text). Applicability of these techniques to silicates was extensively investigated in our previous studies (8, 25, 30, 31).

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Supporting Information

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SI Text

Structure Models for Ultrahigh-Pressure Phase of SiO$_2$ and Other Compounds. We examined initially 15 different structural models relevant to high-pressure phases of silica: α-PbO$_2$ (1), pyrite (FeS$_2$) (1), baddelyite (α-ZrO$_2$) (2), orthorhombic-I (2), fluorite (CaF$_2$) (2), P$_2$/m structure (3), cotunnite (α-PbCl$_4$) (4), Fe$_3$P (4), P$_1$ structure (3), MoSi$_2$ (3), CrSi$_2$ (5), Cmcm structure (3), Ni$_3$In (4), MgZn$_2$ (4), and MgCu$_2$ (4), for SiO$_2$ in this study (Fig. S1). Their unit cells consist of 4, 4, 4, 4, 8, 4, 4, 4, 3, 6, 1, 3, 4, 2, 4, and 8 formula units with space groups Pbcm, Pn$ar{3}$m, P$ar{6}$m2m, P$\bar{1}$, I$ar{4}$mmn, P$\bar{6}$22, Cmcm, Pnma, P$\bar{6}$m/mmc, and Fd$ar{3}$m, respectively. The cation coordination number (CoN) is indicated in parentheses in Fig. S1, from 6 in α-PbO$_2$ and pyrite to 12 in MgZn$_2$ and MgCu$_2$. The six structures of α-PbO$_2$, pyrite, baddelyite, orthorhombic-I, fluorite, and cotunnite are known to be applicable to oxides and/or halides, and the other six of Fe$_3$P, MoSi$_2$, CrSi$_2$, Ni$_3$In, MgZn$_2$, and MgCu$_2$ are appropriate for metallic and/or intermetallic compounds including Laves phases. Among these structures, cotunnite is well recognized as the currently established final dense phase in several oxides, but Ni$_3$In is suggested to be a possible postcotunnite phase of some fluorides (6), and the P$_2$/m, P$_1$, and Cmcm structures are reported to be postcotunnite phases in TeO$_2$ (3).

Perovskite (Pv) and postperovskite (pPv) structures (Fig. S2) for MgSiO$_3$ consist of 4 and 2 formula units with Pbcm and Cmcm symmetry, respectively (7). Although the Ppv structure is identical in CaSiO$_3$, we applied the tetragonal I4/mcm Ppv structure to Ca-Pv, because it has been reported to be the most stable under high pressure (8). B1 (NaCl) and B2 (CsCl)-type MgO and CaO (Fig. S2) both consist of one formula unit with Fm3m and Pm3m symmetry, respectively.

Ab Initio Computational Details. Our calculation methods were based on the density functional theory (9, 10) with the local density approximation (11, 12) and the generalized gradient approximation (13). Plane-wave basis and pseudopotentials were applied to represent electronic structures. By means of these base methods, so far we have reported high-P-T phase diagrams of various major Earth and planetary materials including SiO$_2$ (14), MgSiO$_3$ (7), Al$_2$O$_3$ (15), the spin system of ferropericlase [(Mg, Fe)O] (16), and also a binary system of MgSiO$_4$-Al$_2$O$_3$ (17). We applied the same techniques in this study.

However, to avoid core overlapping in calculations involving the structure search, we constructed unique pseudopotentials with sufficiently small core radii by using the ultrasoft scheme (18), and to represent the electronic structures under strong compression correctly, we included some core states in the pseudopotentials. Detailed conditions of the pseudopotentials are as follows. For Mg, Ca, Si, and O, electronic configurations of 2$s^2$ 2$p^6$ 3$s^2$ 3$p^4$ 3$d^0$, 3$s^2$ 3$p^4$ 3$d^0$ 4$s^2$ 4$p^0$, 2$s^2$ 2$p^6$ 3$s^2$ 3$p^4$ 3$d^0$, and 2$s^2$ 2$p^4$ 3$d^0$ configurations are pesudorated, respectively. The small cutoff radii of 1.4 a.u., 1.8 a.u., 1.2 a.u., and 1.0 a.u. were applied for all quantum numbers l in each atom of Mg, Ca, Si, and O, respectively, to sufficiently guarantee no core overlapping even under the significant compression. However, as reported in the main text, interatomic distances in the stable ultrahigh-pressure structures such as Fe$_3$P are surprisingly large, even with significantly small volumes. The plane-wave cutoff energy was set to 400 Ry. These conditions are basically the same as those applied in a previous study (19). We applied variable-cell-shape molecular dynamics (20) for structure searches and optimization. Calculations were carried out using the QUANTUM ESPRESSO package (21).

To obtain full convergence in total energies, pressures, and atomic forces, we applied the Monkhorst–Pack method (22) to sample 8, 4, 16, 4, 10, 24, 6, 12, 24, 63, 14, 18, 21, 10, and 10 k points in the irreducible wedges of Brillouin zones of the model structures, α-PbO$_2$, pyrite, baddelyite, orthorhombic-I, fluorite, P$_2$/m structure, cotunnite, Fe$_3$P, P$_1$ structure, MoSi$_2$, CrSi$_2$, Cmcm structure, Ni$_3$In, MgZn$_2$, and MgCu$_2$, respectively. Using these conditions, total energies converge within 0.01 eV/atom. The effects of using a larger number of k points on the calculated properties are found to be insignificant.

Static enthalpy differences relative to the pyrite phase are shown in Fig. S3 and Fig. L4 as a function of pressure. The seven relatively unstable (high-enthalpy) phases are shown in Fig. S2, and the seven relatively stable (low-enthalpy) phases are shown in Fig. L4. All seven of the phases shown in Fig. S3A have enthalpies always a great deal higher than pyrite, implying no possibility of a phase change, though some of them were reported to stabilize in other AX$_2$ compounds. The MgCu$_2$-type structure was found to have an enthalpy more than 1500 K/mol higher than that of pyrite; therefore, it is excluded in these figures. We further applied ab initio meta-dynamics simulations (23) to find out structural derivatives from all the optimized structures with more efficient exploration in free energy space. However, this did not derive any other stable structures. The Fe$_3$P-type form is therefore the strong candidate for the previously uncharacterized multimegabar pressure phase of SiO$_2$. We also analyzed each component of enthalpy, the total energy ($E_{\text{tot}}$) and PV term, of the Fe$_3$P phase relative to that of cotunnite, in order to find a clue to the stabilization mechanism of the Fe$_3$P phase. Fig. S3B indicates that the difference of PV term is always negative and has important contributions to stabilize the Fe$_3$P, even though the volume contrast between cotunnite and Fe$_3$P is subtle (~0.5%) (Fig. 2). Fig. S3B shows that the difference of $E_{\text{tot}}$ term also decreases with increasing pressure. These clearly mean that the Fe$_3$P-type structure is more suitable to SiO$_2$ under ultrahigh-pressure condition than cotunnite.

On the other hand, 4, 15, and 6 k points were sampled in the irreducible wedges of Brillouin zones of Mg-Pv, Ca-Pv, and Ppv, respectively, and 10 k points were sampled in the irreducible wedges of Brillouin zones of the B1 and B2 phases. Because B2-CaO has a metallic ground state as mentioned below, we applied Fermi–Dirac smearing with a small energy width of 0.001 Ry to occupations of the electronic states near the Fermi level and a sufficiently dense k-point sampling with 220 points in order to correctly obtain the self-consistent convergence of the electronic structure. These are important, especially to calculate the correct phonon frequencies.

Calculated static enthalpies of the MgSiO$_3$ and CaSiO$_3$ systems are shown in Fig. S4 with references to the Ppv and Ppv phases, respectively. These indicate that in MgSiO$_3$, Ppv first changes to Ppv at low pressure of ~0.1 TPa, which remains stable until 1.0 TPa, and eventually it collapses to the Fe$_3$P-type SiO$_2$ phase plus B2-type MgO at 1.09 TPa, not to cotunnite plus MgO, which was suggested previously for MgSiO$_3$ (19) and also for some low-pressure analogs such as CaSiO$_3$ (24) and NaMgF$_2$ (19). In CaSiO$_3$, Ppv remains until 0.53 TPa, which transforms to Ppv similarly with MgSiO$_3$ at 0.72 TPa, but it immediately collapses also to the Fe$_3$P-type SiO$_2$ phase plus B2-type CaO. For the ultrahigh-pressure phase evolution of both silicates, there are
no stability fields for either pyrite or cotunnite, at least for the static condition.

Apart from these calculations, we have additionally examined the possible elemental dissociations of SiO$_2$ itself into Si and O, MgO into Mg and O, and CaO into Ca and O. This was executed by comparing static enthalpies of proposed ultrahigh-pressure phases, Fe$_3$P-type SiO$_2$, hexagonal closed pack (hcp) Si (25), hcp Mg (26), and hcp Ca (27), and $\zeta$-phase of O$_2$ (28, 29). The calculated enthalpy of Fe$_3$P-SiO$_2$ was found to be 1982 kJ/mol lower than the total enthalpy of hcp Si plus $\zeta$-O$_2$, even at 2 TPa, which confirmed no molecular dissociation of $\zeta$-O$_2$ as reported previously (29), and this further increased with pressure. Also, at 2 TPa, B$_2$-MgO and B$_2$-CaO were found to be 2187 kJ/mol and 600 kJ/mol more stable than the mixture of hcp-Mg + 1/2$\zeta$-O$_2$ and hcp-Ca + 1/2$\zeta$-O$_2$, respectively. These considerably positive dissociation enthalpies strongly suggest that the elemental dissociations are still highly unlikely even at such ultrahigh-pressure conditions.

Strong compression under multimegarbar conditions can also affect the bonding properties and electronic structures considerably. Electronic partial density of states calculated at multimegarbar pressures are shown in Fig. S5. Even at remarkable pressures beyond 1 TPa, large energy gaps of 6 ~ 10 eV still remain in SiO$_2$, MgSiO$_3$, and MgO, which is consistent with previous works (19). It is widely known that the traditional density functional calculations systematically underestimate electronic band gaps, so that the gaps of ~15 eV can be expected in the actual systems. The wide gap of Fe$_3$P-SiO$_2$ is particularly surprising when considering basic physical arguments that indicate every material tends to transform to metal under strong compression. But the structural properties of Fe$_3$P-SiO$_2$ with long Si-O distances (see main text) support this behavior, though significant broadening of O protons and Boltzmann constant, respectively. Then, pressure values at finite temperatures are calculated from the thermodynamic relation $P(\zeta;T) = -\frac{1}{\zeta} \frac{\partial F(\zeta;T)}{\partial \text{V}^\zeta}$, which approximates neglects the temperature dependence of phonon frequencies, so that it becomes invalid at too high of a temperature. In this study, a practical evaluation of its high-temperature validity limit was applied by carefully examining the temperature dependence of thermal expansivity $\alpha$ as in our previous studies (33). Then, the deep super-Earths’ mantle $P,T$ conditions (Fig. 3) were found to fall mostly in the QHA validity range because of the large suppression of anharmonicity by strong compression. Gibbs free energy is converted from Helmholtz energy as

$$G(P,T) = F(V,T) + P(V,T)\text{V},$$

where the pressure $P(V,T)$ is calculated from $P(V,T) = -\frac{\partial F(V,T)}{\partial V}$ by interpolating $F(V,T)$ by fitting to the $E$-$V$ form of the third-order Birch–Murnaghan equation (34).

$$E(V) = -\frac{9}{16} B_0 \left[ \left( 4 - B''_0 \right) \frac{V^2}{V_0^2} - (14 - 3B''_0) \frac{V^{7/3}}{V_0^{7/3}} \right] + \left( 16 - 3B''_0 \right) \frac{V^{5/3}}{V_0^{5/3}} \right] + \text{constant.}$$

Other quantities listed in Table I were calculated based also on general thermodynamic identities.

**Density Variation of a Representative Pyrolytic Aggregate and a Phase Transition Buoyancy Parameter.** Although super-Earths’ mantle composition is still highly unclear, here we try to evaluate density variation of a pyrolytic composite, one of the most representative mineralogical models for the differentiated mantle of terrestrial bodies, represented approximately by MgSiO$_3$ : MgO : CaSiO$_3$ = 0.55 : 0.38 : 0.07 in moles (35), along the super-Earth’s adiabat (Fig. 3). Four distinct layers are found from 0.3 to 1.5 TPa depending on constituent phases. Layer I is composed of pPv-MgSiO$_3$, B1 (NaCl)-type MgO, and pPv-CaSiO$_3$, and MgO transforms to the B2 form in Layer II over 0.48 TPa, which is consistent with a recent calculation (36). pPv-CaSiO$_3$ then dissociates into B2-CaO plus pyrite-type SiO$_2$, but silica reacts back with B2-MgO and forms additional pPv-MgSiO$_3$ in Layer III. pPv-MgSiO$_3$ eventually collapses over 1.04 TPa, and thus B2-MgO, F$_2$P-SiO$_2$, and B2-CaO compose Layer IV. Two major discontinuities associated with the silicate breakdowns are predicted, which produce large density jumps of $+3.6\%$ and $+2.3\%$ at the boundaries between the second-third and third-fourth regions in Fig. S7, respectively.

So-called phase transition buoyancy parameter ($P_b$) (37) is defined as

$$P_b = \Gamma(\Delta \rho / \rho).$$
where $\gamma$, $g$, and $h$ are the Clapeyron slope ($dP_c/dT$), gravity, and scale of convection, respectively. Negatively large $P_c$ tends to produce a layered-type convection, so that two separated convections occur, whereas small values suggest no separation of the convection cell. Each physical parameter applied here is calculated for the second one of $\gamma$ of the convection cell. Each physical parameter applied here is calculated to produce a layered-type convection, so that two separated $\gamma$-type convection cells occur in the earth's lower mantle. Earth Planet Sci Lett 224:241–248.


MgO phase diagram (36) are clearly needed for quantitative understanding of the mantle convection in super-Earths. However, their magnitudes are smaller than the $P_c$ for the postspinel boundary of about $-0.2$ corresponding to the 660 km discontinuity in the Earth (37), though computations taking care of more realistic situations (40) are clearly needed for quantitative understanding of the effects of dissociation transitions on the superEarths' internal activity.


In total, 15 different dense packing initial structure models with the AX$_2$ stoichiometry examined in this study on the structure search for the possible ultrahigh-pressure phase of SiO$_2$. Red spheres and blue polyhedra are O and SiO$_2$, respectively. Apparent O-coordination numbers around Si are shown in parentheses, which are relatively high, from 6 to 12, which is suitable to ultrahigh-pressure phases. These are not only the dioxide and dihalide structures (A–G, I, and L), but also the structures for intermetallic compounds (H, J, K, and M–O). Among these structures, cotunnite has been thought to be the final high-pressure phase in dioxide, but very recently structures F, I, and L are suggested to be the post-cotunnite phase of TeO$_2$ (3).

Crystal structures for the other five phases of Mg-Pv (orthorhombic Pv-type with Pbnm symmetry) (A), Ca-Pv (tetragonal Pv-type with I4/mcm symmetry) (B), pPv (CaIrO$_3$-type with Cmcm) (C), B1 (NaCl-type with Fm3m) (D), and B2 (CsCl-type with Pm3m) (E). Large ocher (sky blue) spheres, small red spheres, and blue polyhedra indicate Mg (Ca), O, and SiO$_2$, respectively. Structures of pPv of CaSiO$_3$, B1, and B2 of CaO are isostructural to those of the corresponding MgSiO$_3$ and MgO phases.
Fig. S3. Static enthalpy differences of seven high-enthalpy structure models of SiO$_2$ relative to that of the pyrite phase (A), and the differences in each component of enthalpy ($H = E_{\text{tot}} + PV$) between cotunnite and Fe$_2$P phases (B). In A, the MgCu$_2$-type structure is more than 1500 kJ/mol higher than pyrite, so that its enthalpy is excluded. Results clearly indicate no stabilization relative to pyrite in any phases up to 1.5 TPa. On the other hand, static enthalpy differences of seven low-enthalpy structure models are presented in Fig. 1B and indicate that negative difference in the $PV$ contribution is the important factor to stabilize the Fe$_2$P phase.

Fig. S4. Static enthalpy differences in the MgSiO$_3$ (A) and CaSiO$_3$ (B) systems relative to those of the pPv and Ppv phases, respectively. Close-ups around dissociation pressures are shown in Insets. Dissociation pressures of silicates into Fe$_2$P-SiO$_2$ plus B2-MgO or CaO, which are found prior to dissociations to cotunnite-SiO$_2$ and B2-MgO or CaO even slightly. We also examined further elemental dissociations of these oxides, but no stability was found in all cases at least up to 2 TPa (see Lattice Dynamical Properties of Stable Phases).
Fig. S5. Electronic projection density of states for each stable phase that appears in the pyrolitic composite above 0.6 TPa. The top of the valence bands is set to the zero energy level. pPv-MgSiO$_3$, Fe$_2$P-SiO$_2$, and B2-MgO are still evidently insulating with gaps of more than several eV (shaded gray bands), whereas only B2-CaO shows a band gap closure and a metallic ground state already at 0.4 TPa far before the collapse of CaSiO$_3$. This is due to the significant broadening of the Ca 3d band (shaded blue area).

Fig. S6. Vibrational density of states of (relatively) stable phases that appear in the pyrolitic composite above 0.4 TPa. All phases including metastable orthorhombic-I of SiO$_2$ show vibrational and mechanical stability. However, if B2-CaO is calculated without correct treatment as a metal, it gives unstable phonons with significant imaginary frequencies, as shown by the dashed line. Using these data with QHA, finite temperature thermodynamics and ultra-high-$P,T$ phase diagrams were calculated. We also examined orthorhombic-I at high temperatures, but no stability field of this phase was found in any $P,T$ range.
Fig. S7. Density variation of the pyrolitic mineral assemblage calculated along the assumed mantle adiabat for the super-Earth with $10M_\oplus$ (38). Silicate breakdown occurs at the pressures indicated by arrows. A corresponding super-Earth’s cross section is also shown.