

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Mechanistic study of pressure and temperature dependent structural changes in reactive formation of silicon carbonate

Bingyan Qu¹, Dongdong Li¹, Lei Wang¹, Jili Wu¹, Rulong Zhou^{1*}, Bo Zhang^{1,2*}, and
Xiao Cheng Zeng^{3*}

¹*Laboratory of amorphous materials, School of Materials Science and Engineering, Hefei University of Technology, Hefei, Anhui 230009, P. R. China*

²*Anhui Provincial Key Lab of Advanced Functional Materials and Devices, Hefei University of Technology, Hefei, Anhui 230009, P. R. China*

³*Department of Chemistry and Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, Lincoln, Nebraska 68588*

*rlzhou@hfut.edu.cn; *bo.zhang@hfut.edu.cn; *xzeng1@unl.edu;

Abstract

The discovery of the silicon carbonate through chemical reaction between the porous SiO₂ and gaseous CO₂ addressed a long-standing question regarding whether the reaction between CO₂ and SiO₂ is possible. However, the detailed atomic structure of silicon carbonate and associated reaction mechanism are still largely unknown. We explore structure changes of silicon carbonate with pressure and temperature based on systematic ab initio molecular dynamics simulations. Our simulations suggest that the reaction proceeds at the surface of the porous SiO₂. Increasing number of CO₂ molecules can take part in the reaction by increasing either the pressure or temperature. The final product of the reaction exhibits amorphous structures, where most C atoms and Si atoms are 3-fold and 6-fold coordinated, respectively. The fraction of differently coordinated C (Si) atoms is pressure dependent, and as a result, the structure of the final product is pressure dependent as well. When releasing the pressure, part of the reaction product decomposes into CO₂ molecules and SiO₂ tetrahedrons. However more than 50% C atoms are still in 3-fold coordination, implying that stable silicon carbonate may be obtained via repeated annealing under high pressure. The mechanism underlying this chemical reaction is predicted with two possible reaction pathways identified. Moreover, the reaction transition curve is obtained from the extensive simulation, which can be useful to guide the synthesis of

silicon carbonate from the reaction between SiO₂ and CO₂.

Introduction

Both CO₂ and SiO₂ are ubiquitous on earth and both compounds have attracted extensive research attention in chemistry, atmospheric science, and geoscience. Although both compounds belong to the group IV oxides and have the same stoichiometric ratio of the constituent atoms, a stark contrast between the two is that in the ambient conditions CO₂ is a molecular gas in which the C atom is *sp*-hybridized and connected with two O atoms via the double bonds [1], whereas the SiO₂ is a covalent solid with rich crystalline polymorphs, *e.g.*, quartz, coesite, and cristobalite [2]. In the SiO₂ polymorphs, Si atom is typically *sp*³-hybridized and bonded with four O atoms. In the ambient conditions, CO₂ and SiO₂ cannot react with each other due to fully occupied bonding orbitals in CO₂ and SiO₂. However, at high pressure and temperature, the reaction between the two compounds can occur [3].

It is known that high pressure may greatly alter the structural, chemical, and mechanical properties of matter, as well as may give rise to novel materials with new structures [4]. At medium pressure, CO₂ can exist in several possible molecular crystalline forms, such as CO₂-I, CO₂-III and CO₂-VII [1, 5, 6]. At high pressure, these molecular crystalline phases can transform into extended covalent solids such as CO₂-V [7-12], CO₂-VI [13] and coesitelike CO₂ [14], whose crystalline structures are in close resemblance to the SiO₂ polymorphs. Moreover, the amorphous structure of CO₂ solids has also been found at high pressure [15, 16]. In view of the structural similarity between the high-pressure crystalline structure of CO₂ and the polymorphs of SiO₂, mixed CO₂ and SiO₂ solids may exist at high pressures, thereby calling for synthetic efforts to achieve the mixed SiO₂-CO₂ compounds. Based on the first-principles computation, Aravindh *et al.* [17] studied the relative stability of hypothetical Si_xC_{1-x}O₂ compounds, constructed via replacing the Si atoms in β-cristobalite by C atoms. Various compositions ranging from $x = 0$ to $x = 1$ were considered. The computed formation energies of all the structures were found to be positive, suggesting that the mixed structures are thermodynamically unstable at the

ambient pressure. However, because the computed formation energies of most structures at ambient pressure are close to zero, stable compounds may be formed under high pressures and still be stable at ambient conditions. Santoro *et al.* [3] successfully synthesized the SiO₂-CO₂ compounds via the chemical reaction between porous SiO₂ and CO₂ molecules at high pressure and temperature. The product is an amorphous with most C atoms threefold coordinated. Although only disordered structures of the mixed SiO₂-CO₂ compounds were achieved in the experiment, it is believed that stable crystalline structures of mixed SiO₂-CO₂ compounds can be formed under high pressures because crystalline phases are expected to be energetically more stable than amorphous phases. Later, Santoro *et al.* [18] obtained the crystalline CO₂-SiO₂ solid solution by cooling the liquid CO₂ and silica from > 4000 K and 16-22 GPa. In the final structure, both C and Si are in fourfold coordination. These experimental results imply the reacted product is sensibly dependent on the temperature and pressure in the reacting process. To predict the possible stable crystalline structure of the mixed SiO₂-CO₂ compound, Morales-García *et al.* [19] examined the structure of UB₂O₆, and theoretically studied structures and stability of the SiO₂-CO₂ alloys at high pressure. They predicted that SiC₂O₆ is the most plausible stoichiometry with the C and Si atoms being 3-fold and 6-fold coordinated, respectively. We have also performed an extensive structure search, using an evolutionary algorithm [20], for the low-enthalpy structures of the SiO₂-CO₂ compounds at various stoichiometric ratios and under the high pressure of 20 GPa. A slab like structure of SiC₂O₆ was predicted to be very stable to resist decomposition into the reactants SiO₂ and CO₂. In most of the predicted low-enthalpy structures, C and Si atoms form CO₃ and SiO₆ structure motif, respectively, indicating that C and Si favor the three-fold and six-fold coordination, respectively, under the high pressure. Despite of these efforts, the detailed atomic structure of the mixed crystals and the reaction mechanism are yet to be studied.

In this work, we performed comprehensive *ab initio* molecular dynamics (AIMD) simulations to explore the chemical reaction between SiO₂ and CO₂ at high pressures and temperatures, and to understand pressure- and temperature-dependent structural

changes and reaction mechanism underlying this process. Our simulation demonstrates that the reaction proceeds at the surface of the porous SiO_2 and more and more CO_2 molecules can take part in the reaction with increasing the pressure or temperature. In the product (silicon carbonate) of the reaction, the C atoms and Si atoms favor the 3-fold and 6-fold coordinated local structures, respectively, although 2-fold and 4-fold coordinated C atoms as well as 4-fold and 5-fold coordinated Si atoms also exist. This newly formed product is constructed *via* the higher-coordinated Si and C atoms through sharing O atoms whose coordination numbers increase correspondingly. The final product is an amorphous and its structure is pressure dependent due to the coordination numbers of C, Si, and O atoms being pressure dependent. When the pressure is released, the reaction product decomposes into CO_2 molecules and SiO_2 , implying the amorphous silicon carbonate is unstable at the ambient pressure, consistent with the observation in experiment [3]. The reaction mechanism underlying this reaction is also investigated.

Model and methods

The crystalline structure of silicalite SiO_2 as used in experiments is built by the corner-sharing SiO_4 tetrahedrons. These tetrahedrons form four-, five-, six- and ten-membered rings with the pores as large as 5.5 Å [21]. A main reason for this structure being selected in the previous experiments is that all the SiO_4 tetrahedrons are on the surface of the micropores. However, this structure (288 atoms in the unit cell) is somewhat too large for the ab initio molecular dynamics (AIMD) simulations. Instead, we choose another porous SiO_2 with RHO-type structure, as shown in Fig.1. This structure is a cubic crystal with the space symmetry of Im-3m (Space Group No. 229) and the lattice constant of about 14.92 Å. It is also constructed by SiO_4 tetrahedrons similar to the silicalite. Moreover, the corner-sharing building units form microcages located at the corners and center of the cubic cell. These microcages connect with their neighboring microcages through the micropores formed by the big eight-membered rings (with the diameter of about 6.70 Å), which ensures the CO_2 molecules can transfer easily between microcages. More importantly, in this structure,

all the SiO_4 tetrahedrons are on the surface of the micropores or microcages, which is crucial for enhancing the chemical reaction. Initially, CO_2 molecules are randomly distributed in the microcages and micropores with the distances between different CO_2 molecules and those between CO_2 and SiO_2 as large as possible. The stoichiometric ratio of SiO_2 and CO_2 is 1:1, and the total number of atoms in the simulation system is 288.

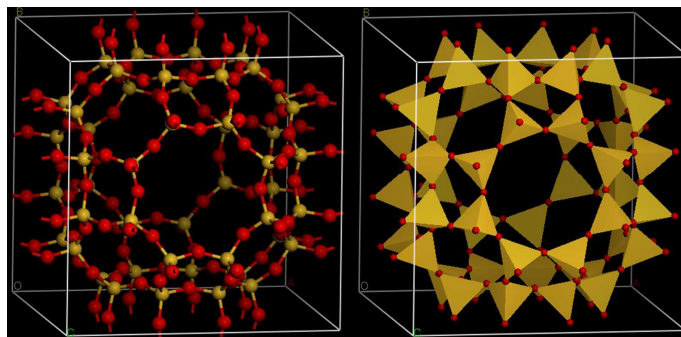


Fig. 1 Schematic representation of the crystalline structure of RHO-type SiO_2 . Atoms in gold and red colors are Si and O, respectively.

All the AIMD simulations are carried out using the Born-Oppenheimer molecular dynamics method implanted in the CP2K package [22]. The wave-function is described using a combination of Gaussian DZVP basis sets and the plane wave basis sets [23] with the energy cutoff of 280 Ry. The convergence criterion for the self-consistent field (SCF) is 10^{-5} . The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerof (PBE) exchange-correlation functional [24] was selected. The AIMD simulations are performed in the NVT ensemble with the periodic boundary conditions applied in all the three spatial dimensions. The hydrostatic pressures is applied by compressing the simulation cell homogeneously. The temperature is controlled with the Nose-Hoover thermostat. The MD time step is 2 fs and each simulation is performed over 50 ps.

Results and Discussions

I. Structural evolution with the increase of pressure

First, the AIMD simulations with the initial structure are performed at the temperature of 800 K, in view of the fact that the reaction between CO₂ and SiO₂ were observed in the experiments at this temperature. Through step-wise compression of the system, we can obtain the structural evolution with increasing the pressure. As seen in Fig. 2 (black line), the volume decreases continuously as increasing pressure. When the pressure reaches in the range of 43.28 - 45.14 GPa, a sudden volume contraction of about 11.1% occurs, indicating a major structural change of the system. Further increase of the pressure only results in smooth decrease of the volume.

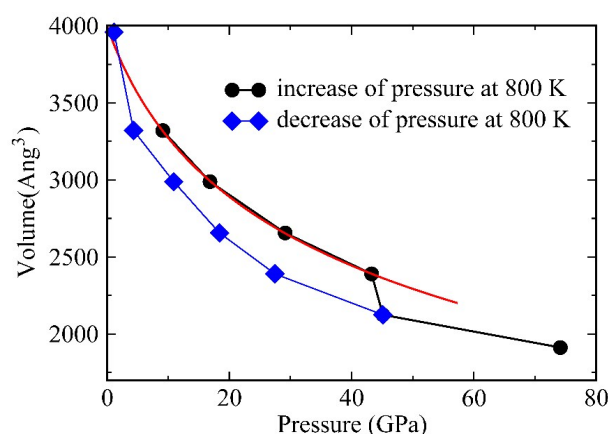


Fig. 2 The volume of system at 800 K *versus* the hydrostatic pressure. The black and blue lines represent the processes of increasing and decreasing pressure, respectively. The red line is a fit to the third-order Birch-Murnaghan equation of state.

To gain more insights into the major structural change in the pressure range of 43.28 - 45.14 GPa, we compare the structures under limiting two pressures in this range. For the structure under the pressure of 43.28 GPa, some C atoms are bonded with three O atoms, forming sp^2 -hybridized local structure. These three-fold coordinated C atoms connect with Si or other C atoms via the bridge of O atoms. However, most C atoms are still in the sp hybridization and each of them is bonded with only two O atoms. For Si atoms, although most of them are in four-fold coordination, some five-fold or six-fold coordinated Si atoms are seen, forming polyhedrons with more than four faces. On the other hand, three-fold coordinated O

atoms are observed. Compared with the initial structure in which all CO₂ are in molecular form and all the Si atoms are 4-fold coordinated, this result strongly indicates that some CO₂ molecules have already reacted with the SiO₂ at 43.28 GPa. However, the reaction is only limited on the surface of SiO₂ while most CO₂ remain in the molecular form. Also, the overall framework of SiO₂ exhibits little change, even though some structural deformation and twist are observed.

For the structure under the pressure of 45.14 GPa, most C atoms are bonded with three or four O atoms, resulting in either sp^2 - or sp^3 -hybridization, and very few C atoms are in the sp -hybridization. The C atoms with higher coordination also connect with other C and Si atoms via the bridge of O atoms. Many Si atoms are in the six-fold or five-fold coordination, although four-fold Si atoms still exist. The Si-O polyhedrons construct a new structure while the microcages in the initial structure disappear. The interconnected threefold and fourfold coordinated C atoms fill in the space among the SiO₂ polyhedrons. Moreover, this newly formed structure is amorphous without any symmetry. It clearly indicates that nearly all the SiO₂ and CO₂ in the system participate in the chemical reaction. From the structural analysis, we come to the conclusion that the large volume contraction (black line in Fig. 2) stems from the major structural transition due to the chemical reaction between CO₂ and SiO₂.

Next, we analyze the structural evolution of the system with increase of the pressure, including the bond lengths, bond angles, and coordination numbers (see Fig. 3). The bond lengths of C-O and Si-O are determined from the first maximum of the C-O and Si-O pair correlation functions, and the coordination number is defined as the number of atoms surrounding a given atom within a specific cut-off distance. The latter is chosen as the first minimum of the corresponding partial pair correlation function. In Fig. 3(a), the nearest distance between O atoms is also plotted. Since the O atoms may be initially bonded to C or Si atoms, in Fig. 3, we distinguish the two kinds of O atoms by the notations O_C and O_{Si}, respectively. When the pressure < 29.14 GPa, the bond lengths of C-O and Si-O as well as the nearest distances of O_C-O_C and O_{Si}-O_{Si} (Fig. 3(a)) are nearly unchanged with increasing pressure.

Meanwhile, the bond angles of O-Si-O and O-C-O (Fig. 3(b)) are nearly constants as well, but the bond angles of Si-O-Si decrease notably. These changes are caused by the continuous contraction of the system volume as shown in Fig. 2 (the black line). The bond angles of O-Si-O and O-C-O are about 109° and 173° , respectively, which are very close to the bond angles in the perfect SiO_4 tetrahedron and CO_2 linear molecule. The coordination numbers of Si and C are shown in Fig. 3(c), which are 4 and 2, respectively, indicating that SiO_2 maintains in the form of SiO_4 tetrahedrons and CO_2 is in molecular form. In other words, the reaction between CO_2 and SiO_2 does not occur.

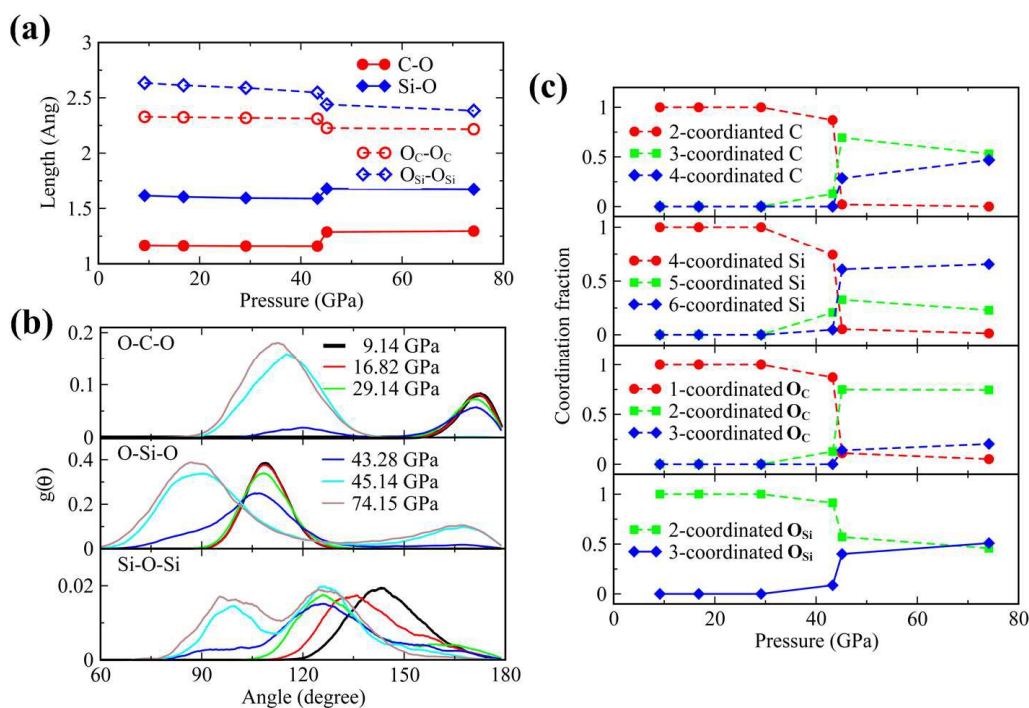


Fig. 3 (a) The bond lengths of C-O and Si-O as well as the nearest distances of O_C-O_C and O_{Si}-O_{Si} versus the pressure. (b) The partial bond angle correlation functions of O-C-O, O-Si-O and Si-O-Si versus the pressures. (c) The fractions of differently coordinated C, Si and O atoms versus the pressure.

When the pressure reaches to the range of 43.28 - 45.14 GPa, the structure of the system is largely altered: (1) The volume contracts sharply, as shown in Fig. 2; (2) The bond lengths of C-O and Si-O increase while the nearest distances of O_C-O_C and

$O_{Si}-O_{Si}$ decrease. (3) The number of 3-fold coordinated C atoms increase abruptly at the expense of 2-fold coordinated C atoms, resulting in a change of bond angle of O-C-O from about 173° to 117° . Besides, the fraction of 4-fold coordinated C atoms reaches 28.5% at the pressure of 45.14 GPa. The highest fraction of 3-coordinated C at 45.14 GPa clearly indicates that the most stable structure of C atom at this pressure is in sp^2 -hybridization. The increase of C-O bond length and the decrease of the nearest distances of O_C-O_C are also a result of the change in coordination number. Meanwhile, the 1-fold coordinated O_C atoms, as seen in CO_2 molecules, nearly disappear at 45.14 GPa, while 2-fold coordinated O_C atoms, which could connect the C atoms to other C atoms or Si atoms, increase largely. (4) At the pressure of 45.14 GPa, most Si atoms are in 6-fold coordination, leading to the bond angle of O-Si-O appearing at around 90° , as well as the increase of the bond lengths of Si-O and the decrease of the nearest distance of $O_{Si}-O_{Si}$. The appearance of higher coordinated C and Si confirms that the reaction does occur at 43.28 GPa, and so does the major structure change.

With further increasing the pressure, the bond lengths of C-O and Si-O, the bond angles of O-C-O, O-Si-O and Si-O-Si, as well as the volume of system only change slightly. However, for the coordination number as shown in Fig. 3(c), large changes are seen. The fraction of 3-fold coordinated C atoms is 53.1% at 74.15 GPa, much lower than 69.4% at 45.14 GPa. The fraction of 4-fold coordinated C atoms increases to 46.9% at 74.15 GPa, close to that of 3-fold coordinated C atoms, and the fraction of 4-fold coordinated C atoms would exceed that of 3-fold coordinated C atoms at even higher pressure. It is expected that the fraction of differently coordinated atoms is correlated with the relative stabilities of these atoms at this conditions. The largest fraction of 3-fold coordinated C atoms suggests that 3-fold coordinated C atoms are more stable in the pressure range of 43.28 - 74.15 GPa. The 2-fold and 4-fold coordinated C atoms are more stable at lower and higher pressure, respectively. This result is consistent with the view that the 3-coordinated C atoms may be a precursor to the formation of the 4-coordinated C [25].

For the Si atoms, the fraction of 6-fold coordinated Si increases further with further increasing of the pressure, which is 65.7% at the pressure of 74.15 GPa, accompanying with the decrease of 5-fold coordinated Si atoms. The 4-fold coordinated Si atoms mostly disappear. Compared with the fraction of 5-fold coordinated Si atoms, the fraction of 6-fold coordinated Si atoms is much higher than that of 5-fold coordinated Si atoms when the pressure is higher than 43.28 GPa. This result indicates that at high pressure, the 6-fold coordinated Si atoms are more favorable, and the 5-fold coordinated Si atoms may be important to understand the transition from state with 4-fold to state with 6-fold coordinated Si atoms. The fraction of 3-fold coordinated O_{Si} atoms is over 50%, necessary for the connection of SiO_6 octahedrons.

The detailed analysis above shows that differently coordinated C, Si and O atoms are coexistence in the final structure and the fraction of differently coordinated atoms is pressure-dependent. The final product represents a competition among these differently coordinated C, Si and O atoms, and thus is also pressure-dependent. Moreover, the simulations suggest that the structure at high pressure is amorphous with short-ranged order. This short-ranged order can be identified through the partial pair correlation function of Si-Si and C-C. As shown in Fig. 4, at low pressure, the narrow peaks at relatively long-distance in the Si-Si pair correlation function strongly indicates existence of a long-range order in the system. With increasing the pressure, the amplitude of all the peaks becomes lower and the peaks at relatively long distance gradually disappear, indicating the loss of the long-ranged order and the amorphization at high pressure. In the case of C-C pairs, at relatively low pressure no sharp peaks arise in the partial pair correlation function due to random distribution of CO_2 molecules. When the pressure increases beyond 45.14 GPa, surprisingly, a peak at the distance of 2.3 Å appears, implying the short-ranged order in such a high pressure system. From the partial bond angle correlation function of C-O-C, we find that although O atoms are 2-coordinated, the bond angle of C-O-C largely deviates from 180° but is close to 120° . Similar results are also seen for the Si-C pair (see Fig. 4).

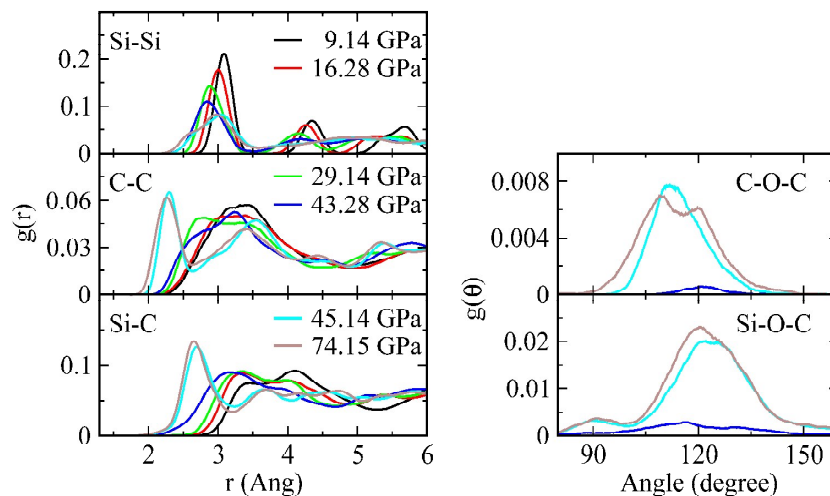


Fig. 4 The partial pair correlation functions of Si-Si, C-C and Si-C, and the partial bond angle correlation functions of C-O-C and Si-O-C at different pressures.

To understand the reaction mechanism between CO_2 and SiO_2 , we attempt to find out the reaction pathway underlying in this process by examining the structure evolution of the system. Two possible reaction pathways are identified as shown in Fig. 5(a) and (b), respectively. Initially, the O_{Si} atom is in twofold coordination with the Si-O-Si bond angle $\sim 144^\circ$ (Fig. 3(b)). This O_{Si} atom accepts two electrons from the Si atoms bonded to it and its bonding-orbitals are fully occupied. As such, the O_{Si} and Si atom in this structure are inactive. On the other side, the C atom is 2-fold coordinated and donates its four valence electrons to the O_{C} atoms bonded with due to its low electronegativity. Thus, the atoms in CO_2 molecule are also inert. At high pressure, the volume of the system shrinks and the bond angle of Si-O-Si decreases considerably, from 144° to 126° (Fig. 3(b)), while the bond length of Si-O is nearly unchanged. Meanwhile, the total energy of the system increases due to the decrease of the Si-O-Si bond angle. Hence, the O_{Si} atom in the compressed system becomes more active. Moreover, the average distance between the O_{Si} and C atoms decreases in such a compressed system. With the C atom being closer to the more active O_{Si} atom, a new covalent bond can be formed between the O_{Si} and C atoms as a result of the reaction. We denote the two reacted atoms as $\text{O}_{\text{Si-1}}$ and C-1, respectively. $\text{O}_{\text{Si-1}}$

receives additional electrons from C-1 to form the C-O bond. The redistribution of valance electrons between O_{Si-1} and C-1 results in two effects: (1) It enhances the activity of the O_C atoms bonded to C-1 atoms because some valance electrons of C-1 transfer to O_{Si-1} . The O_C atoms bonded to C-1 can no longer receive enough valance electrons such that the strength of the C-O bonds becomes weaker, leaving the p orbitals of these O atoms not fully occupied. So the activity of these O_C atoms is enhanced. The more active O_C atoms can bond with other C atoms if the distance between them is short enough. In this process, more and more CO_2 molecules would take part in the reaction. (2) The redistribution of valance electrons can weaken the strength of bond between O_{Si-1} and Si atoms. Since O_{Si-1} has received some valance electrons from C-1 atom, O_{Si-1} atom would draw less number of electrons from Si atom. So the bond strength becomes much weaker while the bond length becomes longer. At some distance, the weakened Si-O bond can be broken, as shown in Fig. 5(a). Once the Si-O bond is broken, the Si atom becomes more active, which not only can attack other O atoms, but also influence the bond strength of other Si-O bonds nearby. Following this process, the initial SiO_2 structure is disrupted.

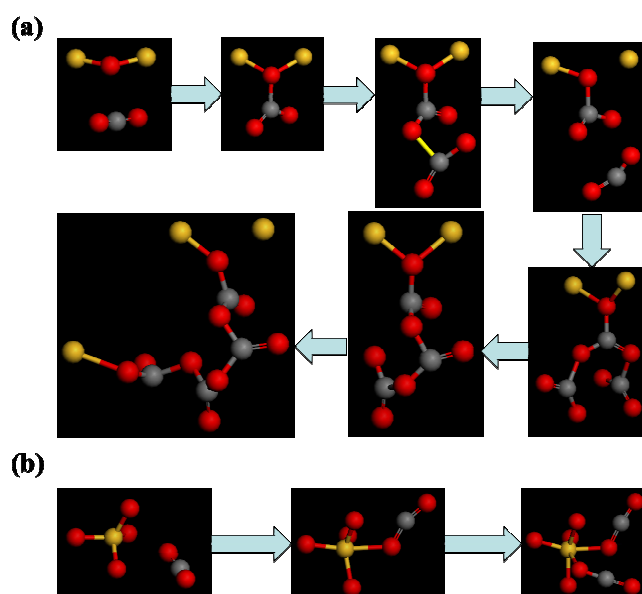


Fig. 5 Two possible reaction pathways (a) and (b) from CO_2 and SiO_2 to silicon carbonate.

The Si, O and C atoms are denoted as the gold, red and gray balls, respectively.

The second possible reaction pathway is shown in Fig. 5(b). At high pressure, the O_C atom of a CO_2 molecule is closer to a Si atom bonded with four O_{Si} atoms. Three of the four O_{Si} atoms are pushed towards the fourth O_{Si} atom, leading to the bond angle of O-Si-O deviated from that of the perfect SiO_4 tetrahedron 109.47° (see Fig. 3). Such a deviation can enhance the activity of the Si atom. Once the distance between the Si atom and O_C atom becomes short enough, a new Si-O bond can be formed. Because of different electronegativity between Si and O atom, the redistribution of valence electrons should happen, resulting in weakened bond strength of Si-O and C-O and enhanced activity of C, Si and O atoms in the CO_2 molecule and SiO_4 tetrahedron. As in the case of the first reaction pathway, the weakened Si-O bond can break more easily and the more active C, Si and O atoms can react with other SiO_4 tetrahedrons and CO_2 molecules. As such, the silicon carbonate is formed.

Note that in our simulation with temperature controlled at 800 K, the reaction between CO_2 and SiO_2 starts at the pressure of 43.28 GPa, much higher than that of experimental pressures (18-26 GPa). Such a deviation may be due in part to the different SiO_2 solid used as indicated previously, or to the different stoichiometric ratio of SiO_2 and CO_2 between the experiment and simulation. In the experiment [3], half of the sample was taken by porous SiO_2 with the pores were filled by CO_2 , while the other half was CO_2 solid. Such a high $CO_2:SiO_2$ ratio is impractical in our ab initio molecular dynamic simulations.

II. Structural evolution with the increase of temperature

The analysis of the reaction mechanism above suggests that the electron redistribution of SiO_4 tetrahedrons, due to large deviation of the O-Si-O or Si-O-Si bond angles from the ideal values, plays a key role to the reaction. High pressures can largely change the structure of the SiO_2 framework such that the activity of Si and O atoms can be enhanced. Besides the high pressures, high temperatures can also enhance the activity of Si and O atoms due in part to stronger motions of atoms and molecules at high temperature. To better understand how the temperature affects the

reaction between SiO_2 and CO_2 , we select the system at 43.28 GPa and 800 K as the starting structure. By raising the temperature from 800 K to 2400 K in steps while keeping the volume of the system fixed, a relation between temperature T and averaged pressure P for the system can be obtained (see Fig. 6). The blue line in Fig. 6 indicates that the pressure increases with the temperature initially from 800 K to 1000 K. This result is reasonable because of the stronger motions of atoms and molecules at higher temperature. But at 1300 K, interestingly, the pressure is 31.70 GPa, much lower than that at 1000 K. Such a sharp drop in pressure suggests a major structure change for the system at 1300 K. Further increase of the temperature results in graduate increase of the pressure again.

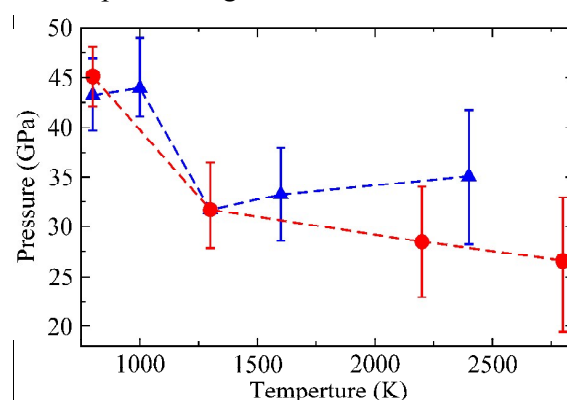


Fig. 6 The blue line represents the relation between the temperature and pressure at a constant volume, and the red dashed line represents an approximate transition curve of CO_2 and SiO_2 with stoichiometric ratio of 1:1.

To understand the major structural change, structural evolution as a function of temperature is analyzed (Fig. 7). As mentioned above, the reaction can occur at 43.28 GPa and 800 K, where the bond angle correlation function shows that most O-C-O bond angles are valued on 173° , while a small portion of them are near 120° , consistent with the appearance of 3-coordinated C atoms. For the O-Si-O bond angles, although most are valued on the 109° , a low shoulder at low angles can be seen, due to the appearance of higher coordinated Si atoms. From 800 to 1000 K, little change occurs for the angle distributions, implying that even at 1000 K the reaction between

CO₂ and SiO₂ are still limited at the surface of the microcages and micropores, and only a few CO₂ molecules take part in the reaction.

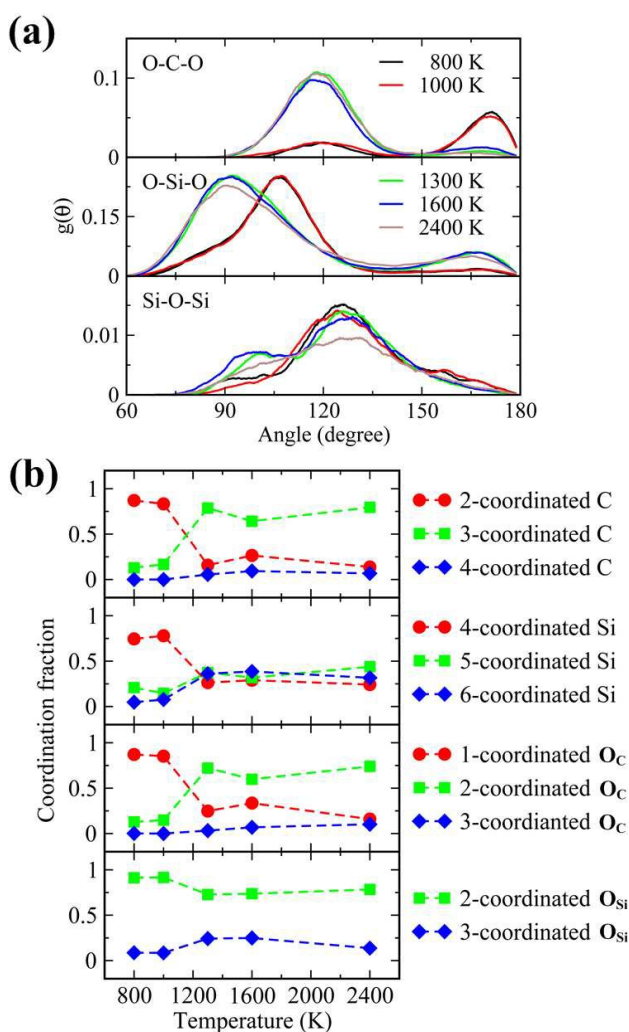


Fig. 7 (a) The partial bond angle correlation functions of O-C-O, O-Si-O and Si-O-Si *versus* temperature. (b) Fraction of differently coordinated C, Si and O atoms *versus* temperature.

When the temperature is increased to 1300 K, the fraction of O-C-O at 120° increases significantly while only few O-C-O are valued at 173°. Meanwhile the 3-fold coordinated C atoms increase greatly with the decrease of the 2-fold coordinated C atoms. The 4-fold coordinated Si atoms decrease rapidly while the 5-fold and 6-fold coordinated Si atoms increase, accompanying with the decrease of the bond angle of O-Si-O from 109° to ~90°. These results show that most SiO₂ and

CO₂ already participate in the reaction, and the temperature is another important factor that can promote the reaction between CO₂ and SiO₂.

Further increase of the temperature beyond 1300 K results in little change in the fraction of differently coordinated C atoms and Si atoms, suggesting comparable stabilities of these atoms. The fraction of 3-fold coordinated C atoms is the largest among differently coordinated C atoms and is little affected by the higher temperature. Overall, the temperature has much less influence on the relative stabilities of differently coordinated atoms in this temperature range.

III. The transition curve

Thus far, we obtain two transition points, one at (800 K, 45.14 GPa) and another at (1300 K, 31.70 GPa). Through selecting another two different volumes, and repeating the process performed in section II, we obtain another two transition points. As a result, an approximate transition curve of SiO₂ and CO₂ with stoichiometric ratio of 1:1 can be plotted in Fig. 6 (the red dashed line). When the temperature is below 1300 K, the pressure decreases rapidly with increasing the temperature. Further increase of the temperature beyond 1300 K leads to slower decrease of pressure. This result indicates co-influence of temperature and pressure on the reaction. Note that in this process, the pressure needed for the reaction is very high. Even for the highest temperature considered, the pressure still exceeds 20 GPa, confirming that high pressure is essential to synthesize silicon carbonate.

Note also that when the temperature is higher than 2200 K, the CO₂ molecules can react with each other directly. An O_C atom of a CO₂ can move towards to a C atom of another CO₂. At certain moment, the distance between the two atoms may become short enough to form a new C-O bond. So, a 3-coordinated C atom arises. However, this reaction mechanism cannot be responsible to the 3-dimensional silicon carbonate formation because this newly formed C-O bond is very unstable. The bond would be broken in the next few simulation steps. So, the reaction mechanism at higher temperature is expected to be the same as that analyzed above.

IV. Stability of product

It has been found from experiments that after releasing the pressure, the silicon carbonate decomposes into CO₂ molecules and SiO₂ in a few days, implying that the reaction product was unstable at the ambient pressure. To gain insights into the structural evolution in this process, we select the structure at 45.14 GPa and 800 K as initial structure in which nearly all the CO₂ and SiO₂ have participated in the reaction. In view of the decomposition rate in the experiment is very low, in the new simulation, we keep the temperature at 800 K to accelerate the decomposition. By releasing the pressure, we obtain the relation between the volume and pressure, as shown in Fig. 2 (the blue line). The volume increases with the decrease of the pressure. When the pressure is low, the volume of the product is very close to that marked by the red line, the third-order Birch-Murnaghan equation of state fit to the initial structure, indicating that the product may decompose.

To detect the structural change in the decomposition, we examine the structural evolution with the decrease of pressure. As shown in Fig. 8, the fraction of 4-fold and 3-fold coordinated C atoms decrease with decreasing the pressure, while the fraction of 2-fold coordinated C atoms increases and approaches to as large as 37.5% as the pressure close to 0 GPa. The bond-angle correlation function shows that although most bond angles of O-C-O are around 120°, the fraction of the bond angles around 180° increases continuously with decreasing the pressure. For Si, with the decrease of pressure, the fraction of 4-fold coordinated Si atoms increases at the expense of the fraction of 5-fold and 6-fold coordinated Si atoms, accompanying with the appearance of the bond angle of O-Si-O at 109°. Moreover, at low pressure, some Si-O-Si bond angles are at 140°, very close to that of the initial structure. Compared with the structure at 45.14 GPa, these results clearly show that part of the product decomposes into CO₂ molecules and SiO₄ tetrahedrons, consistent with the experimental results. Hence, we confirm that the amorphous phase of silicon carbonate formed via the reaction between SiO₂ and CO₂ under high pressures is indeed unstable when the pressures are released. Note that even under ambient pressure, there are still more than 50% 3-fold coordinated C left in the sample. In other words, the sample cannot

fully decompose into the original SiO_2 structure and CO_2 molecules. This is because the original SiO_2 framework is entirely destroyed after reacting with CO_2 under high pressures and cannot be recovered after the pressure is released. On the other hand, it may be possible to obtain stable silicon carbonate via repeatedly annealing under pressures and temperatures.

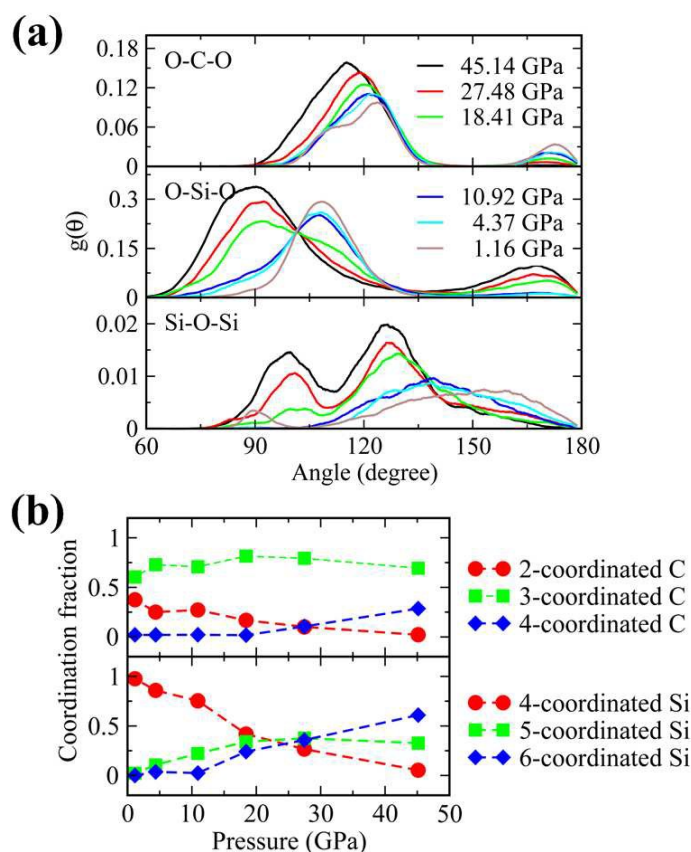


Fig. 8 (a) Partial bond angle correlation functions of O-C-O, O-Si-O and Si-O-Si *versus* pressure. (b) Fraction of different coordinated C and Si atoms *versus* pressure.

Conclusion

We have studied structural evolution of silicon carbonate with pressure and temperature and the mechanism underlying the formation reaction using the AIMD simulations. Through analyzing the structures at different pressures and temperatures, we find the reaction occurs at the surface of the porous SiO_2 at 43.28 GPa and 800 K. With increasing the pressure or temperature, more and more CO_2 molecules

participate in the reaction to form the new structure, an amorphous consisting of 2-fold, 3-fold and 4-fold coordinated C atoms, and 4-fold, 5-fold and 6-fold coordinated Si atoms. The number of differently coordinated C (Si) atoms is pressure dependent, and the final product is a result of the competition among these differently coordinated C (Si) atoms. When releasing the pressure, although part of the product decomposes, more than 50% CO₃ units are retained, suggesting that it is possible to obtain stable silicon carbonate via repeated annealing under high pressure and temperature. The mechanism underlying the reaction is revealed with two possible reaction pathways being identified. Both paths begin with the electron redistribution due to the large change of the bond angles of Si-O-Si or O-Si-O in SiO₄ tetrahedrons caused by high pressure or temperature. An approximate reaction transition curve is obtained based on the extensive simulations, which can be informative to guide the synthesis of silicon carbonate from porous SiO₂ and CO₂ molecules.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (Grant No: 11104056, 51171055, and 11404085), and the Natural Science Foundation of HFUT (NO. JZ2014HGBZ0039). The computer simulations were carried out in the University of Nebraska Holland Computing Center and the Supercomputing Center of University of Science and Technology of China.

References

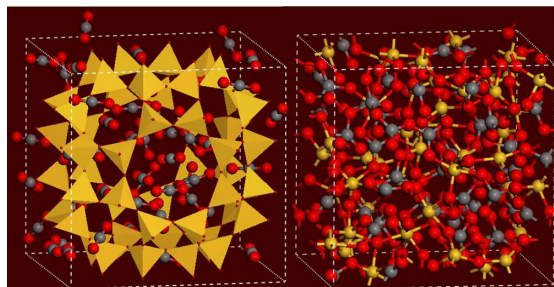
- [1] M. Santoro and F. A. Gorelli, *Chem. Soc. Rev.* 2006, **35**, 918-931.
- [2] F. Liu, S. H. Garofalini, D. King-Smith and D. Vanderbilt, *Phys. Rev. B* 1994, **49**, 12528-12534.
- [3] M. Santoro, F. Gorelli, J. Haines, O. Cambon, C. Levelut and G. Garbarino, *Proc. Natl. Acad. Sci. USA* 2011, **108**, 7689-7692.
- [4] P. F. McMillan, *Chem. Soc. Rev.* 2006, **35**, 855-857.
- [5] K. Aoki, H. Yamawaki, M. Sakashita, Y. Gotoh and K. Takemura, *Science* 1994, **263**,

356-358.

- [6] V. M. Giordano and F. Datchi, *Europhys. Lett.* 2007, **77**, 46002.
- [7] C. S. Yoo, H. Cynn, F. Gygi, G. Galli, M. Nicol, D. Hausermann, S. Carlson and C. Mailhot, *Phys. Rev. Lett.* 1999, **83**, 5527-5530.
- [8] V. Iota, C. S. Yoo and H. Cynn, *Science* 1999, **283**, 1510-1513.
- [9] S. Serra, C. Cavazzoni, G. L. Chiarotti, S. Scandolo and E. Tosatti, *Science* 1999, **284**, 788-790.
- [10] M. Santoro, F. A. Gorelli, R. Bini, J. Haines, O. Combon, C. Levelut, J. A. Montoya and S. Scandolo, *Proc. Natl. Acad. Sci. USA* 2012, **109**, 5176-5179.
- [11] F. Datchi, B. Mallick, A. Salamat and S. Ninet, *Phys. Rev. Lett.* 2012, **108**, 125701.
- [12] C. S. Yoo, M. Kim, W. Morgenroth and P. Liermann, *Phys. Rev. B* 2013, **87**, 214103.
- [13] V. Iota, C. S. Yoo, J. H. Klepeis, J. Zsolt, W. Evans and H. Cynn, *Nat. Mater.* 2007, **6**, 34-38.
- [14] A. Sengupta and C. S. Yoo, *Phys. Rev. B* 2010, **82**, 012105.
- [15] M. Santoro, F. A. Gorelli, R. Bini, G. Ruocco, S. Scandolo and W. A. Crichton, *Nature* 2006, **441**, 857-860.
- [16] J. A. Montoya, R. Rousseau, M. Santoro, F. Gorelli and S. Scandolo, *Phys. Rev. Lett.* 2008, **100**, 163002.
- [17] A. Aravindh, et al. *Solid State Commun.* 2007, **144**, 273-276.
- [18] Mario Santoro, Federico A. Gorelli, Roberto Bini, Ashkan Salamat, Gaston Garbarino, Claire Levelut, Olivier Cambon and Julien Haines, *Nat. Commun.* 2014, **5**, 3761
- [19] A. Morales-García, M. Marqués, J. M. Menéndez, D. Santamaría-Pérez, V. G. Baonza and J. M. Recio, *Theor. Chem. Acc.* 2013, **132**, 1308.
- [20] R. L. Zhou, B. Y. Qu, J. Dai and X. C. Zeng, *Phys. Rev. X*, 2014, **4**, 011030.
- [21] J. Haines, C. Levelut, A. Isambert, P. Hébert, S. Kohara, D. A. Keen, T. Hammouda and D. Andrault, *J. Am. Chem. Soc.* 2009, **131**, 12333-12338.
- [22] J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing and J. Hutter, *Comput. Phys. Commun.* 2005, **167**, 103-128.
- [23] G. Lippert, J. Hutter and M. Parrinello, *Mol. Phys.* 1997, **92**, 477-488.
- [24] G. Lippert, J. Hutter and M. Parrinello, *Theor. Chem. Acc.* 1999, **103**, 124-140.

[25] F. Tassone, G. L. Chiarotti, R. Rousseau, S. Scandolo and E. Tosatti, *ChemPhysChem* 2005, **6**, 1752-1756.

TOC Graphics



The structure changes of silicon carbonate with pressure and temperature are explored based on systematic ab initio molecular dynamics simulations.