

## The structural properties of synthetic Sr-åkermanite, $\text{Sr}_2\text{MgSi}_2\text{O}_7$

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*Crystal structure /  $\text{Sr}_2\text{MgSi}_2\text{O}_7$*

**Abstract.** The crystal structure of  $\text{Sr}_2\text{MgSi}_2\text{O}_7$  with tetragonal,  $a = 7.9957(10)$ ,  $c = 5.1521(9)$  Å,  $Z = 2$ , space group  $P\bar{4}2_1m$  has been refined to  $R = 4.3\%$  from three-dimensional single-crystal, X-ray diffraction data by full-matrix least-squares calculations. This compound is completely isomorphous with åkermanite,  $\text{Ca}_2\text{MgSi}_2\text{O}_7$ , and the Mg and Si atoms are distributed respectively in the T(1) and T(2) sites of the melilite structure. The tetrahedral Mg–O bond length (1.942 Å) is clearly longer than that in  $\text{Ca}_2\text{MgSi}_2\text{O}_7$  (1.915 Å), which exhibits the flexibility of T(1) site in melilite structures. In the system  $\text{Ca}_2\text{MgSi}_2\text{O}_7 - \text{Sr}_2\text{MgSi}_2\text{O}_7$  the tetragonal parameters of the solid solutions are linear functions of molar compositions, which implies that this solid solution is continuous.

All of the rare silicates with tetrahedrally coordinated Mg cations contain alkali or alkali-earth cations in their structures and the ratios Mg:Si are below one.

### Introduction

Complete substitution of Sr for Ca in melilites was first demonstrated by the synthesis of strontio-gehlenite  $\text{Sr}_2\text{Al}_2\text{SiO}_7$  by Dear (1957), and by Brisi and Abbattista (1960), while strontio-åkermanite  $\text{Sr}_2\text{MgSi}_2\text{O}_7$  was also synthesized by Dear (1960). The amount of strontium in natural melilites is seldom analyzed, and it rarely exceeds 1% (by weight) SrO. Gold (1966), for example, reported 1.59% SrO in a melilite from Oka carbonatite. Fitton and Hughes (1981), however, found strontium-rich (up to 16 wt% SrO) melilite occurring as microphenocrysts in a nosean-leucite-nephelinite lava from Etinde, Cameroon, and its melilite is richer in Al than in Mg. Recently single crystal of  $\text{Sr}_2\text{MgSi}_2\text{O}_7$  was synthesized from the melt by the Czochralski method (Liebertz and Stähr, 1982). The ionic radius of  $\text{Sr}^{2+}$  (1.26 Å) in eight

coordination is between those of Ca<sup>2+</sup> (1.12 Å) and Ba<sup>2+</sup> (1.42 Å) and is somewhat smaller than the Pb<sup>2+</sup> radius (1.29 Å) (Shannon, 1976). Therefore, in a number of minerals and artificial compounds, Sr is replaced by these atoms and also replaces them.

It is the scope of this study to describe the structural properties of synthetic Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> in comparison with those of åkermanite, and to discuss mineralogical behavior of strontium in melilites.

### Experimental

The compound Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> was prepared by solid-state reaction between appropriate quantities of SrCO<sub>3</sub>, MgO and SiO<sub>2</sub>. A single crystal was selected from a sample which had been heated at 1400°C for 15 days. The crystal used for collection of the intensity data is of 0.07 × 0.08 × 0.06 mm in size and of irregular shape, and was mounted in an arbitrary orientation. The orientation matrix was found automatically. Intensity data were collected on a computer-controlled RIGAKU four-circle diffractometer with a generator rotaflex Ru-200 and a scintillation counter. MoK $\alpha$  radiation from a graphite monochromator was used in conjunction with a pulse-height analyser. The diffractometer was controlled by a PANAFACOM U-100 computer. 732 independent nonzero reflections below  $2\theta = 90^\circ$  were collected. The data were corrected for Lorentz and polarization factors but absorption effects were neglected because of the small size and irregular shape of the crystal.

The (Sr,Ca)<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> solid solutions were prepared by mixing the appropriate amounts of SrCO<sub>3</sub>, CaCO<sub>3</sub>, Mg(OH)<sub>2</sub> and SiO<sub>2</sub>, grinding the mixtures in an agate mortar under acetone and heating at 1400°C 9 days. Their cell parameters were determined from powder X-ray diffraction patterns by the method of least-squares using silicon as internal standard.

### Crystal data

Approximate unit-cell parameters were determined from precession photographs, which yielded space-group extinctions compatible with  $P\bar{4}2_1m$ . The lattice parameters used in the least-squares refinement are determined by using a four-circle single-crystal X-ray diffractometer. Twenty-two reflections in the  $2\theta$  region from 25–50° were selected to calculate the lattice parameters with  $\lambda(\text{MoK}\alpha_1) = 0.70926 \text{ \AA}$ . These results and other physical constants for Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> are given in Table 1. The lattice parameters determined are very close to those of the Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> ( $a = 8.01$ ,  $c = 5.18 \text{ \AA}$ ) previously published (Brisi and Abbattista, 1960).

The mean refractive index of Sr-åkermanite was calculated by using the Gladstone-Dale relationship (Mandarino, 1981), according to which, the

**Table 1.** Crystallographic data for Sr-åkermanite

Formula	Sr <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub>
mol wt.	367.71
Symmetry	tetragonal
Space group	$P\bar{4}2_1m$
<i>a</i>	7.9957(10) Å
<i>c</i>	5.1521(9) Å
Volume	329.54(8) Å <sup>3</sup>
<i>Z</i>	2
<i>D</i> <sub>cal.</sub>	3.707 g cm <sup>-3</sup>
<i>F</i> (000)	344

index (1.636) is somewhat larger than that (1.612) of åkermanite. This implies that the replacement of Ca by Sr in åkermanite is accompanied by an increase in the refractive indices.

### Refinement

The positional parameters of åkermanite (Kimata and Ii, 1981) were used as starting parameters for refinements. The structural parameters were refined by the least-squares techniques using a modified version of the ORFLS program of Busing, Martin and Levy (1962). The computations were performed on HITAC M-200H at the Computer Center of the University of Tokyo. The atomic scattering factors for Sr<sup>2+</sup>, Mg<sup>2+</sup>, and Si<sup>4+</sup> cations were taken from International Tables for X-ray Crystallography Vol. IV (1974), and from Tokonami (1965) for O<sup>2-</sup>. 143 amplitudes which were classed as unobserved ( $F = 3 \times \text{e.s.d.}$ , where the standard deviation was based on counting statistics) were excluded from the refinement. The final refinement with anisotropic temperature factors resulted in  $R = 0.043$  and  $R_w = 0.047$  for 589 observed  $F_{hkl}$ 's.

The refined positional and thermal parameters are given in Tables 2 and 3, respectively. The bond lengths and angles shown in Table 4 were calculated using the Fortran function and error program RSDA-4 written by Sakurai (1967).

### Discussion

The structure of the Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> is isotypic with those of åkermanite groups (åkermanite Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>, Kimata and Ii, 1981; gugiaite Ca<sub>2</sub>BeSi<sub>2</sub>O<sub>7</sub>, Kimata and Ôhashi, 1982a; hardystonite Ca<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub>, Louisnathan, 1969; Ca<sub>2</sub>CoSi<sub>2</sub>O<sub>7</sub>, Kimata, 1982b and 1983). The magnesium and silicon atoms were distributed respectively in the T(1) and T(2) sites of åkermanite given by Kimata and Ii (1981). The Mg cation is tetrahedrally coordinated by oxygens,

**Table 2.** Final atomic coordinates and their standard deviations (in parentheses)

Atom	Position	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>
Sr	4(e)	$\frac{1}{2}$	0.3345(5)	$\frac{1}{2} - x$	0.5077(1)
Mg	2(a)	$\frac{1}{4}$	0	0	0
Si	4(e)	$\frac{1}{2}$	0.1387(2)	$\frac{1}{2} - x$	0.9438(4)
O(1)	2(c)	$\frac{1}{4}$	0.5	0	0.1603(15)
O(2)	4(e)	$\frac{1}{2}$	0.1396(6)	$\frac{1}{2} - x$	0.2528(10)
O(3)	8(f)	1	0.0793(5)	0.1915(5)	0.8034(7)

**Table 3.** Anisotropic thermal parameters and their standard deviations (in parentheses)

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Sr	0.00265(4)	$\beta_{11}$	0.00564(15)	0.00060(6)	0.00058(9)	$-\beta_{13}$
Mg	0.00145(41)	$\beta_{11}$	0.00324(84)	0	0	0
Si	0.00088(14)	$\beta_{11}$	0.00256(49)	0.00059(17)	$-0.00058(18)$	$-\beta_{13}$
O(1)	0.00199(113)	$\beta_{11}$	0.00479(213)	$-0.00093(78)$	0	0
O(2)	0.00322(52)	$\beta_{11}$	0.00340(142)	$-0.00087(61)$	$-0.00034(63)$	$-\beta_{13}$
O(3)	0.00304(53)	0.00110(49)	0.00526(101)	$-0.00010(36)$	0.00025(36)	$-0.00030(59)$

**Table 4.** Bond lengths and angles in Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>

Bond lengths		Bond angles	
The MgO <sub>4</sub> tetrahedron at point symmetry $\bar{4}$			
Mg—O(3) [4 ×]	1.942(4) Å	O(3)—Mg—O(3') [2 ×]	117.1(1)°
O(3)—O(3') [2 ×]	3.316(6)	O(3)—Mg—O(3'') [4 ×]	105.7(1)
O(3)—O(3'') [4 ×]	3.098(5)	Mean	109.5
The Si <sub>2</sub> O <sub>7</sub> group at point symmetry <i>mm</i> 2			
Si—O(1)	1.658(3)	Mg—O(3)—Si	121.8(2)
Si—O(2)	1.592(5)	Si—O(1)—Si'	142.2(5)
Si—O(3) [2 ×]	1.609(4)	O(1)—Si—O(2)	109.2(3)
O(1)—O(2)	2.651(8)	O(1)—Si—O(3) [2 ×]	102.7(2)
O(1)—O(3) [2 ×]	2.553(4)	O(3)—Si—O(3'')	107.2(2)
O(3)—O(3'')	2.591(5)	O(3)—Si—O(2) [2 ×]	116.5(2)
O(3)—O(2) [2 ×]	2.723(6)	Mean	109.1
The SrO <sub>8</sub> polyhedron at point symmetry <i>m</i>			
Sr—O(3) [2 ×]	2.555(4)	O(2)—Sr—O(3) [2 ×]	70.3(1)
Sr—O(2)	2.565(4)	O(3)—Sr—O(3')	60.9(1)
Sr—O(1)	2.589(5)	O(2)—Sr—O(2')	70.3(1)
Sr—O(3''') [2 ×]	2.776(4)	O(2)—Sr—O(3'') [2 ×]	76.7(1)
Sr—O(2') [2 ×]	2.741(4)	O(2'')—Sr—O(3''') [2 ×]	82.2(1)
O(1)—O(2')	4.103(4)	O(1)—Sr—O(3''') [2 ×]	56.71(9)
O(3''')—O(3'')	5.161(5)	O(1)—Sr—O(2')	105.4(1)
		O(3''')—Sr—O(3''')	150.8(1)

which is rare in silicates. In the tetrahedral MgO<sub>4</sub>, Mg–O distances are 1.942(4) Å, which is somewhat longer than 1.915(2) Å in åkermanite; O–Mg–O angles are close to ideal tetrahedral angle, 109.5° (Kimata and Ii, 1981).

Examination of Table 4 shows that there is a variation of Si–O distances in T(2) site of Sr-åkermanite. This variation is similar to that in åkermanite (Kimata and Ii, 1981), and the mean Si–O distance (1.617 Å) is in good agreement with that (1.619 Å) in åkermanite. It seems that compositional change has no effect on Si–O bond length. Some explanations have been offered for the variation of these T(2)–O distances by the electrostatic valence principle (Pauling, 1960), the same interpretation that has been already given in gugiaite (Kimata and Ōhashi, 1982a).

Distances and distortions of T(1) and T(2) tetrahedra in silicate-melilites are summarized in Table 5. The replacement of Ca cation by Sr brings forth the larger distortion of the T(1) tetrahedron in Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>. In order to magnify to the size of Sr-polyhedron, this is caused by longer T(1)–O distances and two wider O–T(1)–O angles. The lack of tetrahedral edge sharing in that T(1) tetrahedron results in a relatively large-size range of cation substitutions in the T(1) site of that structure. The essential features of these tetrahedra, suggested by Kimata and Ōhashi (1982a), are as follows: (a) the smaller metallic cations occupy T(2) while the larger ones prefer T(1); (b) the distortion of the T(1) tetrahedron is always smaller than that of T(2); (c) generally divalent cations prefer the completely ordered distribution together with Si cations, while trivalent cations cause the partially disordered distribution. This synthetic Sr-åkermanite embodies all those features. The relationship between distortions of the T(1) and T(2) tetrahedra in silicate-melilites is represented in Figure 1. Distortion of these sites in this Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> displays the relation of crystallographically mutual compensation (Kimata and Ōhashi, 1982a). Moreover the distortion of the T(2) site in Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> is the smallest, and the difference between distortions of the T(1) and T(2) sites is the minimum, which may imply the structural limitation in silicate-melilites.

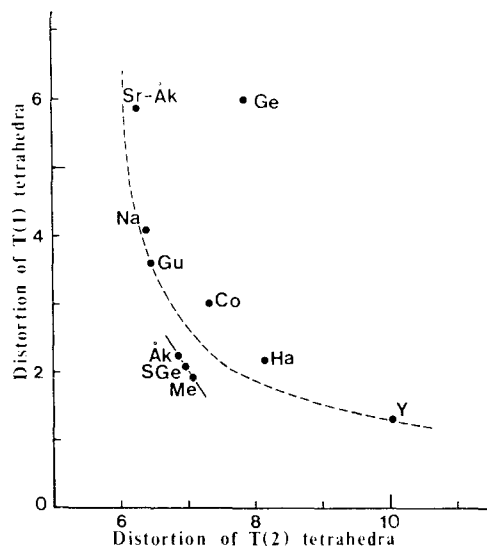
The 8-coordinated site of Sr cation in Sr-åkermanite shows a similar variation to that of the Ca–O bond lengths in åkermanite (Kimata and Ii, 1981). Here the geometrical effect is due to the similarity of crystallochemical properties of Sr and Ca cations. The Sr cations produce very little effect on the Si tetrahedra but a powerful effect on those of Mg. The lengthening of the Mg–O distance in Sr-åkermanite demands the interpretation that Sr causes a higher ionicity of the Mg–O bond than Ca in åkermanite.

The ionic radii of Sr<sup>2+</sup> and Ca<sup>2+</sup> are within the tolerance limits usually set forth for isomorphous, ionic, solid-solution replacement. Examples of such replacement are known; e.g., the metasilicates of calcium and strontium (Eskola, 1922). Tetragonal cell parameters for the solid solutions Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>–Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> are given in Table 6 and Figure 2. From åker-

**Table 5.** T–O distance and distortion in the tetrahedra of melilites

	T(1) site			T(2) site			$\sigma_1 - \sigma_2$	Reference
	Oc- cupying atom	Distance	$\sigma_1^a$	Oc- cupying atom	Distance	$\sigma_2^a$		
Melilite	Mg,Al	1.87(1) Å	1.93	Al,Si	1.63(1) Å	7.08	–5.15	Smith (1953)
Y-melilite	Si	1.67(2)	1.29	Be	1.63	10.04	–8.75	Bartram (1969)
Hardystonite	Zn	1.937(4)	2.17	Si	1.617	8.14	–5.97	Louisonathan (1969)
Na-melilite	Al	1.762(3)	4.08	Si	1.622(3)	6.39	–2.31	Louisonathan (1970)
Gehlenite	Al	1.785(2)	5.98	Al,Si	1.691	7.85	–1.87	Louisonathan (1971)
Åkermanite	Mg	1.915(2)	2.35	Si	1.619(2)	6.86	–4.51	Kimata and Ii (1981)
Gugiaite	Be	1.654(1)	3.59	Si	1.622(2)	6.47	–2.88	Kimata and Ôhashi (1982a)
Co-åkermanite	Co	1.926(5)	3.00	Si	1.608(5)	7.33	–4.33	Kimata (1982b)
Gehlenite (syn.)	Al	1.747(1)	2.07	Al,Si	1.684(1)	6.98	–4.91	Kimata and Ii (1982c)
Sr <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub>	Mg	1.942(4)	5.88	Si	1.617(4)	6.25	–0.37	This study

<sup>a</sup> The distortion of tetrahedra proposed by Robinson et al. (1971)



**Fig. 1.** The relationship between distortions of the T(1) and T(2) tetrahedra in silicate-melilites. Abbreviations: Me, melilite; Y, Y-melilite; Ha, hardystonite; Na, Na-melilite; Åk, åkermanite; Gu, gugiaite; Ge, gehlenite; SGe, synthetic gehlenite; Co, Co-åkermanite; Sr-Åk, Sr-åkermanite

**Table 6.** Tetragonal parameters for åkermanite–Sr-åkermanite

Mol% åkermanite	100	75	50	25	0
Mol% Sr-åkermanite	0	25	50	75	100
$a$ (Å)	7.835(1)	7.887(1)	7.933(1)	7.970(1)	7.9957(10)
$c$ (Å)	5.010(1)	5.045(1)	5.083(1)	5.122(1)	5.1521(9)
Volume (Å <sup>3</sup> )	307.5(1)	313.8(1)	319.9(1)	325.4(1)	329.54(8)
$c/a$	0.6394(2)	0.6397(2)	0.6407(2)	0.6427(2)	0.6408(1)

manite to Sr-åkermanite  $a_0$  increases linearly by 0.161 Å and  $c_0$  increases linearly by 0.142 Å, which indicates that continuous crystalline solution exists between these åkermanites. Moreover the increasing ratio in  $c_0$  is somewhat smaller than that, 0.206 Å, between  $c_0$  of gehlenite and Sr-gehlenite (Dear, 1961). The five-membered rings in åkermanite are larger than those in gehlenite (Kimata and Ii, 1982c), and so the Sr cation sandwiched between two tetrahedral five-membered rings occurs in the melilite structure. This schematic model is the same as in the mica structure, their flattening accounting for the almost constant dimension of the  $c_0$  axis of the biotite solid-solution series, in spite of the expected chemical expansion by the larger cations (Takeda and Morosin, 1975).

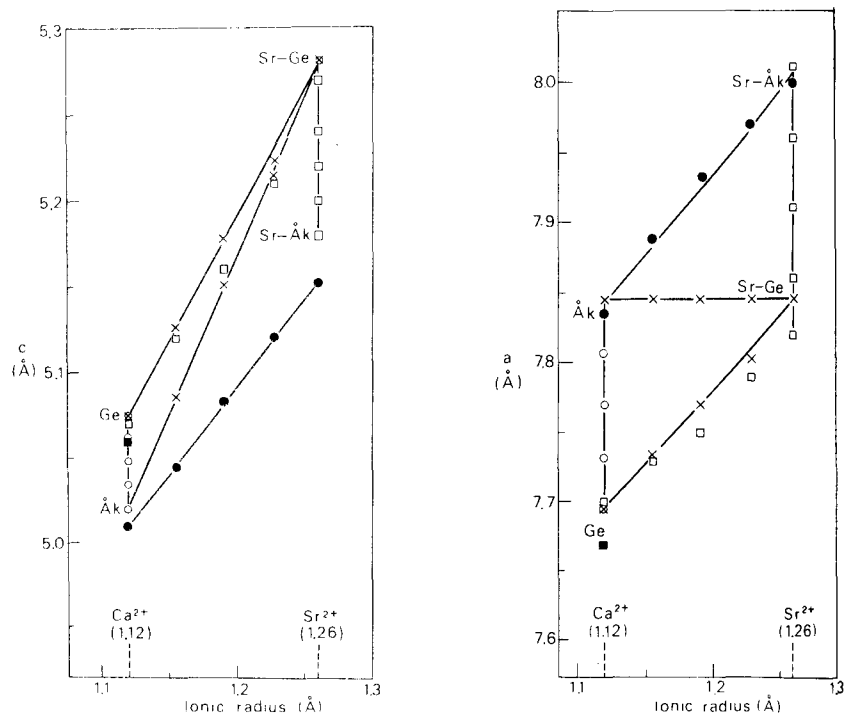


Fig. 2. Variation of tetragonal cell parameters with ionic radii for synthetic Ca/Sr melilites. Abbreviations: Ge, gehlenite; Sr-Ge, Sr-gelenite; Åk, åkermanite; Sr-Åk, Sr-åkermanite. Symbols: ●, this study; □, Brisi and Abbattista (1960); ×, Dear (1961 and 1969); ○, Ervin and Osborn (1949); ■, Kimata and Ii (1982c). Note, intermediate ionic radii between those of Ca and Sr cations were calculated by interpolation method through the correspondence of composition to ionic radius

Åkermanite,  $\text{Ca}_2\text{MgSi}_2\text{O}_7$ , is a rare silicate mineral in nature (Valley and Essene, 1980), but it usually forms the continuous solid solutions of melilite groups among the following composition series;  $\text{Ca}_2\text{MgSi}_2\text{O}_7$ – $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ,  $\text{Ca}_2\text{MgSi}_2\text{O}_7$ – $\text{Sr}_2\text{MgSi}_2\text{O}_7$  and  $\text{Ca}_2\text{MgSi}_2\text{O}_7$ – $\text{Sr}_2\text{Al}_2\text{SiO}_7$ , which are illustrated in Fig. 2. It is possible that the continuity of this solid solution is due to the flexibility of the T(1)–O distance in melilite structures, which results in accepting various interlayer cations with different valences, for examples,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Y}^{3+}$  (Louisnathan, 1970; Dear, 1957; Bartram, 1969). This behavior is reflected in natural occurrences, and the Sr-melilite reported by Fitton and Hughes (1981) contains appreciable amounts of various cations, for examples as an interlayer cation,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$ , and as a T(1) cation,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ . Thanks to the enlargement of tetrahedral Mg–O distance, my results can be explained by ideal mixing of Ca and Sr in the 8-coordination sites in åkermanite system.



**Table 7.** Crystallographic data for Mg tetrahedra in silicates

	T—O distance	$\sigma^a$	Mg/Si	Synthetic temperature	References
Ca <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub>	1.915(2) Å	2.35	1/2	1550	Kimata and Ii (1981)
Sr <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub>	1.942(4)	5.88	1/2	1400	This study
K <sub>2</sub> Mg <sub>5</sub> Si <sub>12</sub> O <sub>30</sub>	1.955(2)	17.55	5/12	790°C (2 kb)	Kahn et al. (1972)
Na <sub>2</sub> Mg <sub>2</sub> Si <sub>6</sub> O <sub>15</sub>	1.965(10)	18.56	1/3	1029°C	Cradwick and Taylor (1972)
Na <sub>2</sub> MgSiO <sub>4</sub>	1.945(1)	2.20	1	900–1000°C	Baur et al. (1981)

<sup>a</sup> The distortion of tetrahedra proposed by Robinson et al. (1971)

The rare silicates with tetrahedrally coordinated Mg cation are summarized in Table 7. This table leads to the following common features:

- (1) All of these silicates contain alkali or alkali-earth cations in their structures.
- (2) They are free from Al cation.
- (3) They are crystallized at relatively higher temperature.
- (4) The ratio Mg:Si is below one.

These features can be regarded as the conditions yielding the Mg tetrahedra in silicates. In nature, observations were recently reported that åkermanite Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> exists in an unusual calc-silicate xenolith in anorthosite (Valley and Essene, 1980), and that eifelite KNa<sub>2</sub>Mg<sub>4.5</sub>Si<sub>12</sub>O<sub>30</sub> occurs in druses of eruptive bombs in the Bellerbery volcano (Abraham et al., 1980). Yang (1973) found 0.7–0.9 wt% MgO in anorthites from the Vigarano and Allende meteorites. Smith's suggestion (1974) is that the nearest approach to an MT<sub>4</sub>O<sub>8</sub> formula of feldspar occurs if the Mg is mostly or entirely in tetrahedral sites. These behaviors of Mg cation in nature are cases in point for the above conditions.

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