Ana Černok*, Elena Bykova, Tiziana Boffa Ballaran, Hanns-Peter Liermann, Michael Hanfland and Leonid Dubrovinsky

High-pressure crystal chemistry of coesite-I and its transition to coesite-II

Abstract: The high-pressure crystal chemistry of coesite was studied by means of single crystal X-ray diffraction in the pressure interval ~2–34 GPa and at ambient temperature. We compressed the samples using diamond-anvil cells loaded with neon as pressure-transmitting medium and collected X-ray diffraction data using synchrotron radiation. The thermodynamically stable coesite – coesite-I – was observed up to ~20 GPa, with the following unit-cell parameters: $a = 6.6533(12)$ Å, $b = 11.9018(10)$ Å, $c = 6.9336(10)$ Å, $\beta = 121.250(20)^\circ$ and $V = 469.38(15)$ Å³. The volume-pressure data of coesite-I are described by means of a third-order Birch-Murnaghan EoS with parameters $V_0 = 547.26(66)$ Å³, $K_{T0} = 96(4)$ GPa, $K'_{T0} = 4.1(4)$. Above such pressure we witness the formation of a well crystallized coesite-II, previously observed only by spectroscopic studies. The structure of the novel *high-P* polymorph was determined and refined at ~28 and ~31 GPa with final R indices of 8% and 12%, respectively. Coesite-II has $P2_1/n$ symmetry and a unit cell that is “doubled” along the b -axis with respect to that of the initial coesite-I: $a = 6.5591(10)$ Å, $b = 23.2276(14)$ Å, $c = 6.7953(9)$ Å, $\beta = 121.062(19)^\circ$ and $V = 886.84(19)$ Å³ at ~28 GPa. All Si atoms are in tetrahedral coordination. The displacive phase transition I→II is likely driven by the extreme shortening (0.05 Å or 3.2%) of the shortest and the most compressible Si1-O1 bond, related to the stiff 180° Si1-O1-Si1 angle. Under compression the linear angle bends, resulting in two independent angles, one of which, however, retains almost linear geometry (~178°). The requirement of this angle to be close to linear likely causes further Si-O compression down to an extremely short distance of ~1.52 Å which prompts subsequent structural changes, with the formation of a triclinic phase at ~31 GPa, coesite-III.

Keywords: coesite; compressibility; high-pressure; phase transition; Si-O bond.

DOI 10.1515/zkri-2014-1763

Received May 1, 2014; accepted August 29, 2014

Introduction

Coesite is the densest polymorph of silica, SiO₂, that contains silicon atom tetrahedrally coordinated to oxygen. It is thermodynamically stable above ~2.5 GPa and at temperatures in excess of 500 °C. The polymorph was first synthesized by Coes [1] and the structure was determined by Buerger and Zoltai [2]. Coesite was discovered in nature by Chao and coworkers in impact breccia from Meteor Crater [3]. Since then, natural occurrences of coesite were documented in kimberlites [4], high-pressure metamorphic rocks [5], and various materials, including meteorites, that have been subjected to shock-metamorphism.

Coesite ($C2/c$, $Z = 16$) shows nearly hexagonal symmetry at room pressure, with almost equal a and c axes, and a β angle close to 120°. The asymmetric unit contains two distinct silicon and five distinct oxygen atoms. It is a framework silicate comprised of fully polymerized corner-sharing SiO₄ tetrahedra. Building blocks of the framework are four-membered rings (4-rings) of tetrahedra that form chains that run parallel to the c -axis. These chains of 4-rings are linked in such manner that crankshaft-like chains are formed. Due to this arrangement there are five distinct Si-O-Si angles in the structure. The high-pressure structural behavior of coesite was previously studied using in-house based single crystal X-ray diffraction up to 5.2 GPa [6] and up to 8.7 GPa [7] in ethanol-methanol pressure medium, as well as by means of ab initio calculations up to 17 GPa [8]. These studies concluded that the symmetry of the unit cell appears less hexagonal with increasing pressure, compressing in the a direction more than twice as much than in the c direction. Also, the most obvious structural change upon compression was found to be the reduction of four out of five different Si-O-Si angles, with smaller angles undergoing more compression than

*Corresponding author: Ana Černok, Bayerisches Geoinstitut, Universität Bayreuth, Universitätsstrasse 30, D-95440 Bayreuth, Germany, E-mail: Ana.Cernok@uni-bayreuth.de; ana.cernok@gmail.com

Elena Bykova, Tiziana Boffa Ballaran and Leonid Dubrovinsky: Bayerisches Geoinstitut, Universität Bayreuth, Universitätsstrasse 30, D-95440 Bayreuth, Germany

Hanns-Peter Liermann: Photon Sciences, Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, 22607 Hamburg, Germany

Michael Hanfland: European Synchrotron Radiation Facility (ESRF), 6 Rue Jules Horowitz, 38000 Grenoble, France

the larger ones. The Si1-O1-Si1 angle is constrained to 180° due to symmetry requirements. The O1 atom is placed on an inversion center and as long as the symmetry is maintained, the Si1-O1-Si1 linkage remains linear, giving rise to the high stiffness of the structure (e.g., [9]).

Our recent study [10] has shown that coesite, similarly to quartz and cristobalite, can be compressed under (quasi)-hydrostatic conditions to very high pressures and at ambient temperatures without undergoing amorphization. Earlier spectroscopic studies observed structural changes in coesite near ~ 23 GPa [11], and one more near ~ 34 GPa, with the latter polymorph remaining crystalline at least up to ~ 51 GPa [10]. Reconstructive transitions to the stable high-pressure polymorphs consisting of SiO_6 octahedra (e.g., stishovite, CaCl_2 -structured silica, or seifertite) are often hindered due to high kinetic barriers associated with the relatively strong Si-O bonding within the tetrahedra (e.g., [12]). As a consequence, compression of phases with tetrahedrally coordinated silicon without sufficient heating results in formation of complex metastable phases, leading in particular to persistence of SiO_4 -based phases far out of their stability fields. Experimental challenge in studying the structure and the formation of these phases arises from the sluggish transitions, enhanced metastability regions, and formation of poorly crystallized materials. Such conditions usually give rise to weak X-ray diffraction patterns that are difficult to interpret, often resulting in contradictory interpretations. Although spectroscopic studies have indicated phase transitions to coesite-II and III, crystallographic analyses of these phases have not yet been reported.

In this work we were motivated to understand in detail the high-pressure crystal chemistry of thermodynamically stable coesite (hereafter coesite-I) and the mechanisms that lead to its structural transformation induced by pressures exceeding 20 GPa. We report single-crystal X-ray diffraction data collected with diamond-anvil cells (DACs) at ten different pressures up to ~ 34 GPa using synchrotron radiation. Our data confirm the phase transition above ~ 20 GPa and give insight into the structure of the novel high-pressure polymorph coesite-II. Appearance of extra reflections above ~ 30 GPa suggests a subsequent transition to a phase with lower, possibly triclinic, symmetry – coesite-III – in agreement with our previous Raman spectroscopy data.

Experimental

Synthesis conditions and the starting material used to synthesize the coesite crystals for this study have been described in a

previous study [10]. We selected coesite single crystals of typical size $10 \times 20 \times 30 \mu\text{m}^3$ at the Bayerisches Geoinstitut (BGI), using a rotating anode high-brilliance Rigaku diffractometer with Mo $K\alpha$ radiation, equipped with an Osmic focusing X-ray optics and a Bruker Apex CCD detector.

The structural behavior of coesite-I was investigated in the pressure region between 2.4 and ~ 34 GPa at ambient temperature using piston-cylinder BX90 type diamond anvil cells (DAC) produced at BGI [13]. We used Boehler-Almax diamond anvils with $250 \mu\text{m}$ culet size and apertures of 80° [14], to allow for large reciprocal space coverage in the single crystal X-ray diffraction experiments. Crystals of coesite were loaded together with a $\sim 5 \mu\text{m}$ in diameter ruby sphere into a cylindrical pressure chamber of $30\text{--}40 \mu\text{m}$ height and $\sim 125 \mu\text{m}$ diameter drilled in a pre-indented rhenium gasket. Neon, used as pressure transmitting medium, was loaded into the DAC using the BGI gas loading system [15].

High-pressure single crystal X-ray diffraction experiments were performed at the beamline ID09A, at ESRF (Grenoble, France) and at the Extreme Conditions Beamline (ECB, P02.2) at PETRA III in Hamburg. At each pressure point, wide-scan diffraction images were collected in the ω range of $\pm 40^\circ$ for 3 s. In addition, 80 independent step-scan diffraction frames were collected with time exposure of 1 s/step in the same ω range. At ESRF, data were collected at seven different pressure points from 2.42(5) up to 20.30(15) GPa, using $30 \mu\text{m}$ X-ray beam with a wavelength of $0.4144 \text{ \AA}$ and a Mar555 flat panel detector, located at the distance of 309.5 mm from the sample. At PETRA III we performed an experiment on another crystal, obtaining single crystal data at 27.52(13), 30.94(41) and 34.20(28) GPa, using $2 \times 4 \mu\text{m}^2$ (FWHM) X-ray beam with a wavelength of $0.29004 \text{ \AA}$. The detector used was a MAR345 online Image Plate (IP), located at the distance of 400.8 mm. Pressure was determined using the ruby pressure gauge [16] both before and after collection of X-ray data. At ECB at PETRA III, in addition to the ruby pressure scale, we determine pressure also by using neon EOS reported by Fei et al. [17]. Single-crystal data have been reduced with the CrysAlis software package [18] and analyzed with the SHELX97 program package [19] as implemented in the WingX software [20]. Isotropic structure refinements of coesite-I were performed based on F^2 starting from the atomic coordinates for coesite at ambient conditions, reported by Angel et al. [7]. The structure of coesite-II was solved by direct method using SHELXS and refined by full matrix least-squares in the isotropic approximation using SHELXL, both programs being implemented in SHELX97 software.

Results

Wide-scan exposure images indicate that the single crystal of coesite remain well-crystallized up to the maximal pressures attained in this study (~ 34 GPa) with an abrupt change in the diffraction pattern between ~ 20 and ~ 28 GPa (Figure 1). The change is characterized by an increase in the number of reflections and an overall decrease in their intensities. This is in agreement with the Raman spectroscopy observations of a pressure-induced structural transformation from coesite-I to a lower-symmetry phase coesite-II [10, 11]. We investigated the compressibility and the structural evolution of coesite-I from 2.42(5) GPa up to 20.30(15) GPa. The structure of the novel polymorph coesite-II was

Fig. 1: Reciprocal space reconstruction of the b^*c^* plane for (A) coesite-I at 20.3 GPa and (B) coesite-II at 27.5 GPa. Some reflections are labeled as example. The reciprocal lattice of coesite-II has a larger c^*/b^* ratio due to the doubling of the unit-cell along the b -axis upon transition. The number of reflections collected for coesite-II increased due to the lower symmetry.

solved using the dataset collected at 27.52(13) GPa and also refined at 30.94(41) GPa. The unit cell parameters of the polymorphs at various pressures are reported in Table 1 and the compressibility data of coesite-I are summarized in Table 2. Details of the refinement procedure are given in Table 3. Refined positional parameters of coesite-I and coesite-II are reported in Tables 4A and B, respectively. Selected bond lengths and angles are given in Tables 5 and 6.

Coesite-I

Compressibility

The smooth and continuous evolution of the coesite-I unit cell volume with pressure (Figure 2) indicates that it remains

stable up to 20.30(15) GPa. By fitting the P - V data with a 3rd-order Birch-Murnaghan equation of state (BM3-EoS) using the EosFit software v5.2 [23], we obtain a room pressure unit cell volume, V_0 , of 547.26(66) Å³, which within uncertainties of our measurements coincides with the V_0 values reported in two other experimental high-pressure studies: i.e., 546.46(5) Å³ by Levien and Prewitt [6] and 546.80(3) Å³ by [22]. The unit cell volume is well within the range of the reported values from various XRD studies at ambient conditions of synthetic, e.g., 549.47 Å³ [23] or 546.4(1) Å³ [24] and natural, e.g., 546.74(30) Å³ [25] or 546.98(13) Å³ [26], samples. The total decrease of the unit cell volume from room pressure up to 20.30(15) GPa is about 14.2%, with a correspondent density increase of about 16.5%.

Although Angel et al. [22] suggested that a 4th-order BM-EoS is necessary to describe adequately the

Tab. 1: Unit-cell parameters of coesite-I and II at various pressures.

P , GPa ^a	a , Å	b , Å	c , Å	β	V , Å ³	ρ , g/cm ³
Coesite-I (C2/c)						
0.00010(1)	7.1436(51) ^b	12.3621(57) ^b	7.1752(19) ^b	120.248(76) ^b	547.26(66) ^b	2.92 ^c
2.42(5)	7.0612(6)	12.2936(5)	7.1417(4)	120.520(9)	534.10(20)	2.99
5.16(6)	6.9837(6)	12.2255(5)	7.1081(4)	120.736(9)	521.60(20)	3.06
9.24(9)	6.8746(6)	12.1220(5)	7.0549(4)	120.965(10)	504.10(20)	3.17
12.14(9)	6.8070(7)	12.0623(5)	7.0223(4)	121.057(11)	493.94(18)	3.23
14.90(25)	6.7549(11)	12.0019(9)	6.9863(7)	121.075(18)	485.11(16)	3.29
17.80(5)	6.6921(11)	11.9470(9)	6.9581(7)	121.179(19)	475.95(15)	3.35
20.30(15)	6.6533(12)	11.9018(10)	6.9336(10)	121.250(20)	469.38(15)	3.40
Coesite-II (P2 ₁ /n)						
27.52(13)	6.5591(10)	23.2276(14)	6.7953(9)	121.062(19)	886.84(19)	3.60
30.94(41)	6.5446(15)	23.0389(17)	6.7325(13)	121.37(3)	866.7(3)	3.68

Note: ^aAverage values of pressures, measured before and after X-ray data collection. ^bValues obtained by fitting BM3 EoS to the P - V dataset with EosFit [21]. ^cLiterature value (Angel et al. [7]); Numbers in parentheses are the esd's in the last decimal place of each value.

Tab. 2: Parameters of the 3rd order Birch-Murnaghan EoS fit to coesite-I data.

Volume compressibility	$V_0, \text{\AA}^3$	K_0, GPa	K'	K'', GPa^{-1}	χ^2_{weighted}
Unit cell volume	547.26(66)	96(4)	4.11(38)	[−0.042]	0.7355
SiO ₄ tetrahedra					
Si1	2.1465(71)	283(23)	[4]	[−0.014]	1.2560
Si2	2.1428(40)	445(31)	[4]	[−0.008]	0.9840
Axial compressibility	$L_0, \text{\AA}$	K_0, GPa	K'	K'', GPa^{-1}	χ^2_{weighted}
X1 a^*	6.1710(51)	52(2)	3.7(3)	[−0.070]	1.2676
X2 b	12.3621(57)	143(8)	3.6(8)	[−0.026]	4.1513
X3 c	7.1751(19)	173(7)	2.5(6)	[−0.026]	1.9640

Note: Data used for BM3 EoS are reported in Table 1. Numbers in square brackets are implied values. X1 compressional direction is parallel to $a^* = a \sin \beta$. Numbers in parentheses are the esd's in the last decimal place of each value.

Fig. 2: Unit-cell volumes, normalized with respect to the V_0 BM3 parameter, plotted against pressure. Literature data are reported for comparison. The dashed line is a 3rd order Birch-Murnaghan EoS (BM3) fitted to the coesite-I P - V data from this study. The gray line is the 4th order BM EoS reported by [22] for the sample X3 P - V data.

high-pressure behavior of coesite, the normalized stress, F_E , vs. Eulerian strain, f_E , plot [21] constructed from our P - V data shows a linear trend consistent with a 3rd-order BM-EoS (Figure 3). The intersection of the linear fit through the F_E data points with the F_E -axis suggests a value of the bulk modulus, K_{T_0} , of about 95 GPa and the slope of such linear fits yields its pressure derivative K'_{T_0} of 4.3. Such results are in good agreement with the BM3-EoS parameters obtained by fitting our P - V data, which are the following: $V_0 = 547.26(66) \text{\AA}^3$, $K_{T_0} = 96(4) \text{GPa}$, $K'_{T_0} = 4.1(4)$. The value of the bulk modulus is very close to that reported by Levin and Prewitt [6]: $K_{T_0} = 96(3) \text{GPa}$, which was obtained using a BM3 fit to their data collected up to 5.1 GPa. However, their

Fig. 3: Pressure-volume data of coesite-I collected up to 20.3 GPa, plotted as normalized pressure, F_E , against Eulerian strain, f_E . Our data (circles) are compared with those of the X3 sample (diamonds) from Angel et al. (2001): both data sets are plotted using their original V_0 (full symbols), as well as by substituting the values of V_0 (see text). The uncertainties in F_E and f_E were calculated by propagation of the experimental uncertainties in volume and pressure, according to Heinz and Jeanloz [28]. The reported relationships are the linear fit through our data with the BM3 EoS V_0 (top) and with the V_0 from X3 sample (bottom). The two bulk moduli so obtained differ only slightly.

pressure derivative is significantly larger [$K'_{T_0} = 8(2)$]. Our data are in excellent agreement with the BM3-EoS parameters obtained from the fit to the data collected up to ~9 GPa by [22]: i.e., $K_{T_0} = 97.4(6) \text{GPa}$ and $K'_{T_0} = 4.3(2)$. The F_E - f_E plot calculated for the P - V data of [22] is also shown in Figure 3, for comparison. Our data are significantly more scattered than those from [22], but clearly do not show the curvature of the data presented by [22]. Since the values of V_0 can

have a strong effect on the F_E - f_E plot [27] we have considered two further F_E - f_E plots: one using our volume data with V_0 from the X3 sample of [22], and one using the data from [22] with the V_0 values from this study (Figure 3). The different V_0 does not significantly affect the linear trend of our data and gives EoS parameters which are indistinguishable within the uncertainties. On the contrary, the F_E - f_E data of [22] are clearly more dependent on the choice of V_0 and the slight increase in V_0 of $0.4 \text{ \AA}^3$ results in a F_E - f_E plot which is more similar to that of our data (Figure 3).

The evolution of the unit-cell axes under pressure is in good agreement with previous studies, as illustrated by comparison to the X3 data set of [22] and it implies that the axial compression of coesite-I is very anisotropic (Figure 4). Due to the monoclinic symmetry, one of the principal axis

of compression is constrained to lie along the b -axis, and the other two principal axes must lie in the (010) plane. Previous analyses of the strain ellipsoid [22] showed that in the case of coesite, the principal axes of compression lie within uncertainties parallel to the $a^* = a \sin \beta$, b and the c axes, with the a^* being the most compressible and the b and c axes showing similar compressional rates. We confirm this compressional regime (Figure 4) and find that the axes of the strain ellipsoid rotate only $\sim 2^\circ$ up to 20.3 GPa, i.e., less than the uncertainty on their position. The axial F_E - f_E plots are compared to the values from [22] in a way similar to the unit cell volume (Figure 5). The linear trend of our data is less affected by the variation of zero-pressure values, particularly in the case of the least compressible b -axis. The axial F_E - f_E plots constructed for the X3

Fig. 4: Compressibility of the unit-cell parameters of coesite-I and II. Half-values of the b -constant for coesite-II is reported. Literature values are given for comparison. In addition to the relative unit cell constants, we also plot $a^* = a \sin \beta$, which is the most compressible direction in coesite. Dotted lines are BM3 fits through our experimental data. BM3 fit of the β -angle was obtained from the BM3 fit to the a^* values.

Fig. 5: Axial F_E - f_E plots of coesite-I up to 20.3 GPa along the principal axes of the compression ellipsoid ($a^* \sin \beta$, b and c). Similarly to Figure 3, our data (circles) are compared to those of the X3 sample (diamonds) from Angel et al. (2001) and both data sets are plotted using their original zero-pressure value (full symbols) as well as by substituted zero-pressure values.

dataset using our zero-pressure values indicate linearity that corresponds closer to our data. Following Angel [21], estimates of the zero-pressure lattice constants as well as the linear moduli along the crystallographic axes have

been obtained by fitting the cubes of the unit-cell parameters with a 3rd-order Birch-Murnaghan EoS. The resulting linear EoS parameters are the following: $a_0 = 7.1436(51)$ Å, $K_0(a) = 67(3)$ GPa, $K' = 3.3(3)$; $b_0 = 12.3621(57)$ Å, $K_0(b) = 143(8)$ GPa, $K' = 3.6(9)$; $c_0 = 7.1752(19)$ Å, $K_0(c) = 173(7)$ GPa, $K' = 2.5(6)$ and $a^*_0 = 6.1710(56)$, $K_0(a^*) = 52(2)$ GPa, $K' = 3.7(3)$. The linear moduli and their respective pressure derivatives obtained from the BM3 fits are in good agreement with the values determined from the axial F_E - f_E plots.

Mechanisms of compression

The structure of coesite-I shown in Figure 6A and B is illustrating the characteristic features and the nomenclature in detail. As in previous studies, we find no evidence of kinking of the linear Si1-O1-Si1 angle throughout the pressure range of the coesite-I stability field. The rate of compression of the four other Si-O-Si angles (Figure 7), with the smaller angles being more compressible, is in good agreement with the experimental studies at lower pressures [6, 7]. The ab initio calculations [8] suggest compressional rates similar to those obtained in all of experiments, although the calculated angles appear to be smaller than those measured. Decrease of the smallest Si1-O5-Si2 angle from 137.44° (ambient, Angel et al. [7]) to 125.54° at ~20 GPa contributes to the shortening along the b -axis. Kinking of the Si2-O2-Si2 angle (142.69° ambient to 127.70° at 20 GPa) brings the four-membered rings closer along [001]. However, the internal shape of the 4-rings in coesite-I is controlled by the much faster decrease of the Si1-O3-Si2 angle with respect to the Si1-O4-Si2, which results in shearing of the rings along [001]. An increase of the O3-O3 ring diagonal by ~5% up to the transition pressure contributes to the large stiffness along the c -axis, giving rise to its stiffest linear modulus (Table 6).

Two neighboring (010) planes of the rings can be seen as two semi-close-packed planes of O3 and O4 oxygen atoms connected by the linear Si1-O1-Si1 angle (Figure 6A). The spacing between these oxygen planes increases with pressure up to 12 GPa, in agreement with the lower pressure studies [7] but it levels off above ~12 GPa (Figure 6A). This is probably a consequence of the fact that Si2 tilting has reached a limiting value and Si1 cannot rotate further around the Si1-Si1 axis. Further tilting of Si2 would invoke the Si1 to tilt as well, which is unfeasible due to the symmetry of coesite-I.

Tetrahedral distortion

The two symmetrically distinct SiO₄ tetrahedra of the coesite-I structure respond differently to compression up

Fig. 6: Structure of coesite-I at 20.3 GPa and of coesite-II at 27.5 GPa viewed in different directions. (A) Coesite-I seen down the c -axis. Dominant features are the symmetric hollow channels that run parallel to $[001]$, placed between the linear Si1-O1-Si1 angles. Dashed lines indicate semi-close-packed O3 and O4 planes of oxygens in (010) and the plot on the right shows the O3 and O4 distance under pressure. (B) Coesite-I seen along the b -axis. Characteristic features are the four-membered rings of corner sharing SiO_4 tetrahedra. Each ring consists of two opposite Si1 and two Si2 tetrahedra connected by O3 and O4 atoms. Neighboring rings are connected by O2 atoms to form chains aligned parallel to the c -axis. The chains are not connected with the neighboring chains within the same (010) plane. Instead, they are linked to the chains from a plane above and a plane below alternately by O1 or O5 atoms. Dotted lines indicate various O-O distances (nomenclature after Angel et al. [7]) between unconnected chains within the same (010) plane and within the 4-rings (O3-O3 and O4-O4 diagonals). The values of these distances are reported in Table 6. (C) Coesite-II seen down the c -axis. The hollow channels parallel to the c -axis are asymmetric and are places between Si7-O4-Si5 ($\sim 178^\circ$) and Si2-O15-Si3 ($\sim 153^\circ$) angles. Few distinct Si tetrahedra are labeled. (D) Planes of 4-rings in coesite-II seen along the b -axis. Each ring consists of four distinct Si tetrahedra. Dotted lines indicate similar O-O distances as in coesite-I, with oxygen nomenclature of coesite-II. Small sketch on the right illustrates two different sizes of 4-rings in coesite-II.

to ~ 20 GPa, following a trend similar to that observed at lower pressures [6, 7]. The Si1 tetrahedron shows a volume decrease of about 5.4% and the Si2 of 4.4% in the investigated pressure range. A larger increase in angular variance and quadratic elongation with pressure shows that the Si1 tetrahedron undergoes much more distortion than the Si2 tetrahedron (Table 5).

The compression and distortion of the Si1 tetrahedron are accommodated by highly anisotropic shortening of the Si-O bonds, with the shortest Si1-O1 bond [$1.5859(13)$ Å at 2.42 GPa] undergoing the largest compression (3.2%, Figure 8). Similarly, the shortest O1-O4 distance [$2.5841(30)$ Å at 2.42 GPa] is the most compressible

tetrahedron edge of the coesite-I structure, showing a decrease of 4.9% up to 20.3 GPa. This is a consequence of the larger distortion of the O1-Si1-O4 angle with respect to the rest of the tetrahedral (O-Si-O) angles (Table 5). In spite of large Si1-O1 bond compressibility and the absence of Si1-O1-Si1 kinking, the Si1-Si1 distance remains the longest cation-cation distance throughout the compression of coesite-I. The Si2 tetrahedron shows less anisotropic compressional behavior, with smaller changes in Si-O and O-O distances with pressure (Figure 8), as well as smaller changes of O-Si2-O angles (Table 5). In contrast to Si1 and according to the expected behavior with pressure, the shortest Si2-O3 bond is the stiffest bond

Tab. 3: Parameters of isotropic refinements of coesite-I and coesite-II structures at various pressures.

P, GPa	2.42	5.16	9.24	12.14	14.90	17.80	20.30	27.52	30.94
Total number/unique reflections	627 / 439	667 / 427	518 / 396	563 / 405	637 / 412	609 / 396	600 / 393	2019 / 1123	1781 / 1002
R_{int}/R_{σ}	0.0220/0.0296	0.0189/0.0291	0.0159/0.0261	0.0129/0.0189	0.0150/0.0193	0.0128/0.0162	0.0116/0.0185	0.0405/0.0459	0.0628/0.0611
$[F_{obs} > 4\sigma(F_{obs})]/\text{restraints/parameters}$	376/0/24	348/0/24	329/0/24	351/0/24	366/0/24	355/0/24	345/0/24	811/0/97	715/0/97
Goodness of fit on $F^2 [S]$	1.057	1.123	1.078	1.161	1.148	1.109	1.139	1.124	1.045
Final R indices $[F_{obs} > 4\sigma(F_{obs})] R_w/wR_2$	0.0553 / 0.1622	0.0346 / 0.0907	0.0302 / 0.0789	0.0344 / 0.1021	0.0340 / 0.0981	0.0375 / 0.1097	0.0372 / 0.1023	0.051 / 0.1369	0.0959 / 0.2636
Final R indices R_w/wR_2 for all data	0.0608 / 0.1622	0.0445 / 0.0907	0.0384 / 0.0789	0.0400 / 0.1021	0.0378 / 0.0981	0.0415 / 0.1097	0.0422 / 0.1023	0.0787 / 0.1369	0.1221 / 0.2636
Largest diff. peak and hole (e / Å ³)	0.86 and -0.76	0.53 and -0.43	0.37 and -0.38	0.46 and -0.47	0.58 and -0.67	0.54 and -0.51	0.65 and -0.58	0.64 and -0.71	1.32 and -1.01
Systematic absences violations	0	0	0	0	0	0	0	0	1
Inconsistent equivalents	9	5	2	7	11	14	1	6	17
Recommended weighting	0.1270	0.0487-1.2285	0.0429-1.2410	0.0706	0.0615-0.9135	0.0684-1.8125	0.0593-1.8117	0.0568-6.2280	0.1958

of the Si2 tetrahedron and of the entire structure (0.1% compression).

The major difference in compressibility of the two tetrahedral sites is clearly reflected in their respective bulk moduli, calculated for the tetrahedral volume changes: 283(23) GPa for Si1O₄ and 445(31) GPa for Si2O₄. The Si1 tetrahedral site is anomalously compressible relative to SiO₄ tetrahedra in other silicates. To our knowledge, the only other common silicate minerals for which the reported bulk moduli of the tetrahedral Si sites are comparable to that of Si1 tetrahedron in coesite-I are zircon and forsterite (summarized in Smyth et al. [31]). Note, however, that in such structures the tetrahedra do not form three-dimensional framework as in the case of coesite.

Phase transition and the structure of coesite-II

The displacive phase transition from coesite-I to coesite-II is characterized by a change of symmetry from C2/c to P2₁/n (Figure 6A and C). Due to the rearrangement of the atoms, doubling along the *b*-axis is achieved, resulting in the disappearance of the C-centering after the transition, in a doubled unit cell volume, and in a number of molecular units *Z* = 32 per unit cell. The asymmetric unit of coesite-II contains eight silicons and sixteen oxygens. The effect of the symmetry reduction can be better understood by observing the changes that occur within the hollow channels that run parallel to the *c*-cell edge (Figure 6A and C). In the coesite-I structure these chains are separated by the linear Si1-O1-Si1 linkages, and they appear symmetric due to a 2-fold axis in [010] perpendicular to a mirror plane in (010). The mirror plane is placed in the middle of the channels, running exactly through the O1 atoms. After the phase transition and distortion of the linear Si1-O1-Si1 angle (Figure 7), the shape of these channels is distorted with consequent disappearance of the mirror plane and loss of the C center. Bending of the linear Si1-O1-Si1 angle results in four non-equivalent silicon atoms connected by two non-equivalent oxygens, thus forming two independent angles. These are Si7-O4-Si5 (~178°) and Si2-O15-Si3 (~153°). Very likely, the extreme compression of the shortest Si1-O1 bond drives the bending of the Si1-O1-Si1 angle and the consequent loss of the mirror plane. Above the transition, those Si-O distances within the Si5 and Si7 tetrahedra, which are related to an angle still very close to 180°, compress down to ~1.52 Å at 30.94(41) GPa (Figure 8). In the case of the Si2-O15-Si3, the previously

Tab. 4A: Fractional atomic coordinates and isotropic displacement parameters of coesite-I at various pressures.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{iso}</i>
2.42 GPa				
Si1	0.13887(24)	0.10923(10)	0.07142(18)	0.00571(41)
Si2	0.50807(22)	0.15748(10)	0.54309(17)	0.00523(41)
O1	0.0000	0.0000	0.0000	0.01073(92)
O2	0.5000	−0.11219(36)	0.2500	0.00772(86)
O3	0.73923(60)	0.12738(27)	0.56621(47)	0.00866(66)
O4	0.31575(62)	0.10210(27)	0.32678(47)	0.01032(71)
O5	−0.02328(65)	0.21177(27)	0.02517(50)	0.00921(69)
5.16 GPa				
Si1	0.13660(19)	0.11018(8)	0.07000(15)	0.00524(25)
Si2	0.50930(18)	0.15704(8)	0.54508(14)	0.00510(25)
O1	0.0000	0.0000	0.0000	0.01032(73)
O2	0.5000	−0.10878(27)	0.2500	0.00635(65)
O3	0.74830(49)	0.13069(20)	0.57351(39)	0.00891(51)
O4	0.31886(49)	0.10081(20)	0.32531(40)	0.00964(53)
O5	−0.02687(51)	0.21251(20)	0.02911(40)	0.00853(49)
9.24 GPa				
Si1	0.13451(19)	0.11145(7)	0.06828(14)	0.00513(23)
Si2	0.50985(18)	0.15649(7)	0.54689(13)	0.00529(24)
O1	0.0000	0.0000	0.0000	0.01190(67)
O2	0.5000	−0.10426(23)	0.2500	0.00643(60)
O3	0.75574(48)	0.13439(17)	0.58087(37)	0.00782(45)
O4	0.32389(50)	0.09922(18)	0.32404(40)	0.00992(49)
O5	−0.03370(47)	0.21271(18)	0.03181(36)	0.00844(45)
12.14 GPa				
Si1	0.13325(19)	0.11217(7)	0.06720(13)	0.00570(27)
Si2	0.50994(17)	0.15615(7)	0.54780(12)	0.00553(28)
O1	0.0000	0.0000	0.0000	0.01353(68)
O2	0.5000	−0.10218(24)	0.2500	0.00669(59)
O3	0.76001(47)	0.13676(18)	0.58549(35)	0.00841(45)
O4	0.32622(50)	0.09864(18)	0.32287(39)	0.00979(47)
O5	−0.03741(47)	0.21258(18)	0.03317(35)	0.00875(47)
14.90 GPa				
Si1	0.13137(19)	0.11291(7)	0.06571(13)	0.00487(25)
Si2	0.50954(17)	0.15583(7)	0.54838(13)	0.00445(26)
O1	0.0000	0.0000	0.0000	0.01368(69)
O2	0.5000	−0.10041(24)	0.2500	0.00606(58)
O3	0.76338(49)	0.13854(18)	0.58882(37)	0.00784(45)
O4	0.32655(53)	0.09786(18)	0.32154(41)	0.00905(47)
O5	−0.04076(49)	0.21284(18)	0.03394(36)	0.00796(46)
17.80 GPa				
Si1	0.13063(21)	0.11348(8)	0.06491(16)	0.00970(29)
Si2	0.50958(21)	0.15565(8)	0.54919(16)	0.00937(30)
O1	0.0000	0.0000	0.0000	0.01782(77)
O2	0.5000	−0.09804(27)	0.2500	0.00994(66)
O3	0.76676(58)	0.13999(20)	0.59224(44)	0.01264(53)
O4	0.32846(60)	0.09716(20)	0.32088(46)	0.01338(54)
O5	−0.04371(56)	0.21274(21)	0.03537(42)	0.01253(54)
20.30 GPa				
Si1	0.13034(21)	0.11379(8)	0.06437(16)	0.00636(28)
Si2	0.50942(21)	0.15551(8)	0.54951(16)	0.00582(28)
O1	0.0000	0.0000	0.0000	0.01697(81)
O2	0.5000	−0.09678(28)	0.2500	0.00683(65)
O3	0.76866(57)	0.14133(21)	0.59464(43)	0.00901(52)
O4	0.33018(60)	0.09676(21)	0.32117(48)	0.01081(53)
O5	−0.04608(56)	0.21279(21)	0.03575(43)	0.00925(53)

Note: Numbers in parentheses are the esd's in the last decimal place of each value.

Tab. 4B: Fractional atomic coordinates and isotropic displacement parameters of coesite-II at various pressures.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{iso}</i>
27.52 GPa				
Si1	0.20478(40)	−0.20401(8)	0.46914(35)	0.00559(47)
Si2	0.32858(42)	−0.32003(8)	0.47855(36)	0.00543(46)
Si3	0.62880(42)	−0.06085(8)	0.94771(35)	0.00486(46)
Si4	0.70453(40)	−0.30081(8)	0.38018(35)	0.00517(46)
Si5	0.89180(41)	−0.07579(7)	0.58105(34)	0.00510(46)
Si6	0.77086(40)	0.04027(8)	0.55025(34)	0.00515(46)
Si7	0.58700(42)	−0.18435(7)	0.37450(36)	0.00516(45)
Si8	0.72817(41)	0.05686(8)	0.94088(35)	0.00533(46)
O1	0.44079(104)	−0.30040(19)	0.33058(88)	0.00631(104)
O2	0.14544(104)	−0.27186(19)	0.45578(85)	0.00657(105)
O3	0.88777(104)	−0.32975(19)	0.61640(88)	0.00662(105)
O4	0.73734(109)	−0.12909(20)	0.47533(91)	0.00902(111)
O5	0.47143(110)	−0.19929(20)	0.52022(93)	0.00864(107)
O6	0.73618(113)	−0.02535(19)	0.59720(90)	0.00888(110)
O7	0.81220(100)	−0.00947(19)	1.01289(85)	0.00539(104)
O8	0.53945(106)	−0.06247(19)	1.12206(88)	0.00699(107)
O9	1.08814(105)	−0.09258(18)	0.84076(86)	0.00531(104)
O10	0.20972(105)	−0.16994(19)	0.67212(87)	0.00607(103)
O11	0.02704(105)	−0.17197(19)	0.24174(89)	0.00708(108)
O12	0.76450(110)	−0.23356(19)	0.39227(90)	0.00832(109)
O13	0.72586(103)	0.07886(20)	0.71930(87)	0.00705(107)
O14	0.39220(108)	−0.04909(20)	0.71465(92)	0.00973(114)
O15	0.71371(107)	−0.11932(19)	0.90380(92)	0.00928(114)
O16	0.97940(115)	−0.05569(20)	0.41236(94)	0.01028(112)
30.94 GPa				
Si1	0.20106(51)	−0.20373(10)	0.46011(47)	0.00753(78)
Si2	0.32239(54)	−0.32007(10)	0.46922(50)	0.00774(79)
Si3	0.63015(53)	−0.06046(10)	0.94741(48)	0.00756(77)
Si4	0.70065(54)	−0.30134(10)	0.37210(48)	0.00802(77)
Si5	0.88998(52)	−0.07636(11)	0.58174(46)	0.00699(76)
Si6	0.77115(50)	0.03963(10)	0.55068(45)	0.00665(78)
Si7	0.58594(54)	−0.18504(10)	0.37046(50)	0.00748(75)
Si8	0.72692(51)	0.05769(10)	0.93825(47)	0.00772(78)
O1	0.43607(141)	−0.29983(25)	0.32223(120)	0.00780(142)
O2	0.13900(134)	−0.27178(25)	0.44832(114)	0.00807(142)
O3	0.88562(143)	−0.33040(27)	0.61051(125)	0.01114(150)
O4	0.73619(143)	−0.13020(27)	0.47243(124)	0.01374(161)
O5	0.46907(150)	−0.19970(27)	0.51681(132)	0.01224(157)
O6	0.73390(139)	−0.02588(25)	0.59980(118)	0.00862(140)
O7	0.81109(136)	−0.00919(27)	1.01288(120)	0.01181(151)
O8	0.54118(142)	−0.06344(26)	1.12732(122)	0.01114(152)
O9	1.08697(140)	−0.09403(26)	0.84255(113)	0.00807(152)
O10	0.20496(129)	−0.16907(25)	0.66384(109)	0.00666(143)
O11	0.01992(151)	−0.17140(27)	0.23066(133)	0.01397(160)
O12	0.76065(142)	−0.23402(25)	0.38418(130)	0.01025(150)
O13	0.72485(130)	0.07951(26)	0.71142(114)	0.00849(143)
O14	0.38789(138)	−0.04672(27)	0.71732(118)	0.01091(148)
O15	0.70703(151)	−0.11848(28)	0.88842(136)	0.01630(169)
O16	0.97500(142)	−0.05568(27)	0.41117(123)	0.01185(155)

Note: Numbers in parentheses are the esd's in the last decimal place of each value.

Tab. 5: Selected tetrahedral distances (Å) and angles (°) in coesite-I at various pressures.

<i>P</i> , GPa	2.42	5.16	9.24	12.14	14.90	17.80	20.30
Si1 tetrahedron							
Bond length							
Si1-O1	1.5865(13)	1.5770(10)	1.5665(9)	1.5602(9)	1.5537(9)	1.5484(10)	1.5440(10)
Si1-O4	1.6063(34)	1.6017(28)	1.5985(28)	1.5944(27)	1.5915(29)	1.5879(32)	1.5884(33)
Si1-O3	1.6174(32)	1.6087(26)	1.6034(24)	1.6030(23)	1.5993(23)	1.5953(26)	1.5948(25)
Si1-O5	1.6201(37)	1.6167(29)	1.6137(26)	1.6085(25)	1.6041(26)	1.6004(29)	1.6012(29)
<Si(1)-O>	1.6076	1.6010	1.5955	1.5915	1.5872	1.5830	1.5821
Edge length							
O1-O3	2.6368(44)	2.6164(35)	2.6048(33)	2.6004(31)	2.5939(33)	2.5851(37)	2.5848(37)
O1-O4	2.5841(30)	2.5607(23)	2.5284(22)	2.5085(22)	2.4852(22)	2.4663(26)	2.4568(27)
O1-O5	2.6222(37)	2.619(25)	2.6088(22)	2.5991(22)	2.5932(22)	2.5846(25)	2.5791(25)
O3-O4	2.6488(55)	2.6485(44)	2.6519(43)	2.6538(38)	2.6512(42)	2.6522(47)	2.6575(47)
O3-O5	2.6196(59)	2.5981(57)	2.5977(52)	2.5923(49)	2.5885(52)	2.5851(59)	2.5853(48)
O4-O5	2.6306(46)	2.6303(34)	2.6402(33)	2.6380(32)	2.6365(33)	2.6331(38)	2.6364(39)
<O-O> in Si1	2.6237	2.6122	2.6053	2.5987	2.5914	2.5844	2.5833
Intratetrahedral angles							
O3-Si1-O1	110.74(14)	110.54(10)	110.51(9)	110.58(9)	110.70(9)	110.62(11)	110.81(11)
O4-Si1-O1	108.43(14)	107.38(10)	106.04(9)	105.34(9)	104.39(9)	103.69(11)	103.29(11)
O5-Si1-O1	109.61(17)	110.28(13)	110.23(12)	110.21(12)	110.40(12)	110.33(13)	110.13(13)
O3-Si1-O4	110.52(20)	111.37(16)	111.83(15)	112.19(15)	112.38(15)	112.85(18)	113.17(17)
O5-Si1-O3	107.93(17)	107.53(14)	107.07(12)	107.65(12)	107.81(12)	107.99(14)	107.94(14)
O5-Si1-O4	109.60(18)	109.77(14)	110.55(13)	110.90(12)	111.18(12)	111.35(14)	111.48(14)
Tetrahedral volume	2.1380	2.0985	2.0803	2.0632	2.0444	2.0265	2.0228
Quadratic elongation	1.0004	1.0008	1.0015	1.0020	1.0026	1.0032	1.0037
Angle variance	1.3210	2.6823	4.6662	6.3271	8.4654	10.5368	12.1043
Si2 tetrahedron							
Bond length							
Si2-O4	1.6010(35)	1.5994(29)	1.5874(28)	1.5818(27)	1.5815(29)	1.5771(32)	1.5680(33)
Si2-O2	1.6070(19)	1.6033(15)	1.5996(14)	1.5949(14)	1.5889(14)	1.5884(17)	1.5860(17)
Si2-O3	1.5984(37)	1.6080(30)	1.6030(30)	1.5993(28)	1.6009(29)	1.5978(34)	1.5941(33)
Si2-O5	1.6187(36)	1.6096(27)	1.6069(24)	1.6086(23)	1.6046(24)	1.6042(27)	1.6018(27)
<Si(2)-O>	1.6063	1.6051	1.5992	1.5962	1.5940	1.5919	1.5875
Edge length							
O2-O3	2.6172(48)	2.6232(40)	2.6089(39)	2.5982(36)	2.5905(38)	2.5830(44)	2.5766(44)
O2-O4	2.6197(33)	2.6129(26)	2.5993(26)	2.5955(26)	2.5910(27)	2.5854(33)	2.5756(34)
O2-O5	2.6456(56)	2.6428(41)	2.6418(32)	2.6412(30)	2.6362(33)	2.6409(40)	2.6398(40)
O3-O4	2.6061(50)	2.6142(40)	2.5968(39)	2.5909(38)	2.5969(38)	2.5876(44)	2.5784(45)
O3-O5	2.6193(59)	2.6173(46)	2.6088(41)	2.6018(41)	2.5955(41)	2.5919(48)	2.5849(48)
O4-O5	2.6289(46)	2.6232(34)	2.613(31)	2.6103(30)	2.6066(31)	2.6068(35)	2.6003(35)
<O-O> in Si2	2.6228	2.6223	2.6114	2.6063	2.6028	2.5993	2.5926
Intratetrahedral angles							
O2-Si2-O4	109.34(15)	109.25(12)	109.30(11)	109.58(11)	109.62(11)	109.52(13)	109.46(14)
O3-Si2-O4	108.81(18)	109.16(14)	108.96(13)	109.07(13)	109.38(13)	109.18(15)	109.25(15)
O5-Si2-O4	109.33(18)	109.56(14)	109.77(13)	109.81(13)	109.79(13)	110.05(15)	110.19(16)
O3-Si2-O2	109.63(14)	109.48(11)	109.10(10)	108.86(10)	108.61(10)	108.33(12)	108.19(12)
O5-Si2-O2	110.46(18)	110.54(14)	110.95(12)	111.07(11)	111.27(12)	111.62(13)	111.76(13)
O5-Si2-O3	109.24(18)	108.83(14)	108.73(12)	108.40(12)	108.13(13)	108.09(15)	107.93(14)
Polyhedral volume	2.1261	2.1249	2.0984	2.0860	2.0775	2.0688	2.0528
Quadratic elongation	1.0001	1.0001	1.0002	1.0003	1.0003	1.0005	1.0006
Angle variance	0.2276	0.3618	0.6527	0.8729	1.1825	1.6556	1.9684

Note: Quadratic elongation and tetrahedral variance calculated using PROGRAM METRIC Ver. 6.1 by Bartelmehs et al. [29], which is based on Robinson et al. [30]. Numbers in parentheses are the esd's in the last decimal place of each value.

Tab. 6: Selected intertetrahedral distances (Å) and angles (°) in coesite-I at various pressures.

P, GPa	2.42	5.16	9.24	12.14	14.90	17.80	20.30
Si1-O1-Si1	180	180	180	180	180	180	180
Si2-O2-Si2	139.46(31)	136.76(25)	133.36(20)	131.82(19)	130.50(20)	128.64(22)	127.70(22)
Si1-O3-Si2	143.13(24)	140.76(20)	138.32(17)	136.67(17)	135.61(18)	134.33(21)	133.41(20)
Si1-O4-Si2	149.40(23)	149.15(19)	148.28(16)	147.91(15)	147.28(16)	146.63(18)	146.17(18)
Si1-O5-Si2	134.62(27)	133.14(22)	130.26(18)	128.77(18)	127.65(18)	126.44(20)	125.54(20)
Si2-Si2	3.9109(17)	3.8825(14)	3.8416(12)	3.8165(12)	3.7914(12)	3.7717(14)	3.7560(14)
Si1-Si1	7.0601(6)	6.9829(6)	6.8746(6)	6.8070(7)	6.7549(11)	6.6921(11)	6.6548(15)
O3-O4 planes	2.9953(54)	3.0163(38)	3.0243(34)	3.0348(34)	3.0341(34)	3.0335(39)	3.0345(39)
O(1)-O(1)	3.5703(2)	3.5535(2)	3.5274(2)	3.5111(2)	3.4931(3)	3.4791(3)	3.4679(5)
O(3)-O(3)	4.0372(39)	4.1094(31)	4.1555(31)	4.1860(25)	4.2051(32)	4.2216(33)	4.2299(36)
O(4)-O(4)	3.3062(68)	3.2064(56)	3.0910(55)	3.0243(55)	2.9836(54)	2.9304(66)	2.8983(66)
O(1)-O(2)	3.3401(21)	3.2815(15)	3.2072(10)	3.1655(10)	3.1337(11)	3.0929(15)	3.0686(17)
O(1)-O(3)	3.1052(31)	3.0627(24)	3.0177(23)	2.9927(19)	2.9719(23)	2.9495(24)	2.9346(25)
O(1)-O(4)	3.2932(47)	3.2953(38)	3.2850(37)	3.2775(37)	3.2622(37)	3.2513(44)	3.2440(44)
O5a-O5b	3.0561(59)	2.9664(47)	2.8680(44)	2.8162(35)	2.7754(43)	2.7299(44)	2.7042(43)
O5a-O5c	3.1797(71)	3.0718(59)	2.9137(49)	2.8314(47)	2.7615(48)	2.6931(56)	2.6452(56)
O5a-O5d	3.6448(44)	3.6028(35)	3.5494(31)	3.5209(28)	3.4965(32)	3.4700(35)	3.4501(37)

Note: Si1-Si1 and Si2-Si2 are distances across the hollow channels. O3-O4 planes are marked in Figure 6. Number in parentheses are the esd's in the last decimal place of each value.

linear angle decreases by nearly 30° and the related Si-O bonds increase to ~ 1.55 Å.

Upon completion of the phase transition, the planes described by the O3 and O4 oxygens do not appear semi-close-packed as in coesite-I (Figure 6D) and all tetrahedra of coesite-II are subjected to tilting resulting in a steady reduction in Si-O-Si angles down to extreme values, the smallest being $\sim 120^\circ$ (Figure 7). The kinking enables the structure of the four-membered rings to become “loose” and less coplanar. The non-planar (i.e., outside of 010 plane) distortion of the rings contributes to the compression in all directions and the structure of coesite-II appears much more compressible than that of coesite I. Unlike coesite-I, which consists of only one characteristic 4-ring, there are two distinct rings, i.e., two alternating layers consisting of two different sizes of the 4-rings in the structure of coesite-II (Figure 6D).

Volume reduction of the coesite structure is most efficiently achieved by reducing the distance between the unconnected chains within the (010) plane. This is illustrated by the reduction of the distances between the six closest oxygen atoms (Table 6). The rate of this reduction is quite anisotropic. The greatest reduction is achieved along the *a*-axis, i.e., the O5a-O5c distance (O12-O2b in coesite-II) that compresses about $\sim 23\%$ down to ~ 2.4 Å (at 30.94 GPa). This oxygen-oxygen distance between the chains is shorter than the average tetrahedral O-O edge at this pressure. High reduction is achieved along *c*, as well,

Fig. 7: Kinking of the five characteristic Si-O-Si angles in coesite-I and their evolution above the phase transition (coesite-II). Open symbols are experimental literature data and the gray line is a trend obtained by ab initio calculations. Few angles are labeled in coesite-II, the rest is omitted for clarity. All values are given in Table 5. Two highlighted bonds Si7-O4-Si5 and Si2-O15-Si3 result from the tilting of the linear Si1-O1-Si1 angle.

Fig. 8: Si-O bonds for Si1 (left) and Si2 (right) tetrahedra in coesite-I. For the Si1 tetrahedron we also show the evolution of the shortest Si1-O1 bond above the phase transition in coesite-II. The two bonds related to the almost linear Si5-O4-Si7 angle are compressed down to ~ 1.52 Å at 30.9 GPa. Full symbols are this study, open symbols are Angel et al. [7] and the solid grey line is Gibbs et al. [8].

by $\sim 14\%$ reduction in O5a-O5b (O12-O2a) distance down to ~ 2.6 Å at 30.94 GPa.

its stability field, suppressing the formation of the more stable high-pressure polymorph cristobalite II [32].

Further phase transitions

At 30.94(41) GPa we observe reflections that, albeit weak, can be indexed by a triclinic unit cell coexisting with the coesite-II phase. The unit cell parameters of this phase are $a = 6.788(4)$ Å, $b = 7.040(4)$ Å, $c = 8.714(5)$ Å, $\alpha = 69.47(5)^\circ$, $\beta = 82.26(5)^\circ$, and $\gamma = 80.89(5)^\circ$ at 30.94(41) GPa. At 34.20(28) GPa the intensities of the reflections for this triclinic phase are much stronger. At this highest pressure point we still observe some coesite-II reflections, but their intensities are too weak to allow for proper integration. The appearance of a triclinic phase is consistent with our previous Raman spectroscopy observation [10] that indicates a structural change near ~ 34 GPa to a phase with symmetry lower than that of coesite-II. This additional structural change is probably related to the bending of the remaining stiff Si5-O4-Si7 angle driven by the extremely short Si5-O4 and Si7-O4 bonds, which are highly unlikely to compress any further.

A possible explanation for the presence of two phases at ~ 31 GPa may reside on the fact that, although the triclinic phase is more stable than coesite-II at such pressure, the complete transition is hindered due to the slow kinetics of the transformation. If this is the case, coesite II appears above 31 GPa as an “overpressurized” phase out of its (meta)stability field. A similar behavior was seen in cristobalite I, which compresses smoothly far out of

Conclusion

The displacive phase transition from coesite-I to coesite-II above ~ 20 GPa is driven by extreme shortening of the shortest and most compressible Si1-O1 bond (Figure 8). In order to allow more compression of this individual bond the Si1-O1-Si1 angle, constrained by symmetry to be 180° in coesite-I, starts to bend with consequent breaking of the symmetry from $C2/c$ to $P2_1/n$ and formation of two different, independent angles. One of the angles remains close to 180° , though, whereas the other one decreases by nearly 30° . The tetrahedra in coesite-II are rearranged in such a way that two slightly different 4-membered rings are created (Figure 6D). Our previous Raman spectroscopy study on the pressure-induced phase transition in coesite reveals that the main A_g vibration mode of coesite at ~ 521 cm^{-1} is a breathing mode of the 4-membered rings. The two rings in coesite-II with two slightly different sizes are expected to have breathing modes at slightly different frequencies, and we indeed observed appearance of a doublet in the experimental Raman spectra upon the coesite-I to coesite-II transition [10]. The computational spectra of coesite-I under pressure reveal that two modes become most unstable between 20 and 30 GPa: a B_g Raman active mode at 77 cm^{-1} and an A_u infrared active mode at 111 cm^{-1} (see the computed spectra in WURM database for details, <http://www.webcitation.org/6NAE01G6>). The

softening of the Raman active mode was previously considered to be related to the structural instability [11]. The computational data, however, clearly indicate that the A_u mode involves large atomic displacement of the O1 atom from the linear Si-O-Si angle, while the B_g mode has no impact on it. Therefore, we conclude that the softening of the A_u mode is more likely responsible for the symmetry breakdown and the bending of the Si-O-Si angle.

The very short Si-O bond found in coesite and its high compressibility is a good example of how such bonds are restricted to the (almost) linear Si-O-Si geometry, and appear highly unfavorable in other Si-O-Si arrangements. This experimental evidence conforms well to theoretical predictions. For example, Oberhammer and Boggs [33] ascribed short Si-O lengths to the highly ionic character of the bond and found that the ionicity of the bond increases as the length of the bond decreases. A later calculation by Nicholas et al. [34] contributed to this conclusion, by finding that the ionicity of the bond increases by ~25% if the Si-O-Si angle widens from 130° to 180° and the Si-O shortens. In general, the force field that governs the Si-O bond length and the related Si-O-Si angle, as well as their respective stretching and bending, can be seen as independent from the long-range forces of an entire crystal [35]. Therefore, the sequence of the phase transitions and symmetry breakdowns in coesite under pressure is most likely controlled by highly compressible S1 tetrahedron and, in particular, by its most compressible Si1-O1 bond.

Acknowledgments: This work was partially funded by Bavarian Elite Network (ENB) Graduate Program *Oxides*. Portions of this research were carried out at the light source PETRA III at DESY, a member of the Helmholtz Association (HGF). The samples were partially analyzed at the beamline ID09 at European Synchrotron Radiation Facility (ESRF) in Grenoble. A.Č. is very thankful to Mattia Gianini for his help with software installation and application.

References

- [1] L. A. Coes, *Science* **1953**, 118, 131.
- [2] M. J. Buerger, T. Zoltai, *Z. Kristallogr. Krist.* **1959**, 111, 129.
- [3] E. C. T. Chao, E. M. Shoemaker, B. M. Madsen, *Science* **1960**, 132, 220.
- [4] J. Smyth, C. Hatton, *Earth Planet Sci. Lett.* **1977**, 34, 284.
- [5] C. Chopin, *Contr. Miner. Petrol.* **1984**, 86, 107.
- [6] L. Levien, C. Prewitt, *Am. Miner.* **1981**, 66, 324.
- [7] R. J. Angel, C. S. J. Shaw, G. V. Gibbs, *Phys. Chem. Min.* **2003**, 30, 167.
- [8] G. V. Gibbs, M. B. Boisen, K. M. Rosso, D. M. Teter, M. S. T. Bukowski, *J. Phys. Chem. B.* **2000**, 104, 10534.
- [9] R. M. Thompson, T. D. Robert, *Am. Miner.* **2010**, 95, 104.
- [10] A. Černok, T. Boffa Ballaran, R. Caracas, N. Miyajima, E. Bykova, V. Prakapenka, H. P. Liermann, L. Dubrovinsky, *Am. Miner.* **2014**, 99, 755.
- [11] R. J. Hemley, Pressure Dependence of Raman Spectra of SiO₂ Polymorphs: α -Quartz, Coesite, and Stishovite, in *High-Pressure Research in Mineral Physics* (Eds., M.H. Manghnani and Y. Syono), Wiley/Terrapub, Tokyo, p. 347, **1987**.
- [12] J. Haines, J. M. Léger, F. Gorelli, M. Hanfland, *Phys. Rev. Lett.* **2001**, 87, 155503.
- [13] I. Kantor, V. Prakapenka, A. Kantor, P. Dera, A. Kurnosov, S. Sinogeikin, N. Dubrovinskaya, L. Dubrovinsky, *Rev. Sci. Instrum.* **2012**, 83, 125102.
- [14] R. Boehler, K. De Hantsetters, *High Pressure Res.* **2004**, 24, 391.
- [15] A. Kurnosov, I. Kantor, T. Boffa-Ballaran, S. Lindhardt, L. Dubrovinsky, A. Kuznetsov, B. H. Zehnder, *Rev. Sci. Instrum.* **2008**, 79, 045110.
- [16] H. K. Mao, J. Xu, P. M. Bell, *J. Geophys. Res.* **1986**, 91, 4673.
- [17] Y. Fei, A. Ricolleau, M. Frank, K. Mibe, G. Shen, V. Prakapenka, *PNAS* **2007**, 104, 9182.
- [18] Oxford Diffraction, CrysAlis CCD, Oxford Diffraction Ltd, Abingdon, England, **2006**.
- [19] G. M. Sheldrick, *Acta Crystallogr. A.* **2008**, A64, 112.
- [20] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, 32, 837.
- [21] R. J. Angel, Equations of State, in *High-Temperature and High-Pressure Crystal Chemistry* (Eds., R. Hazen and R. T. Downs), Reviews in Mineralogy and Geochemistry, Mineralogical Society of America and Geochemical Society, Washington, DC, Vol. 47, p. 445, **2000**.
- [22] R. J. Angel, J. Mosenfelder, C. S. Shaw, *PEPI* **2001**, 124, 71.
- [23] T. Araki, T. Zoltai, *Z. Kristallogr. Krist.* **1969**, 129, 381.
- [24] G. V. Gibbs, C. T. Prewitt, K. J. Baldwin, *Z. Kristallogr. Krist.* **1977**, 145, 108.
- [25] J. R. Smyth, J. V. Smith, G. Artioli, A. Kvick, *J. Phys. Chem.* **1987**, 91, 988.
- [26] D. Ikuta, N. Kawame, S. Banno, T. Hirajima, K. Ito, J. F. Rakovan, R. T. Downs, O. Tamada, *Am. Miner.* **2007**, 92, 57.
- [27] R. J. Angel, J. M. Jackson, *Am. Miner.* **2002**, 87, 558.
- [28] D. L. Heinz, R. Jeanloz, *J. Appl. Phys.* **1984**, 55, 885.
- [29] K. Bartelmehs, M. B. Boisen, G. V. Gibbs, R. T. Downs, PROGRAM METRIC Ver. 6.1, **2002**.
- [30] K. Robinson, G. V. Gibbs, P. H. Ribbe, *Science* **1971**, 172, 567.
- [31] J. R. Smyth, S. D. Jacobsen, R. M. Hazen, Comparative Crystal Chemistry of Orthosilicate Minerals, in *High-Temperature and High-Pressure Crystal Chemistry* (Eds. R. Hazen and R. T. Downs), Reviews in Mineralogy and Geochemistry, Mineralogical Society of America and Geochemical Society, Washington, DC, Vol. 41, p. 187, **2000**.
- [32] P. Dera, J. D. Lazars, V. B. Prakapenka, M. Barkley, R. T. Downs, *Phys. Chem. Min.* **2011**, 38, 517.
- [33] H. Oberhammer, J. E. Boggs, *J. Am. Chem. Soc.* **1980**, 102, 7241.
- [34] J. B. Nicholas, R. E. Winans, R. J. Harrison, L. E. Iton, L. A. Curtiss, *J. Phys. Chem.* **1992**, 96, 7958.
- [35] G. V. Gibbs, J. W. Downs, M. B. Jr. Boisen, The Elusive SiO Bond, in *SILICA—Physical Behavior, Geochemistry and Materials Applications* (Eds., P. J. Heaney, C. T. Prewitt and G. V. Gibbs), Reviews in Mineralogy, Mineralogical Society of America, Washington, DC, Vol. 29, p. 331, **2000**.