

Mechanism of Chemical Reactions between SiO₂ and CO₂ under Mantle Conditions

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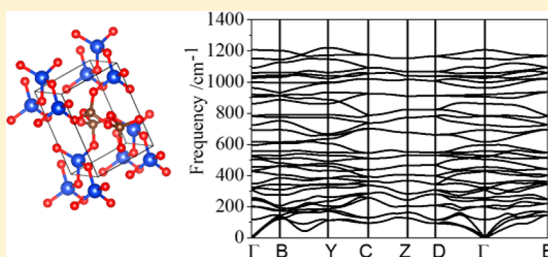
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Supporting Information

ABSTRACT: Silica (SiO₂) is a major component of many minerals on the Earth. Under ambient conditions, silica does not react with carbon dioxide (CO₂). However, at high pressure and temperature, the stability of silica may be affected by CO₂, which becomes supercritical fluid CO₂ under extreme conditions and can percolate into the Earth's mantle to react with silica. Here, we investigated the chemical reactions between zeolite SSZ-56 as a model silicate and CO₂ under temperature and pressure conditions close to those of the mantle transition zone using density functional theory and molecular dynamics calculations. The reactions occurred on the SiO₂ surface forming the zeolite's cavities. In the melt, CO₂ and SiO₂ mixed closely and, upon cooling, formed a solid with disordered Si and C sites similar to a cristobalite SiO₂–CO₂ solid-solution structure. This structure was thermodynamically stable with respect to α -cristobalite and solid CO₂ above 9 GPa.

KEYWORDS: silica, DFT, chemical reaction, high pressure, Earth's mantle, mineral



1. INTRODUCTION

Carbon dioxide and silica are two fundamental components of the Universe. Both are group IV oxides. Molecular CO₂ is the main greenhouse gas, and the current amount in the Earth's atmosphere has become a severe challenge to human life. The presence of CO₂ in the Earth's mantle also plays an important role in volcanic and seismic activities. The CO₂ molecule has strong C=O bonds, so it is chemically inert under ambient conditions. However, the π bond and the properties of CO₂ can be significantly affected by pressure.¹ At low pressures, CO₂ crystallizes into several van der Waals molecular solids. At high pressures and high temperatures (>41 GPa and >1800 K), the CO₂ molecules rehybridize and transform into an extended solid with single (sp³) bonded C–O¹ sharing a similar structure with the β -cristobalite polymorph of SiO₂. In addition, CO₂ fluid becomes supercritical, when it is held above its critical temperature and critical pressure, and can percolate into most materials. Under ambient conditions, CO₂ and SiO₂ do not react with each other, but reactivity is expected to be promoted by high pressures and high temperatures. The similarity between CO₂ and SiO₂ at high pressures has stimulated several recent studies to investigate the possible reactions between them.^{2,3} Such chemical reactions, on one hand, are of fundamental importance for understanding the deep carbon cycle; on the other hand, such reactions may have important practical applications. For example, injecting CO₂ underground has been proposed as a new and efficient way of removing extra

CO₂ from the atmosphere.^{4–6} The possibility of forming three-dimensional extended covalent solids may help stabilize the reaction products that, in themselves, may even be potential candidates as high-energy content materials. In fact, silicon–oxygen polyhedra bonded to carbonates have been found in carbon bearing silicate melt.⁷ The exploration of the chemical reaction between CO₂ and SiO₂ at high pressures will help the development of new chemistry between these two chemical species. However, experimental and theoretical studies on this subject are limited.^{2,3,8–10}

Santoro et al.² reported the first observation of a disordered silicon carbonate formation by compressing a sample of microporous silica (zeolite) with CO₂-filled voids at pressures of 18–26 GPa and temperatures between 600 and 980 K. No detailed information about the structure or the reaction mechanism was presented. Later, the same group³ reported the observation of a SiO₂–CO₂ solid solution from the reaction of CO₂ and a silica melt at pressures around 16–22 GPa and temperatures of >4000 K. The report was challenged.^{3,11,12} Here, we propose a novel mechanism on the formation of a SiO₂–CO₂ solid solution. We have undertaken a theoretical investigation of the reactions between CO₂ and porous zeolite

Received: December 12, 2017

Revised: March 5, 2018

Accepted: March 19, 2018

Published: March 19, 2018

SSZ-56 SiO_2 under mantle transition zone conditions using density functional (DFT)-based *ab initio* molecular dynamics (AIMD) simulations and total energy calculations. The theoretical results helped to identify the reaction products and provide an atomistic description of the reaction mechanisms. We also performed a detailed investigation of the structure and energy of the reaction product obtained from quenching the silica melt and CO_2 and the potential cristobalite SiO_2 - CO_2 solid solution at high pressures.

2. COMPUTATIONAL METHODOLOGY

We investigated the chemical reaction of CO_2 in SSZ-56 with AIMD calculations. The computational model was constructed from a unit cell of the zeolite SSZ-56,^{2,13} a member of the SFS zeolite family with a crystal structure consisting of 56 SiO_2 molecules that is structurally similar to the zeolite used in the experiment. The empty zeolite structure was optimized at 0 GPa, and afterward, 40 CO_2 molecules were inserted into the channels (Figure 1) to create the same chemical composition as

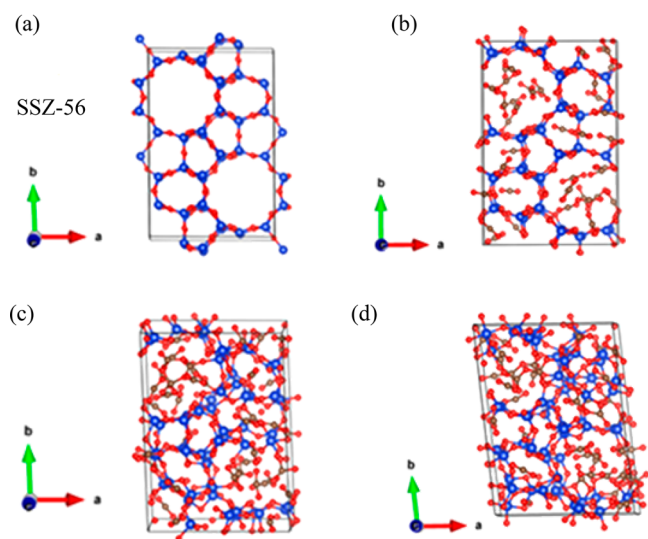


Figure 1. (a) Structure of empty SSZ-56. (b) Final snapshot of SSZ SiO_2 - CO_2 after NVT MD simulation at 0 GPa and 100 K and NPT MD simulation at (c) 26 GPa and 1000 K and (d) 30 GPa and 500 K (Si, blue; C, gray; O, red).

that of the system studied in the experiment. Therefore, the model consisted of 56 SiO_2 and 40 CO_2 molecules and 288 atoms in total. Following the experimental conditions,² the zeolite SiO_2 - CO_2 model system was equilibrated for 3 ps at 500 K and then to 1000 K at 0 GPa with microcanonical ensemble constant-volume constant-temperature (NVT) MD simulations using a Nosé–Hoover thermostat to control the temperature. After equilibration, an isobaric–isothermal canonical ensemble (NPT) MD calculation was performed under the experimental condition² of 26 GPa and 1000 K. In the NPT simulation, the Parrinello–Rahman barostat and Langevin thermostat are employed to control the pressure and temperature, respectively. A fictitious mass of 10 is employed for lattice degrees of freedom. To assess the effects of pressure and temperature, an additional calculation was performed at 30 GPa and 500 K. In each case, the MD simulation lasted for at least 13 ps. To ensure that the reaction was complete, a total 25 ps NPT simulation was performed for the system at 26 GPa and 1000 K. Notably, the pressure and temperature considered here

are far below those of the molecular to nonmolecular transformation of CO_2 (41 GPa and 1800 K, respectively).

To test the hypothesis of SiO_2 - CO_2 solid-solution formation under high pressures,³ we examined the structure of the quenched melt of the SSZ-56 SiO_2 - CO_2 model by melting the structure at 25 GPa and 4000 K and then quenching it to 500 K. In addition, the stability of a potential SiO_2 - CO_2 solid solution structure was constructed from crystalline α -cristobalite SiO_2 by randomly replacing half of the Si atoms with C atoms. Static geometry optimization at different pressures was performed. The infrared and Raman spectra, electronic band structure, optical spectrum, elastic modulus, and hardness of this α -cristobalite SiO_2 - CO_2 solid solution were calculated. The optical spectrum was computed by solving the Bethe–Salpeter equation (BSE) using GW-corrected eigenvalues. The elastic constants were computed by the strain–stress method, and the bulk modulus and shear modulus were derived from the Voigt–Reuss–Hill averaging scheme.^{14,15}

All calculations were performed with the Vienna *ab initio* simulation package, VASP,^{16–19} which is a plane wave basis electronic structure code using projected augmented (PAW) wave potentials for the atoms. An energy cutoff at 400 eV is used for the plane wave basis set expansion. The PAW²⁰ treats 3s and 3p orbitals of Si, 2s and 2p orbitals of O, and C atoms as valence electrons. The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional²¹ was employed. An $8 \times 8 \times 8$ Monkhorst–Pack *k*-point mesh was used to sample the Brillouin zone for geometry optimization, and energy calculations on the SiO_2 - CO_2 solid solution with the total energy converged to better than 1 meV/atom. A single Γ point was used for Brillouin zone sampling for MD calculation. A time step of 1.0 fs was used to integrate the equations of motion in MD calculations. The MD trajectories were examined to identify the reaction mechanisms and products.

3. RESULTS AND DISCUSSION

3.1. Reaction of CO_2 Trapped in the Zeolite SSZ-56 Cavities. Silicalite zeolites are microporous and can be synthesized with pores of different sizes formed from linking of four-, five-, six-, and ten-membered channels formed by SiO_4 tetrahedra. The porous framework structures can be filled with small molecules through physical absorption.²² This unique property has been exploited industrially for gas separation and storage.²³ As reported elsewhere,²⁴ the chemical reaction between CO_2 and mineral quartz and stishovite proceeds only at the interface. Compared to these minerals, microporous SiO_2 has a much larger surface and channel to accommodate the CO_2 molecules. The large surface area of the cavities exposed to the encaged CO_2 molecules may facilitate reactions at lower pressures and temperatures. Recently, zeolite filled with CO_2 and compressed under external pressures was studied by infrared spectroscopy, and a disordered silicon carbonate was successfully synthesized at 18–26 GPa and 600–980 K.² The objective here is to identify the mechanism and the reaction products with AIMD.

A zeolite (SSZ-56)/ CO_2 model (Figure 1b) with a SiO_2 : CO_2 ratio close to the experimental stoichiometry was constructed and studied with AIMD. SSZ-56 is made of five-, six-, and ten-membered Si–O channels. During thermal equilibrium, no reaction between the microporous framework and the CO_2 was uniformly observed (Figure 1b). Upon compression to 26 and 30 GPa using NPT MD simulation, the lattice constants

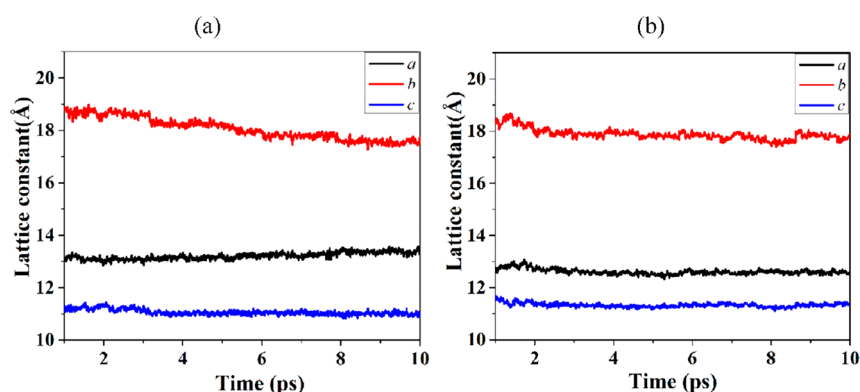


Figure 2. Temporal evolution of the lattice constants in the MD simulations performed at (a) 26 GPa and 1000 K and (b) 30 GPa and 500 K.

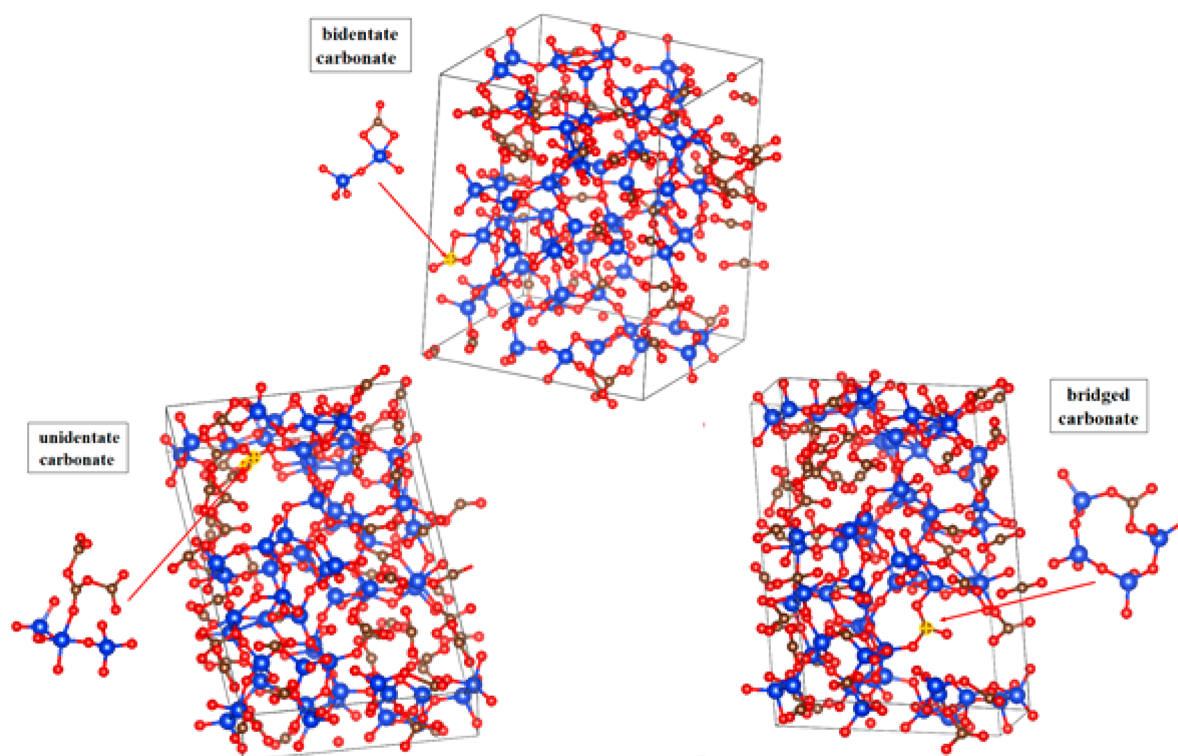


Figure 3. Final structure of the $\text{SiO}_2\text{--CO}_2$ model from the *NPT* simulation at 1000 K and 26 GPa, with unidentate, bidentate, and bridged carbonate fragments extracted from the final structure.

decreased most noticeably in the b axes with a small increase in the a axes (Figure 2a,b). This indicated that the porous SiO_2 framework had shrunk and the SiO_2 framework began to distort. At 30 GPa, the a lattice constant (x -direction) shortened more than the b lattice constant, as compared to 26 GPa. In both calculations, the compressed structure helped to bring the SiO_2 and CO_2 closer, promoting the initial chemical interaction. Reactions occurred only between CO_2 and SiO_2 (Figures 1c,d and 3) on the channel surfaces, forming unidentate, bidentate, and bridged carbonates (Figure 3). This observation is exactly the same as that suggested in the experimental study.² After 8 ps, the model system equilibrated and there was no more change in the lattice constants. This is also reflected from the evolution of the total energy with time (Figure S1) where there is little change after 8 ps. No new reactions were detected up to 25 ps. The reason that no more reaction occurs is that the exposed SiO_2 surface is already covered by reacted CO_2 and those free molecules are no longer

able to interact with the SiO_2 and the reaction ceased. Polycarbonate (CO_3) chains composed of --O--(C=O)--O-- were formed in the large channel (10-member Si--O ring channel) with some unreacted CO_2 molecules. The product consisted of three coordinated carbonate (CO_3) groups with an average C--O bond length of 1.45 Å. Remarkably, even after the reaction, the SFS framework was only slightly distorted, and the gross zeolite structure was maintained (Figure 4). The reactions between SiO_2 and CO_2 resulted in an increase in the local Si--O coordination number to five.

To understand the reaction mechanism, we analyzed the temporal atom positions from the MD trajectory. For both simulations (i.e., 26 GPa at 1000 K and 30 GPa at 500 K), similar results were found. The temporal variation of the lattice constants plotted in Figure 2 shows a slowly decreasing trend, indicating that the reaction between SiO_2 and CO_2 proceeded gradually. At high pressures and high temperatures, some of the CO_2 exhibited large-amplitude and fluxional O--C--O bending

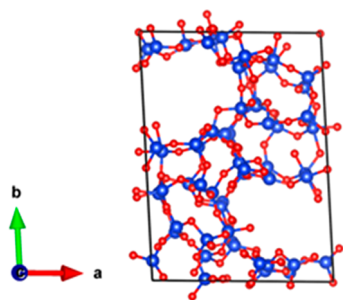


Figure 4. SiO_2 framework of the final structure of the $\text{SiO}_2\text{--CO}_2$ model from the *NPT* MD calculation at 26 GPa and 1000 K, with CO_2 molecules and polycarbonate chains removed.

motions, as evidenced by a large $\text{O}=\text{C}=\text{O}$ angle distribution shown in Figure S2. The distribution function has a broad distribution between 150° and 180° showing substantial fluxional bending of the CO_2 . When the bent CO_2 moved closer to the surface of the SiO_2 , forming the channels, the O of CO_2 started to bond with the Si forming 5-Si-O coordinated Si centers (Figure 5a). The C hybridization changed from sp to sp^2 . This initial reaction occurred near the five-membered ring pores. This is not unreasonable as the bent CO_2 needed to migrate only a short distance before reaching the SiO_2 in the channel. The reacted CO_2 was trapped and immobilized in the channels. In the subsequent step, the C reacted with the bridging O of two corner-shared SiO_4 tetrahedra (Si–O–Si linkage) and formed the bidentate carbonates (Figure 5b). The reaction was then paused, and no further reaction was observed for 3.5 ps, even though the lattice constants were decreased further. After 3.5 ps, similar reactions between CO_2 and SiO_2 in the 10-membered ring pores were observed (Figure 5c). Because the large pores (ten-membered ring) are more spacious, the reacted CO_2 can orient parallel to the channel. When more free CO_2 molecules were diffused into the channel, additional reactions were observed (Figure 5d,e). Unidentate carbonates formed when the CO_2 molecules were situated perpendicular to the channel surface (Figure 5d). Bidentate carbonates formed in the large pores (Figure 5d,e). Up to 6.1 ps, the carbonates in the large channels continued to react further when the additional CO_2 , brought closer by diffusion, led to the formation of polycarbonate chains attached to the channel surface (Figure 5f–h). No further reactions (Figure S2) were found even when the MD simulation was extended to 25 ps. A similar reaction mechanism was also observed at 30 GPa and 500 K. Therefore, the pressure and temperature collaborated to drive the chemical reactions.

Examination of the atom trajectories showed that the reaction between CO_2 and SiO_2 can be organized into three stages (Scheme 1). (i) At high temperatures, the CO_2 molecule bends. (ii) The initial reaction was between the O of the CO_2 and the Si of the SiO_4 tetrahedra on the surface of the channels, where the lone pair of the O interacted with the empty σ^* orbital of SiO_2 (see Scheme 2) and the C bonded to the bridging Si–O–Si forming CO_3 . (iii) Finally, subsequent reactions with other free CO_2 produced the polymer structure.

3.2. Formation of a Cristobalite-like $\text{SiO}_2\text{--CO}_2$ Solid Solution. Although the high-pressure crystalline polymorphs of CO_2 and SiO_2 share several similar structural features, there is a significant difference in the C–O and Si–O bond lengths. The formation of a $\text{SiO}_2\text{--CO}_2$ crystalline would not intuitively be expected to form a stable cristobalite-like solid, as it would

require both C and Si to have compatible coordination environments. Therefore, it was unexpected that a crystalline solid, composed of similar stoichiometric amounts of CO_2 and SiO_2 , was reported from the reaction of CO_2 with melted zeolite SSZ-56 at 16–22 GPa and 4000 K.³ Even more remarkably, this new material was shown to be recoverable under close to ambient conditions. X-ray diffraction measurements³ suggested this new phase can be assigned to an α -cristobalite structure with both C and Si 4-fold coordinated to the O atoms. Later, this conclusion was challenged as it was found that the experimental diffraction pattern may also be attributed to β - ReO_2 due to the reaction of the Re gasket with CO_2 at high pressures and high temperatures.¹² This new finding has led to the retraction of the claim.³ Nevertheless, it is of great interest to investigate the potential formation of a $\text{SiO}_2\text{--CO}_2$ solid solution.

To explore the possibility of formation of a $\text{SiO}_2\text{--CO}_2$ solid solution, the reaction product of CO_2 in zeolite SSZ-56 described above was melted at 4000 K using an AIMD simulation in the *NVT* ensemble. Quenching of the molten structure was conducted by decreasing the temperature slowly in steps of 100–500 K followed by a long 20 ps annealing. In the melt, both Si and C atoms were found to be distributed evenly (Figure 6). Once quenching had occurred, a structure composed of linked, corner-sharing CO_4 and SiO_4 tetrahedra (the basic structural feature of the cristobalite structure) and the remaining CO_3 were found (Figure 6). It is not surprising or unexpected that the calculations did not reproduce the observed crystal structure. However, the essential structural motif of the $\text{SiO}_2\text{--CO}_2$ solid solution, i.e., the occurrence of linked CO_4 and SiO_4 tetrahedra, was clearly observed. Apparently, it is indeed possible to form a solid with connected CO_4 and SiO_4 tetrahedra.

To examine the stability of the proposed crystalline $\text{SiO}_2\text{--CO}_2$ solid solution, we constructed an α -cristobalite-type structure with equal amounts of CO_2 and SiO_2 , i.e., $\text{Si}_2\text{C}_2\text{O}_8$. The model was constructed by replacing half of the Si atoms with C atoms randomly. The model structure was then fully optimized at selected pressures. The optimized model has a monoclinic $P2_1$ space group (Figure 7a), but the unit cell angles were very close to 90° . The optimized lattice parameters at 9 GPa were as follows: $a = 4.389 \text{ \AA}$, $b = 4.181 \text{ \AA}$, and $c = 5.983 \text{ \AA}$, $\beta = 90.5^\circ$. The theoretical structure, accounting for the distortion in the crystal structure due to the disordered C and Si positions, is in fair agreement with the experimentally observed cristobalite-type tetragonal $P4_12_12$ structure with a ($=b$) $= 4.594(1) \text{ \AA}$ and $c = 5.938(3) \text{ \AA}$ at 7 GPa. The result agrees with a previous structural prediction calculation in which a similar $P2_1$ structure is found to be stable at 20 GPa.¹⁰

Significantly, the predicted structure is dynamically stable (Figure 7b) and can be quenched recoverably, as no soft mode was found in the calculated phonon band structure computed at 0 GPa shown in Figure 7b. The calculated infrared (IR) and Raman spectra at 9 GPa are shown in panels a and b of Figure 8, respectively. Remarkably, the single dominant sharp peak observed³ at 540 cm^{-1} due to C–O–Si bending vibration in the experimental Raman spectrum is reproduced by the calculations. In the calculated Raman spectrum, the peaks around 450 cm^{-1} can be assigned to Si–O–Si bending of the zeolite frame; the vibrations in the range of $800\text{--}970 \text{ cm}^{-1}$ belong to the O–C–O bending modes, and the weak peaks at $1060\text{--}1150 \text{ cm}^{-1}$ are the asymmetric $\nu(\text{C–O–C})$ stretch modes. In the IR spectrum, the peaks at $600\text{--}800 \text{ cm}^{-1}$ belong

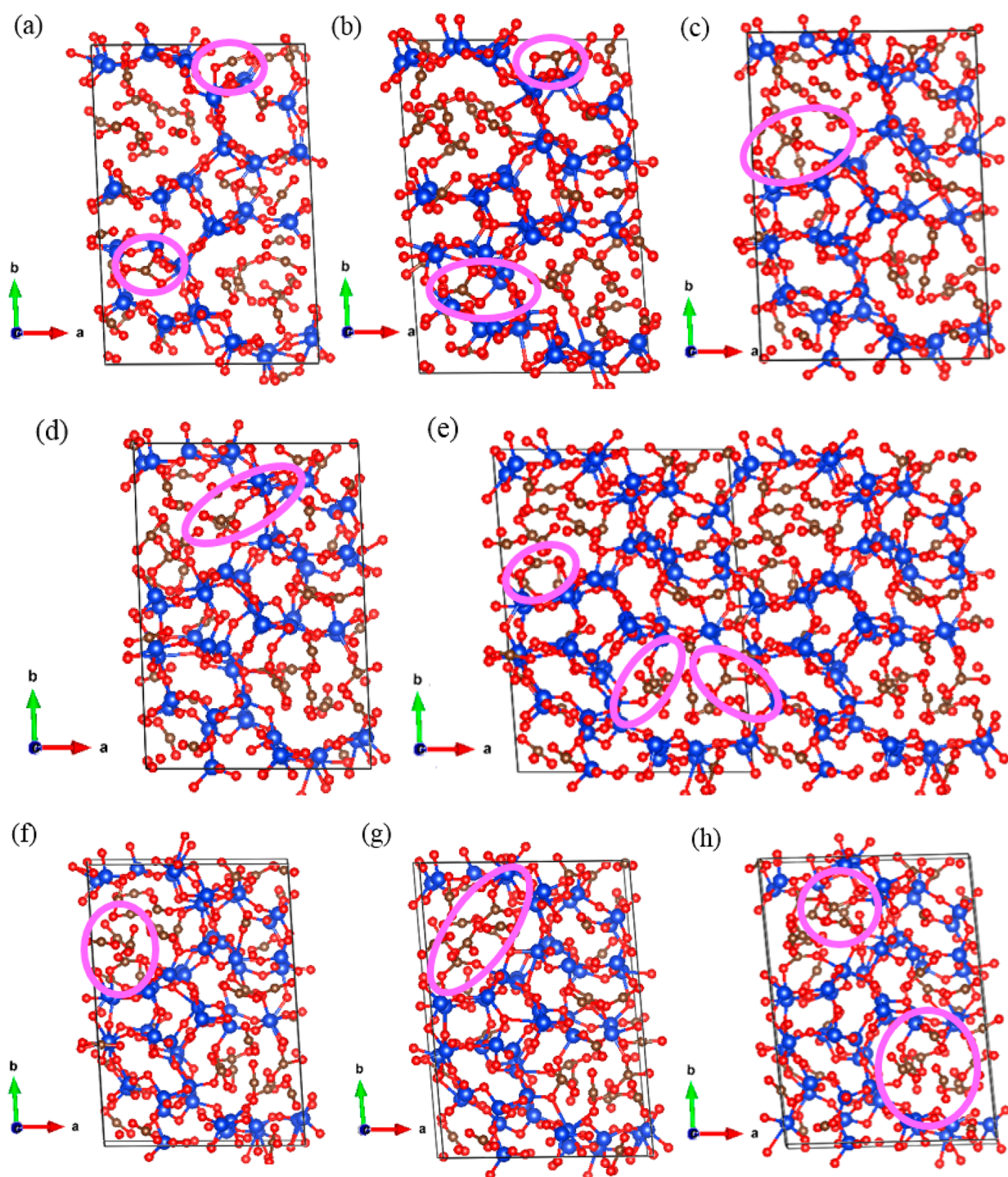
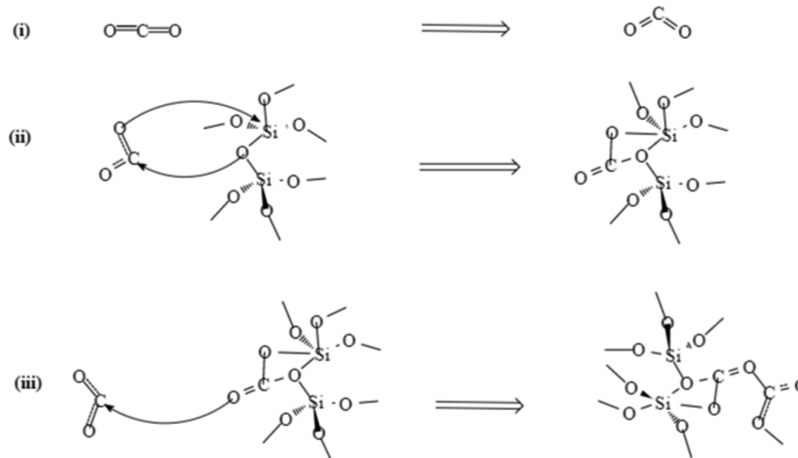


Figure 5. Snapshots of the $\text{SiO}_2\text{--CO}_2$ model system at different stages from the NPT calculation at 26 GPa and 1000 K at (a) 479, (b) 749, (c) 3501, (d) 3821, (e) 6101, (f) 6131, (g) 6201, and (h) 8000 fs. The purple circles highlight the structural changes described in the text.

to $\text{O--C--O } \nu_2$ while the peaks at 800–1000 are those of O--Si--O . Peaks at 1100 can be assigned to the Si--O--C mixed stretch modes. The calculated vibration spectra provide the evidence that an α -cristobalite $\text{SiO}_2\text{--CO}_2$ solid solution may have been formed in the previous experiment. Noting that the experiment may be contaminated by ReO_2 ,¹¹ the theoretical results presented here encourage further experimental work to investigate the possible formation of a $\text{SiO}_2\text{--CO}_2$ solid solution.

The thermodynamic stability of the $\text{SiO}_2\text{--CO}_2$ solid solution with the α -cristobalite structure in the pressure range of 2–25 GPa is determined from a comparison between the calculated enthalpies of the $\text{SiO}_2\text{--CO}_2$ model and the sum of (i) $\text{CO}_2\text{--III}$ and quartz and (ii) $\text{CO}_2\text{--III}$ and α -cristobalite (Figure 8c). Solid $\text{CO}_2\text{--III}$ was chosen for reference because it is the stable solid phase in this pressure range. The results show that the solid solution is thermodynamically unstable with respect to CO_2 and quartz but is thermodynamically stable with respect to $\text{CO}_2\text{--III}$ and α -cristobalite. This is reasonable because the

Scheme 1. Three Primary Reactions of (i) the Bent CO₂ at High Temperatures and High Pressures, (ii) the O of the Bent CO₂ That Bonded with Si of SiO₄ Tetrahedra on the Surface of the Zeolite Channel Forming a Five-Coordinate Si Center, and (iii) the Other O Atom of the CO₂ That Interacted with Additional CO₂ Molecules and Initialized Polymerization



Scheme 2. Orbital Interaction Diagram of the Initial Chemical Reaction between CO₂ and SiO₂

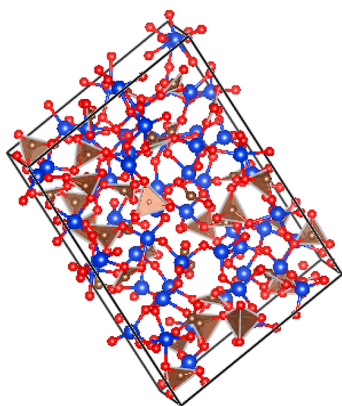
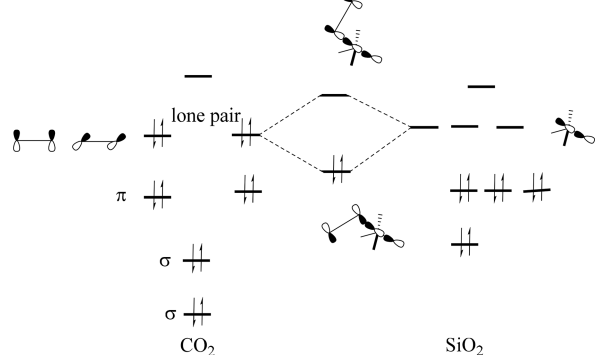


Figure 6. SiO₂–CO₂ model at 26 GPa obtained from melting zeolite SiO₂–CO₂ at 4000 K and quenched to 500 K. The connected CO₄–SiO₄ units are shown as shaded tetrahedra.

quartz is the stable phase of the four Si–O coordinated phase.²⁵ Therefore, in principle, an α -cristobalite SiO₂–CO₂ solid solution can form at high temperatures and pressures higher than 10 GPa and become metastable and recoverable under ambient conditions.

The band structure calculation shows this novel SiO₂–CO₂ solid solution is an insulator with a direct band gap of 6.0 eV (Figure 9a). The band gap is smaller than those of the SiO₂

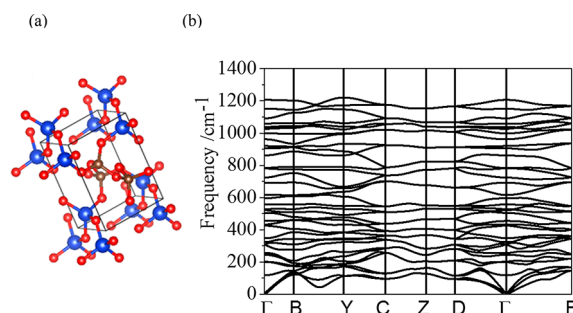


Figure 7. (a) Optimized α -cristobalite-like SiO₂–CO₂ solid solution at 9 GPa and (b) phonon spectrum for the recovered structure at 0 GPa.

analogues (under ambient conditions, the band gap of polycrystalline SiO₂ is 8.9 ± 0.2 eV;¹⁵ that of the thermally grown amorphous SiO₂ film is 9.3 eV,²⁶ and that of amorphous SiO₂ is 9.7 eV²⁶). Furthermore, crystalline silica α -quartz, β -quartz, α -cristobalite, β -cristobalite, and β -tridymite show similar electronic band structures and band gaps.^{27–30} In the SiO₂–CO₂ solid solution, the dispersions of the valence electronic bands are surprisingly flat throughout the entire Brillouin zone. The calculated absorption spectrum (Figure 9b) also shows band-edge absorption around 6.0 eV with a broad main absorption at 12 eV. The reflectivity (Figure 9c) is quite small at a low frequency as the compound is transparent. The calculated low-frequency refractive index is $n(\omega) = 1.17$, which is much smaller than that of α -quartz (1.46).³¹ Thus, the SiO₂–CO₂ solid solution may also be a good glass material. The SiO₂–CO₂ solid at 0 GPa is predicted to have a bulk modulus B of 55.62 GPa, which is higher than that of quartz (36.4 GPa).³² The calculated Vickers hardness (H_v) is ~ 11.0 GPa, which is comparable to that of quartz (9.81–11.3 GPa).³³ The larger bulk modulus and hardness compared to those of quartz are due to the stronger C–O bonds in the structure.

4. CONCLUSION

In this study, novel reactions among SSZ-56, a microporous SiO₂ zeolite, and CO₂ molecules trapped in the cavities were observed under the pressure and temperature conditions of the Earth mantle. We have made several contributions. (i) Under high-pressure and -temperature conditions, CO₂ should be a

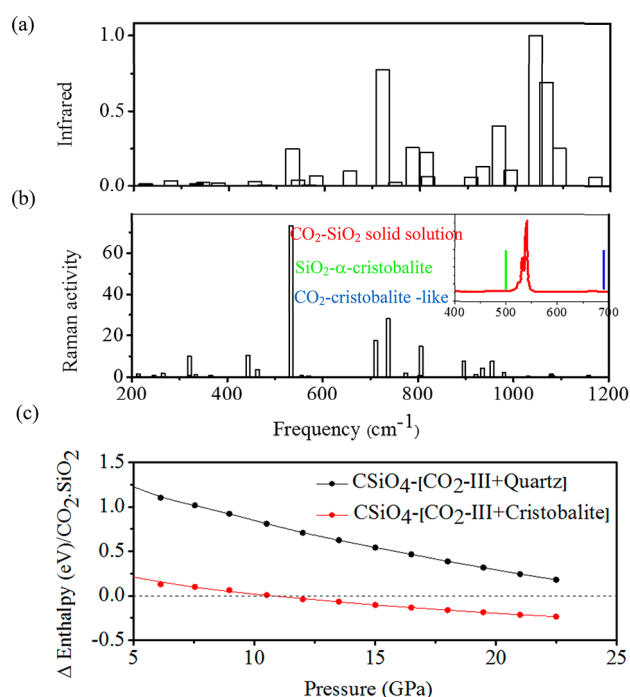


Figure 8. Calculated (a) IR and (b) Raman spectra for the studied $\text{SiO}_2\text{-CO}_2$ solid solution at 0 GPa. The inset is adopted from ref 3, where the red and blue peaks correspond to the $\text{SiO}_2\text{-}\alpha\text{-cristobalite}$ and cristobalite-like CO_2 , respectively. (c) Formation enthalpy for the $\alpha\text{-cristobalite-like}$ $\text{SiO}_2\text{-CO}_2$ solid solution with respect to phase III of CO_2 and quartz and $\alpha\text{-cristobalite}$.

supercritical fluid, yet we found no percolation of CO_2 into the bulk solid. Chemical reactions were observed at 26 GPa and

1000 K with only the SiO_2 on the surface of the cavities of zeolite SSZ-56. (ii) The vibrational modes of the chemical species proposed in the experimental Raman and infrared spectra are identified. (iii) The mechanisms of formation of these species, particularly the polycarbonates, are elucidated from the analysis of the molecular dynamics trajectories. It was found that the formation of 5 Si–O coordinated Si atoms plays a critical role in promoting the reactions between CO_2 and SiO_2 . The reactions occurred only at the pore surface through an initial interaction between the Si and O with a thermally excited bent CO_2 . Subsequent reactions eventually led to the formation of polycarbonate chains. (iv) We provided energetic and spectroscopic evidence of the formation of the $\text{CO}_2\text{-SiO}_2$ solid solution upon cooling from the melt. The thermodynamic stability of the cristobalite structure above 9 GPa is confirmed with the calculated Raman spectrum in substantial agreement with experiment. The theoretical results lend support to the possible synthesis and existence of this novel structure that has been suggested earlier. The solid solution is also predicted to be quench recoverable. It is a hard material with interesting electronic properties. The new results will potentially stimulate further experimental exploration of this system.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsearthspacechem.7b00144.

Evolution of temperature and total energy of $\text{SiO}_2\text{-CO}_2$ from NPT simulation at 26 GPa and 1000 K (Figure S1) and O–C–O angle distribution of the product from the chemical reactions at 26 GPa and 1000 K (Figure S2) (PDF)

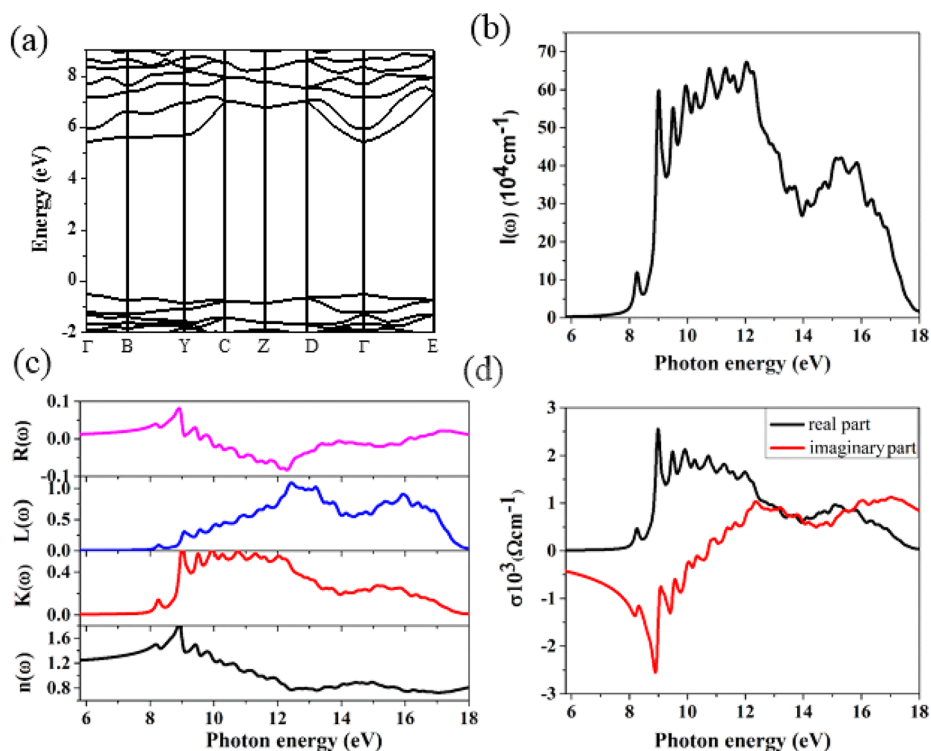


Figure 9. Calculated (a) electronic band structure, (b) absorption spectrum, (c) refractive index, energy-loss spectrum, extinction coefficient, and refractive index, and (d) optical conductivity for the cristobalite-like $\text{SiO}_2\text{-CO}_2$ solid structure.

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge WestGrid for providing computational resources.

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