

# Synthetic Mn-kilchoanite—a new development in polymorphism of melilite

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**ABSTRACT.** Two compounds with the chemical composition  $\text{Ca}_{2.32}\text{Mn}_{0.68}\text{Si}_{2.00}\text{O}_7$  were synthesized from a molten carbonating silicate with the melilite composition. The synthetic samples were subsequently characterized by X-ray powder diffraction, IR absorption and EPMA, and they proved to be the anhydrous phases isomorphous with kilchoanite  $\text{Ca}_3\text{Si}_2\text{O}_7$  and åkermanite  $\text{Ca}_2\text{MgSi}_2\text{O}_7$  respectively, and to be polymorphous with each other. Their crystallochemical properties suggest that Mn-åkermanite is a high-temperature structure type of Mn-kilchoanite. Substitution of  $\text{Mn}^{2+}$  with an intermediate ionic radius between those of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  cations establishes the polymorphic relationship between åkermanite  $\text{Ca}_2\text{MgSi}_2\text{O}_7$  and kilchoanite  $\text{Ca}_3\text{Si}_2\text{O}_7$ .

**KEYWORDS:** kilchoanite, åkermanite, manganese.

**MELILITE** with a tetragonal symmetry, a continuous solid solution between åkermanite,  $\text{Ca}_2\text{MgSi}_2\text{O}_7$ , and gehlenite,  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  (Andrew, 1948), is characteristic mineral of alkaline rocks, meteorites, and slags (Edgar, 1984) and its crystal structure type has been observed even in sialons and sulphide compounds, for example  $\text{Y}_2\text{Si}(\text{Si}_2\text{O}_3\text{N}_4)$  (Jack, 1976) and  $\text{SrLaAl}_3\text{S}_7$  (Lozac'h, 1972). Mg/Si disorder in åkermanite has been disproved from refinement of the crystal structure (Kimata, 1983), but the existence of polymorphs due to Al/Si order-disorder in gehlenite is open to controversy (Huckenholtz, 1977; Kimata and Ii, 1982). On the other hand, dicalcium silicate,  $\text{Ca}_3\text{Si}_2\text{O}_7$ , in nature, yields dimorphs, kilchoanite with an orthorhombic symmetry and monoclinic rankinite (Agrell and Gay, 1961). The paragenesis of kilchoanite and åkermanite has been described by Agrell (1965), and the coexistence of those dimorphs with gehlenite was observed by Henmi *et al.* (1975). In spite of contamination by spurrite and calcite, the structural formulae of their dimorphs are close to the ideal composition  $\text{Ca}_3\text{Si}_2\text{O}_7$ . Furthermore, phase equilibrium data for the ternary system  $\text{CaO-MnO-SiO}_2$  led Glasser (1962) to suggest that the  $\text{Ca}_3\text{Si}_2\text{O}_7$  structure does not admit appreciable amounts of  $\text{Mn}^{2+}$ .

The purpose of this study is to provide information on new polymorphs in the melilite series.

*Experimental.* The materials used in the syntheses of melilite analogues consisted of powdered chemicals—reagent-grade chemicals with the following stoichiometry:  $\text{CaCO}_3 : \text{MnO} : \text{SiO}_2 = 2 : 1 : 2$ . The chemicals were mixed with acetone in an agate mortar. The mixture was put in a Pt-crucible and reacted in an electric muffle furnace with siliconites. Through solid-state reactions, by heating this mixture for 24 hrs  $1600^\circ\text{C}$  in air, two kinds of crystals and a glass crystallized at a cooling rate of  $20^\circ\text{C}/\text{day}$  between 1600 and  $1300^\circ\text{C}$ .

The products were examined under a petrographic microscope, and subsequently X-ray powder diffraction analysis was carried out by a Rigaku Geigerflex diffractometer with a Rotaflex RU-200 generator and a scintillation counter. Ni-filtered  $\text{Cu-K}\alpha$  radiation from a graphite monochromator was monitored in conjunction with a pulse-height analyser. The diffractometer was calibrated against a silicon standard.

The chemical analyses were made with a computer-controlled electron probe X-ray microanalyser, a JXA-50 (Jeol) instrument and ACPS-XR (Elionix) counting equipment. Standards used were a variety of natural and synthetic oxides, and silicates:  $\text{SiO}_2$  for Si,  $\text{MnFe}_2\text{O}_4$  for Mn and  $\text{CaSiO}_3$  for Ca. The data were corrected on-line by the method of Sweatman and Long (1969).

The infra-red spectra of synthetic compounds in KBr pellets were recorded by means of a Hitachi Infra-red Spectrophotometer type 260-30 covering the range from  $4000$  to  $400\text{ cm}^{-1}$ . Correction of the frequencies was made by reference to the polystyrene absorption bands.

*Results.* Examination of the products under a petrographic microscope showed a paragenesis of three phases. The major crystals were colourless and transparent, lath-shaped with 1 mm maximum length, whilst very small crystals of a similar shape were dark blue transparent; the third phase was a dark-brown glass. These crystalline phases were characterized by comparison with mineral samples of melilite and kilchoanite.

*X-ray crystallography.* Tables I and II list the indexed X-ray powder diffraction data for the crystalline phases. The diffraction patterns of blue

Table II. X-ray powder diffraction data for synthetic Mn-kilchoanite and natural kilchoanite.

Mn-kilchoanite				kilchoanite <sup>1</sup>		kilchoanite <sup>2</sup>		hkl
d <sub>obs</sub>	I <sub>obs</sub>	d <sub>calc</sub>	I <sub>calc</sub>	d <sub>obs</sub>	I <sub>obs</sub>	d <sub>obs</sub>	I <sub>obs</sub>	
5.673 Å	4	5.677 Å	1	-	-	-	-	200
5.036	13	5.036	20	5.07 Å	2	5.17 Å	m	202
4.575	5	4.581	1	4.79	1	-	-	110
4.222	2	4.224	2	4.27	1	4.26	w	112
4.123	9	4.124	8	4.18	1	-	-	013
3.934	12	3.933	10	3.97	2	4.00	w	204
3.700	12	3.701	10	-	-	-	-	211
3.508	62	3.508	71	3.56	4	3.56	ms	114
3.336	6	3.337	5	3.38	3	3.39	vw	213
3.064	9	3.062	11	-	-	-	-	206
3.017	100	3.019	68	3.05b	10	3.07	S <sub>3</sub>	310
2.911	8	2.910	8	-	-	-	-	312
2.849	90	2.848	100	2.88	8	2.89	S <sub>1</sub>	116
-	-	-	-	2.86	2	-	-	215
2.748	9	2.747	9	2.76	2	2.77	vw	402
2.728	6	2.727	10	-	-	-	-	008
2.642	69	2.642	77	2.67	8	2.68	S <sub>2</sub>	314
2.503	7	2.504	10	2.54	2	2.55	m	020
2.454	11	2.454	11	2.48	2	2.48	m	411
2.429	4	2.430	4	-	-	-	-	121
2.398	27	2.398	19	2.43	2	2.42	m	217
2.343	15	2.344	6	2.35b	1	2.36	ms	118
2.323	19	2.323	11	-	-	-	-	316
-	-	-	-	2.255	1	2.26	vs	222
2.240	9	2.238	4	-	-	-	-	406
2.183	3	2.182	2	-	-	-	-	0010
2.150	2	2.149	2	-	-	-	-	415
2.111	3	2.112	3	-	-	-	-	224
2.098	3	2.098	2	-	-	-	-	510
2.036	3	2.037	2	-	-	-	-	219
2.024	2	2.024	2	-	-	-	-	318
2.006	3	2.007	1	-	-	-	-	323
1.9697	6	1.9700	7	-	-	-	-	1110
1.9387	20	1.9382	32	-	-	-	-	226
1.8777	20	1.8776	20	-	-	-	-	420
1.8434	8	1.8443	7	-	-	-	-	028
1.8169	4	1.8183	6	-	-	-	-	0012
1.7982	11	1.7978	11	-	-	-	-	516
1.7880	13	1.7879	10	-	-	-	-	604
.7545	14	1.7541	10	-	-	-	-	228
1.7319	11	1.7317	12	-	-	-	-	2012
1.6902	4	1.6901	3	-	-	-	-	1112
1.6791	14	1.6787	11	-	-	-	-	606
1.6689	8	1.6684	6	-	-	-	-	426
1.6474	4	1.6480	2	-	-	-	-	518
1.5809	6	1.5804	5	-	-	-	-	134
1.5588	12	1.5586	12	-	-	-	-	0014
1.5284	8	1.5279	5	-	-	-	-	712
1.5038	7	1.5035	5	-	-	-	-	136
1.4712	8	1.4713	8	-	-	-	-	0212

Table I. X-ray powder diffraction data for synthetic Mn-melilites.

Mn-åkermanite				Sr <sub>2</sub> MnSi <sub>2</sub> O <sub>7</sub> *			
d <sub>obs</sub>	I <sub>obs</sub>	d <sub>calc</sub>	I <sub>calc</sub>	d <sub>obs</sub>	I <sub>obs</sub>	hkl	
5.598 Å	4	5.600 Å	5	5.74 Å	6	110	
5.022	20	5.022	14	-	-	001	
4.242	12	4.241	15	4.34	5	101	
3.955	3	3.960	2	4.06	6	200	
3.738	29	3.739	14	3.83	29	111	
3.542	6	3.542	4	3.63	6	210	
3.108	61	3.109	43	3.19	48	201	
2.895	100	2.894	100	2.96	100	211	
2.799	8	2.800	10	2.87	8	220	
-	-	-	-	2.57	34	002	
2.505	30	2.504	18	-	-	310	
2.445	9	2.446	8	-	-	221	
2.394	13	2.394	8	2.45	6	102	
2.335	6	2.337	8	2.39	7	301	
2.291	6	2.291	4	-	-	112	
2.241	6	2.241	1	-	-	311	
-	-	-	-	2.17	3	202	
2.049	20	2.048	7	2.10	24	212	
1.9786	2	1.9798	1	2.03	5	400	
1.9198	7	1.9207	5	1.966	13	410	
-	-	-	-	1.913	15	330	
1.8708	12	1.8694	8	-	-	222	
-	-	1.8418	2	1.886	6	401	
1.7956	17	1.7940	6	1.838	17	411	
-	-	-	-	-	-	420	
1.7731	34	1.7732	26	1.815	28	420	
1.7491	7	1.7496	4	1.794	15	331	
1.6734	4	1.6749	1	-	-	003	
1.6524	4	1.6532	3	-	-	322	
1.6040	6	1.6039	3	-	-	113	
1.5418	5	1.5419	1	1.579	5	203	
1.5137	7	1.5135	3	1.551	11	213	
1.4841	4	1.4837	3	1.512	7	511	
1.4112	6	1.4113	5	1.446	13	521	

\* Brisi and Abbattista (1961).

1. Black (1969). 2. Agrell and Gay (1961)

and transparent crystals were found to be very similar to those of Sr<sub>2</sub>MnSi<sub>2</sub>O<sub>7</sub> melilite (Brisi and Abbattista, 1961) and kilchoanite (Agrell and Gay, 1961; Black, 1969), respectively. X-ray single-crystal studies, using the precession method, showed the space group of the former to be *P*4̄2<sub>1</sub>*m*. On the other hand, the four possible space groups of the latter were examined by Taylor (1971), whose packing considerations suggested that the space group and orientation described by the symbol *I*2*c**m* were the most likely. Taylor's identification is compatible with the present precession photographs, the crystal structure having been refined successfully in this symmetry. Using isotropic temperature factors, the refinement converged to an unweighted conventional residual of 0.061 for 1238 reflections greater than 3σ<sub>F</sub> collected by the automated Rigaku four-circle diffractometer. Table III shows the refined atomic coordinates and isotropic temperature factors of the present Mn-kilchoanite from which its X-ray powder diffraction pattern

was calculated with the aid of the program POWD5 (Smith and Johnson, 1973). The wavelength used in all calculation was Cu-Kα = 1.54178 Å. This pattern makes no significant difference from the result calculated on the basis of the atomic coordinates and temperature factors of kilchoanite (Taylor, 1971). The diffraction pattern of this Mn-åkermanite was also calculated by the same method, using atomic coordinates and isotropic temperature factors for Sr<sub>2</sub>MnSi<sub>2</sub>O<sub>7</sub> melilite (Kimata, 1985*a, b*). The agreement with the observed patterns is satisfactory. We may, therefore, conclude that these crystals are of melilite- and kilchoanite-structure types.

Cell parameters, determined by refinement of the X-ray powder data with the RSLC-3 of UNICS computer program (Sakurai, 1967), are shown in Table IV. These parameters are in good agreement with those obtained by refinement of the setting angles of the crystals mounted on a Rigaku automatic four-circle diffractometer. Cell parameters of

Table III. Positional coordinates of the atoms in Mn-kilchoanite used for calculating the X-ray powder diffraction pattern.

	x	y	z	B(A)
Ca1	0.0167	0.	0.	0.92
Ca2	0.3097	0.9949	1/4	0.73
Ca3	0.0349	0.0034	0.1700	0.49
Ca4*	0.2447	0.4943	0.1059	1.02
Si1	0.1182	0.4220	1/4	0.82
Si2	0.4371	0.9382	0.1026	0.78
Si3	0.2716	0.	0.	0.82
O1	0.1845	0.2842	0.1909	1.46
O2	0.9854	0.2803	1/4	1.03
O3	0.1166	0.7511	1/4	1.24
O4	0.3731	0.7992	0.1597	0.85
O5	0.0626	0.7022	0.0948	1.13
O6	0.3633	0.8162	0.0421	0.84
O7	0.4326	0.2543	0.0988	1.02
O8	0.1899	0.1838	0.0409	1.15

\* Assumed to be 0.68Mn + 0.32Ca occupancy.

Table IV. Cell dimensions of melilite- and kilchoanite-isomorphs.

Method	Mn-akermanite		Sr <sub>2</sub> MnSi <sub>2</sub> O <sub>7</sub> <sup>1</sup>		Ca <sub>2</sub> ZnSi <sub>2</sub> O <sub>7</sub> <sup>2</sup>	
	powder	single	powder	single	powder	single
a(A)	7.919(1)	7.9191(7)	8.12	7.8279(10)		
c(A)	5.022(1)	5.0218(6)	5.16	5.0138(6)		
V(A <sup>3</sup> )	314.9(1)	314.93(5)	340.2	307.22		
V/Z*	157.47	157.465	170.1	153.61		

Method	Mn-kilchoanite		kilchoanite <sup>3</sup>
	powder	single	powder
a(A)	11.3568(12)	11.356(2)	11.42
b(A)	5.0071(6)	5.007(1)	5.09
c(A)	21.8190(20)	21.817(3)	21.95
V(A <sup>3</sup> )	1240.5(3)	1240.4(3)	1276.
V/Z*	155.4	155.95	159.5

\* Molar volume, where the symbol Z stands for the number of times the formula unit is contained in the unit cell.

1. Brisi and Abbattista (1961).
2. Louisnathan (1963).
3. Agrell and Gay (1961).

the melilite-like phase are intermediate between those of Ca<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub> and Sr<sub>2</sub>MnSi<sub>2</sub>O<sub>7</sub> melilites. This is due to the size relation of cations: both of Ca<sup>2+</sup> and Mn<sup>2+</sup> are larger in ionic radius than Zn<sup>2+</sup>, whereas both are smaller than Sr<sup>2+</sup> (Shannon, 1976). Shrinkages of the parameters in this kilchoanite-like phase, compared with those in natural kilchoanite, are interpreted as due to substitution of Mn<sup>2+</sup> which is of a smaller ionic radius than Ca<sup>2+</sup> (Shannon, 1976).

**Chemical composition.** The resultant chemical values are presented in Table V. The data yield the following empirical formulae, based on seven oxygens: Ca<sub>2.33</sub>Mn<sub>0.67</sub>Si<sub>2.00</sub>O<sub>7</sub> (transparent crystal) and Ca<sub>2.33</sub>Mn<sub>0.68</sub>Si<sub>1.99</sub>O<sub>7</sub> (blue crystal). In comparison, the matrix glass is richer in Mn and poorer in Ca. Åkermanite and kilchoanite have the ideal chemical composition Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> and Ca<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, respectively. As the EPMA results are consistent with the X-ray evidence, the resultant crystals can be identified as Mn-ilchoanite and

Mn-åkermanite. Mn is assumed to be Mn<sup>2+</sup> because of the dark-blue colour of Mn-åkermanite, in contrast to the colourless, transparent nature of åkermanite. This blue colour is in agreement with the visible spectrum of four-coordinated Mn<sup>2+</sup> for the crystal structure of Sr<sub>2</sub>MnSi<sub>2</sub>O<sub>7</sub> melilite determined by Kimata (1985a, b). Therefore it is proved that Mn<sup>2+</sup> in melilite is four-coordinated, whereas in kilchoanite it may be six-coordinated owing to its colourless, transparent property. Moreover, the excess Ca in the Mn-åkermanite may indicate occupancy by four-coordinated Ca<sup>2+</sup> cations, which is a new suggestion in the crystal chemistry of silicates.

Table V. Electron microprobe analyses of run products

	1	2	3
SiO <sub>2</sub>	40.22	40.03	40.46
MnO	15.86	16.06	26.19
CaO	43.71	43.67	31.12
Total	99.79	99.71	97.77

Number of cations on the basis of 7(O)			
Si	2.00	1.99	/
Mn	0.67	0.68	/
Ca	2.33	2.33	/

1. Mn-kilchoanite.
2. Mn-åkermanite.
3. The matrix glass.

**Infra-red spectroscopy.** The spectra of Mn-kilchoanite and Mn-åkermanite are illustrated in fig. 1. The spectrum of the former, apart from a shift of the absorption bands below 600 cm<sup>-1</sup> towards the lower wavenumber side, is very similar to that of synthetic kilchoanite Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> reported by Roy (1958). This shift can be explained by substitution of Mn<sup>2+</sup> for Ca<sup>2+</sup>, namely the reduced mass effect of Mn. One Mn in a Ca site perturbs their IR vibrations from 953 to 945 cm<sup>-1</sup>. This perturbation is the same as the effect of Mn<sup>2+</sup> partially substituting for Ca<sup>2+</sup> in fluorapatite (Suitch *et al.*, 1985). Further confirmation is found in that Mn-kilchoanite does not include the H<sub>2</sub>O and CO<sub>2</sub> molecules coordinated crystal-structurally. Ortho-silicates do not usually adsorb in the region around 765 cm<sup>-1</sup> (Farmer, 1974), which is common to this Mn-kilchoanite, too. The spectrum of Mn-åkermanite closely parallels that of hardystonite Ca<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub> (Kimata, 1980), which implies the ordered distribution of both tetrahedral Mn<sup>2+</sup> and Si<sup>4+</sup> cations, judging from the IR spectrum of gehlenite isomorphs with partially disordered

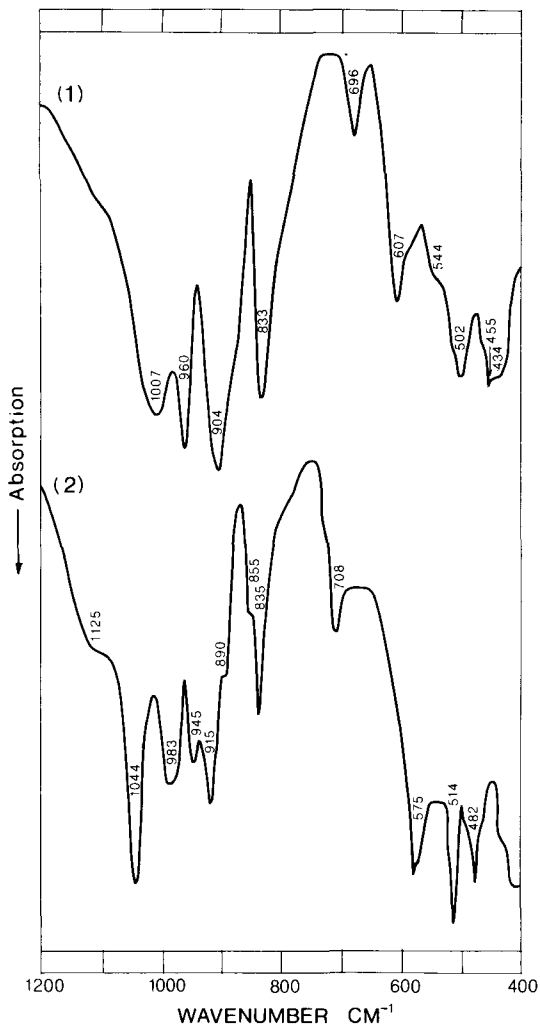


FIG. 1. Infra-red absorption spectra of Mn-åkermanite (1) and Mn-kilchoanite (2).

tetrahedral cations (Kimata, 1980). The infra-red results are thus consistent with the X-ray evidence.

*Polymorphic development of melilite.* The reason why the phase isostructural with rankinite, dimorphous with kilchoanite, does not occur in the present syntheses is essential for systematizing the 'crystallo-chemical evolution of a mineral' (Kimata, 1985a, b). Heating experiments on natural kilchoanite at 1000°C for 10 hr confirmed that the single crystal transforms into a polycrystalline aggregate of rankinite (Agrell, 1965). It is evident from the natural occurrence that kilchoanite represents a lower temperature, retrograde phase of rankinite (Baker and Black, 1980). Inasmuch as

$Mn^{2+}$  is of smaller ionic radius than  $Ca^{2+}$  (Shannon, 1976), substitution of Mn for Ca coincides with shrinkage of the Ca-polyhedra due to temperature lowering. Furthermore, the crystal structure determination of these dimorphs proved that the averaged Ca-O bond length, 2.376 Å, in kilchoanite (Taylor, 1971) is clearly shorter than 2.445 Å in rankinite (Saburi *et al.*, 1976). Kilchoanite has the six-coordinated site more suitable for  $Mn^{2+}$  with a smaller ionic radius. Accordingly, appearance of Mn-kilchoanite instead of the corresponding rankinite is crystallo-chemically possible. The above result is in accordance with the suggestion by Hazen (1977) that certain temperature-pressure-composition isostructural surfaces may coincide with phase boundaries.

The crystal structures of polymorphs are sensitive to external secondary conditions, such as formation temperature, pressure, and impurities, but if the external conditions are the same, their crystallo-chemical properties hold the key to determining the stability relation between their polymorphs. The euhedron of natural kilchoanite has been unknown (Taylor, 1971), but examination under a petrographic microscope shows that the present Mn-kilchoanite, enclosed by the brown glass, is lath-shaped and Mn-åkermanite is of a similar shape. As shown in Table IV, the molar volume of Mn-åkermanite is clearly larger than that of Mn-kilchoanite. Moreover four-coordinated Mn cations in the former contrast with six-coordinated Mn cations in the latter. The general concept that high temperatures and low pressures favour low coordination (Mason, 1966) can be considered to apply to the behaviour of  $Mn^{2+}$  cation in these silicates. The average Ca-O distance in the eight-coordinated Ca of åkermanite is 2.576 Å (Kimata and Ii, 1981) whilst that in kilchoanite is 2.51(2) Å (Taylor, 1971). The former polyhedron is of a more expansive type than the latter. However, several heating experiments on Mn-kilchoanite did not cause the transformation into Mn-kilchoanite. Melilite has tetrahedral sites except for the Si sites, whereas kilchoanite has six-coordinated sites. Changing the coordination number of Mn cations between these phases requires a large activation energy. This transformation may therefore be sluggish (Buerger, 1951). The general rule that a symmetry of the high-temperature form is higher than that of the low-temperature form (Buerger, 1951), as evident from Table IV, is favourable for identifying the present polymorphous forms. The crystallo-chemical evidence for the polymorphic relationship between these two compounds is summarized in Table VI. We may, therefore, reasonably conclude that Mn-åkermanite is a higher temperature structure type of Mn-kilchoanite.

Table VI. Evidence in favour of the polymorphic relationship between Mn-akermanite and Mn-kilchoanite.

	Mn-akermanite	Mn-kilchoanite
Symmetry	tetragonal	orthorhombic
Space group	$P\bar{4}_2m$	I2cm
Molar volume(A <sup>3</sup> )	157.465	155.05
C.N. of Mn <sup>2+</sup>	IV	VI
Ca-O distance(A)	2.576*	2.51(1)**
Polymorphic type	high form	low form

\* Kimata and Ii (1981).

\*\* Taylor (1971).

The existence of reconstructive-type polymorphs in melilite compounds will play a new and important role in systematizing the crystal chemistry of rock-forming minerals, as well as silicates and sulphide compounds. As evident from the intermediate substitution of Mn<sup>2+</sup> between Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> and Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>:  $Mg^{2+} \rightleftharpoons (Ca^{2+} + Mn^{2+}) \rightleftharpoons Ca^{2+}$ , it may well be that this type of substitution can be prerequisite to developing the polymorphic relationship between minerals or solid compounds. In conclusion, we recommend thorough study of this type of substitution to take advantage of the possibility that it provides important clues to systematizing the different crystal structures of minerals with similar formulae.

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