Silicon—Oxygen Bond Lengths, Bridging Angles Si—O—Si and Synthetic Low Tridymite

By Werner H. Baur

Department of Geological Sciences, University of Illinois, Chicago, IL 60680, USA

The crystal structure of synthetic low tridymite has been re-refined to an $R = 0.076$ for 4117 F(obs) with data collected by Kato & Nukui [*Acta Cryst.* (1976), B32, 2486–2491]. The structure is monoclinic, space group Cc, with $a = 18.494$ (8), $b = 4.991$ (2), $c = 23.758$ (8) Å, $\beta = 105.79$ (2)°, $Z = 12$. The mean Si—O distance measures 1.597 (10) Å and the mean Si—O—Si angle is 150.0 (7.4)°. The structure of this synthetic Cc low tridymite and that of the recently refined meteoritic low tridymite are identical within the margin of experimental error. A regression analysis of data from tridymite, quartz, cristobalite, coesite, zunyite, hemimorphite, benitoite, beryl, emerald, $Sc_2Si_2O_7$, $Yb_2Si_2O_7$ and $Er_2Si_2O_7$ shows that the correlation coefficient between the Si—O bond length and the negative secant of the angle Si—O—Si is 0.19; consequently only 4% of the variation in Si—O can be explained by the dependence on $-\sec(Si-O-Si)$. Therefore the null hypothesis that the Si—O bond lengths do not depend on $-\sec(Si-O-Si)$ can be accepted at the 2.5% risk level. For a given Si—O bond length the lower limit of possible Si—O—Si angles is determined by the shortest possible non-bonding Si—Si contact. Therefore this lower limit is a function of the Si—O bond length and not *vice versa* as required by π-bonding theory.

Introduction

The crystal structure of meteoritic low tridymite has recently been solved by Dollase & Baur (1976) in space group Cc, with $a = 18.524$ (4), $b = 5.0032$ (15), $c = 23.810$ (8) Å, $\beta = 105.82$ (2)°, $Z = 12$. The refinement of 1260 Mo $K\alpha$ reflections gave an $R = 0.069$. The 48 individual, crystallographically independent Si—O distances range from 1.55 to 1.65 Å, with a mean value of 1.601 Å, and a standard deviation from this mean of 0.017 Å. Kato & Nukui (1976) determined the structure of the corresponding synthetic tridymite and refined it for 4117 Mo $K\alpha$ reflexions to $R = 0.085$ [Cc, $a = 18.494$ (8), $b = 4.991$ (2), $c = 25.832$ (8) Å, $\beta = 117.75$ (2)°, $Z = 12$]. The 48 individual Si—O distances range from 1.552 to 1.634 Å, with a mean value of 1.595 (20) Å. The data used by Dollase & Baur were collected in a range up to $\sin \theta/\lambda = 0.7$ Å^{-1}. The Kato & Nukui data range up to a $\sin \theta/\lambda = 1.0$ Å^{-1}, and their refinement should be more reliable. However, the standard deviation from Kato & Nukui's mean Si—O value is larger than for the mean value obtained by Dollase & Baur. Because of computer-memory limitations Kato & Nukui (1976) could not refine all parameters in the same cycle. This might have hindered proper convergence.

Re-refinement of synthetic tridymite

The two different unit cells used for meteoritic and synthetic tridymite are related by the transformation matrix (1,0,0/0,−1,0/−1,0,−1). Since the choice of origin in Cc is arbitrary for x and z the relationships for the positional parameters are $x_{DB} = x_{KN} - z_{KN} - 0.2606$, $y_{DB} = 0.75 - y_{KN}$ and $z_{DB} = -z_{KN}$ (where DB and KN refer to the Dollase & Baur and Kato & Nukui settings respectively). The re-refinement of Kato & Nukui's data was performed in the setting of Dollase & Baur. In this setting the dimensions of the unit cell of synthetic tridymite are: $a = 18.494$ (8), $b = 4.991$ (2), $c = 23.758$ (8) Å, $\beta = 105.79$ (2)°. The scattering factors of Si^{2+} and O^- were taken from *International Tables for X-ray Crystallography* (1974). A simultaneous, full-matrix, unit-weight refinement of all 323 adjustable parameters yielded in three cycles an $R = 0.076$ for 4117 F_{obs}.

Discussion of the structure

The new positional parameters (Table 1) lead to Si—O distances (Table 2) ranging from 1.576 to 1.622 Å, with a mean of 1.597 (10) Å. The range of 0.046 Å is appreciably smaller than for either the Dollase & Baur (0.10 Å) or the Kato & Nukui (0.082 Å) refinements. It is only slightly larger than the range of 0.033 Å

Table 1. *Synthetic low tridymite: positional and thermal parameters* ($\times 10^4$)

The temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. KN# indicates the numbers of the atoms used by Kato & Nukui (1976). The x and z parameters of Si(11) were not varied, in order to define the origin (*).

	KN#	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si(1)	6	5477(2)	5433(7)	5653(2)	3(1)	87(7)	4(.3)	0(2)	1(.3)	2(2)
Si(2)	4	7003(2)	9458(7)	7381(2)	7(1)	73(8)	4(.3)	3(2)	2(.3)	7(2)
Si(3)	5	4171(2)	5508(7)	6236(2)	6(1)	82(7)	4(.3)	-1(2)	1(.3)	-8(2)
Si(4)	3	5724(2)	0464(7)	7977(2)	8(1)	74(7)	3(.3)	5(2)	1(.3)	-4(2)
Si(5)	10	9219(2)	5503(7)	6987(2)	6(1)	79(8)	3(.3)	-4(2)	1(.3)	-1(2)
Si(6)	12	7622(2)	9414(7)	5393(2)	6(1)	77(8)	4(.3)	-1(2)	0(.3)	-5(2)
Si(7)	9	7997(2)	4474(7)	7670(2)	7(1)	85(8)	4(.3)	0(2)	3(.3)	7(2)
Si(8)	11	6428(2)	0393(7)	6042(2)	5(1)	76(7)	3(.3)	6(2)	1(.3)	-1(2)
Si(9)	2	8493(2)	4614(7)	9030(2)	5(1)	94(8)	3(.3)	-2(2)	0(.3)	1(2)
Si(10)	7	9454(2)	9637(7)	9375(2)	6(1)	72(8)	3(.3)	-5(2)	0(.3)	0(2)
Si(11)	1	7216*	5607(7)	9618*	5(1)	54(8)	4(.3)	2(2)	0(.3)	2(2)
Si(12)	8	5663(2)	5457(7)	8716(2)	6(1)	88(8)	3(.3)	-1(2)	2(.3)	-1(2)
O(1)	5	5723(6)	3471(18)	8204(4)	20(3)	137(29)	7(1)	3(7)	5(1)	-4(5)
O(2)	4	5665(5)	8457(15)	8494(4)	18(2)	41(20)	9(1)	5(5)	7(1)	5(4)
O(3)	1	7297(5)	1394(16)	4864(3)	24(3)	60(23)	5(1)	1(6)	0(1)	3(4)
O(4)	2	7488(5)	6415(16)	5160(4)	13(2)	68(23)	9(1)	3(5)	-2(1)	0(4)
O(5)	8	4133(6)	3504(16)	6752(4)	25(3)	52(22)	9(1)	1(7)	8(2)	-4(4)
O(6)	7	4096(5)	8505(16)	6444(3)	16(2)	83(23)	6(1)	-7(1)	0(1)	-12(4)
O(7)	14	8748(4)	1625(16)	9225(4)	6(1)	108(25)	9(1)	10(5)	2(1)	10(4)
O(8)	13	9130(5)	6633(16)	9375(3)	14(2)	76(23)	7(1)	-15(5)	0(1)	-1(4)
O(9)	17	7714(5)	1484(18)	7566(4)	12(2)	98(26)	14(2)	-8(6)	2(2)	-4(6)
O(10)	16	7302(5)	6442(16)	7437(4)	11(2)	62(22)	12(2)	-2(5)	-1(1)	-10(5)
O(11)	20	6177(4)	3391(14)	5856(3)	8(2)	48(20)	6(1)	8(4)	-1(1)	3(4)
O(12)	19	5789(5)	8410(16)	5670(4)	14(2)	77(24)	10(1)	-5(6)	1(1)	8(5)
O(13)	12	4958(4)	5109(18)	6083(4)	6(1)	280(46)	8(1)	4(6)	4(1)	-2(5)
O(14)	9	3506(4)	4920(17)	5653(4)	5(1)	251(44)	7(1)	-10(5)	1(1)	-20(5)
O(15)	18	6524(5)	0009(21)	6721(4)	10(2)	300(59)	6(1)	21(7)	1(1)	16(5)
O(16)	11	6490(5)	9945(21)	7809(4)	11(2)	348(51)	5(1)	3(7)	4(1)	-8(5)
O(17)	23	8607(6)	4970(22)	7324(5)	22(3)	311(50)	12(2)	-28(8)	14(2)	-11(6)
O(18)	15	8377(6)	5008(19)	8341(4)	20(3)	284(57)	3(1)	8(8)	2(1)	0(5)
O(19)	6	5040(5)	0017(20)	7408(4)	14(2)	250(36)	8(1)	6(7)	-2(1)	-9(5)
O(20)	3	6355(4)	4979(18)	9279(4)	4(1)	240(45)	7(1)	-4(5)	-1(1)	11(5)
O(21)	22	9900(5)	9898(21)	8887(4)	8(2)	333(52)	5(1)	-15(6)	1(1)	4(5)
O(22)	21	5003(5)	4741(16)	4999(4)	8(2)	168(24)	4(1)	3(6)	2(1)	-1(5)
O(23)	24	7219(5)	9882(17)	5902(4)	9(2)	199(37)	7(1)	9(5)	2(1)	-6(4)
O(24)	10	7712(5)	5206(20)	9163(4)	9(2)	256(40)	9(1)	8(6)	6(1)	14(5)

observed for Si—O distances in well refined SiO_4 tetrahedra in which all O atoms are bridging between two Si atoms each (see entries with NC = 4 in Table 3). The mean change in Si—O bond lengths achieved by the re-refinement is 0·012 Å, which is more than the estimated standard deviation for an individual Si—O bond of 0·008 Å reported by Kato & Nukui (1976). Since the standard deviation from the mean of these bond lengths is now half as large as it was before the re-refinement, it is believed that the new results are physically meaningful. Kato & Nukui (1976) noted the large thermal amplitudes of their atoms O(11), O(12) and O(18) and suggested that these might be due to positional disorder. The re-refinement of their data does not reveal anything particular about the thermal parameters of O(13), O(15) and O(16) (using the numbering system of Table 1). It is remarkable that in the Kato & Nukui refinement the ratio between the largest and the smallest β_{22} parameter of the O atoms is 765, whereas after re-refinement this ratio is reduced to

8 or by two orders of magnitude. Therefore it is not necessary to assume disorder for these atoms. An inspection of the β_{22} parameters of the O atoms reveals that O(1) to O(12) have a small thermal amplitude parallel to the b axis, whereas the remaining O atoms, O(13) to O(24), have a high amplitude in this direction. The latter group correspond to the bridging O atoms in the chains of SiO_4 tetrahedra running parallel to the pseudohexagonal axis, |201| [see Fig. 1 in Dollase & Baur (1976)].

With three exceptions the Si—O distances and the Si—O—Si angles in meteoritic low tridymite (Dollase & Baur, 1976) and in the re-refined synthetic low tridymite are within two pooled e.s.d.'s of each other. The exceptions are: Si(2)—O(15) and the angles around O(15) and O(18). This close similarity between the results of the refinements indicates that the structures indeed are identical, even though their unit-cell constants differ slightly: up to six times the estimated standard deviations.

Table 2. *Synthetic low tridymite,* Si—O *bond lengths,* Si—O—Si *angles and* Si—Si *distances*

(1) Si O distances (Å) (mean e.s.d. 0·008 Å)

Si(1)—O(13)	1·589	Si(5)—O(17)	1·576	Si(9)—O(24)	1·588
O(12)	1·590	O(5)	1·591	O(7)	1·595
O(22)	1·600	O(19)	1·594	O(8)	1·596
O(11)	1·615	O(6)	1·598	O(18)	1·604
mean	1·599	mean	1·590	mean	1·596
Si(2)—O(16)	1·586	Si(6)—O(3)	1·584	Si(10)—O(22)	1·584
O(10)	1·597	O(4)	1·592	O(21)	1·600
O(15)	1·602	O(23)	1·599	O(7)	1·601
O(9)	1·622	O(14)	1·603	O(8)	1·615
mean	1·602	mean	1·595	mean	1·600
Si(3)—O(6)	1·593	Si(7)—O(9)	1·578	Si(11)—O(3)	1·599
O(5)	1·599	O(18)	1·581	O(4)	1·606
O(13)	1·606	O(17)	1·586	O(20)	1·608
O(14)	1·608	O(10)	1·592	O(24)	1·609
mean	1·602	mean	1·584	mean	1·606
Si(4)—O(16)	1·594	Si(8)—O(15)	1·585	Si(12)—O(2)	1·588
O(1)	1·594	O(11)	1·593	O(21)	1·596
O(19)	1·596	O(23)	1·606	O(20)	1·597
O(2)	1·611	O(12)	1·609	O(1)	1·598
mean	1·599	mean	1·598	mean	1·595

(2) Si—O—Si angles (°) (mean e.s.d. 0·6°) and corresponding Si—Si distances (Å) (mean e.s.d. 0·004 Å)

Si(4)—O(1)—Si(12)	148·0	3·069	Si(1)—O(13)—Si(3)	151·2	3·095
Si(12)—O(2)—Si(4)	147·8	3·074	Si(6)—O(14)—Si(3)	145·2	3·064
Si(6)—O(3)—Si(11)	148·5	3·063	Si(8)—O(15)—Si(2)	153·7	3·103
Si(6)—O(4)—Si(11)	148·9	3·080	Si(2)—O(16)—Si(4)	155·9	3·110
Si(5)—O(5)—Si(3)	146·9	3·058	Si(5)—O(17)—Si(7)	179·1	3·162
Si(3)—O(6)—Si(5)	146·3	3·054	Si(7)—O(18)—Si(9)	155·3	3·111
Si(9)—O(7)—Si(10)	143·4	3·034	Si(5)—O(19)—Si(4)	155·5	3·117
Si(9)—O(8)—Si(10)	143·9	3·053	Si(12)—O(20)—Si(11)	148·1	3·081
Si(7)—O(9)—Si(2)	147·3	3·070	Si(12)—O(21)—Si(10)	149·8	3·085
Si(7)—O(10)—Si(2)	147·0	3·058	Si(10)—O(22)—Si(1)	155·4	3·110
Si(8)—O(11)—Si(1)	145·6	3·064	Si(6)—O(23)—Si(8)	144·8	3·056
Si(1)—O(12)—Si(8)	142·7	3·031	Si(9)—O(24)—Si(11)	150·8	3·093
			means	150·0	3·079

Angle Si—O—Si *versus* distance Si—O

In numerous crystal structures individual bond lengths Si—O depend on the bond-strength variation $\Delta p(O)$ of the O atoms (Baur, 1970, 1976). In cases where $\Delta p(O) = 0·0$ the bond-length variation obviously cannot depend on $\Delta p(O)$; such instances are useful for studying other bonding effects (Baur, 1971). In tridymite there are 12 crystallographically independent four-connected SiO_4 tetrahedra in which all O atoms are valence-balanced; that is their $\Delta p(O)$ is zero. These 12 tetrahedra can be added to the five such tetrahedra previously known in the literature (see Table 3) in order to test the dependence of individual Si—O bond lengths on the negative secant of the bridging angle Si—O—Si, as discussed by Gibbs, Hamil, Louisnathan, Barteil & Yow (1972). In addition this correlation was tested for a data set which included not only the tetrahedra from tridymite, low quartz, low cristobalite, coesite and zunyite, but also Si—O bonds to charge-balanced O atoms in several disilicates, ring silicates and the remaining Si—O bond in zunyite (Table 3). In either case the correlation coefficients are small (13 and 19%)

and the slope of the Si—O bond length with the negative secant (see Table 4) is much smaller than found by Gibbs *et al.* (1972). The null hypothesis (that the correlation coefficient and the slope equal zero) can be accepted at the 0·025 risk level because neither value of $|t|$ exceeds $t(77,0·05) \sim t(66,0·025) \simeq 1·99$ (one-tailed test). For the larger sample, $|t|$ barely reaches $t(77,0·05) \sim 1·67$. This is a small consolation since less than 4% of the variations in Si—O are explained by the dependence on sec(Si—O—Si). The difference between the two results is partly due to the inclusion of the zunyite data (Louisnathan & Gibbs, 1972), which were not present in the data set analyzed by Gibbs *et al.* Actually the correlation would be fair if the data for zunyite, $Er_2Si_2O_7$ and $Yb_2Si_2O_7$ were not included (Fig. 1). Considering the presently available empirical evidence, however, the Si—O *vs* sec(Si—O—Si) correlation cannot be viewed as a general property of charge-balanced bridging O atoms in silicates.

O'Keeffe & Hyde (1976) have recently pointed out that bridging angles between tetrahedral groups of Si and other first, second and third row elements in structures of cristobalite type depend mostly on the

Table 3. *Individual distances* Si—O *and* Si—Si (Å) *and angles* Si—O—Si (°) *in crystal structures in which all* O *atoms are charge-balanced* $[\Delta p(O) = 0.0]$

The connectivity of the SiO_4 tetrahedra, NC, is the number of bridging (Si—O—Si) O atoms per tetrahedron. The estimated standard deviations of all Si—O bonds are 0·010 Å or smaller. All distances and angles have been recalculated from the positional parameters *etc.*, in the original papers.

Compound	Si—O	Si—O—Si	Si—Si	NC	Compound	Si—O	Si- O—Si	Si—Si	NC
Cristobalite[1]	1·601	146·8	3·076	4	Zunyite[4]	1·628	180·0	3·258	4
	1·608	146·8	3·076	4		1·630	180·0	3·258	1
Low quartz[2]	1·603	143·6	3·057	4	$Yb_3Si_3O_7$[5]	1·626	180·0	3·252	1
	1·615	143·6	3·057	4	$Er_2Si_2O_7$[5]	1·632	180·0	3·265	1
Coesite[3]	1·598	180·0	3·196	4	$Sc_2Si_2O_7$[6]	1·604	180·0	3·208	1
	1·608	143·8	3·056	4	Hemimorphite[7]	1·627	150·4	3·145	1
	1·607	145·0	3·077	4	Benitoite[8]	1·630	132·9	3·005	2
	1·619	145·0	3·077	4		1·648	132·9	3·005	2
	1·598	150·5	3·116	4	Beryl[9]	1·594	168·8	3·174	2
	1·625	150·5	3·116	4		1·595	168·8	3·174	2
	1·631	136·1	3·012	4	Emerald[9]	1·585	169·3	3·176	2
	1·617	136·1	3·012	4		1·604	169·3	3·176	2

References: (1) Dollase (1965). (2) Zachariasen & Plettinger (1965). (3) Araki & Zoltai (1969). (4) Louisnathan & Gibbs (1972). (5) Smolin & Shepelev (1970). (6) Smolin, Shepelev & Titov (1973). (7) McDonald & Cruickshank (1967). (8) Fischer (1969). (9) Gibbs, Breck & Meagher (1968).

Table 4. *Regression equations for* Si—O *on* —sec(Si—O—Si): *source of data, sample size, intercept* (a), *slope* (b), *correlation coefficient* (r), *percent variation explained* (%), $|t|$

Data source	Tables 2 and 3		Gibbs *et al.* (1972)	
	NC = 4	NC = 1,2 and 4	NC = 4	NC = 1,2 and 4
Sample size	68	79	12	27
a	1·578 (23)	1·573 (19)	1·539	1·545
b	0·020 (19)	0·027 (16)	0·06 (2)	0·06 (2)
r	0·126	0·187	0·57	0·58
%	1·6	3·5	32	34
$|t|$	1·03	1·67	2·3	3·6

non-bonded cation—cation contacts [based on Glidewell's (1975) radii]. In order to test this hypothesis the shortest possible Si—Si distance between neighboring tetrahedra must be determined. It occurs in benitoite, which is not surprising since, in the tight curvature of the Si_3O_9 rings, the Si atoms are forced together more closely than in most other silicate geometries. Therefore, if we assume (a) that Si atoms in silicates with charge-balanced O atoms cannot approach each other closer than 3·0 Å and (b) that both Si—O bonds in the Si—O—Si bridge are of the same length, then no data points should occur
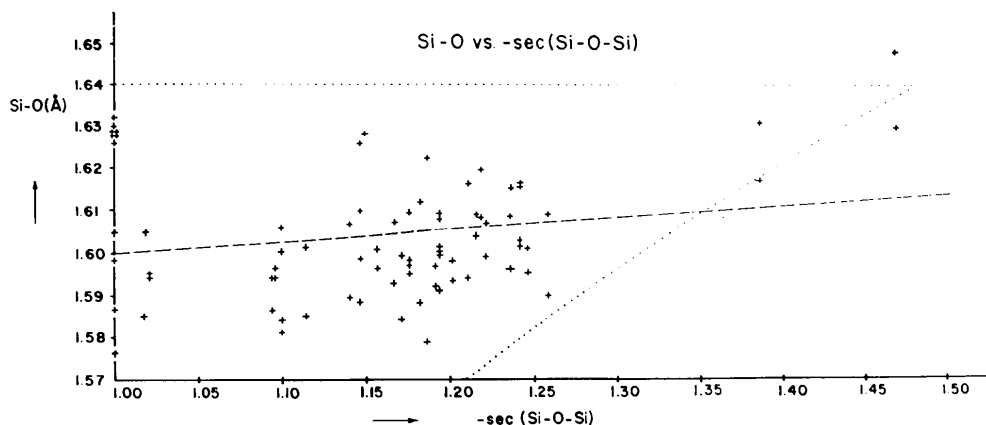

Fig. 1. Si—O bond lengths *versus* —sec(Si—O—Si) for 17 four-connected tetrahedra and 11 Si—O bonds of other bridging O atoms. The data are from Tables 2 and 3. The dashed line corresponds to the regression equation for the sample consisting of 79 values (see Table 4). For the explanation of the dotted lines see text.

below the dotted diagonal curve in Fig. 1. An upper limit for possible data points is given by the dotted horizontal line in Fig. 1 at Si–O = 1·64 Å, because Si–O distances involving charge-balanced O atoms rarely exceed this value. The only data outside these limits are the benitoite points and one coesite point, which do not conform to assumption (b). The averages of the two Si–O bridging bonds in both cases fall within the bounds. It is particularly impressive that the longest Si–O distances of approximately 1·63 Å occur over the whole range of bridging angles from 180 to 133° with essentially constant values. It is equally interesting to see that straight Si–O–Si bonds can occur for Si–O bonds ranging from 1·576 to 1·632 Å. This covers almost the whole range of Si–O bond lengths, since only one Si–O bond in the whole sample is outside these limits. The 79 data points are distributed over all the allowed space; however, they are not uniformly distributed. Therefore, regression calculations, especially when they ignore points in the upper left of the diagram, tend to give positive correlations between Si–O and –sec(Si–O–Si). The diagonal dotted curve in Fig. 1 is calculated from the general expression relating one angle to the three sides of a triangle. Since this expression is, within the limits of interest, not far from being linear with the secant of the Si–O–Si angle, it is not surprising that Gibbs et al. (1972) found a linear relationship between Si–O and the secant of Si–O–Si. Analysis of small samples which have no or few values with long Si–O distances at straight or nearly straight Si–O–Si angles yields significant correlations between Si–O and –sec(Si–O–Si) (Prewitt, Baldwin & Gibbs, 1974). Such correlations disappear when larger, less biased samples are studied. For cases where the Si–Si distance is close to the nonbonding contact length of 3·0 Å the correlation between Si–O distances and Si–O–Si angles does exist because of the dependence of the angle Si–O–Si on the Si–O distances and not vice versa as required by π-bonding theory (Glidewell, 1975). Therefore it appears that the approach of O'Keeffe & Hyde (1976) is useful to obtain a lower limit of possible Si–O–Si angles, even though it cannot give us an upper limit. For Si–O bonds ranging in length from 1·576 to 1·632 Å the upper limit of Si–O–Si is empirically found to be 180°. Angles larger than the lower limit may be imposed by packing constraints of the crystal structures (Baur, 1972).

Note added in proof:—After this paper was submitted for publication a short communication by Glidewell (1977) was published. The non-bonded atomic radius of Si has been used there to rationalize the Si–O–Si angles in the silica polymorphs.

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