UC Davis
UC Davis Previously Published Works

Title

Carbon substitution for oxygen in silicates in planetary interiors

Permalink

https://escholarship.org/uc/item/7216f1c5

Journal

Proceedings of the National Academy of Sciences of the United States of America, 110(40)

ISSN

0027-8424

Authors

Sen, Sabyasachi
Widgeon, Scarlett J
Navrotsky, Alexandra
et al.

Publication Date

2013-10-01

DOI

10.1073/pnas.1312771110

Peer reviewed

Carbon substitution for oxygen in silicates in planetary interiors

Sabyasachi Sen[a], Scarlett J. Widgeon[a,b], Alexandra Navrotsky[a,b,1], Gabriela Mera[c], Amir Tavakoli[b], Emanuel Ionescu[c], and Ralf Riedel[c]

[a]Department of Chemical Engineering and Materials Science and [b]Peter A. Rock Thermochemistry Laboratory and Nanomaterials in the Environment, Agriculture, and Technology Organized Research Unit, University of California, Davis, CA 95616; and [c]Institut für Materialwissenschaft, Technische Universität Darmstadt, D-64287 Darmstadt, Germany

Amorphous silicon oxycarbide polymer-derived ceramics (PDCs), synthesized from organometallic precursors, contain carbon- and silica-rich nanodomains, the latter with extensive substitution of carbon for oxygen, linking Si-centered SiO_xC_{4-x} tetrahedra. Calorimetric studies demonstrated these PDCs to be thermodynamically more stable than a mixture of SiO_2, C, and silicon carbide. Here, we show by multinuclear NMR spectroscopy that substitution of C for O is also attained in PDCs with depolymerized silica-rich domains containing lithium, associated with SiO_xC_{4-x} tetrahedra with nonbridging oxygen. We suggest that significant (several percent) substitution of C for O could occur in more complex geological silicate melts/glasses in contact with graphite at moderate pressure and high temperature and may be thermodynamically far more accessible than C for Si substitution. Carbon incorporation will change the local structure and may affect physical properties, such as viscosity. Analogous carbon substitution at grain boundaries, at defect sites, or as equilibrium states in nominally acarbonaceous crystalline silicates, even if present at levels at 10–100 ppm, might form an extensive and hitherto hidden reservoir of carbon in the lower crust and mantle.

carbon in silicates | Li-Si-O-C ceramics | deep Earth

The carbon cycle is one of the most important components in the sustenance of life and the evolution of the environment on our planet. The exchange of carbon between the atmosphere, biosphere, and oceans primarily controls the near-surface carbon cycle in the short term (decades to millennia) (1, 2). However, a large fraction of the carbon in the planet is stored at a greater depth (i.e., in the crust, mantle, core), and it exchanges with the surficial carbon only on much longer time scales (millions of years) through processes involving subduction and volcanic activity (3, 4). The form of stored carbon in these deep reservoirs and the amounts of carbon in various reservoirs, as well as the balance between the inward and the outward fluxes of carbon from them, are poorly constrained (3, 4). In the crust and upper mantle under relatively oxidizing conditions, CO_3^{2-} provides the familiar trigonal (sp^2) coordination environment for carbon in carbonates, mixed CO_2-H_2O fluid phases and carbonatite-forming melts. Under more reducing conditions, graphite, diamond, and methane become important and carbonate becomes less important or absent. The substitution of tetrahedral (sp^3) carbon for silicon in silicate minerals and melts has often been suggested as a possibility at high pressure (5–13), but there was little experimental evidence for it until recent phase equilibrium studies indicated that CO_2 can undergo transformation from a molecular gas to an extended solid at very high pressure and temperature to form a cristobalite-like structure consisting of a network of corner-sharing CO_4 tetrahedra (13, 14). Recent studies have also indicated the possibility of a chemical reaction between SiO_2 and CO_2 to form a silicon carbonate phase under pressure (12) and the possibility of amorphous solid phases (7, 11). However, the experimental results and their structural interpretations have remained somewhat controversial, and, in any event, such reactions appear to require pressures near a

megabar, probably making them unimportant for most of the crust and mantle.

Here, we propose an alternate and facile mode of carbon incorporation into silicates in the crust and mantle under moderately reducing conditions, namely, its substitution not for silicon but for oxygen in a silicate tetrahedron. This mechanism of substitution is well documented in so-called "polymer-derived ceramics" (PDCs; recently reviewed in ref. 15), X-ray amorphous but nanoheterogeneous solids in the Si-C-O system that are prepared over a wide range of compositions via pyrolysis of organometallic polymer precursors (Fig. 1 *A* and *B*). Their nanostructure, characterized extensively by solid-state NMR and other spectroscopic techniques, small angle X-ray scattering, and transmission electron microscopy, consists of interconnected domains of relatively disordered sp^2 carbon layers (ranging from graphene sheets to turbostratic graphite) and amorphous silica-rich regions (Fig. 1*C*). The latter are not pure SiO_2 but contain several percent carbon, which substitutes for oxygen in the tetrahedra, forming a mixture of SiO_4, SiO_3C, SiO_2C_2, $SiOC_3$, and SiC_4 species (15). Because all these silicon-centered tetrahedra are bonded through their oxygen and carbon atoms to the neighboring tetrahedra, the network remains fully connected by corner sharing. Indeed, the carbon tends to bond to four silicon atoms (and not to oxygen), whereas oxygen bonds to two silicon atoms; thus, the network is even more cross-linked, making local structure different and somewhat heterogeneous on the nanometer scale (15). Nevertheless, the structure can be considered to be a new amorphous phase with a high concentration of mixed-bond tetrahedra and not an intergrowth of separate silicon carbide and silicon oxide nanophases. The absence of carbon-oxygen bonds in these structures argues against carbon incorporation as a species related to CO or CO_2.

It has been established that these SiOC PDCs are stable energetically (and presumably in free energy as well, because they
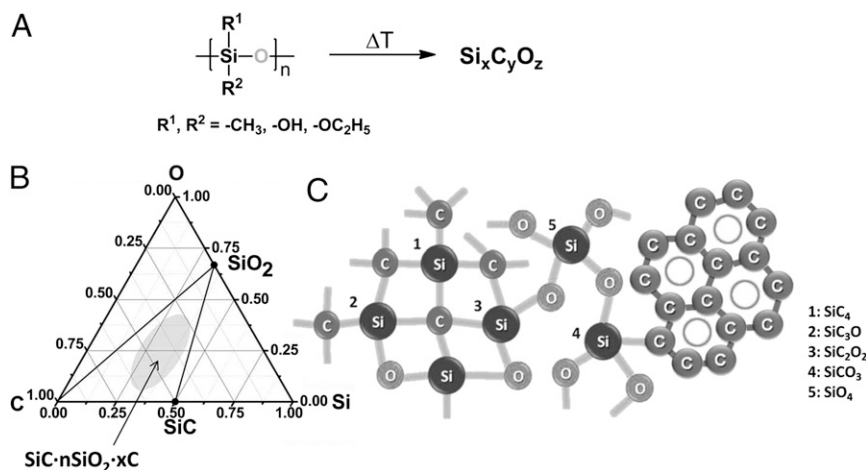
Significance

Carbon is an important element in the Earth and other planets, but its concentration, chemical and structural form, and dynamics throughout the crust, mantle, and core are incompletely known. Based on the thermodynamic stability of a class of synthetic materials, the polymer-derived ceramics containing Si, C, and O, and on new NMR data for such systems containing a network-modifying metal (Li), this paper suggests that the substitution of C for O (rather than C for Si) in molten, amorphous, and crystalline silicate structures may provide a hitherto hidden reservoir of carbon in planetary interiors.

Fig. 1. Polymer-derived SiOC ceramics: synthesis by the pyrolysis of polysiloxanes (*A*), composition diagram (*B*), and nanodomain structure and silicon coordination in the ceramic state (*C*).

are disordered) with respect to a mixture of SiO_2 (glass or cristobalite), C (graphite), and silicon carbide (SiC) (15). This is a critical observation for the present argument because such thermodynamic stability suggests that although the organometallic precursor route may be kinetically necessary to overcome barriers to synthesize SiOC ceramics at atmospheric pressure and at low enough temperatures to avoid carbothermic reduction of silica by graphite by the reaction $SiO_2 + 3C = SiC + CO$ (gas), it may not be thermodynamically necessary and the SiOC materials may not be metastable because they are favored by both energetic and entropic (disorder) factors. Furthermore, pressure of even 1 GPa will strongly disfavor carbothermic reduction and extend the stability field of the SiOC materials. This is because the driving force in the free energy for such reduction is the large positive entropy (and volume) increase in forming gaseous products. At pressures of roughly 1 GPa and above, the molar volume of CO (and CO_2) is more like that of a liquid or solid (tens of cubic centimeters per mole rather than tens of

liters), and the entropy has likewise diminished greatly. Indeed, the major effect on raising the temperature of the reduction reaction will occur in the low-pressure range, where the volume of the products is decreasing most rapidly. This argument will continue to hold, with minor changes in slopes of free energy curves, if phase transitions occur (e.g., graphite to diamond, dense CO or CO_2 fluids to more polymerized phases). Indeed, it has already been shown that SiOC PDCs at moderate pressures of ~20 MPa can withstand temperatures as high as 1,600 °C (16, 17). Thus, we hypothesize that given the high temperature and pressure, long time scale for chemical reaction, and relatively low oxygen fugacity characteristic of the lower crust and mantle, substitution of carbon for oxygen may be a viable mechanism of carbon incorporation into molten, glassy, and perhaps even crystalline silicates, as well as into grain boundaries.

Realizing that the silicate network in minerals and melts is often partially depolymerized with charge balance largely involving aluminum, iron, and alkali and alkaline earths, we must
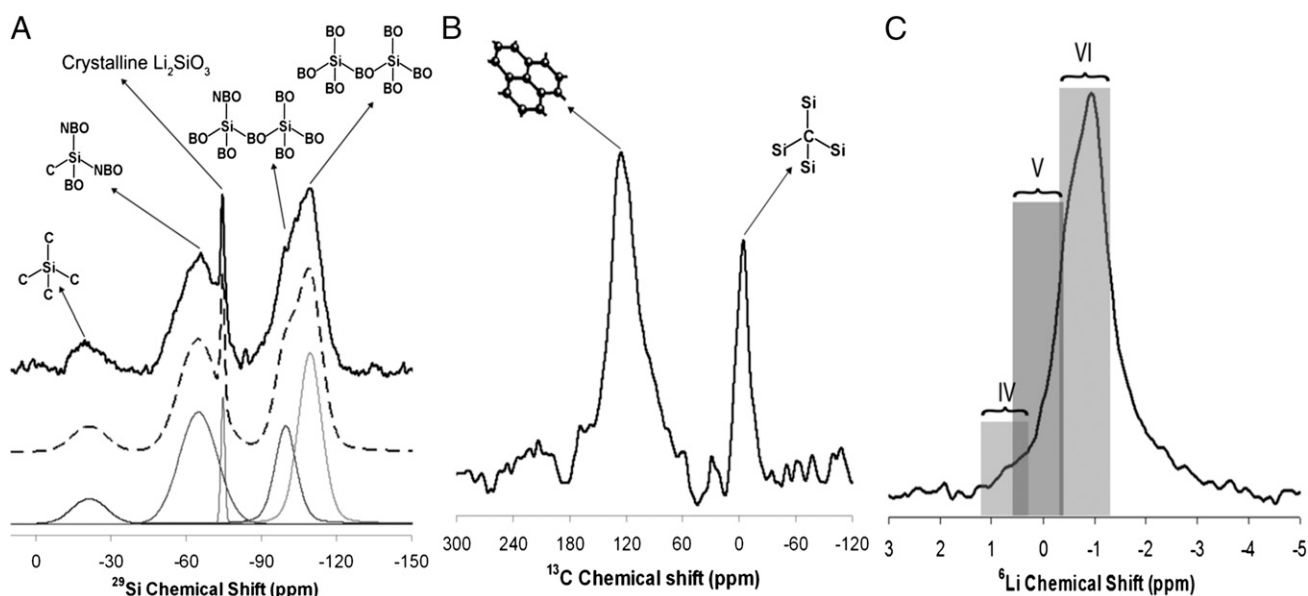
Fig. 2. (*A*) ^{29}Si MAS NMR spectra of Li-SiOC-700. The experimental spectrum is shown as the bold black line (*Top*), the simulation is shown as the bold dashed line (*Middle*), and the individual peak components are shown with thin solid lines (*Bottom*). (*B*) ^{13}C MAS NMR spectrum of Li-SiOC-700. (*C*) ^{6}Li MAS NMR spectrum of Li-SiOC-700. The ^{6}Li NMR chemical shift ranges characteristic of 4-, 5-, and 6-coordinated Li in oxides, as reported in the literature (20), are shown.
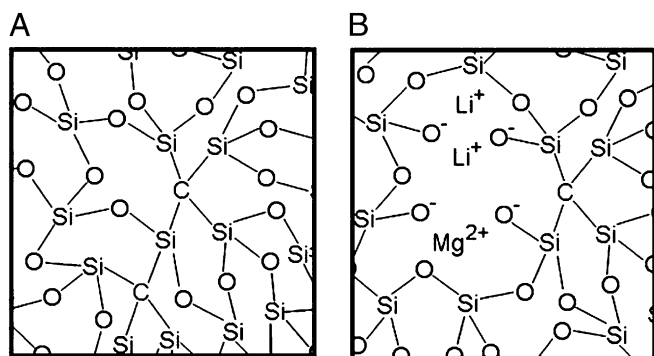
Fig. 3. Schematic representations of the local structural scenarios corresponding to the various modes of carbon incorporation via substitution of oxygen in silicate structures. (*A*) SiOC networks characterized by corner-shared SiC_xO_{4-x} tetrahedra without any C-O and C-C bonding. (*B*) Depolymerized SiOC network formed from addition of modifier cations, such as alkali and alkaline earths, where the SiC_xO_{4-x} tetrahedra may contain one or more NBOs.

ask whether this mode of carbon incorporation can be maintained in less polymerized environments. Here, we present the results of a structural study of alkali (Li)-containing Si-O-C ceramics that confirm and provide insight into this mechanism of incorporation of C in silicate structures. A multinuclear ([6]Li, ^{13}C, and [29]Si) NMR spectroscopic approach was taken to investigate the local structure and bonding around Li, C, and Si atoms to obtain a comprehensive structural picture of these materials.

The Li-SiOC sample was synthesized via pyrolysis of preceramic organic-inorganic hybrid polymers (*Materials and Methods*). Chemical analyses indicated a composition of $SiLi_{0.52}O_{2.50}C_{0.84}$. Powder X-ray diffraction (XRD) (Fig. S1) confirmed the predominantly amorphous nature of the material with a small fraction of Li_2SiO_3 nanocrystallites dispersed in the amorphous matrix. The [29]Si magic angle spinning (MAS) NMR spectrum of the Li-SiOC sample is shown in Fig. 2*A*. It contains multiple broad peaks centered at chemical shifts of around −110, −100, −91, −64, and −21 ppm and a relatively sharp peak centered at −75 ppm. The latter can be readily assigned to the presence of a small amount of Li_2SiO_3 crystals (18), consistent with the powder XRD result. The broad peaks at −110 and −100 ppm can be assigned to various tetrahedral SiO_4 environments typical of glassy silicates that are usually denoted as Q^n species, where n denotes the number of bridging oxygens (BOs) that are shared between two SiO_4 tetrahedra. The peaks at −110 and −100 ppm are characteristic of Q^4 environments bonded to other Q^4 and Q^3 species, respectively (19). The [29]Si isotropic chemical shift for $SiCO_3$ tetrahedra with three BOs and one bridging carbon nearest neighbors is typically located near −71 ppm in Li-free SiOC ceramics (20). Therefore, it is reasonable to assign the major peak at −64 ppm to $SiCO_3$ tetrahedra with one or two nonbridging oxygens (NBOs). This species is denoted as Q^{NBO}-C in the subsequent discussion. The presence of the Q^{NBO}-C species implies depolymerization of the SiOC network due to the addition of an archetypal modifier oxide, such as Li_2O. Because the NBO on this species is expected to be bonded to the Li^+ ions, it also suggests a close spatial association of Li with C atoms in the structure. Finally, the broad peak at −21 ppm can be assigned to SiC_4 tetrahedra in the network. Simulation of this spectrum with Gaussian line shapes and assuming that the Q^{NBO}-C species contains 1 NBO atom yields the following relative fractions (atom %) of various Si species: 53% Q^4, 36% Q^{NBO}-C 6.4% SiC_4, and 4.6% Q^2 in crystalline Li_2SiO_3, leading to overall NBO per Si atom, NBO/Si = 0.45, consistent with the chemical composition of the sample characterized by a Li/Si ratio of ∼1:2.

The ^{13}C MAS NMR spectrum (Fig. 2*B*) consists of two well-resolved but relatively broad peaks at ∼120 and −3 ppm. The former peak can be readily assigned to sp^2-bonded carbon environments as in amorphous or turbostratic graphite. On the other hand, the latter peak with a ^{13}C isotropic chemical shift of −3 ppm represents sp^3-bonded carbon sites in SiC. ^{13}C NMR signals corresponding to these two C environments have also been reported in the literature for Li-free Si-O-C samples (20), although in those cases, the ^{13}C isotropic chemical shifts for the sp^2 and sp^3 sites are shifted to somewhat higher frequencies (∼140 and 12 ppm, respectively).

The [6]Li MAS NMR spectrum is shown in Fig. 2*C*. The isotropic chemical shift of the [6]Li resonance (−0.85 to −0.95 ppm) indicates that the majority of the Li^+ ions are in sixfold coordination with oxygen (21). The chemical shift range spanned by the [6]Li MAS NMR spectrum also suggests that Li-C bonding in the PDC would be unlikely because such resonances are expected to be shifted significantly to higher frequencies (22).

Based on these observations, we suggest that the substitution of C for O in silicate tetrahedra must be considered as a significant possibility for the interior of the Earth and other planets. Such modes of carbon incorporation include (*i*) formation of Si–O–C networks characterized by corner-shared SiC_xO_{4-x} tetrahedra without any C-O and C-C bonding, where C and O atoms are only bonded to four and two Si atoms, respectively, and (*ii*) formation of a depolymerized Si-O-C network upon incorporation of modifier cations, such as alkali and alkaline earths, where the SiC_xO_{4-x} tetrahedra may contain one or more NBOs. These structural scenarios are shown schematically in Fig. 3. Although these modes of carbon incorporation can be easily envisaged for amorphous or liquid silicates (magmas), chemical substitution of O by C in a crystalline silicate would require the formation of local defect structures either in the interior of a crystal grain or near grain boundaries and would likely involve
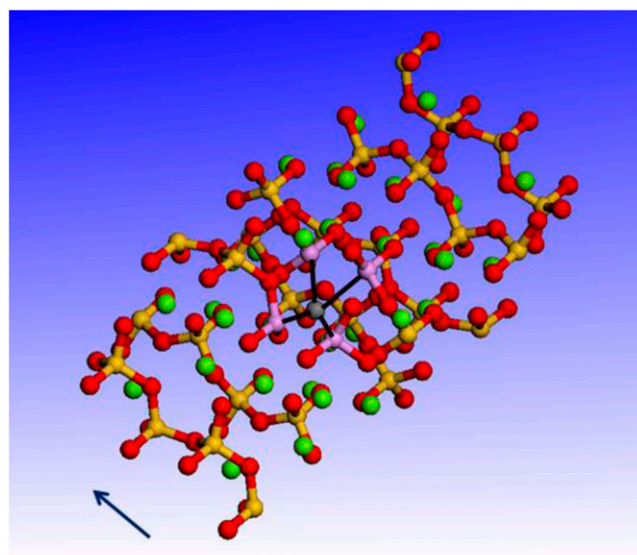
Fig. 4. Schematic representation of a "defect" created by the replacement of oxygen by carbon in the lattice of an ortho-enstatite ($MgSiO_3$) structure. The Si, O, Mg, and C atoms are shown in yellow, red, green, and dark gray, respectively. The chains of Q^2 SiO_4 tetrahedra in the structure are oriented along the crystallographic *c* axis indicated by the arrow. Two BO atoms connecting two pairs of SiO_4 tetrahedra in the neighboring chains have been substituted by the carbon atom that now bonds to four Si atoms (shown in pink) and cross-links the two chains. This substitution results in the formation of four SiO_3C tetrahedra, as shown. Although not shown here, the structure near the defect is expected to relax in response to this substitution.

significant local rearrangement of the lattice. A schematic representation of one such possible substitution is shown in Fig. 4 for the $MgSiO_3$ chain silicate structure, where two BO atoms in two Q^2 chains are replaced by an sp^3 carbon atom, resulting in local cross-linking of the two chains.

Annealing the Li-SiOC sample at a higher temperature (1,100 °C) caused extensive crystallization of lithium silicate and apparent disruption of the Si-O-C network. Differential scanning calorimetry showed only a strong crystallization exotherm above 800 °C with no evidence of a glass transition in the amorphous Si-O-C domains. No mixed bonded tetrahedra in the crystalline lithium silicate phases could be detected by NMR, although such substitution at trace levels, below a few percent, would not be easily detected. Thus, the extent of substitution of carbon for oxygen in crystalline silicates remains open. However, even if this substitution occurs at a low level (e.g., on the order of 10–100 ppm), the large volumes of silicates resident in the lower crust and mantle would provide an extensive "hidden" reservoir for carbon in nominally acarbonaceous phases, analogous to that of H_2O in nominally anhydrous phases as discussed extensively in the recent literature (23). If melts (magmas) in contact with graphite (and in the absence of significant carbonate) or amorphous phases in grain boundaries are also present, this reservoir could be greatly enhanced.

It is not yet possible to quantitate the extent and importance of such a reservoir both because the degree of carbon incorporation by this mechanism in natural systems is not yet known and because the carbon inventory of the lower crust, mantle, and core is poorly constrained (4). However, one should note that a low level of substitution would decrease the thermodynamic activity of the C (or SiC) component in the solid or liquid phase where carbon occurs. As an example, if the carbon activity (similar to or likely smaller than its concentration) is 10^{-3}, the oxygen fugacity for oxidation to CO_2 by the reaction C (in solid or melt) + O_2 = CO_2 would be increased by three orders of magnitude. This would extend the oxygen fugacity range over which such carbon incorporation could occur, at low concentration, to more common mantle conditions. Thus, some trace carbon incorporations into silicates by this mechanism could occur at oxygen fugacities higher that those needed to maintain silicon carbide, graphite, or diamond. Of course, at the upper end of the oxygen fugacity range, carbon incorporation by CO_2 (and/or CO) solubility will become dominant. Furthermore, considering the strongly reducing conditions likely to have existed in the Hadean era, including the period of core formation and several possible magma ocean episodes (24), the proposed mechanism of carbon incorporation may have been more widespread in primordial times and could have played an important role in setting the carbon inventory of the crust, mantle, and core. The major hypothesis of this paper is simply that such a mechanism of incorporating carbon in silicates merits further consideration by both experimental and theoretical approaches.

Materials and Methods

Synthesis and Chemical Analyses. The synthesis of ceramic SiLiOC materials was performed starting from a chemically modified siloxane by pyrolysis in argon atmosphere of a chemically modified and commercially available poly-methylsilsesquioxane (MK Belsil PMS; Wacker GmbH). The lithium-containing preceramic polymer was synthesized in air as follows: 8 g of MK-polymer dissolved in acetone was mixed with 7.06 g of 97% molar lithium acetyl acetonate (Sigma–Aldrich Chemie GmbH) and stirred at room temperature for 8 h. The resulting white powder was dried in vacuum and cross-linked via warm-press at 250 °C and 60 MPa in 2×2-cm^2 pellets. The pellets were pyrolyzed in argon at 700 °C for a dwell time of 2 h using standard Schlenk techniques. Elemental analyses for carbon and oxygen were performed by means of hot gas extraction techniques using a LECO C-200 analyzer and a LECO TC-436 analyzer, respectively. The Li and Si contents of the ceramics were analyzed at the Mikroanalytisches Labor Pascher (Remagen, Germany).

MAS NMR Spectroscopy. The ^6Li, ^{29}Si, and ^{13}C MAS NMR spectra of the Li-SiOC-700 sample were collected using a Bruker Avance solid-state spectrometer operating at the Larmor frequencies of 73.6, 99.3, and 125.7 MHz, respectively, for these nuclides. Crushed sample was loaded in a ZrO_2 rotor and spun at a rate of 14 kHz using a 4-mm Bruker cross-polarization magic-angle-spinning (CPMAS) probe. All NMR spectra were externally referenced to tetramethylsilane for ^{29}Si and ^{13}C, and ^6Li was referenced to LiCl.

^6Li one-pulse MAS NMR spectra were collected using $\pi/3$ (2.7 µs) rf pulses and 60-s recycle delay. Approximately 1,200 free induction decays (FIDs) were averaged and Fourier-transformed to obtain each ^6Li spectrum. ^{29}Si MAS spectra were obtained by using $\pi/2$ (2.5 µs) rf pulses and a 60-s recycle delay. Approximately 400 FIDs were averaged and Fourier-transformed to obtain each ^{29}Si spectrum. ^{13}C (direct polarization) MAS NMR spectra with high-power proton decoupling were collected using a $\pi/2$ pulse length of 2.5 µs and a recycle delay of 60 s. A two-pulse phase modulation (TPPM15) pulse sequence was used for proton decoupling with a pulse duration of 6.5 µs. Approximately 2,000 FIDs were collected and averaged to obtain each ^{13}C MAS NMR spectrum.

1. Falkowski P, et al. (2000) The global carbon cycle: A test of our knowledge of earth as a system. *Science* 290(5490):291–296.
2. Crowley TJ (2000) Causes of climate change over the past 1000 years. *Science* 289(5477):270–277.
3. Walter MJ, et al. (2011) Deep mantle cycling of oceanic crust: Evidence from diamonds and their mineral inclusions. *Science* 334(6052):54–57.
4. Dasgupta R (2013) Ingassing, storage, and outgassing of terrestrial carbon through geologic time. *Reviews in Mineralogy and Geochemistry* 75:183–229.
5. Oganov A, Hemley R, Hazen R, Jones A (2013) Structure, bonding, and mineralogy of carbon at extreme conditions. *Reviews in Mineralogy and Geochemistry* 75:47–77.
6. Santoro M, Gorelli FA (2006) High pressure solid state chemistry of carbon dioxide. *Chem Soc Rev* 35(10):918–931.
7. Santoro M, et al. (2006) Amorphous silica-like carbon dioxide. *Nature* 441(7095):857–860.
8. Bonev S, Gygi F, Ogitsu T, Galli G (2003) High-pressure molecular phases of solid carbon dioxide. *Phys Rev Lett* 91(6):065501.
9. Holm B, Ahuja R, Belonoshko A, Johansson B (2000) Theoretical investigation of high pressure phases of carbon dioxide. *Phys Rev Lett* 85(6):1258–1261.
10. Serra S, Cavazzoni C, Chiarotti GL, Scandolo S, Tosatti E (1999) Pressure-induced solid carbonates from molecular CO_2 by computer simulation. *Science* 284(5415):788–790.
11. McMillan PF (2006) Solid-state chemistry: A glass of carbon dioxide. *Nature* 441(7095):823.
12. Santoro M, et al. (2011) Silicon carbonate phase formed from carbon dioxide and silica under pressure. *Proc Natl Acad Sci USA* 108(19):7689–7692.
13. Santoro M, et al. (2012) Partially collapsed cristobalite structure in the non molecular phase V in CO_2. *Proc Natl Acad Sci USA* 109(14):5176–5179.
14. Datchi F, Mallick B, Salamat A, Ninet S (2012) Structure of polymeric carbon dioxide CO_2-V. *Phys Rev Lett* 108(12):125701.
15. Mera G, Navrotsky A, Sen S, Kleebe H, Riedel R (2013) Polymer-derived SiCN and SiOC ceramics-structure and energetics at the nanoscale. *Journal of Materials Chemistry* 1:3815–3825.
16. Esfehanian M, Oberacker O, Fett T, Hoffmann M (2008) Development of dense filler-free polymer-derived SiOC ceramics by field-assisted sintering. *J Am Ceram Soc* 91:3803–38015.
17. Linck C, et al. (2012) Corrosion behavior of silicon oxycarbide-based ceramic nano-composites under hydrothermal conditions. *International Journal of Materials Research* 103:31–39.
18. Clayden N, Esposito S, Jayasooriya U, Sprunt J, Pernice P (2012) Solid state ^{29}Si NMR and FT Raman spectroscopy of the devitrification of lithium metasilicate glass. *Journal of Non-Crystalline Solids* 224:50–56.
19. Sen S, Youngman R (2003) NMR study of Q-speciation and connectivity in K_2O-SiO_2 glasses with high silica content. *Journal of Non-Crystalline Solids* 331:100–107.
20. Widgeon S, et al. (2010) ^{29}Si and ^{13}C solid-state NMR spectroscopic study of nano-meter-scale structure and mass fractal characteristics of amorphous polymer derived silicon oxycarbide ceramics. *Chem Mater* 22:6221–6228.
21. Xu Z, Stebbins JF (1995) ^6Li nuclear magnetic resonance chemical shifts, coordination number and relaxation in crystalline and glassy silicates. *Solid State Nucl Magn Reson* 5(1):103–112.
22. Gerald R II, Sanchez J, Johnson C, Klingler R, Rathke J (2001) In situ nuclear magnetic resonance investigations of lithium ions in carbon electrode materials using a novel detector. *J Phys Condens Matter* 13:8269–8285.
23. Smyth J, Jacobsen S (2006) *Nominally Anhydrous Minerals and Earth's Deep Water Cycle*, Geophysical Monograph (American Geophysical Union, Washington, DC), Vol 168, pp 1–11.
24. Marty B, Alexander C, Raymond S (2013) Primordial origins of Earth's carbon. *Reviews in Mineralogy and Geochemistry* 75:149–181.