# Crystal Structures of Three Polymorphs of Co<sub>2</sub>SiO<sub>4</sub>

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#### Abstract

The crystal structures of three polymorphs of Co<sub>2</sub>SiO<sub>4</sub> have been studied in detail. Relevant data are:

		Cell	dimensions	s (Å)		Space	Mean distances (Å)		
Phase	Structure type	а	b	c	$\boldsymbol{Z}$	group	Si-O	Co-O	
$\alpha$ $\beta$	olivine modified spinel	4.782	10.302	6.003	4	Pbnm	1.627	2.134	
γ	or β-Mn₂GeO₄ normal spinel	5.753 8.138	11.524	8.340	8	Imma Fd3m	1.642 1.646	2.114 2.104	

The site occupancy refinement of the  $\gamma$ -phase indicates that  $3.4 \pm 0.8$  percent of the total silicon atoms are at the octahedral sites, and the *u*-parameter of the oxygen atoms is 0.3666(4).

The close-packed structures of the three polymorphs are explained as differences in stacking of bands composed of Co octahedra and Si tetrahedra. The change of polyhedra around Co and Si atoms in the transformations induced by pressure is also discussed.

#### Introduction

High pressure phase transformations of silicates and germanates have been extensively studied for clues to possible phase transformations in the Earth's mantle. Among the silicates and germanates subjected to pressures of more than 100 kbar, several olivine-type structures ( $\alpha$ -phases) were transformed to their spinel polymorphs ( $\gamma$ -phases). The structures of  $\alpha$ -phases belonging to the Mg<sub>2</sub>SiO<sub>4</sub>-Fe<sub>2</sub>SiO<sub>4</sub> system have been studied in detail by Birle *et al* (1968). Ma (1972) studied a polycrystalline Ni<sub>2</sub>SiO<sub>4</sub> spinel and indicated that  $8 \pm 6$  percent of the total silicon ions are octahedrally coordinated. However, the structure of a silicate  $\gamma$ -phase has never been studied by single crystal methods.

Kamb (1968) first discussed the relative stability and structural relations between olivine and spinel. He gave an explanation for the stability of olivine structure compared with spinel structure at atmospheric pressure based on Pauling's rules for edgesharing by coordination polyhedra.

A new modification of a spinel-type structure with orthorhombic symmetry (β-phase) was found at high pressures in Co<sub>2</sub>SiO<sub>4</sub>, Mg<sub>2</sub>SiO<sub>4</sub>, Mn<sub>2</sub>GeO<sub>4</sub>, and Zn<sub>2</sub>SiO<sub>4</sub> (Akimoto and Sato, 1968; Ringwood and Major, 1970; Morimoto *et al*, 1969, 1970; Syono, Akimoto, and Matsui, 1971). Morimoto *et al* (1969,

1970), and Moore and Smith (1969, 1970) have shown that this modification has a modified spinel structure with a peculiar atomic arrangement. Because Pauling's electrostatic balance rule is not obeyed for some oxygen atoms in the  $\beta$ -phase, the stability of this phase has been seriously questioned. However, recent calculations on the electrostatic energy of the three polymorphs of Co<sub>2</sub>SiO<sub>4</sub>, based on their preliminary structures, reveal that the modified spinel ( $\beta$ ) structure is not necessarily unstable relative to the spinel  $(\gamma)$ structure (Tokonami et al, 1972), Syono, Tokonami, and Matsui (1971) studied the crystal field effect on the olivine-spinel transformation, and suggested that the structure of the  $\beta$ -phase could be more stable than that of the  $\gamma$ -phase at high pressure without crystal field stabilization when the ionic radius ratio of divalent and tetravalent cations has a high value.

Although the stability of the three polymorphs in the  $\alpha \to \beta \to \gamma$  transformation has been studied extensively, the precise crystal structures of the three polymorphs have not been previously described. In this paper, we report the crystal structures of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -Co<sub>2</sub>SiO<sub>4</sub> in detail and discuss their crystal-chemical relationships. Preliminary descriptions of the present work have already appeared (Morimoto *et al*, 1969, 1970; Tokonami *et al*, 1970, 1972).

### **Experimental**

The cell dimensions, space groups, and densities at atmospheric pressure are given for the three polymorphs of Co<sub>2</sub>SiO<sub>4</sub> (Table 1). The cell dimensions measured on the four-circle diffractometer are in good agreement with those measured by the powder method (Akimoto and Sato, 1968).

## (a) α-Co<sub>2</sub>SiO<sub>4</sub>

Data collection. A mixture of  $Co_3O_4$  and quartz in the proper stoichiometric ratio was used as starting material. The mixture was melted at 1500°C in air and cooled slowly to room temperature. Good single crystals of orthorhombic  $\alpha$ - $Co_2SiO_4$  were found in the product. Cell dimensions are compared with those of  $\alpha$ -phases of  $Mg_2SiO_4$  and  $Mn_2GeO_4$  in Table 1. The diffraction aspect is  $Pbn^*$ , giving the space group Pbnm of olivines.

A nearly spherical crystal (diameter 0.03 mm), was used for collecting intensity data. Using a RIGAKU automatic four-circle diffractometer and Zr-filtered Mo $K\alpha$  radiation ( $\lambda=0.71069$  Å), intensities of 501 symmetrically independent reflections were measured out to a maximum diffraction range of  $\sin\theta/\lambda=0.72$  by the  $\omega-2\theta$  scan method. The scanning width  $\Delta\omega$  was given by the relation:  $\Delta\omega=0.60+0.30$  tan  $\theta$  (degrees). Of these reflections, 24 were the same as or less than the background value and were regarded to be zero in intensity. The intensities were corrected for Lorentz and polarization effects. No absorption correction was made.

Structure Refinement. The initial atomic coordinates and isotropic temperature factors were taken from those of the fayalite structure described by

Birle et al (1968). The refinement was carried out by a full-matrix least-squares method using a FACOM 230-60 version of the program ORFLS of Busing, Martin, and Levy (1962). The function minimized in this refinement was  $\Sigma 1/\sigma_{hk1}^2 |s(F_o - F_c)|$ , where  $\sigma_{hk1}$  is the value given by the counting statistics when  $|F_0| \neq 0$ , and is 10.0 when  $|F_0| = 0$ ; s is the scale factor. Only the final refinement was carried out using equal weight for all reflections, as described later. Scattering factors and the real and imaginary anomalous dispersion corrections for Co2+ and those for Si<sup>4+</sup> were taken from International Tables for X-ray Crystallography (1962), while scattering factors for O<sup>2</sup> were taken from the values reported by Tokonami (1965). Anomalous dispersion corrections for O<sup>2-</sup> were assumed to be zero.

Three cycles of refinement of the atomic coordinates and one scale factor were made with individual isotropic temperature factors, and after three further cycles of refinement in which the scale factor, one secondary extinction factor, atomic coordinates, and the anisotropic temperature factors were varied, no further change of parameters took place. The final unweighted and weighted residuals are 0.046 and 0.035, respectively, for all 501 reflections.

The final parameters, the individual anisotropic temperature factors, and the equivalent isotropic temperature factors are listed with their estimated standard deviations in Table 2.  $F_o$  and  $F_o$  values are listed in Table 3.

# (b) β-Co<sub>2</sub>SiO<sub>4</sub>

Data Collection. The single crystals used for the structure study were synthesized at  $1420^{\circ}$ C and 81 kbar from  $\alpha$ -Co<sub>2</sub>SiO<sub>4</sub>. The cell dimensions and

TABLE 1. A Comparison of Crystallographic Data for α-, β-, γ-Co<sub>2</sub>SiO<sub>4</sub> with Mg-, Co-, and Fe-Olivine

Polymorph	a (Å)	b(Å)	c (Å)	Space group	Density $(g \cdot cm^{-3})$
α-Co <sub>2</sub> SiO <sub>4</sub>	4.782(4)	10.302(4)	6.003(4)	Phnm	4.73
B-Co <sub>2</sub> SiO <sub>4</sub>	5.753(4)	11.524(4)	8.340(2)	Imma	5.05
γ-Co <sub>2</sub> SiO <sub>4</sub>	8.138(3)	_	-	Fd3m	5.17
Composition				Ref	Terences
Mg <sub>2</sub> SiO <sub>4</sub>	4.7553(6)	10.1977(14)	5.9820(7)	Matsui and S	Syono (1968)
Co2SiO4	4.782(4)	10.302(4)	6.003(4)	This study (	
Fe <sub>2</sub> SiO <sub>4</sub>	4.821(1)	10.477(1)	6.086(1)	_	Fujisawa (1968)

The standard deviations in parentheses are expressed in the unit of the last digit stated.

Table 2. Final Atomic Coordinates, Anisotropic Temperature Factors, and Equivalent Isotropic Temperature Factors for Atoms in α-Co<sub>2</sub>SiO<sub>4</sub> and β-Co<sub>2</sub>SiO<sub>4</sub>

Atom	x	У	z	β <sub>11</sub>	β <sub>22</sub>	β <sub>33</sub>	<sup>β</sup> 12	β31	β23	B equiv
				(	x-Co <sub>2</sub> SiO <sub>4</sub>					
Co(1)	0 .9917(3)	0 .2765(1)	0 1/4	.0038(4)	.0015(1) .0013(1)	.0034(3)	.0001(2) .0001(2)	0002(4)	0002(1) 0	.49 .51
Si	.4292(5)	.0951(3)	1/4	.0025(10)	.0013(2)	.0033(6)	.0001(3)	0	0	.42
D(1) D(2) D(3)	.7662(13) .2121(13) .2835(8)	.0924(6) .4504(6) .1639(4)	1/4 1/4 .0349(7)	.0087(29) .0085(28) .0068(16)	.0017(6) .0020(6) .0017(4)	.0041(18) .0032(15) .0042(12)	.0010(12) 0006(11) 0001(7)	0 0 .0007(13)	0 0 0002(6)	.70 .69 .66
					β-Co <sub>2</sub> SiO <sub>4</sub>					
Co(1)	0	0	0	.0030(7)	.0005(2)	.0019(2)	0	0	0001(1)	.40
20(2)	0	1/4	0286(2)	.0050(8)	.0008(2)	.0014(2)	0	0	0	.49
20 (3)	1/4	.1241(1)	1/4	.0037(3)	.0008(1)	.0019(3)	0	0002(2)	0	.48
Si	0	.1211(3)	.6169(3)	.0029(5)	.0008(1)	.0009(3)	0	0	0001(2)	.35
0(1)	0	1/4	.2175(11)	.0016(30)	.0014(7)	.0025(13)	0	0	0	.55
0(2)	Ō	1/4	.7154(11)	.0017(31)	.0018(7)	.0012(12)	0	0	0	.51
0(3)	Ō	0141(5)	.2567(8)	.0054(27)	.0017(5)	.0013(9)	0	0	.0002(6)	.66
0(4)	.2663(6)	.1227(7)	0083(5)	.0073(11)	.0002(3)	.0021(5)	.0002(13)	0005(8)	0002(3)	.55

The estimated standard deviations, in parentheses, are expressed in units of the last digit.

space group are compared with the other polymorphs in Table 1. A single prism,  $0.1 \times 0.06 \times 0.06$  mm, was used for collecting intensity data. Three-dimensional intensities with  $\sin \theta/\lambda < 0.71$  were obtained as already described for  $\alpha\text{-Co}_2\mathrm{SiO}_4$ . Of the observed 485 reflections, 36 were the same (or less) than the background values and were thus regarded to be zero in intensity. The intensities were corrected for Lorentz and polarization factors. No absorption correction was made.

Structure Refinement. A least-squares refinement, using the same procedures as for α-Co<sub>2</sub>SiO<sub>4</sub>, was initiated using the atomic coordinates and isotropic temperature factors of β-Mn<sub>2</sub>GeO<sub>4</sub> described by Morimoto et al (1972). After several cycles of refinement in which atomic coordinates, isotropic temperature factors, and one scale factor were varied, the R value for 485 reflections reached 0.109. Temperature factors were then converted to anisotropic form, and four cycles of refinement-varying the scale factor, atomic coordinates, and anisotropic temperature factors, and one secondary extinction factor—further reduced the R value to 0.053 for all reflections. The weighted R value is 0.032. The final parameters, the individual anisotropic temperature factors, and the equivalent isotropic temperature factors are listed with their estimated standard deviations in Table 2.  $F_{\rm o}$  and  $F_{\rm c}$  values are listed in Table 3.

## (c) y-Co<sub>2</sub>SiO<sub>4</sub>

Data Collection. The single crystals of  $\gamma$ -Co<sub>2</sub>SiO<sub>4</sub> were synthesized at 850°C and 68 kbar from  $\alpha$ -Co<sub>2</sub>SiO<sub>4</sub>. An approximately spherical crystal (diameter  $\sim$ 0.03 mm) was used for collecting the three-dimensional intensity data. 670 reflections with  $\sin \theta/\lambda < 1.0$  were measured using the procedures described above. Taking the average of the observed structure factors of symmetrically equivalent reflections, 136 independent  $F_{\rm o}$ 's were obtained. We assigned to  $\sigma_{hkl}$ , the larger of the two values of  $\sigma_{\rm equi}$  or  $\sigma_{\rm st}$ , where  $\sigma_{\rm equi}$  is the standard deviation of  $F_{\rm o}$  values of equivalent reflections and  $\sigma_{\rm st}$  is the largest estimated standard deviation given by counting statistics.

Structure Refinement. For the determination of the spinel structure, only one geometrical parameter of oxygen atoms—the u-parameter—is necessary. Structure refinement began with u=0.365, a value proposed by Kamb (1968) for Fe<sub>2</sub>SiO<sub>4</sub> spinel, and with the isotropic temperature factors obtained for the final structure of  $\beta$ -Co<sub>2</sub>SiO<sub>4</sub>.

Four cycles of refinement of one scale factor and the *u*-parameter were made with isotropic temperature factors, and four more cycles were made with anisotropic temperature factors. The final *R* value is 0.079 and the weighted residual is 0.037. The final positional parameter, anisotropic temperature factors, and

Table 3. Observed and Calculated Structure Factors ( $\times 10$ ) for  $\alpha$ -,  $\beta$ -, and  $\gamma$ -Co<sub>2</sub>SiO<sub>4</sub>

TABLE 3a. α-Co<sub>2</sub>SiO<sub>4</sub>

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equivalent isotropic temperature factors are given with their standard deviations in Table 4(a).  $F_{\rm o}$  and  $F_{\rm c}$  values are listed in Table 3.

An attempted refinement of the site occupancies of Si and Co atoms in the octahedral and tetrahedral sites was carried out using Finger's RFINE program (1969) using the 88 most significant reflections. The refinements were initiated with the values obtained in the above refinement and without changing the site occupancy. The R-factor is 0.037 and the weighted R-factor is 0.029. The next four cycles were made by changing the site occupancy of Si atoms in the octahedral site under compositional constraint but by keeping the atomic coordinates constant at the values obtained in the last refinement. The final R-value is

Table 3b. β-Co<sub>2</sub>SiO<sub>4</sub>

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5	7	414 338	28 432		10 12 14	2	46 B2 0	55 39 48		0 2	1.5	235	160 224 2047		3	1	386	- 6
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16	1 2 2	174 246	195 228		1	7	315 786	49 314 805 651 252 226		2 4	4	1076 93 166	1067 95 178	7	2 0 2 4 6	Ē	160 279 0	1
3 5 7	2 2 2	351 267	332 262 192		3 5 7	7	644 252 226	651 252		8	4	89 789	80 775 42 79 206		6	1	376 0	17
	2	104 245 132	96 253 125		11	7 8	226 602 79 265	594 41		12	4	53 205	79		1	2 2	242 82 167	-
11 13 15	2 2 2	132	125		2	8	265			3	**********	563 535 249	560		5	2	122 94 505	1
0 2	3	101 1010 74	108 989 89		4 6 8	8	222 75	615 223 49		7	5	249 116 359	240 90 367 153		0 2	3	505 26 138	4
15 0 2 4 6	3	560	555 40		10	B 9 9 9	629 222 75 183 473 82 33 382	180		21	6		367 153		6	3.7	36	1
10 12 14	3	673 86 282	680 81 283		5 7	9	33 382	465 104 36 374		4 6	6.0	67 562 65 86	63 576		3 5	-	36 134 171 145	1
		331	339		9	9	390	378		8	0.	86 366	96 360		0	-	454	- 4
1357	4	418 354 202	415 373 204		4	10 10 10	430 115 192	428 124 206		9.5	7 7	366 48 51	360 40 37		4	5	45 48 181	1
9.		202	204 204 217		6 B 3	10	380	107 368 285		6	7 7 8	340 271	335 266 898	В	0 2	6	57 930	8
11 13 15	4	200 214 194 100	217 185 92 762	3	5 0 2	11	290 259 586	285 255 585		2	1 1	340 271 939 245 373	239		4	0 1	181 57 930 25 127 102	1
0 2	5	758 113 231	762 109 243	,	4	1	42 805 71	801		8 1	10 10 10 10 10 10 10 10 10 10 10 10 10 1	159 753 0	152 731 10		3	1	153	1
0 2 4 E	5 5 5	231 57 579	243 54 51		6 8 10	1 1	71 371 ±8	36 381 21		11.5	9 9	308 335	10 293 320					

TABLE 3c. γ-Co<sub>2</sub>SiO<sub>4</sub>

H	B.	L										_							
0	C	4	2001	1995	2	6	12	124	116	8	10	10	42	122	3	3	11	477	481
	· C	, 0	1456	1462		6	14	354	304	2,	1	1.	572	576		3	13	272	287
	0	12	591	579		8	8	57	46		1	3	1156	1098		3	15	238	20
	.0	16	601	567		8	10	139	129		1	- 5	785	786			5 7 9	591	61
	2	2	413	393		В	12	46	48		1	7	369	388		ununn	7	287	28
	23.3	6	263	268		6	14	12	69		1	9	166	165		- 5		126	15
	- 2	10	183	202		10	10	346	329		1	11	466	464		- 2	3.1	418	39:
	2	14	190	96		10	12	31	77		1	13	301	275		- 5	11	236	26
	4	4	2045	2092	4	4	4	1173	1181		1	15	198	187		- 4	15	209	165
		8	838	852		4	6	52	17		3	3	593	595		2	7	553	56
	4	12	842	618		4	В	1110	1150		3	5	354	388		7		426	386
	6	6	249	269		4	10	124	10		3	7	711	732		7	21	183	238
	6	10	61	111		4	12	532	512		3	9	451	471		7	13	133	126
	5	14	152	137		4	1.4	2	5		3	11	257	242		9	9	274	29
	3	8	937	953		6	6	141	172		3	13	139	129		9	11	158	16
	64498	12	489	460		6	8	105	22		3	15	318	317		9	11	71	9
		10	225	166		6	10	71	178		5	5	255	231		11	11	344	32
2	10 22 22	2	787	747		6	12	42	22		5	7	567	579	5	45	5	496	47
	2	4	320	291		6	14	120	56		5	9	369	387	-	5	7	215	22
	2	6	686	712		В	8	618	584		5	11	221	212		5	. 6	50	9
	7	8	215	214		8	10	54	14		5	13	168	83		5	21	352	35
	- 2	10	439	480		8	12	654	641		5	15	297	285			11	240	212
	2	12	114	126		10	10	50	55		7	7	278	294		5	7	481	46
	- 2	14	339	337		10	12	2	15		7	ģ	177	187		4	- 2	346	340
	2 2 2	16	40	80		6	6	487	475		7	11	424	400		-	11	204	18
	7	4	7.3	29		6	В	158	164		ż	13	266	260		-	2.0	48	120
	- 7	6	225	249		6	10	401	363		ý	9	156	99		120	13	135	24
	- 2	8	46	30		6	12	101	81		9	11	350	306			9 11		
	- 30	10	187	141		8	8	2	36		9	13	225	200		17	LL	167	15:
	- 2	12	31	28		8	10	103	76		11	11	109	186	7	130	7	206	26
	- 7	14	145	108		8	12	171	39	3	2,7	3	1032	1035		- 3		171	17
	- 2	6	555	580		10	10	308	298	3	3	5	745	752		4	11	348	361
	- 0	8	164	160	0.5	10	8	711	720		3	7				- 2	9	101	12
	- 2	10	390	414		8	10	29	24		3	9	375	385	452	. 2	11	342	264
		~0	290	474			10	29	24		3	9	223	217	9	- 5	9	80	5

0.037 and the weighted R-value is 0.027. About  $3.4 \pm 0.8$  percent of the Si atoms were octahedrally coordinated, which means that  $1.7 \pm 0.4$  percent of Co atoms were tetrahedrally coordinated.

The positional parameters, site occupancies, anisoropic temperature factors, and the equivalent isotropic temperature factors are given with the estimated standard deviations in Table 4(b).

The bond distances and angles for three polymorphs (Tables 5, 6, and 7) were calculated by using the FACOM 230-60 version of the program RDA4 of the UNICS system (Sakurai, 1967).

Table 4. Final Atomic Coordinates plus Anisotropic and Equivalent Temperature Factors for γ-Co<sub>2</sub>SiO<sub>4</sub>

Atom		site cupancy	x (=y,z)	$(=\beta_{22}=\beta_{33})$	$(=\beta_{31}^{\beta_{12}})$	B (equiv.)
(a)	Refin	ement with	nout site o	ccupancy cha	nge	
Со			5/8	.0013(1)	0	0.38
Si			0	.0009(2)	0	0.25
0			.3668(3)	.0019(2)	.0006(4)	0.50
(b)	Refir	nement wit	h site occu	pancy change		
М	Co Si	.984(4) .016(4)	5/8	.0013(1)	0	0.34
Т	Co Si	.032(8)	0	.0014(2)	0	0.37
0			.3666(3)	.0019(2)	.0005(4)	0.50

M and T represent octahedral and tetrahedral sites, respectively. The standard deviation,  $\sigma_i$  in parentheses are expressed in units of the last digit.

### Discussion of the Structures

## (a) α-Co<sub>2</sub>SiO<sub>4</sub>

This structure consists of hexagonal closest-packed oxygen atoms with half of the otcahedral sites occupied by Co atoms and one eighth of the tetrahedral sites occupied by Si atoms. The distortion of the Co octahedra in the structure resembles that found in the Mg<sub>2</sub>SiO<sub>4</sub>-Fe<sub>2</sub>SiO<sub>4</sub> system (Birle *et al*, 1968). The

TABLE 5. Interatomic Distances and Angles in α-Co<sub>2</sub>SiO<sub>4</sub>

			$SiO_4$ tetrahedron	
Si-	-O(3) 1.629(4) Å -O(1) 1.612(6) -O(2) 1.638(7) -O(3) 1.629(4)	0(1)-0(2) 0(1)-0(3) 0(2)-0(3) 0(3)-0(3)	2.715(9) Å 2.745(7) [×2] 2.551(6) [×2] 2.582(6)	O(1)-Si-O(2) 113.4(3)° O(1)-Si-O(3) 115.8(2) [×2] O(2)-Si-O(3) 102.7(2) [×2] O(3)-Si-O(3) 104.9(2)
me	ean 1.627 Å	mean	2.648 Å	mean 109.2°
			CoO <sub>6</sub> octahedron	
Co(1)-O(1) Co(1)-O(2) Co(1)-O(3)	2.100(4) Å [×2] 2.100(4) [×2] 2.175(4) [×2]	0(1)-0(2) 0(1)-0(2) 0(1)-0(3) 0(1)-0(3) 0(2)-0(3) 0(2)-0(3)	2.893(9) Å [×2] 3.045(2) [×2] 2.886(7) [×2] 3.154(6) [×2] 3.431(7) [×2] 2.551(6) [×2]	0(1)-Co(1)-O(2) 87.1(2)° [×2 O(1)-Co(1)-O(2) 92.9(2) [×2 O(1)-Co(1)-O(3) 84.9(2) [×2 O(1)-Co(1)-O(3) 95.1(2) [×2 O(2)-Co(1)-O(3) 73.3(2) [×2 O(2)-Co(1)-O(3) 106.7(2) [×2
mean	2.125 Å	mean	2.993 Å	mean 90.0°
Co(2)-O(1) Co(2)-O(2) Co(2)-O(3) Co(2)-O(3)	2.182(5) Å 2.078(6) 2.073(4) [×2] 2.227(4) [×2]	0(1)-0(3) 0(1)-0(3) 0(2)-0(3) 0(2)-0(3) 0(3)-0(3) 0(3)-0(3)	2.886(7) Å [×2] 3.040(6) [×2] 3.240(7) [×2] 2.917(6) [×2] 3.008(5) [×2] 3.421(6) 2.582(6)	O(1)-Co(2)-O(3) 91.2(1)° [x2 O(1)-Co(2)-O(3) 81.7(2) [x2 O(2)-Co(2)-O(3) 89.3(1) [x2 O(2)-Co(2)-O(3) 97.6(2) [x2 O(3)-Co(2)-O(3) 88.7(2) [x2 O(3)-Co(2)-O(3) 111.2(3) O(3)-Co(2)-O(3) 70.9(2)
mean	2.143 Å	mean	3.015 Å	mean 89.9°

Table 6. Interatomic Distances and Angles in β-Co<sub>2</sub>SiO<sub>4</sub>

6.		S	i <sub>2</sub> 0 <sub>7</sub> group		
Si-O(2) Si-O(3) Si-O(4)	1.697(5) Å 1.626(7) 1.623(4) [×2]	O(2)-O(3) O(2)-O(4) O(3)-O(4) O(4)-O(4) mean	2.734(6) Å 2.633(8) [×2] 2.693 [×2] 2.692(5) 2.688 Å	O(2)-Si-O(4) 10 O(3)-Si-O(4) 11 O(4)-Si-O(4) 11	0.7(4)° 04.9(3) [×2] 1.9(3) [×2] 2.1(2) 09.4°
		CoC	octahedron		
0(1)-0(3)	2.144(7) Å [×2] 2.088 [×4]	O(3)-O(4) O(3)-O(4) O(4)-O(4) O(4)-O(4)	3.115(8) Å [×4] 2.865(7) [×4] 2.841(11) [×2] 3.061(5) [×2]	O(3)-Co(1)-O(4) O(3)-Co(1)-O(4) O(4)-Co(1)-O(4) O(4)-Co(1)-O(4)	85.2(1)° [×4 94.8(1) [×4 85.7(3) [×2 94.3(3) [×2
ean	2.107	mean	2.977	mean	90.0
o(2)-O(1) o(2)-O(2) o(2)-O(4)	2.053(9) Å 2.138(9) 2.125(6) [×4]	O(1)-O(4) O(2)-O(4) O(4)-O(4) O(4)-O(4)	2.834(8) Å [×4] 3.133(8) [×4] 3.061(5) [×2] 2.930(11) [×2]	O(1)-Co(2)-O(4) O(2)-Co(2)-O(4) O(4)-Co(2)-O(4) O(4)-Co(2)-O(4)	85.4(1)° [×4 94.6(1) [×4 87.1(2) [×2 92.1(2) [×2
ean	2.115	mean	2.988	mean	89.9
co (3) -0 (1) co (3) -0 (3) co (3) -0 (4)	2.062(2) Å [×2] 2.146(4) [×2] 2.155(3) [×2]	0(1)-0(1) 0(1)-0(3) 0(1)-0(4) 0(1)-0(4) 0(3)-0(3) 0(3)-0(4) 0(3)-0(4)	2.927(3) Å 3.061(6) [×2] 2.834(8) [×2] 3.136(9) [×2] 2.878(2) 2.952(8) [×2] 3.115(8) [×2]	O(1)-Co(3)-O(1) O(1)-Co(3)-O(3) O(1)-Co(3)-O(4) O(1)-Co(3)-O(4) O(1)-Co(3)-O(4) O(3)-Co(3)-O(3) O(3)-Co(3)-O(4)	90.4(1)° 92.3(1) [×2 86.7(2) [×2 84.4(3) [×2 96.0(3) [×2 84.2(2) 92.8(2) [×2
nean	2.121	mean	3.000	mean	89.9

Co-O distances of the two octahedra vary from 2.075 to 2.227 Å with a mean value of 2.134 Å. Thus the sizes of the Co octahedra are in good agreement with the sizes of the Mg/Fe-octahedra in hyalosiderite and hortonolite (Birle *et al*, 1968).

## (b) β-Co<sub>2</sub>SiO<sub>4</sub>

This structure is isostructural with that of  $\beta$ -Mn<sub>2</sub>GeO<sub>4</sub> (Morimoto *et al*, 1972) and is based on a cubic closest packed arrangement of oxygen atoms, with the Si atoms in tetrahedral and the Co atoms in octahedral sites. Two SiO<sub>4</sub> tetrahedra, which would be isolated in the spinel structure, now share an oxygen

atom to produce an  $Si_2O_7$  group. One oxygen atom in the structure is therefore not bonded to a Si atom. The structural relationship between the  $\beta$ - and  $\gamma$ -phases was first discussed by Morimoto *et al* (1970) and later by Moore and Smith (1970).

The Si-O distances range from 1.623 to 1.697 Å with a mean value of 1.642 Å. The Si<sub>2</sub>O<sub>7</sub> group is schematically shown in Figure 1 with the bond distances and angles. The bridging Si-O bonds are much longer than the non-bridging bonds. The bond angle Si-O(2)-Si is  $122^{\circ}$ , in good agreement with that of Ge-O-Ge ( $121^{\circ}$ ) in  $\beta$ -Mn<sub>2</sub>GeO<sub>4</sub>. The Co-O distances vary from 2.053 to 2.155 Å with a mean value of 2.114 Å.

TABLE 7. Interatomic Distances and Angles in γ-Co<sub>2</sub>SiO<sub>4</sub>

	$\mathtt{SiO}_{4}$ tetrahedron										
Si-O	1.646(3)	° [×2]	0-0	2.688(4)	Å	[×6]	0-Si-0	109.5(1)°	[×6]		
			Co	00 <sub>6</sub> octah	edr	ron					
Co-0	2.104(3)	å [×6]		3.066(4) 2.880(4)	Å	[×6] [×6]	0-Co-0 0-Co-0	93.6(1)° 86.4(1)°			
mean	2.104 Å	*	mean	2.973 Å			mean	90.0°			

### (c) γ-Co<sub>2</sub>SiO<sub>4</sub>

The u-parameter of the cubic closest-packed oxygen atoms in  $\gamma$ -Co<sub>2</sub>SiO<sub>4</sub> is 0.3668(3). This is the first u-parameter of a silicate spinel determined by single crystal methods and is in good agreement with the value (0.365) deduced by Kamb (1968) for Mg<sub>2</sub>SiO<sub>4</sub> spinel based on its cell dimension.

The Si atom has a smaller isotropic temperature factor than the large, octahedrally coordinated cations in most silicates and in other polymorphs of Co<sub>2</sub>SiO<sub>4</sub>. With Si and Co atoms in tetrahedral and octahedral sites, respectively, we have normal isotropic temperature factors for all atoms. However, as a result of the site occupancy refinement, Si atoms in tetrahedral coordination showed higher equivalent isotropic temperature factors than those for Co atoms in octahedral coordination. Because of (1) the reverse change between the isotropic temperature factors for Si and Co atoms, and (2) the small percent of octahedral Si atoms obtained in the refinement, we consider that γ-Co<sub>2</sub>SiO<sub>4</sub> is a perfectly normal spinel. This result is not consistent with the prediction by Ma (1972) based on the structure of Ni<sub>2</sub>O<sub>4</sub> spinel.

The Si-O distance in  $\gamma$ -Co<sub>2</sub>SiO<sub>4</sub> is 1.646 Å and the Co-O distance is 2.104 Å. The shared edges (3.066 Å) of the Co octahedra are much longer than the unshared ones (2.880 Å).

#### (d) Structural Relationships of the Three Polymorphs

The structures of the three polymorphs are compared schematically by the populations of octahedra and tetrahedra in the successive layers of close-packed oxygen atoms (Fig. 2, a, b, c). The stacking sequences of layers and the heights of metal atoms represented by numbers in these figures are shown in Figure 3.

Within the three structures, two different key structural units of octahedra and tetrahedra exist. In the first unit, the octahedra share edges with neighboring octahedra to make a serrated chain of octahedra (Fig. 4a; cf Birle et al, 1968). In the second unit, octahedra and tetrahedra share corners to make another serrated chain (Fig. 4b), here called a hybrid chain.

In the  $\alpha$ -structure (Fig. 2a), chains of octahedra (Fig. 4a) are cross linked by SiO<sub>4</sub> tetrahedra to form a two-dimensional layer. Each layer has the same patterns of combination of the two structural units. Two layers, superposed with the displacement of a/2, constitute the unit translation normal to the plane of the drawing.

In the  $\beta$ -structure (Fig. 2b), two chains of octahedra

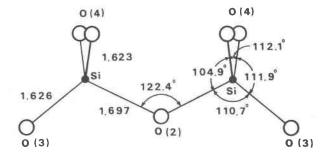


Fig. 1. The Si<sub>2</sub>O<sub>7</sub> group in β-Co<sub>2</sub>SiO<sub>4</sub>.

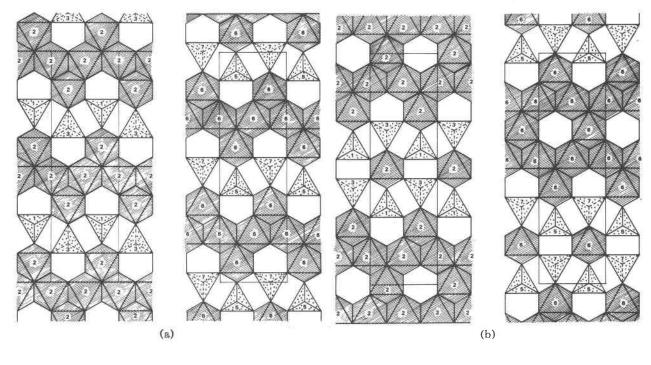
(as in Fig. 4a) are joined together with common salient octahedra, resulting in an extended double chain of octahedra. These chains combine with double hybrid chains consisting of corner-sharing SiO<sub>4</sub> and CO<sub>6</sub> polyhedra by again sharing salient octahedra. Each layer has the same combination of the two structural units. Stacking of six layers constitutes the unit translation (Fig. 4).

In the  $\gamma$ -structure (Fig. 2c) a whole layer is composed only of edge-sharing octahedra. This layer alternates with a layer composed only of cornersharing tetrahedra and octahedra. Three pairs of these layers constitute the unit translation in this structure (Fig. 3).

The actual configuration of the octahedral chain is most distorted in the  $\alpha$ -structure and becomes more regular in the  $\gamma$ -structure and the  $\beta$ -structure, resulting in the different symmetries of the three polymorphs. The translation perpendicular to the stacking in the three polymorphs indicates a greater stacking density for the high-pressure polymorphs.

### Pressure-Induced Phase Transition in Co<sub>2</sub>SiO<sub>4</sub>

Many phase transformations at high pressures involve an increase in the coordination number of the cations. Such phase transformations have been attributed to a change of the radius ratio between the cations and anions as a function of pressure. However, in the  $\alpha \to \beta \to \gamma$  transitions of  $\text{Co}_2\text{SiO}_4$ , the coordination numbers of the cations remain unchanged, being based on the closest packing of oxygen atoms. Thus it has been necessary to introduce new concepts for an understanding of stability of the three polymorphs in the transition (Kamb, 1968; Tokonami et al, 1972; Syono et al, 1971). Because the differences between the preliminary atomic parameters and the final ones of the three polymorphs of  $\text{Co}_2\text{SiO}_4$  are very slight, the conclusions of Tokonami et al (1972)



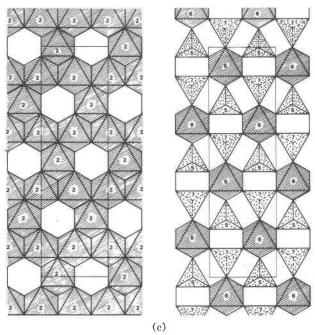


Fig. 2. The crystal structures of the three polymorphs of  $\text{Co}_2 \text{SiO}_4$ , (a)  $\alpha$ -structure, (b)  $\beta$ -structure, and (c)  $\gamma$ -structure, schematically shown by the populations of octahedra and tetrahedra in the successive layers of close-packed oxygen atoms. The standard cell is outlined in each layer. The stacking sequence of layers and the heights of metal atoms represented by numbers are shown in Figure 3. Only one third of the unit translation is shown for the  $\beta$ - and  $\gamma$ -structures normal to the plane of the drawing.

on the stability of the three polymorphs remain unchanged.

However, it is of interest to compare the structures of the three polymorphs of  $\text{Co}_2\text{SiO}_4$  based on the data obtained in the present study, and to propose a general principle for the structural changes in the  $\alpha \to \beta \to \gamma$  transitions using a simple qualitative approach like that of Kamb (1968) for the olivine-spinel transition.

The olivine structure ( $\alpha$ -Co<sub>2</sub>SiO<sub>4</sub>), because of the destabilizing effect of shared edges between the octahedra and tetrahedra (Table 8), appears unstable in respect to the normal spinel structure ( $\gamma$ -Co<sub>2</sub>SiO<sub>4</sub>).

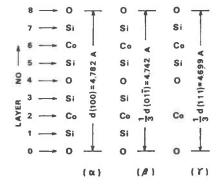


Fig. 3. The stacking sequences of layers and the heights of metal atoms normal to the plane of drawing in Figure 2. Stacking of six layers constitute the unit translation in the  $\beta$ -and  $\gamma$ -structures.

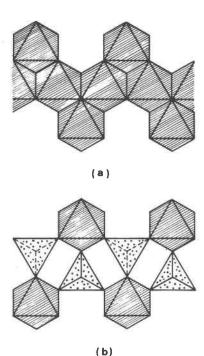


Fig. 4. Two different key structural units of octahedra and tetrahedra in the polymorphs of Co<sub>2</sub>SiO<sub>4</sub>: (a) a serrated chain of octahedra, and (b) a hybrid chain of octahedra and tetrahedra.

Similarly, the sharing of a corner between tetrahedra to form an  $Si_2O_7$  group in the modified spinel structure  $(\beta-Co_2SiO_4)$  seems distinctly unfavorable for its stability.

In the relative stability of the three polymorphs, however, the shortening of shared polyhedral edges must play an important role (Kamb, 1968). This shortening can be seen for the three polymorphs in Table 9. Unshared octahedral edges are much longer than the edges shared between the octahedra in the  $\alpha$ -phase, whereas the unshared edges are shorter than the shared edges in the  $\gamma$ -phase. In the  $\beta$ -phase, the shared and unshared edges have almost the same lengths. The apparently destabilizing factor of the  $\mathrm{Si}_2\mathrm{O}_7$  group in the  $\beta$ -phase, therefore, seems to be partly compensated by a significant shortening of the shared edges of the octahedra.

As indicated by average interatomic distances (Table 10), the SiO<sub>4</sub> tetrahedra clearly increase in size within the higher pressure polymorphs of Co<sub>2</sub>SiO<sub>4</sub> whereas the CoO<sub>6</sub> octahedra display a remarkable decrease in size. Presumably, if the higher pressure structures had been studied at elevated pressures—instead of at one atmosphere—the size decrease in the CoO<sub>6</sub> octahedra would be even more striking. In response to pressure, the SiO<sub>4</sub> tetrahedra thus appear

Table 8. Numbers of Shared Corners and Edges Between Metal Polyhedra in  $\alpha$ -,  $\beta$ -, and  $\gamma$ -Co<sub>2</sub>SiO<sub>4</sub>

	CL.	β	Υ
Co-Co	6(3.65)*	0	0
Co-Si	6(3.32)	10	12(3.37)
Si-Si	0	1(2.97)	0
Co-Co	3(3.22)	6(2.88)	6(2.87)
Co-Si	3(2.76)	0	0
Si-Si	0	0	0
	Co-Si Si-Si Co-Co Co-Si	Co-Co 6(3.65)* Co-Si 6(3.32) Si-Si 0 Co-Co 3(3.22) Co-Si 3(2.76)	Co-Co 6(3.65)* 0 Co-Si 6(3.32) 10 Si-Si 0 1(2.97) Co-Co 3(3.22) 6(2.88) Co-Si 3(2.76) 0

<sup>\*</sup> The numbers in parentheses represent average cationcation distances in Angstroms.

to be more rigid than the CoO<sub>6</sub> octahedra. Interestingly, in low- to high-pigeonite measured at room temperature and at 960°C, respectively, Brown *et al* (1972) observed negligible expansion of the SiO<sub>4</sub> tetrahedra but large expansion of the Fe, Mg, and Ca octahedra. These results suggest that size of SiO<sub>4</sub> tetrahedra is relatively independent of pressure and temperature.

In the  $\alpha \to \beta \to \gamma$  transitions of  $\text{Co}_2 \text{SiO}_4$ , the polyhedra around metal ions generally become more regular in the polymorphs stable at higher pressures. Thus the ranges of bond lengths become smaller in the polymorphs stable at higher pressures (Table 10) even though one of the Si-O bonds in  $\text{Co}_2 \text{SiO}_4$  is exceptionally long because of corner-sharing between two  $\text{SiO}_4$  tetrahedra. The change of the distortion of the polyhedra is quantitatively shown by the tetrahedral and octahedral angle variances. These variances are calculated by the following formulae (Robinson, Gibbs, and Ribbe, 1971):

$$\sigma_{\text{tet}}^2 = \sum_{i=1}^{6} (\theta_i - 109.47^\circ)/5$$

$$\sigma_{\text{oct}}^2 = \sum_{i=1}^{12} (\theta_i - 90^\circ)/11$$

where  $\theta_i$  represents the angles between the metaloxygen bonds in the tetrahedra or in the octahedra (Table 10). The decrease of the variances clearly indicates decrease in polyhedral distortion.

These changes of the polyhedra can be explained qualitatively by the repulsive forces in ionic crystals

Table 9. Mean Values for Shared and Unshared Edges (Å) of Metal Polyhedra in α-, β-, and γ-Co<sub>2</sub>SiO<sub>4</sub>

		α	β	Υ
Со	octahedron { shared unshare	2.84 ed 3.14	2.99	3.08
Si	tetrahedra { shared unshare	2.56 ed 2.74	2.69	2.69

TABLE 10. The Longest and Shortest Interatomic Distances and the Angle Variances in the Metal Polyhedra of α-, β-, and γ-Co<sub>2</sub>SiO<sub>4</sub>\*

	SiO <sub>4</sub> tetrahedra			CoO <sub>6</sub> octahedra		
	S1-0	0-0	σ <sup>2</sup> tet	Co-0	0-0	o <sup>2</sup> tet Co(1) Co(2) Co(3)
α	1.61-1.64(1.63)	2.55-2.75(2.65)	41.5	2.07-2.23(2.13)	2.55-3.43(3.01)	114.5 97.7
β	1.62-1.70(1.64)	2.63-2.73(2.69)	12.2	2.05-2.16(2.11)	2.83-3.14(2.99)	23.5 17.7 26.2
Υ	1.65-1.65(1.65)	2.69-2.69(2.69)	0	2.10-2.10(2.10)	2.88-3.07(2.97)	14.1

which increase very rapidly as interatomic distances approach some constant value. To form crystals of higher density under pressure, therefore, it seems most energetically efficient to bring atoms with longer bond lengths closer and to make all the coordination polyhedra of the cation more regular. In some cases, where the polyhedra behave rigidly with increasing pressure, the average bond lengths of the coordination polyhedra increase to give some space to the oxygen atoms approaching to the central metal atoms, resulting in smaller possible ranges for all bond lengths of the polyhedra (Table 10). This feature is observed for SiO4 tetrahedra, not only in the highpressure polymorphs of Co<sub>2</sub>SiO<sub>4</sub> but also in other silicates which undergo polymorphic transformations at high pressures—for example, in Zn<sub>2</sub>SiO<sub>4</sub> as observed by Marumo and Syono (1971).

More generally, an increase in the coordination number of the cations in the phase transitions at high pressures may be considered as an extension of this tendency, because some next-nearest neighbors become nearest neighbors during the transformations. This produces not only an increase of the coordination number but also of the average bond lengths.

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