STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 74 (2018)

Supporting information for article:

Ionic network analysis of tectosilicates: the example of coesite at variable pressure

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SUPPLEMENTARY MATERIAL to the article entitled *Ionic network analysis of tectosilicates: the example of coesite at variable pressure*

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S1. The relationship between the volume of a tetrahedron and its derived pseudocube

A general result is that the volume of the pseudocube derived from a tetrahedron is exactly three times the volume enclosed by the generating tetrahedron. This may be shown as follows.

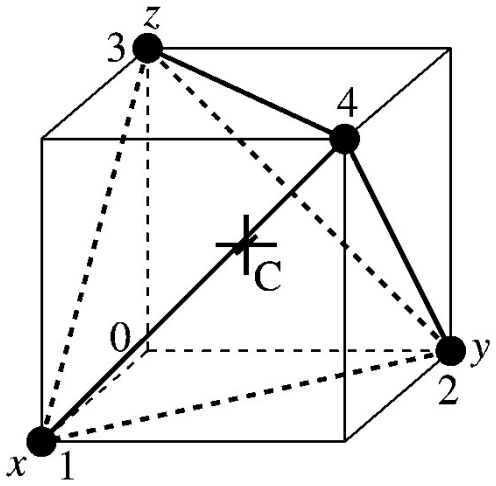


Figure S1 A tetrahedron 1234 and its associated pseudocube. Point C is the centre of coordinates of both tetrahedron and pseudocube.

Points 1,2 and 3 may be represented by vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$, respectively, so that the volume of the pseudocube is $\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}$.

A general result is that the volume of tetrahedron is given by $\frac{1}{3}bh$, where b is the area of one of its bases (such as 123) and h is its perpendicular height, for example the perpendicular distance of vertex 4 from base 123.

The area of base 123 is given by half the magnitude of the vector cross-product of vectors 1→2 and 1→3, *i.e.* $\frac{1}{2}\left|(\mathbf{b}-\mathbf{a})\times(\mathbf{c}-\mathbf{a})\right|$. Similarly, the normal unit vector to plane 123 is given by

$$\frac{(\mathbf{b}-\mathbf{a})\times(\mathbf{c}-\mathbf{a})}{\left|(\mathbf{b}-\mathbf{a})\times(\mathbf{c}-\mathbf{a})\right|}.$$

The perpendicular distance of plane 123 from the origin is given by the projection of vertex 1 on the normal vector, i.e. $\mathbf{a}\cdot\frac{\left((\mathbf{b}-\mathbf{a})\times(\mathbf{c}-\mathbf{a})\right)}{\left|(\mathbf{b}-\mathbf{a})\times(\mathbf{c}-\mathbf{a})\right|}$. Therefore the perpendicular height of vertex 4 above plane

123 is given by $h = \left(\left(\mathbf{a}+\mathbf{b}+\mathbf{c}\right)-\mathbf{a}\right)\cdot\dfrac{\left(\left(\mathbf{b}-\mathbf{a}\right)\times\left(\mathbf{c}-\mathbf{a}\right)\right)}{\left|\left(\mathbf{b}-\mathbf{a}\right)\times\left(\mathbf{c}-\mathbf{a}\right)\right|}$.

The volume of the tetrahedron follows as $\frac{1}{3}bh = \frac{1}{6}\left(\mathbf{b}+\mathbf{c}\right)\cdot\left(\left(\mathbf{b}-\mathbf{a}\right)\times\left(\mathbf{c}-\mathbf{a}\right)\right)$. This expression may be simplified to $\frac{1}{6}\left(-\mathbf{b}\cdot\mathbf{a}\times\mathbf{c}-\mathbf{c}\cdot\mathbf{b}\times\mathbf{a}\right)$, which is equivalent to $\frac{1}{3}\left(\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}\right)$.

S2. Archive of calculated pseudocubic parameters and INA parameters for coesite

The data in Table S1 are the calculated values of the pseudocubic parameters plotted in Fig. 5(a) & (b). The fitting parameters used to construct the curves in Fig. 5(a) are given in Table S2.

Table S1 Pseudocubic parameters in coesite I at eight hydrostatic pressures. *p* =0.00 GPa: data of Angel *et al.* (2003); *p*=2.42-20.30 GPa: data of Černok *et al.* (2014*b*). Parameters above the bold horizontal line refer to pseudocubes enclosing Si(1) ions. Parameters below the line refer to pseudocubes enclosing Si(2) ions.

Parameter	Pressure (GPa)							
	0	2.42	5.16	9.24	12.14	14.90	17.80	20.30
a_{PC}(Å)	1.8521(31)	1.8402(33)	1.8332(26)	1.8164(24)	1.8090(23)	1.7993(24)	1.7933(28)	1.7885(28)
b_{PC}(Å)	1.8781(33)	1.8857(33)	1.8944(25)	1.9002(23)	1.9044(23)	1.9077(23)	1.9082(26)	1.9118(27)
c_{PC}(Å)	1.8432(31)	1.8425(47)	1.8177(37)	1.8116(34)	1.7983(33)	1.7890(34)	1.7795(39)	1.7773(39)
α_{PC}(°)	89.99(14)	90.00(17)	90.32(13)	90.89(13)	90.82(13)	90.94(13)	91.06(15)	91.15(15)
β_{PC}(°)	89.96(13)	90.62(17)	90.89(14)	91.45(13)	91.88(13)	92.33(13)	92.70(16)	92.90(15)
γ_{PC}(°)	89.95(14)	90.62(14)	90.67(11)	90.86(10)	91.19(10)	91.27(11)	91.48(12)	91.72(12)
$V_{tet,Si(1)}$(Å^3)§	2.137	2.131	2.104	2.083	2.063	2.044	2.027	2.022
a_{PC}(Å)	1.8586(34)	1.8545(40)	1.8522(31)	1.8452(28)	1.8460(28)	1.8465(28)	1.8442(33)	1.8393(33)
b_{PC}(Å)	1.8618(42)	1.8589(51)	1.8633(39)	1.8535(36)	1.8539(37)	1.8539(37)	1.8531(42)	1.8504(43)
c_{PC}(Å)	1.8611(38)	1.8509(45)	1.8446(35)	1.8384(31)	1.8290(31)	1.8208(31)	1.8166(36)	1.8090(36)
α_{PC}(°)	89.57(14)	90.15(17)	89.99(14)	90.07(13)	90.27(13)	90.35(13)	90.52(15)	90.53(15)
β_{PC}(°)	90.12(13)	90.13(15)	90.12(12)	90.18(11)	90.14(11)	90.10(12)	90.14(14)	90.20(14)
γ_{PC}(°)	89.49(18)	88.95(23)	89.42(18)	88.84(16)	88.90(16)	89.14(16)	88.83(18)	88.67(19)
$V_{tet,Si(2)}$(Å^3)§	2.147	2.127	2.122	2.095	2.086	2.077	2.069	2.052

§ Volumes of oxygen tetrahedra of Si(1) and Si(2) ions, calculated according to equation (1)

Table S2 Fitting coefficients for the curves in Fig. 5(a)

Parameter i	A_i (Å)	B_i	C_i (Å)	r.m.s. deviation (x10^{-3} Å)
1 (a_{PC})	0.1278	0.6964	1.7240	3.03
2 (b_{PC})	0.0378	2.0173	1.8781	1.90
3 (c_{PC})	0.1574	0.5999	1.6887	10.73
	A_i (°)	B_i	C_i (°)	r.m.s. deviation (°)
4 (α_{PC})	1.656	1.445	89.89	0.29
5 (β_{PC})	7.945	0.452	90.04	0.21
6 (γ_{PC})	2.564	0.896	90.11	0.34

Calculated INA parameters used in the curves of Fig. 7(a) relating to the Si-ion network are contained in Table S3, with the curve-fitting coefficients given in Table S4.

Table S3 Values of the ten INA parameters for the Si ionic network at eight hydrostatic pressures. p=0.00 GPa: data of Angel *et al.* (2003); p=2.42-20.30 GPa: data of Černok *et al.* (2014*b*)

Para-meter	Pressure (GPa)							
	0.00	2.42	5.16	9.24	12.14	14.90	17.80	20.30
1	3.0502(21)	3.0149(29)	2.9817(24)	2.9378(23)	2.9119(21)	2.8858(23)	2.8630(28)	2.8473(28)
2	4.1924(16)	4.1239(26)	4.0504(21)	3.9644(20)	3.9164(20)	3.8774(23)	3.8351(25)	3.8091(26)
3	4.2671(16)	4.2122(25)	4.1527(20)	4.0717(19)	4.0215(19)	3.9769(20)	3.9324(22)	3.9057(23)
4	4.0063(21)	3.9722(32)	3.9323(26)	3.8784(25)	3.8469(24)	3.8115(27)	3.7853(30)	3.7640(31)
5	3.0104(16)	2.9924(24)	2.9753(19)	2.9465(18)	2.9283(17)	2.9180(18)	2.8995(22)	2.8865(22)
6	3.0430(16)	3.0371(24)	3.0321(20)	3.0156(19)	3.0060(18)	3.0007(21)	2.9896(24)	2.9789(25)
7	3.9602(21)	3.9285(31)	3.8960(26)	3.8567(24)	3.8324(23)	3.8077(24)	3.7887(28)	3.7771(28)
8	0.6182(16)	0.5932(17)	0.5729(14)	0.5460(12)	0.5305(12)	0.5151(12)	0.5038(14)	0.4965(13)
9	2.6801(16)	2.6857(17)	2.6940(14)	2.7020(12)	2.7061(12)	2.7103(12)	2.7115(14)	2.7086(14)
10	2.2696(16)	2.2748(17)	2.2730(14)	2.2671(12)	2.2641(12)	2.2604(12)	2.2544(14)	2.2492(14)

Table S4 Fitting coefficients for the curves in Fig. 7(a).

Parameter *i*	a_{i0} (Å)	a_{i1} (Å)	a_{i2} (Å)	a_{i3} (Å)	a_{i4} (Å)	A_i (Å)	B_i	C_i (Å)	r.m.s. deviation (x10^{-3} Å)
1	3.0495	-0.2947	0.1207	-0.0290	0				2.76
2						0.5731	1.1059	3.6197	5.02
3	4.2666	-0.4608	0.0414	0.0809	-0.0235				3.29
4	4.0063	-0.2933	0.0102	0.0493	-0.0087				3.84
5	3.0108	-0.1578	0.0483	-0.0145	0				4.15
6	3.0437	-0.0524	-0.0159	0.0096	-0.0055				4.28
7	3.9596	-0.2665	0.0859	-0.0028	0				3.43
8						0.1802	1.1219	0.4372	2.71
9	2.6791	0.0685	-0.0377	0	0				2.43
10	2.2757	-0.0231	0	0	0				8.02

Calculated INA parameters used in the curves of Fig. 7(b) relating to the O_4(mp)-ion network are contained in Table S5, with the curve-fitting coefficients given in Table S6.

Table S5 Values of the ten INA parameters for the O_4(mp) network at eight hydrostatic pressures. p =0.00 GPa: data of Angel *et al.* (2003); p=2.42-20.30 GPa: data of Černok *et al*. (2014*b*)

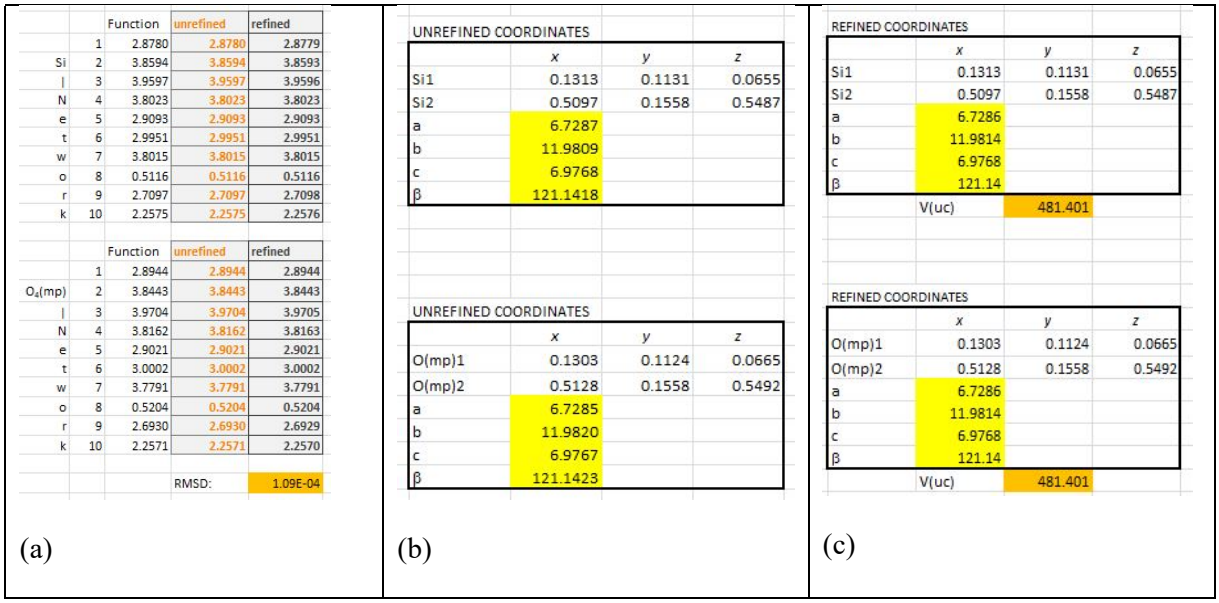
Para-meter	Pressure (GPa)							
	0	2.42	5.16	9.24	12.14	14.90	17.80	20.30
1	3.0721(27)	3.0287(36)	2.9960(29)	2.9560(27)	2.9278(27)	2.9036(28)	2.8815(33)	2.8630(33)
2	4.1939(21)	4.1249(29)	4.0464(24)	3.9557(23)	3.9038(23)	3.8651(26)	3.8191(29)	3.7891(29)
3	4.2668(21)	4.2099(29)	4.1543(23)	4.0811(22)	4.0284(22)	3.9872(23)	3.9429(26)	3.9155(26)
4	4.0085(27)	3.9731(36)	3.9363(30)	3.8852(28)	3.8544(28)	3.8251(31)	3.8014(35)	3.7822(35)
5	3.0074(21)	2.9921(29)	2.9728(23)	2.9378(22)	2.9228(22)	2.9106(22)	2.8929(26)	2.8818(26)
6	3.0366(21)	3.0329(29)	3.0311(24)	3.0173(22)	3.0106(23)	3.0036(25)	2.9945(28)	2.9867(28)
7	3.9518(27)	3.9218(36)	3.8853(29)	3.8448(27)	3.8151(27)	3.7870(28)	3.7624(33)	3.7458(33)
8	0.5929(16)	0.5798(17)	0.5616(14)	0.5420(12)	0.5338(12)	0.5243(12)	0.5154(14)	0.5094(13)
9	2.7194(16)	2.7123(17)	2.7141(14)	2.7051(12)	2.7018(12)	2.6959(12)	2.6874(14)	2.6831(14)
10	2.2808(16)	2.2749(17)	2.2753(14)	2.2719(12)	2.2617(12)	2.2565(12)	2.2553(14)	2.2490(14)

Table S6 Fitting coefficients relating to equations (2.1)-(2.3) for the O_4(mp) network

Param-eter i	a_{i0} (Å)	a_{i1} (Å)	a_{i2} (Å)	a_{i3} (Å)	a_{i4} (Å)	A_i (Å)	B_i	C_i (Å)	r.m.s. deviation (x10^{-3} Å)
1						0.3494	0.8724	2.7187	7.46
2						0.6195	1.0589	3.5754	7.05
3	4.2655	-0.4631	0.1162	-0.0045	0				4.88
4	4.0082	-0.2951	0.0338	0.0580	-0.0228				1.65
5	3.0090	-0.1559	0.0044	0.0358	-0.0110				6.02
6	3.0374	-0.0324	-0.0188	0	0				3.73
7						0.4864	0.5568	3.4654	4.15
8						0.1232	1.1451	0.4705	3.08
9	2.7180	-0.0201	-0.0122	-0.0034	0.0002				4.48
10	2.2801	-0.0211	-0.0102	0	0				5.87

S3. Screenshots from Microsoft® *Excel* relating to §3: Predicting the structure of coesite I at variable pressures by the reverse INA transformation

Information on the interpretation of the following two figures is contained in their respective captions.



		Function	unrefined	refined
	1	2.8780	2.8780	2.8779
Si	2	3.8594	3.8594	3.8593
|	3	3.9597	3.9597	3.9596
N	4	3.8023	3.8023	3.8023
e	5	2.9093	2.9093	2.9093
t	6	2.9951	2.9951	2.9951
w	7	3.8015	3.8015	3.8015
o	8	0.5116	0.5116	0.5116
r	9	2.7097	2.7097	2.7098
k	10	2.2575	2.2575	2.2576

		Function	unrefined	refined
	1	2.8944	2.8944	2.8944
O_4(mp)	2	3.8443	3.8443	3.8443
|	3	3.9704	3.9704	3.9705
N	4	3.8162	3.8162	3.8163
e	5	2.9021	2.9021	2.9021
t	6	3.0002	3.0002	3.0002
w	7	3.7791	3.7791	3.7791
o	8	0.5204	0.5204	0.5204
r	9	2.6930	2.6930	2.6929
k	10	2.2571	2.2571	2.2570
			RMSD:	1.09E-04

(a)

UNREFINED COORDINATES

	x	y	z
Si1	0.1313	0.1131	0.0655
Si2	0.5097	0.1558	0.5487
a	6.7287		
b	11.9809		
c	6.9768		
β	121.1418		

UNREFINED COORDINATES

	x	y	z
O(mp)1	0.1303	0.1124	0.0665
O(mp)2	0.5128	0.1558	0.5492
a	6.7285		
b	11.9820		
c	6.9767		
β	121.1423		

(b)

REFINED COORDINATES

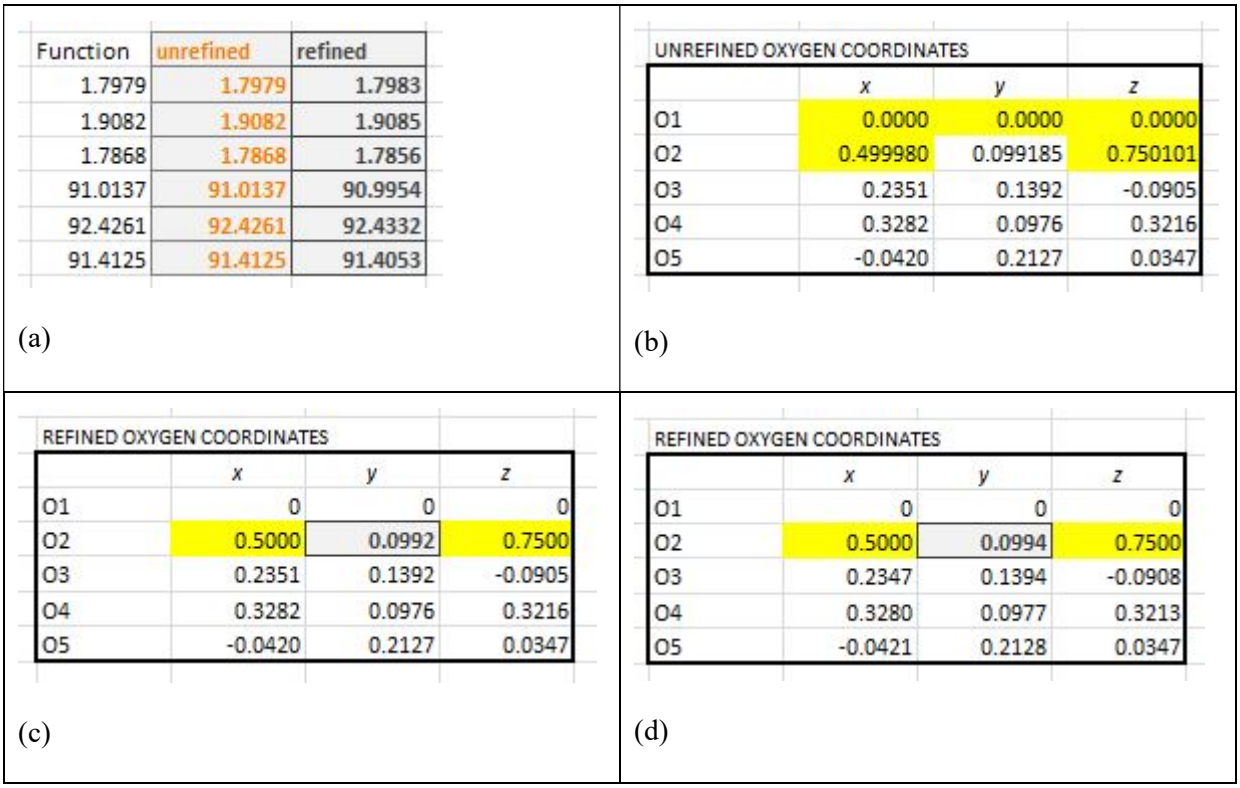
	x	y	z
Si1	0.1313	0.1131	0.0655
Si2	0.5097	0.1558	0.5487
a	6.7286		
b	11.9814		
c	6.9768		
β	121.14		
	V(uc)	481.401	

REFINED COORDINATES

	x	y	z
O(mp)1	0.1303	0.1124	0.0665
O(mp)2	0.5128	0.1558	0.5492
a	6.7286		
b	11.9814		
c	6.9768		
β	121.14		
	V(uc)	481.401	

(c)

Figure S2 Screenshots from the *Excel* spreadsheet for the predicted structure at 16 GPa. (a) Steps 3.1 and 3.2. Values of the ten INA parameters for the Si- and the O_4(mp)-networks calculated from the fitted curves of Figs. 7(a),(b) are listed in the columns headed 'Function' and 'unrefined'. (b) Steps 3.3 & 3.4: crystallographic parameters calculated from the unrefined INA parameters are listed in the upper box for the Si-network and the lower box for the O_4(mp)-network. (c) Step 3.5. The entries in the two boxes of (b) are allowed to refine until both boxes contain identical cell parameters *a*,*b*,*c* and β. The refinement is associated with the minimum RMS deviation between the unrefined and refined INA parameters in (a), i.e. 1.09 x 10^{-4} Å.



Function	unrefined	refined
1.7979	1.7979	1.7983
1.9082	1.9082	1.9085
1.7868	1.7868	1.7856
91.0137	91.0137	90.9954
92.4261	92.4261	92.4332
91.4125	91.4125	91.4053

(a)

UNREFINED OXYGEN COORDINATES

	x	*y*	*z*
O1	0.0000	0.0000	0.0000
O2	0.499980	0.099185	0.750101
O3	0.2351	0.1392	-0.0905
O4	0.3282	0.0976	0.3216
O5	-0.0420	0.2127	0.0347

(b)

REFINED OXYGEN COORDINATES

	x	*y*	*z*
O1	0	0	0
O2	0.5000	0.0992	0.7500
O3	0.2351	0.1392	-0.0905
O4	0.3282	0.0976	0.3216
O5	-0.0420	0.2127	0.0347

(c)

REFINED OXYGEN COORDINATES

	x	*y*	*z*
O1	0	0	0
O2	0.5000	0.0994	0.7500
O3	0.2347	0.1394	-0.0908
O4	0.3280	0.0977	0.3213
O5	-0.0421	0.2128	0.0347

(d)

Figure S3 Prediction of the crystal structure at 16 GPa. (a) Step 3.6. The unrefined parameters for the pseudocubes enclosing Si(1) are equal to the values given by the functional fitting in Fig. 5(a). The refined values shown are obtained in optional Step 3.8. (b) Values for oxygen ion coordinates obtained after Step 3.7. (c) Oxygen ion coordinates x(O(2)) and z(O(2)) are fixed at ½ and ¾ before optional refinement in Step 3.8. (d) Oxygen ion coordinates after refinement in Step 3.8.

END