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# Identification of post-pyrite phase transitions in $SiO_2$ by a genetic algorithm

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Using a first-principles genetic algorithm we predict an $Fe_2P$ phase is the first post-pyrite phase of $SiO_2$ at low temperatures. This contrasts with a recently predicted cotunnite phase. Static enthalpy differences between these two phases are small near the transition pressure (0.69 TPa). While quasiharmonic free energy calculations predict an $Fe_2P$-→cotunnite-type transition with increasing temperature, another phase, NbCoB type, is identified as being structurally and energetically intermediate between $Fe_2P$ and cotunnite phases. This structure suggests a possible temperature-induced gradual transformation between $Fe_2P$ and cotunnite phases. This finding would change our understanding of how planet-forming silicates, for example, $MgSiO_3$ post-perovskite and its solid solutions, dissociate into elementary oxides at thermodynamic conditions expected in the interior of solar giants and exoplanets.

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## I. INTRODUCTION

$MgSiO_3$ is a major constituent of Earth's mantle. The discovery of the post-perovskite (PPV) transition of $MgSiO_3$ near Earth's core-mantle boundary conditions[1–3] reminded us that minerals can have truly unexpected high-pressure behavior. This finding naturally introduced a new question: what is the next high-pressure polymorph of $MgSiO_3$? The answer is fundamental for modeling the interiors of recently discovered exoplanets, particularly the terrestrial type,[4,5] and the cores of the solar giants, where pressures and temperatures can reach 4 TPa and 21 000 K.[6] In 2006 the dissociation of $MgSiO_3$ PPV into CsCl-type MgO and cotunnite-type $SiO_2$ was predicted at 1.1 TPa.[7] This prediction was based on the assumption of a sequence of pressure-induced transitions in $SiO_2$: rutile → $CaCl_2$ → $\alpha$-$PbO_2$ → pyrite → cotunnite phases. Experimentally, only phases up to pyrite-type $SiO_2$ have been observed to date.[8] This sequence of transitions seemed very reasonable because (i) $MgF_2$, a low-pressure analog of $SiO_2$, undergoes the same sequence of pressure-induced transitions from rutile up to pyrite and then transitions to the cotunnite phase[9] preceded by phase X in a very narrow pressure range[10] and (ii) the cotunnite phase has cation coordination number (CN) higher (9) than that of the pyrite phase (6). Nevertheless, it is not guaranteed at all that the cotunnite phase is the real post-pyrite phase of $SiO_2$. The predicted transition pressure to the cotunnite phase (∼0.69 TPa)[7,11] is still too high to be observed in static compression experiments. Prediction of high-pressure phases in the multi-Mbar regime is a difficult problem and behavior of low-pressure analogs is often invoked. Comparison of enthalpies and/or Gibbs free energies of potential structures is the method frequently used (Refs. 11 and 12 for postpyrite $SiO_2$) to predict phases at ultrahigh pressures. However, these strategies do not guarantee that the true stable structure is identified. Structural search using genetic algorithms (GA) are much more likely to catch truly stable phases and this method has been proven to work very efficiently.[13–15] Here we show that a first-principles GA search predicts the $Fe_2P$ phase as the first post-pyrite phase of $SiO_2$. The cotunnite phase has very competitive enthalpy but definitely higher than that of the $Fe_2P$ phase beyond the stability field of the pyrite structure. However, the cotunnite phase is stable at high temperatures according to quasiharmonic (QHA) free-energy calculations.[16] These two structures are very closely related, and the existence of another competitive and structurally intermediate phase, the NbCoB type, suggests a gradual crossover between them. We also discuss the effect of these new phase transitions on the dissociation of $MgSiO_3$ PPV.

## II. COMPUTATIONAL METHOD

First-principles GA structural searches were performed at 0.5 and 2 TPa. The details of our GA algorithm were described elsewhere.[15] The number of structures in the GA pool was 32 or 64. The candidate structure pool was initially generated from experimentally known and randomly generated structures. We considered primitive cells with 1–8 $SiO_2$ formula units (FUs). We used the local density approximation (LDA).[17,18] Two sets of silicon and oxygen pseudopotentials were generated by Vanderbilt's method.[19] For the GA searches we used pseudopotentials generated using the following electronic configurations: $3s^2 3p^1 3d^0$ and $2s^2 2p^4$ with cutoff radii of 1.6 and 1.4 a.u. for silicon and oxygen, respectively. They required a cutoff energy of 40 Ry. Brillouin-zone integration was performed using the Monkhorst-Pack sampling scheme[20] over **k**-point meshes of spacing $2\pi \times 0.05$ Å$^{-1}$. In the structure relaxation steps, constant-pressure variable-cell-shape molecular dynamics[21,22] was used. Candidate structures obtained with the GA were refined and their static enthalpies and QHA free energies were calculated using harder pseudopotentials, more suitable for the extreme pressures addressed here.[7] The valence electronic configurations of these harder pseudopotentials were $2s^2 2p^6 3s^1 3p^0$ and $2s^2 2p^4 3d^0$ with cutoff radii of 1.2 and 1.0 a.u. for silicon and oxygen, respectively.

Their cutoff energy was 400 Ry. We used density-functional perturbation theory to compute dynamical matrices at $2 \times 2 \times 2$ **q**-point mesh for all phases.[23,24] Phonon frequencies were then calculated by interpolation onto **q**-point meshes fine enough to achieve convergence of QHA free energy within 1 mRy/FU. All first-principles calculations were performed using the Quantum-ESPRESSO software distribution,[25] which has been interfaced with the GA scheme in a fully paralleled manner.

## III. RESULTS AND DISCUSSION

The present GA scheme is quite efficient in this system at high pressure. It takes approximately 10 generations at most to reach ground-state configurations for inspected cases. For instance, at 0.5 TPa the GA search using 4-FU $SiO_2$ produces a pyrite ground state in just a few generations (as shown in Fig. 1). At 2 TPa, for 4-FU $SiO_2$, the cotunnite structure is predicted to be the ground state. For 3-FU $SiO_2$ at both 0.5 and 2 TPa, the $Fe_2P$ structure is rapidly predicted. For 6-FU and 8-FU $SiO_2$, $Fe_2P$ and cotunnite structures are predicted, respectively. These results indicate that $Fe_2P$ and cotunnite phases are indeed good candidates for post-pyrite phases of $SiO_2$.

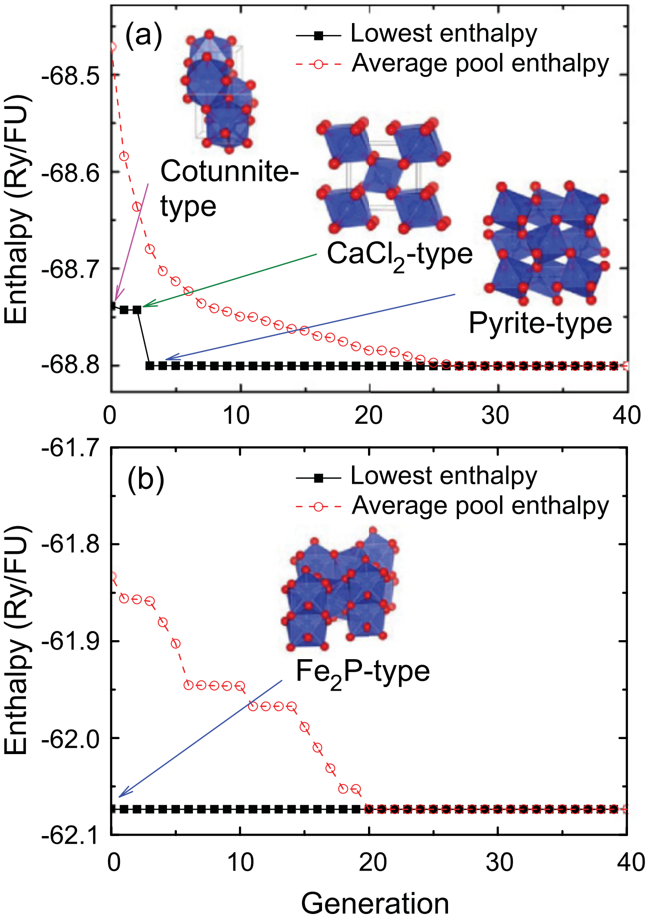

FIG. 1. (Color online) The histories of the lowest energy (enthalpy) and the average pool energy (enthalpy) of (a) 4-FU at 0.5 TPa and (b) 3-FU $SiO_2$ at 2.0 TPa by generation.

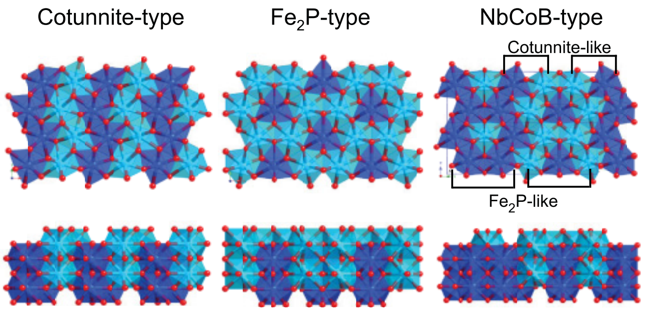

FIG. 2. (Color online) Crystal structures of $Fe_2P$-, cotunnite- and NbCoB-type phases. Blue and light blue spheres denote silicon atoms at different heights. Red small spheres denote oxygen atoms.

$Fe_2P$ and cotunnite structures (Fig. 2) are closely related.[26,27] Both have tricapped triangular prisms as structural units with silicon coordination number (CN) equal to 9 $(= 6 + 3)$. The lower-pressure phases of $SiO_2$ (rutile, $CaCl_2$, $\alpha$-$PbO_2$, and pyrite) consist of Si octahedra. In the $\alpha$-$PbO_2$ structure, shifts of silicons from the octahedral center to the middle of an octahedral face give rise to tricapped triangular prisms.[27] If all silicons shift in the same direction, the $\alpha$-$PbO_2$ structure transforms into the cotunnite structure. If half of silicons shift in the opposite direction, the $\alpha$-$PbO_2$ structure changes into the $Fe_2P$ structure. Several other structures with tricapped triangular prisms can be produced by different shifting patterns. Among them, the NbCoB structure, whose unit cell consists of 10 FUs,[28] is worthy of note because it is intermediate between $Fe_2P$ and cotunnite structures. In this structure $Fe_2P$ and cotunnite structures appear in an alternating pattern (Fig. 2). Therefore the NbCoB phase is also a potential post-pyrite phase. Calculated structural parameters of these three potential post-pyrite phases of $SiO_2$ are given in Table I.

Several other phases appeared in GA pools. Among them, the $Li_2ZrF_6$ structure[29] is also worthy of note. This phase consists of silicon octahedra and is closely related to the $\alpha$-$PbO_2$ structure,[27] in the same way as $Fe_2P$ and cotunnite structures are related. $Fe_2P$ and cotunnite structures with tricapped triangular prisms are structural counterparts of $Li_2ZrF_6$ and $\alpha$-$PbO_2$ structures with octahedra. $Fe_2P$-type $SiO_2$ can be obtained from $Li_2ZrF_6$ type by shifting all silicons in the same direction from octahedral centers to octahedral faces. Similarly to the NbCoB structure, there might be an intermediate phase between $\alpha$-$PbO_2$ and $Li_2ZrF_6$ as well. At 2 TPa, most phases in GA pools, including the baddeleyite phase, are found to consist of capped triangular prisms. Enthalpy calculations with harder pseudopotentials confirm that these phases are metastable over the entire pressure range investigated here; $Li_2ZrF_6$-type $SiO_2$ has higher enthalpy than $\alpha$-$PbO_2$ type at all pressures.

Figure 3 shows relative enthalpies of several phases of $SiO_2$. The PBE-type generalized gradient approximation[30] give rise to the same results as LDA essentially. Calculated transition pressures by PBE is higher by just ~10 GPa, as usually expected.[31] Static calculations show that pyrite-type $SiO_2$ transforms to $Fe_2P$ type at 0.69 TPa, being consistent with Ref. 12. This transition pressure is almost identical to the metastable transition pressure between pyrite-type and

TABLE I. Structural parameters of $Fe_2P$-, cotunnite-, and NbCoB-type $SiO_2$ at 0.8 TPa. Bulk modulus ($B$) and its pressure derivative ($B'$) at 0.8 TPa were obtained by the third-order Birch-Murnaghan equation of states.

| | | |
|---|---|---|
| | $Fe_2P$-type $SiO_2$ | |
| Space group | | $P\bar{6}2m$ |
| $(a,c)$ | | (4.120 Å, 2.222 Å) |
| $Si_1$ | $2c$ | (1/3, 2/3, 0) |
| $Si_2$ | $1b$ | (0, 0, 1/2) |
| $O_1$ | $3f$ | (0.2567, 0, 0) |
| $O_2$ | $3g$ | (0.5903, 0, 1/2) |
| $(B,B')$ | | (2.76 TPa, 2.71) |
| | Cotuninte-type $SiO_2$ | |
| Space group | | $Pnma$ |
| $(a,b,c)$ | | (4.108 Å, 2.191 Å, 4.853 Å) |
| Si | $4c$ | (0.2335, 1/4, 0.1387) |
| $O_1$ | $4c$ | (0.3472, 1/4, 0.4347) |
| $O_2$ | $4c$ | (0.9845, 1/4, 0.6670) |
| $(B,B')$ | | (2.75 TPa, 2.71) |
| | NbCoB-type $SiO_2$ | |
| Space group | | $Pmmn$ |
| $(a,b,c)$ | | (2.218 Å, 12.010 Å, 4.094 Å) |
| $Si_1$ | $4e$ | (1/4, 0.4470, 0.7612) |
| $Si_2$ | $4e$ | (1/4, 0.3500, 0.2629) |
| $Si_3$ | $2b$ | (1/4, 3/4, 0.2375) |
| $O_1$ | $4e$ | (1/4, 0.5675, 0.5202) |
| $O_2$ | $4e$ | (1/4, 0.6287, 0.025) |
| $O_3$ | $2b$ | (1/4, 3/4, 0.6454) |
| $O_4$ | $4e$ | (1/4, 0.4722, 0.1542) |
| $O_5$ | $4e$ | (1/4, 0.3270, 0.6330) |
| $O_6$ | $2a$ | (1/4, 1/4, 0.0198) |
| $(B,B')$ | | (2.75 TPa, 2.71) |

cotunnite-type $SiO_2$. Although cotunnite and NbCoB phases are metastable over all pressures in static calculations, their enthalpies are very competitive. Below 0.64 TPa, the cotunnite phase has lower enthalpy than $Fe_2P$. Above 0.78 TPa, the NbCoB phase has intermediate enthalpy between those of $Fe_2P$ and cotunnite phases. At 1 TPa, enthalpy differences between cotunnite and $Fe_2P$ and between NbCoB and $Fe_2P$ phases are just 0.006 and 0.004 Ry/FU. At 2 TPa, these differences increase to 0.017 and 0.01 Ry/FU (at most ~3000 K). Phonon calculations show that all three phases are dynamically stable beyond ~0.4 TPa.

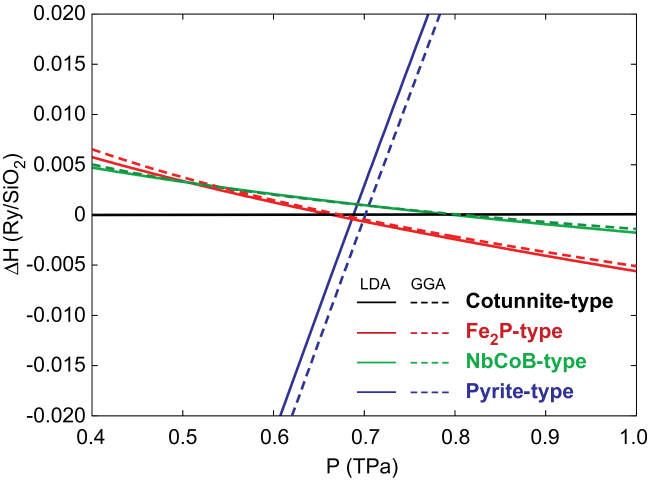

FIG. 3. (Color online) Enthalpies of pyrite-, $Fe_2P$-, and NbCoB-type $SiO_2$ with respect to cotunnite-type $SiO_2$.

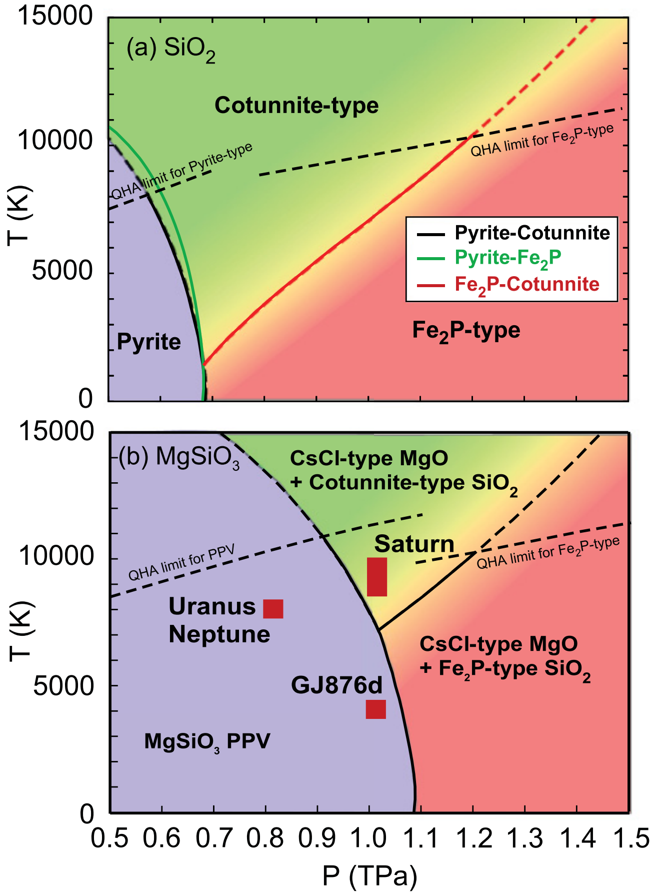

FIG. 4. (Color online) Pressure-temperature phase diagram of (a) $SiO_2$ and (b) dissociation of $MgSiO_3$ PPV into MgO and $SiO_2$. Free energy of $MgSiO_3$ PPV published in Ref. 7 is used. The transformation between $Fe_2P$- and cotunnite-type $SiO_2$ is expected to be gradual (see the text). Red areas denote estimated pressure-temperature conditions at core-envelope boundaries in the solar giants[6] and in the GJ876d.[34] Dashed lines indicate the limit of validity of the QHA.

Figure 4(a) shows the phase diagram of $SiO_2$ predicted by the QHA. Post-pyrite transitions to $Fe_2P$ and cotunnite phases have negative Clapeyron slopes. This results from the increase in CNs and bond lengths in $Fe_2P$ and cotunnite phases, which increases density of states of low-frequency vibrations and vibrational entropies across these post-pyrite transitions.[32] In contrast, the phase boundary between $Fe_2P$ and cotunnite phases has a normal positive Clapeyron slope. Below (above) ~1500 K, pyrite-type $SiO_2$ should transform to a $Fe_2P$-type (cotunnite-type) $SiO_2$. In contrast, the NbCoB phase does not have a stability field. However, entropic stabilization of disordered structural motifs intermediate between $Fe_2P$ and cotunnite is very likely at high temperatures. Therefore the $Fe_2P$ to cotunnite transition might not be sharp but a rather gradual transformation. Actually, the possibility that a fully disordered, mixed, or even dynamically disordered phase is stable at high temperatures cannot be discarded. However, the cotunnite phase is very stable without phonon instabilities in the pressure and temperature range of the phase diagram we presented, suggesting a crossover.

The presence of the $Fe_2P$ phase introduces an additional phase boundary in the dissociation phase diagram of $MgSiO_3$ PPV as shown in Fig. 4(b). In the icy giants, Uranus and Neptune, the dissociation into MgO and $SiO_2$ should not occur. In the gas giants, Saturn and Jupiter, the dissociation into CsCl-type MgO and cotunnite-type $SiO_2$ occurs first. At higher pressures, depending on the internal temperature profiles in these planets, cotunnite-type $SiO_2$ might transform to $Fe_2P$ type. In GJ876d, a terrestrial exoplanet[33] with ∼7.5 Earth masses ($7.5M_{\oplus}$), conditions estimated at the core-mantle boundary[34] are close to the dissociation phase boundary.

Finally, the predicted structural crossover between $Fe_2P$ and cotunnite phases should be fundamental to understanding the high-pressure and high-temperature behavior of $AX_2$-type compounds. Although pressures for the predicted phenomenon in $SiO_2$ are challenging to experiments, low-pressure analogs could be investigated to validate our predictions. $MgF_2$ is particularly suitable because it has a very similar sequence of phase transitions to $SiO_2$. In combination with NaF it forms $NaMgF_3$ perovskite, that has the same sequence of predicted phase transitions as $MgSiO_3$ perovskite,[7,35] including dissociation into elementary fluorides/oxides. There are still unresolved questions in the experimental high-pressure behavior of $NaMgF_3$ and $MgF_2$.[10,36] The structural crossover between $Fe_2P$ and cotunnite phases might be part of the answer.

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