RHODONITE-PYROXMANGITE PERITECTIC ALONG THE JOIN MnSiO$_3$–MgSiO$_3$ IN AIR[1]

JUN ITO, *Department of Geological Sciences, Harvard University, Cambridge, Massachusetts 02138*

ABSTRACT

In the MnSiO$_3$-MgSiO$_3$ join a pyroxmangite-rhodonite peritectic exists on the liquidus at a composition of approximately (Mn$_{0.67}$Mg$_{0.33}$)SiO$_3$ at 1350°C $\pm$ 5°C in air. Unit-cell dimensions are given for the continuous solid-solutions of pyroxmangite at compositional range (Mn$_{0.60}$Mg$_{0.40}$)SiO$_3$—(Mn$_{0.10}$Mg$_{0.90}$)SiO$_3$ and for rhodonite at compositional range (Mn$_{0.60}$Mg$_{0.40}$)SiO$_3$—MgSiO$_3$.

Single crystals of pyroxmangite, (Mn$_{0.50}$Mg$_{0.50}$)SiO$_3$ and rhodonite, (Mn$_{0.80}$Mg$_{0.20}$)SiO$_3$ were grown to a maximum size of 5mm $\times$ 3mm $\times$ 2mm by slow cooling of the melts. At 1200°C in air, the join MnSiO$_3$—MgSiO$_3$ consists of four phases, *i.e.*, triclinic rhodonite, at MnSiO$_3$—(Mn$_{0.55}$Mg$_{0.45}$)SiO$_3$; triclinic pyroxmangite, at (Mn$_{0.50}$Mg$_{0.50}$(SiO$_3$—(Mn$_{0.25}$Mg$_{0.75}$)SiO$_3$; clinopyroxene, at (Mn$_{0.20}$Mg$_{0.80}$)SiO$_3$—(Mn$_{0.15}$Mg$_{0.85}$)SiO$_3$ and orthorhombic protoenstatite, at (Mn$_{0.10}$Mg$_{0.90}$)—MgSiO$_3$. The phase transformation at fixed P and T for (Mn, Mg)SiO$_3$ appears to be controlled by the mean cationic radii for the variable Mn and Mg contents. A narrow but distinct rhodonite-pyroxmangite coexistence region is found below the solidus around (Mn$_{0.50}$Mg$_{0.50}$)SiO$_3$—(Mn$_{0.55}$Mg$_{0.45}$)SiO.

INTRODUCTION

A discontinuous solid-solution (rhodonite-pyroxene[2]) in the join MnSiO$_3$–MgSiO$_3$ under atmospheric pressure, with a break in the liquidus profile at approximately 50 mol percent MgSiO$_3$ and 1330°C, was first noted by Lebedew (1911). The phase equilibrium study by Glasser and Osborn (1960) using a controlled atmosphere (H$_2$ 20 percent and CO$_2$ 80 percent) along this join defined an unbroken rhodonite solid-solution series. It extended from the MnSiO$_3$ end member (incongruent M.P. 1291°C) to compositions containing a maximum of 94.5 wt percent of MgSiO$_3$ at 1454°C. These authors, however, noted that the X-ray powder diffraction pattern of 10 MnSiO$_3$·90 MgSiO$_3$ wt percent appeared significantly different from that of rhodonite, but they presented no crystallographic data.

In the present study quenching and slow cooling carried out in the air at temperatures ranging from 1200°C to 1520°C reveals a pyroxmangite-rhodonite peritectic at 1350°C $\pm$ 5°C at approximately (Mn$_{0.67}$Mg$_{0.33}$)SiO$_3$ as found by Lebedew (1911) at (Mn$_{0.50}$Mg$_{0.50}$)SiO$_3$.

---

[1] Mineralogical Contribution No. 486.

[2] Since pyroxmangite was not established as a valid species until 1913 (Ford and Bradley), Lebedew described the MgSiO$_3$-rich phase as orthorhombic pyroxene, but this was no doubt pyroxmangite.

A tentative phase diagram along this join, the result of the crystal growth attempts for both rhodonite and pyroxmangite, and a crystal chemical discussion on the formation of pyroxenoids are given in this paper.

<div align="center">Experimental Method</div>

Starting materials used for this study were mixtures of the analyzed C. P. grade reagents of silicic acid, manganese carbonate, and magnesium hydroxide. These were thoroughly ground with a small amount of ethyl alcohol in an agate mortar. The charges were placed in a platinum container and were heated in a pre-heated silicon carbide furnace. Temperatures were controlled within 5°C by a proportional controller using a Pt-Rh$_{10}$ percent thermocouple. The products were quenched to room temperature, except in the case of single crystal growth experiments (Table 1) in which the crystals were slowly cooled to room temperature in order to avoid thermal shock. For the synthesis runs approaching two phase boundaries at temperatures considerably below (>50°C) solidus, at least two grindings and repeated heating were necessary to reach equilibrium. Mixtures of crystalline rhodonites and pyroxmangites with the different Mn/Mg ratio obtained by the slow cooling experiments (Table 1) were used as starting materials for the experiments in establishing subsolidus equilibrium between rhodonite and pyroxmangite at 1250°C. The reaction between the rhodonites and the pyroxmangites having the different chemical compositions took place within 100 hours to reach equilibrium. The samples were thoroughly ground every 24 hours. The detailed results of quenching experiments summarized in Table [I] have been deposited with the National Auxiliary Publication Service[1].

Unit-cell dimensions were measured using X-ray powder diffraction (CuKα_1 with Si standard) and refined with a least square computer program written by Dr. Daniel Appleman of the U.S. Geological Survey. Indexing of the diffraction peaks was facilitated using both the existing data of Lindsley and Burnham (1970), Momoi (1969), and Chao *et al.* (1970) and the intensity data observed on the precession single crystal photographs. These were taken at three axes for the natural pyroxmangite from Taguchi, Japan (Momoi, 1964) and two synthetic pyroxmangite crystals grown from melts having the compositions of $(Mn_{0.50}Mg_{0.50})SiO_3$ and $(Mn_{0.20}Mg_{0.80})SiO_3$.

<div align="center">Results and Discussion</div>

Unit-cell Data

The unit-cell dimensions for the eight pyroxmangites synthesized in air within the solid-solution range $Mn_{0.10}Mg_{0.90}SiO_3 - Mn_{0.60}Mg_{0.40}SiO_3$, and the five pyroxmangites synthesized hydrothermally within the solid-solution range $Mn_{0.60}Mg_{0.40} - MnSiO_3$ are listed in Table [II] together with the data for $MnSiO_3$ II (pyroxmangite)

[1] To obtain a copy of this material, order NAPS Document Number 01770 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 866 Third Avenue, New York, New York 10022; remitting $2.00 for microfiche or $5.00 for photocopies, in advance, payable to CCMIC-NAPS.

Table 1. Results of slow cooling of melts.

Melt Composition	Temperature range (°C)			Cooling rate °C per hour	Products
	melt	soaking (hour)	end		
$(Mg_{.80}Mn_{.20})SiO_3$	1500	3	1150	3	Pink pyroxmangite crystals 3x2x2mm.
$(Mg_{.70}Mn_{.30})SiO_3$	1490	5	1200	3	Aggregates of small pyroxmangite crystals.
$(Mg_{.60}Mn_{.40})SiO_3$	1470	5	1200	3	Light brown pyroxmangite crystals 1x1x0.2mm.
$(Mg_{.50}Mn_{.50})SiO_3$	1450	5	1180	3	Large light brown pyroxmangite crystals 5x3x2mm with small rhodonite.
$(Mg_{.45}Mn_{.55})SiO_3$	1500	3	1180	3	Massive pyroxmangite mixed with a small amount of rhodonite.
$(Mg_{.43}Mn_{.57})SiO_3$	1500	2	1180	5	Massive mixture of pyroxmangite and rhodonite with pyroxmangite fringe and rhodonite dome.
$(Mg_{.40}Mn_{.60})SiO_3$	1450	6	1180	6	Massive mixture of pyroxmangite and rhodonite with domes of pure rhodonite.
$(Mg_{.35}Mn_{.65})SiO_3$	1400	3	1300	25	Massive rhodonite and pyroxmangite.
$(Mg_{.34}Mn_{.66})SiO_3$	1400	3	1300	20	Massive rhodonite and pyroxmangite.
$(Mg_{.32}Mn_{.68})SiO_3$	1400	3	1300	20	Massive rhodonite
$(Mg_{.30}Mn_{.70})SiO_3$	1420	6	1180	3	Massive rhodonite.
$(Mg_{.25}Mn_{.75})SiO_3$	1420	5	1180	3	Rhodonite and cristobalite.
$(Mg_{.20}Mn_{.80})SiO_3$	1440	5	1180	10	Crystals of rhodonite 5x4x2mm with opaque inclusion.
$(Mg_{.10}Mn_{.90})SiO_3$	1400	1	1200	10	Crystals of rhodonite and small tridymite.
$(MnSiO_3$	1350	1	1240	5	Massive rhodonite and tridymite.
0.55 MnO + 0.45 SiO_2	1300	6	1200	2	Rhodonite crystals and manganese oxides.

synthesized by Akimoto and Syono (1972) under high-pressure; the same data are presented graphically in Figures 2 and 3.

The unit-cell dimensions for the six synthetic rhodonites within the solid-solution range $Mn_{0.55}Mg_{0.45}SiO_3$—$MnSiO_3$ synthesized in air are given in Table [III] with the other data obtained for $MnSiO_3$ synthesized under H_2O total pressure (Momoi, 1969; present study), and

dry high-pressure (Akimoto and Syono, 1972); the data are also plotted graphically in Figure 4.

Tables [II] and [III] have been deposited with the National Auxiliary Publication Service[1].

The changes observed for the unit-cell dimensions of the pyroxmangite series (Figs. 2 and 3) are almost linear functions of Mn and Mg contents. Yet there is some evidence for lack of linearity. The observed small gap at the composition $Mn_{0.60}Mg_{0.40}SiO_3$ between the two series of pyroxmangites synthesized one in the air (left) and the other under water pressure (right) may not be significant enough to discuss unless more information on the vapor phase activities and the precise compositional data are obtained.

The unit-cell dimensions of the rhodonites series (Fig. 4) are more nearly linear with composition than those of the pyroxmangite series.

Phase Study

The tentative phase diagram for the join $MnSiO_3$–$MgSiO_3$ in air between 1200°C and 1520°C is constructed using the results of the present study (Table 1 and Table [1]). These distinctly show the rhodonite-pyroxmangite peritectic at 1350°C ± 5°C at approximately $(Mn_{0.67}Mg_{0.33})SiO_3$. The region above 1520°C is excluded because of the complexity expected from the results of the detailed study by Glasser and Osborn (1960) at temperatures above 1520°C and compositions between $MgSiO_3$ and $(Mg_{0.90}Mn_{0.10})SiO_3$. On the whole, the results of Glasser and Osborn (1960) and those of the present work agree well except for the peritectic, although the latter experiments were carried out in air; the diagram presented here does not represent a true binary system, since a small amount of higher valency ionic manganese (excess oxygen)—other than divalent manganese—is present, particularly in compositions over $MnSiO_3$ 60 mol percent. The amount of Mn_2O_3 in the bulk sample of $(Mn_{0.70}Mg_{0.30})SiO_3$, mainly due to the admixed unidentified manganese oxides, was found to be 0.2 wt percent, and the amount increases progressively up to 1.5 wt percent at the $MnSiO_3$ composition. However, the compositions having Mg contents higher than 40 mol percent are virtually free from any appreciable amount of Mn_2O_3, especially in the silicate crystals. The amount of higher valency manganese in rhodonite, $MnSiO_3$ quenched at over 1200°C in air is in fact negligible (Muan, 1959). In any case, the phase diagram of this join may require complete restudy under controlled partial pressure of oxygen P_{o_2}.

---

[1] See footnote on page 865.

A significant difference in the composition for the peritectic point, between Lebedew (1911) and the present study, is most likely due to the considerable difference of P_{O_2} in the two experiments. The P_{O_2} in a carbon crucible at high-temperature (used by Lebedew) is considerably lower than that for heating in a platinum container in air.

There is a narrow but distinct two-phase region for rhodonite and pyroxmangite at the solidus composition around $(Mn_{0.52}Mg_{0.48})SiO_3$. In the subsolidus, this two-phase region shifts toward $MnSiO_3$ side as temperature lowers. At 1250°C, equilibrium was reached at the composition around $(Mn_{.55}Mg_{.45})SiO_3$. The fact is consistent with the results of the hydrothermal (Momoi, 1968 and present study) and the dry high-pressure (Akimoto and Syono, 1972) synthesis of rhodonite-pyroxmangite dimorph with composition $MnSiO_3$.

A small subsolidus region for clinopyroxene was also found near the Mg side (Fig. 1) at the temperatures 1200°–1300°C and the composition $Mn_{0.20}Mg_{0.80}SiO_3$ of this diagram. This clinopyroxene belongs to the isomorphous series extending through $(Mn_{0.50}Mg_{0.50})SiO_3$ (hydrothermal) to the end member $MnSiO_3$—III (high-pressure clinopyroxene) synthesized by Akimoto and Syono (1972).

No critical attempt was made to establish the subsolidus equilibrium boundaries between two pyroxenes and pyroxmangite. The two-phase areas given shaded in the left hand side of this diagram (Fig. 1) are synthesis boundaries.

Single Crystal Growth

Single crystals of $(Mn, Mg)SiO_3$ (over Mg_{50} mol percent) pyroxmangite have been obtained by slow cooling of clear melt for some of the compositions within the join $MnSiO_3$—$MgSiO_3$. The largest crystal measures $5 \times 3 \times 2$ mm at $(Mn_{0.50}Mg_{0.50})SiO_3$. Medium size ($3 \times 2 \times 2$ mm) crystals were obtained for $(Mn_{0.20}Mg_{0.80})SiO_3$. Only small crystals were grown of $(Mn_{0.30}Mg_{0.70})SiO_3$ and $(Mn_{0.40}Mg_{0.60})SiO_3$. All the crystals are light amber in color. The color intensifies progressively with increasing amount of manganese in the crystals. The color turns to pink by heating at 1250°C for several hours, due to reduction of the trace amount of higher valency manganese in the crystals.

Single crystals of rhodonite were grown to $5 \times 4 \times 2$ mm for the composition $(Mn_{0.80}Mg_{0.20})SiO_3$ by fairly rapid cooling (in air at 10°C/hour) of melt. Small crystals of $(Mn_{0.90}Mg_{0.10})SiO_3$ and $(Mn_{0.70}Mg_{0.30})SiO_3$ were also obtained. The crystals are dark red in color, and always contain some opaque dots which probably are hausmannite Mn_3O_4; the Mn_2O_3 content of the bulk crystalline aggregates for $(Mn_{0.80}Mg_{0.20})SiO_3$ was found to be 0.5 wt percent. These rhodonites

also turn to bright pink by heating in a reducing atmosphere, as mentioned above.

Single crystals of pure end member rhodonite were grown from a melt having the composition MnO 55 and SiO_2 45 mol percent (congruent melting), in air, by slow cooling from 1300°C to 1200°C at a rate of 5°C per hour; this procedure is based on the phase diagram given by Muan (1959).

Crystal Chemistry

Presence of five and seven silicate chain repeat units in rhodonite and pyroxmangite respectively, has been first found by Liebau (Liebau, 1957, 1959; Liebau, Hilmer, and Lindemann, 1959). Chemical analyses of natural pyroxmangites show ratios of Ca^{2+} to $(Fe^{2+} + Mg^{2+} + Mn^{2+})$ less than 1:6. No rhodonites have Ca contents more than that needed to completely fill one out of five cation sites (Deer, Howie, and Zussman, 1963). In view of its size and coordination, there is no doubt that Ca^{2+} has an important role in limiting compositional range of pyroxenoid structure type. Based on the chemical data, Liebau indicated Ca-ordered structures for both rhodonite and pyroxmangite, but no actual evidence for the ordered structure was given. He suggested the following formulae for rhodonite $Ca_x(Mn, Mg)_{1-x} SiO_3$ with $0 < x < 0.2$ and for pyroxmangite $(Ca, Mg)(Mn, Fe)_6 Si_7O_{21}$.

In the recent crystal structure refinement of rhodonite, Peacor and Niizeki (1963) assigned Ca^{2+} in M_5 site with the largest metal oxygen distance, and Mg^{2+} and Fe^{2+} in M_4 site while the other three sites are predominantly occupied by Mn^{2+}.

In a review paper on pyroxene and pyroxenoid crystal chemistry, Prewitt and Peacor (1964) indicated that pyroxmangite structure may also follow the same trend as rhodonite. In such a structure, Ca^{2+} may enter exclusively one out of seven cation sites.

Until recently, the above ordered structure hypothesis has been well accepted in most of the mineralogical literature. A complete summary made by Chao *et al.* (1970) for the existing chemical analysis of the terrestrial pyroxmangite did not, however, support the formula suggested by Liebau (1957). Furthermore, a rhodonite-pyroxmangite dimorph with the composition $MnSiO_3$ has been synthesized hydrothermally (Momoi, 1968) and under anhydrous high-pressure conditions (Akimoto and Syono, 1972), indicating that Ca or other divalent ions other than Mn^{2+} are not essential for chain repeat units of 5 or 7 silicon tetrahedra.

Single silicate chains that repeat after every nine silicon tetrahedra were found by Burnham (1966) in ferrosilite III, a new pyroxenoid,

$FeSiO_3$ (Lindsley, Davis and MacGregor, 1964). The fact led Lindsley and Burnham (1970) to believe that Ca^{2+} is not essential for the 7 repeats of structure formation of pyroxferroite. They predicted that Ca-free pyroxmangite may be stable on the $FeSiO_3$—$MnSiO_3$ join particularly at Mn-rich compositions.

Latest results of the crystal structure study of lunar pyroxferroite, $Ca_{0.13}Fe_{0.83}Mn_{0.02}Mg_{0.02}Si_{3.00}$ (Burnham, 1971) showed that Ca is distributed over three different sites (M_5, M_6, and M_7) of pyroxmangite type structure, not restricted in a single M_7 site.

The results of the present study now show solid solutions of pyroxmangite over the compositional range $(Mn_{0.50}Mg_{0.50})SiO_3$—$(Mn_{0.10}Mg_{0.90})SiO_3$ and rhodonite over the compositional range $(Mn_{0.55}Mg_{0.45})SiO_3$—$MnSiO_3$, both in air (Fig. 1), along the join $MnSiO_3$—$MgSiO_3$. The isomorphous pyroxmangite series extends all the way to $MnSiO_3$ under hydrothermal conditions (Figs. 2 and 3). The study made by Riboud
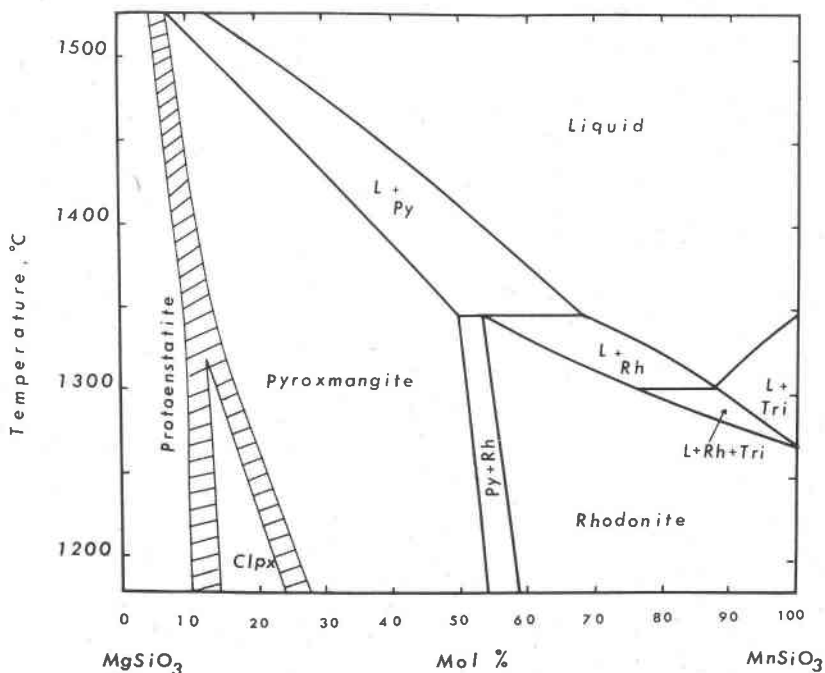
Fig. 1. Phase diagram for the join $MnSiO_3$–$MgSiO_3$ at temperatures between 1200°C and 1520°C in air. Py = pyroxmangite, Rh = rhodonite, Tri = tridymite, Clpx = clinopyroxene, Pr = protoenstatite and L = liquid. Shaded area = two-phase coexisting region. Unidentified manganese oxides observed microscopically at the composition $MnSiO_3$ over 60 mol% are not included.
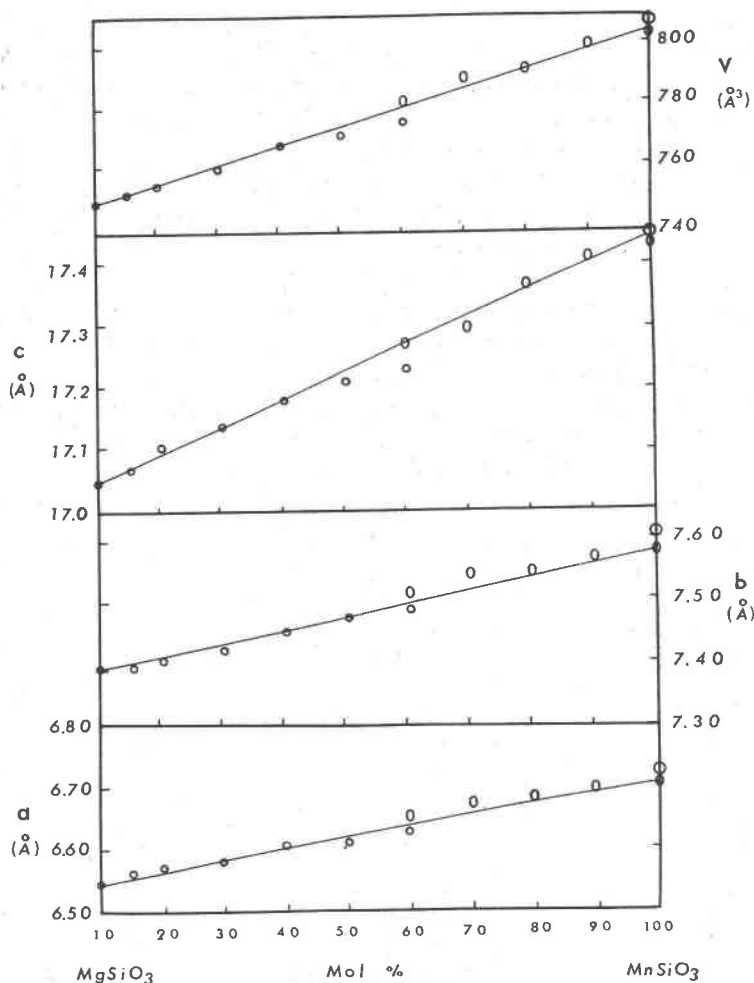
Fig. 2. Unit-cell edges and volumes of synthetic pyroxmangites, $(Mn,Mg)SiO_3$. Small open circles = pyroxmangites synthesized in air at high temperature. Open ellipses = pyroxmangites synthesized hydrothermally. Large open circles = pyroxmangites synthesized at high-pressure and high-temperature (Akimoto and Syono, 1972).

and Muan (1962) under $CO_2/H_2 = 1:1$, 1 atm. showed that rhodonite solid-solution extends to $(Mn_{0.52}Fe_{0.48})SiO_3$ wt percent, but no pyroxmangite phase was observed by them in one atm experiments in the join $MnSiO_3$—$FeSiO_3$. It is known that the original specimen of pyroxmangite described by Ford and Bradley from Iva, South Carolina,

is in fact manganoan pyroxferroite (Chao *et al.*, 1970; Lindsley and Burnham, 1970) with the formula $(Fe_{.55}Mn_{.41}Ca_{.04})SiO_3$, but neither rhodonite nor pyroxmangite containing more than 6 wt percent of MgO has been found in nature. Site occupancies of both Mg and Fe^{2+} in these synthetic pyroxenoids should be investigated.

In a study of the high pressure transformation of $MnSiO_3$, Akimoto and Syono (1972) stated that

When $MnSiO_3$ is subjected to high pressure, the Mn^{2+}/Si^{4+} ionic radius ratio is expected to become smaller since the larger Mn^{2+} ions tend to contract more than the small Si^{4+} ions. Hence, it may be reasonable to presume that high pressure phase of $MnSiO_3$ is turned into the pyroxenoid and pyroxene (rhodonite-pyroxmangite-clinopyroxene) corresponding to the smaller average size of the octahedral cations.

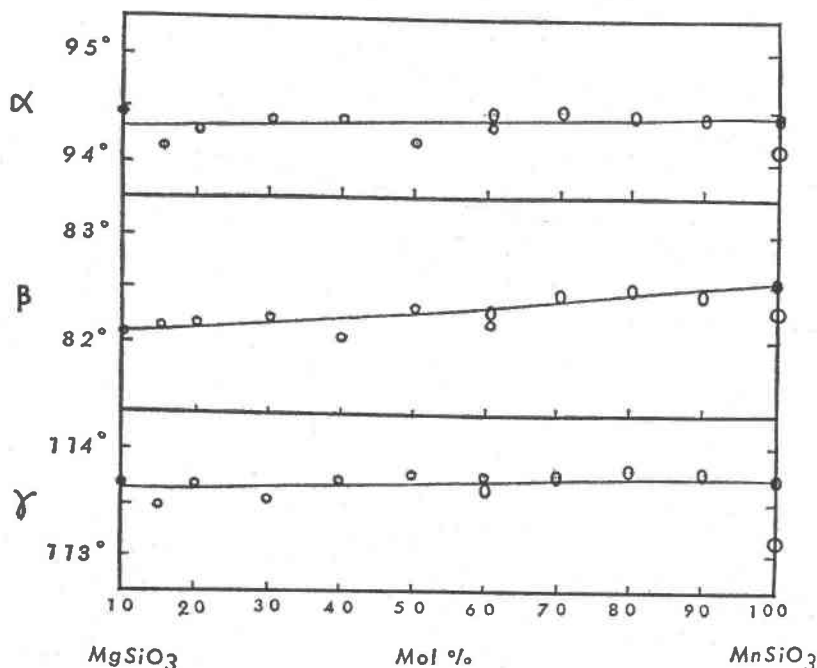The results of the present study have demonstrated analogous trans-

FIG. 3. Unit-cell axial angles α, β, and γ of synthetic pyroxmangites, (Mn, Mg)SiO₃. Small open circles = pyroxmangites synthesized in air at high temperature. Open ellipses = pyroxmangites synthesized hydrothermally. Large open circles = pyroxmangites synthesized at high-pressure high-temperature (Akimoto and Syono, 1972).
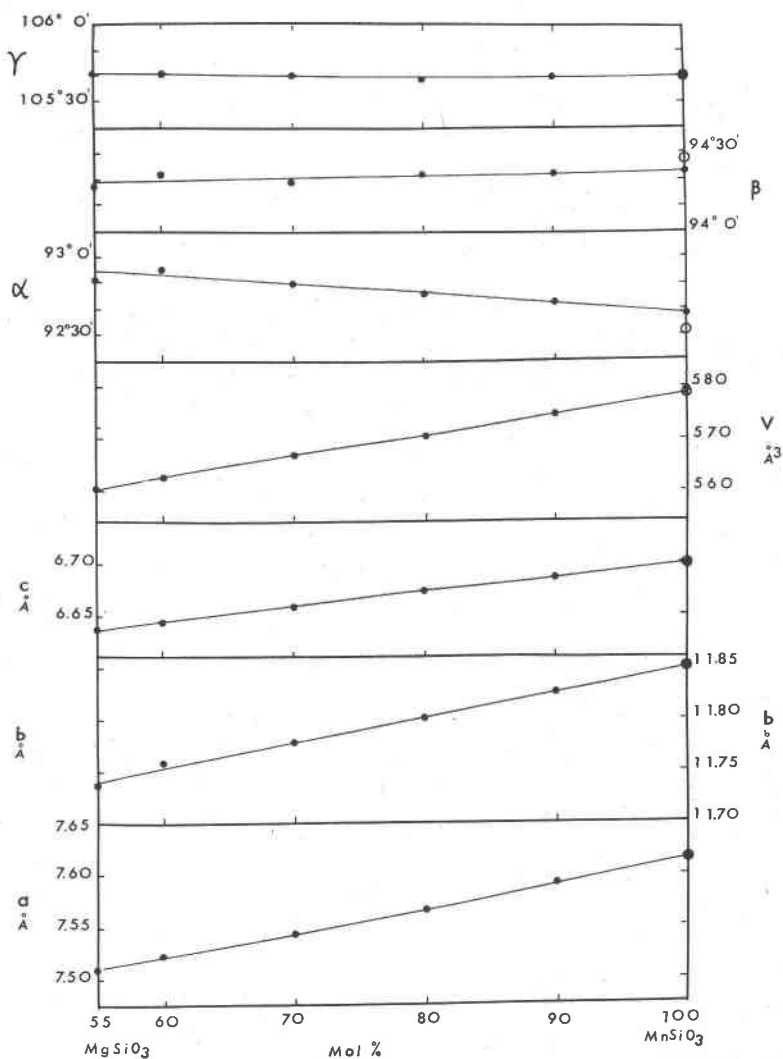
FIG. 4. Unit-cell dimensions of synthetic rhodonites, (Mn, Mg)SiO₃. Black circles = rhodonites synthesized in air at high-temperature. Open circles = rhodonite synthesized hydrothermally.

formations by progressively replacing octahedral Mn^{2+} (0.83Å)[1] by smaller Mg^{2+} (0.72Å)[1] at fixed temperatures under atmospheric pressure. These results thus confirm that the most important controlling factor for these phase transformations is average cation size at given

---

[1] Ionic radii by R. D. Shannon and C. T. Prewitt (1969).

P and *T*. In addition, the presence of wide ranging solid-solution series for pyroxmangites and rhodonites in the join $MnSiO_3$–$MgSiO_3$ suggests that Mg^{2+} ions must be distributed over several sites in the structure of rhodonite and pyroxmangite; they cannot be restricted to a single site.

The garnet-like tetragonal phase with 6-coordinated Si^{4+} obtained by Akimoto and Syono (1972) under ultra-high pressure has not been synthesized under the conditions used for the present study. This suggests, as would be expected, that Si^{4+} does not occupy 6-coordinated sites under low pressure conditions.

Primary crystallization of rhodonite in rhyolite was found at Kesebol, Sweden (Geijer, 1961), but most naturally occuring rhodonites and pyroxmangites have been found in contact metamorphic, metasomatic or pegmatitic rocks in which the crystallization temperatures of these minerals are much lower than those used in this study, and H_2O vapor is always present. Similar crystallization of manganese metasilicates under atmospheric conditions was found in various slags. No serious attempt was made to correlate the results of the experiments in air to any of the natural occurrences. Nevertheless, this study demonstrates that under the proper conditions of pressure, temperature and composition, rhodonite and pyroxmangite can coexist in equilibrium. Although these conditions are undoubtedly rare in nature, this assemblage when found could represent an approach to equilibrium. Such an example of intimate intergrowth of rhodonite and pyroxmangite has been described by Burrell (1942) in specimens from Broken Hill, New South Wales, Australia.

References

AKIMOTO, S., AND Y. SYONO (1972) High pressure transformation in $MnSiO_3$. *Amer. Mineral.* **57**, 76–84.

BURNHAM, CHARLES W. (1966) Ferrosilite III: A triclinic pyroxenoid-type poly-morph of ferrous metasilicate. *Science,* 154, 513–516.

——— (1971) The crystal structure of pyroxferroite from Mare Tranquillitatis. *Proc. 2nd Lunar Sci. Conf.* 1, 47–57, The MIT Press.

BURRELL, H. C. (1942) *A Statistical and Laboratory Investigation of Ore Types at Broken Hill, Australia.* Ph.D. Thesis, Harvard University, pp. 372–373.

DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1963) *Rock-forming minerals. Vol. 2,* John Wiley and Sons, Inc., New York, p. 184, 198, and 202

FORD, W. E., AND W. M. BRADLEY (1913) Pyroxmangite, a new member of the pyroxene group and its alteration products, skemmatite. *Amer. J. Sci., Ser. 4,* 36, 169–174.

GEIJER, PER (1961) The maganese, iron and copper mineralization at Kresbol in Dalsland, Southwestern Sweden. *Bull. Geol. Inst. Univ. Uppsala* 40, 37–49. (Chem. Abstr. 55, 21999i).

GLASSER, F. P., AND E. F. OSBORN (1960) The ternary system MgO-MnO-SiO_2. *J. Amer. Ceram. Soc.* 43, 132–140

LEBEDEW, P. (1911) Schmelzversuche an einigen Bisilikaten. *Z. Anorg. Allgem. Chem.* 70, 301–324.

LIEBAU, VON F. (1957) The crystal structures of rhodonite, $CaMn_4$ [Si_5O_{15}] and pyroxmangite, $(Ca, Mg)(Mn, Fe)_6$ [Si_7O_{21}]. *Acta Crystallogr.* 10, 761.

——— (1959) Über die Kristallstruktur des Pyroxmangits $(Mn, Fe, Ca, Mg)SiO_3$. *Acta Crystallogr.* 12, 177–181.

——— W. HILMER, AND VON G. LINDEMANN (1959) Über die Kristallstruktur des Rhodonits $(Mn, Ca)SiO_3$. *Acta Crystallogr.* 12, 182–187.

LINDSLEY, D. H., AND C. W. BURNHAM (1970) Pyroxferroite: Stability and X-ray crystallography of synthetic $Ca_{.15}Fe_{.85}SiO_3$ pyroxenoid. *Science,* 168, 364–367.

MOMOI, H. (1964) Mineralogical study of rhodonites in Japan with special ref-erence to contact metamorphism. *Mem. Fac. Sci. Kyushu Univ. Ser. D. Geol.* 15, 39–63

——— (1968) Some manganese pyroxenoids. *Jap. J. Mineral. Soc.* 8, 1–5.

——— (1969) Determination of lattice constant by X-ray diffractometer, with an example applied to rhodonite. *Sci. Rep., Fac. Sci. Kyushu Univ., Ser. D. Geol.* 9, 59–65.

MUAN, A. (1959) Phase equilibrium in the system manganese oxide-SiO_2 in air. *Amer. J. Sci.* 257, 297–315.

PEACOR, D. R., AND N. NIIZEKI (1963) The redetermination and refinement of the crystal structure of rhodonite, $(Mn, Ca)SiO_3$. *Z. Kristallogr.* 119, 98–116.

PREWITT, C. T., AND D. R. PEACOR (1964) Crystal chemistry of the pyroxenes and pyroxenoids. *Amer. Mineral.* 49, 1527–1542.

RIBOUD, P. V., AND A. MUAN (1962) Phase equilibria in a part of the system "FeO"-MnO-SiO_2. *Trans. AIME,* 224, 27–33.

SHANNON, R. D., AND C. T. PREWITT (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.* B25, 925–946.