

**Zeitschrift:** Schweizerische mineralogische und petrographische Mitteilungen =  
Bulletin suisse de minéralogie et pétrographie

**Band:** 66 (1986)

**Heft:** 3

**Artikel:** Constraints on some phase relations in the system CaO-MnO-MgO-  
K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O inferred from mineral data from Buritirama,  
Brazil

**Autor:** Schultz-Güttler, R.A. / Peters, Tj. / Valarelli, J.V.

**DOI:** <https://doi.org/10.5169/seals-50896>

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# **Constraints on some phase relations in the system CaO–MnO–MgO–K<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–CO<sub>2</sub>–H<sub>2</sub>O inferred from mineral data from Buritirama, Brazil**

von *R. A. Schultz-Güttler*<sup>1</sup>, *Tj. Peters*<sup>1</sup>, *J. V. Valarelli*<sup>2</sup>

## **Abstract**

Additional mineral data from Buritirama, Pará (Brazil) permit to define some phase relations in the system CaO – MnO – MgO – K<sub>2</sub>O – Al<sub>2</sub>O<sub>3</sub> – SiO<sub>2</sub> – CO<sub>2</sub> – H<sub>2</sub>O. These data complement the earlier ones given by PETERS et al. (1977) and confirm the presence of a clinopyroxene of near MnMgSi<sub>2</sub>O<sub>6</sub> composition, kanoite, at Buritirama.

The data for carbonates, clinopyroxenes and amphiboles constrain the compositions of solid solutions under the given metamorphic conditions of about 550 °C, 3 kbar total pressure. The phase relations shown are valid for high partial pressures of CO<sub>2</sub>.

Coexisting pyroxmangites and rhodonites define a considerable miscibility gap at this locality compared with other occurrences described in the literature.

*Keywords*: Phase relations, manganese, solid solution, Buritirama.

## **Introduction**

As part of a current study of metamorphism of carbonatic-silicatic manganese protoses of Brazil, the manganese deposit of Buritirama in the state of Pará offers a good opportunity to investigate and define some phase relations in the rather complex system CaO–MnO–MgO–K<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–CO<sub>2</sub>–H<sub>2</sub>O.

The geological aspects of this region of the state of Pará are described by ANDERSON, DYER and TORRES (1974); BEISIEGEL et al. (1973); PETERS et al. (1977) and BELLO (1978). The manganese protoses are enclosed in a thick banded series of calc-mica schists and calcsilicatic marbles intercalated with biotite schists. The protoses show varying amounts of manganese (BELLO, 1978), rela-

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<sup>1</sup> Mineralogisch-petrographisches Institut, Universität Bern, Baltzerstr. 1, CH-3012 Bern, Switzerland.

<sup>2</sup> Instituto de Geociencias, University of São Paulo, Brazil.

tively high contents of magnesium and very little iron. The presence of phlogopite or K-feldspar in most samples requires that their chemical composition be represented by the afore mentioned chemical system and not only by CaO-MnO-MgO-SiO<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O.

Previous petrological work by PETERS et al. (1977), COUTINHO et al. (1976) and BELLO (1978) defined some phase relations of the manganese protore and from carbonate thermometry and critical phase relations in the calc-silicatic marbles determined the metamorphic conditions as being about 550°C and 3 kb total pressure. Meanwhile, more X-ray analyses and electronmicroprobe data have permitted to give a more complete picture of the phase relations for this locality. The present study complements the earlier ones and shows a nearly continuous transition in mineralogy from the system CaO-MgO-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O to the extended system CaO-MgO-MnO-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O. The phase relations, as discussed below, can be compared with the ones shown by BROWN et al. (1980) for the subsystems CaSiO<sub>3</sub>-MnSiO<sub>3</sub>-FeSiO<sub>3</sub> and CaSiO<sub>3</sub>-MnSiO<sub>3</sub>-MgSiO<sub>3</sub>. The main difference between both studies lies in the role of partial pressure of CO<sub>2</sub> and the present results refer to relatively high activities of CO<sub>2</sub> stabilizing the presence of carbonates. Furthermore, all assemblages discussed below are formed under the same P,T-conditions.

#### Mineral assemblages

During this complementary study, attention was focused on investigating the quartz-rich mineral assemblages of this locality and verifying the suspected presence of kanoite MnMgSi<sub>2</sub>O<sub>6</sub> at Buritirama (BROWN et al., 1980). Powder diffraction patterns confirmed the presence of a monoclinic phase similar to the one described by KOBAYASHI (1977) and called kanoite. Thin sections showed granoblastic textures in all cases where phlogopite was not a dominant mineral. This fact lends support to thorough metamorphic recrystallisation. Secondary alterations are minor in Buritirama. The following assemblages, listed in order of increasing MnO-content, have been found and investigated by electron-microprobe procedures (appendix):

- 1) Calcite-diopside-tremolite-phlogopite
- 2) Mn-Calcite-Mn-diopside-Mn-tremolite-Mn-phlogopite-spessartite
- 3) Ca-Mn-carbonate-kanoite-tirodite -Mn-phlogopite-spessartite
- 4) Ca-Mn-carbonate-kanoite -Mn-phlogopite-spessartite
- 5) Ca-Mn-carbonate-kanoite-tirodite -pyroxmangite-rhodonite-spessartite
- 6) Ca-Mn-carbonate-kanoite -pyroxmangite-rhodonite-spessartite

## 7) Ca-Mn-carbonate

-pyroxmangite-rhodonite-  
spessartite

Representative analyses of the minerals of these assemblages are given in Table 1 and discussed below. These seven mineral assemblages and the ones listed by PETERS et al. (1977) are sufficient to define the CaO-MgO-MnO relations of the main minerals of interest for petrological purposes and they are shown in Fig. 1. Full lines in Fig. 1 show inferred composition ranges for mineral solid solutions in the system as discussed by BROWN (1980) and dashed tie-lines refer to this investigation. Other coexisting minerals such as garnets,

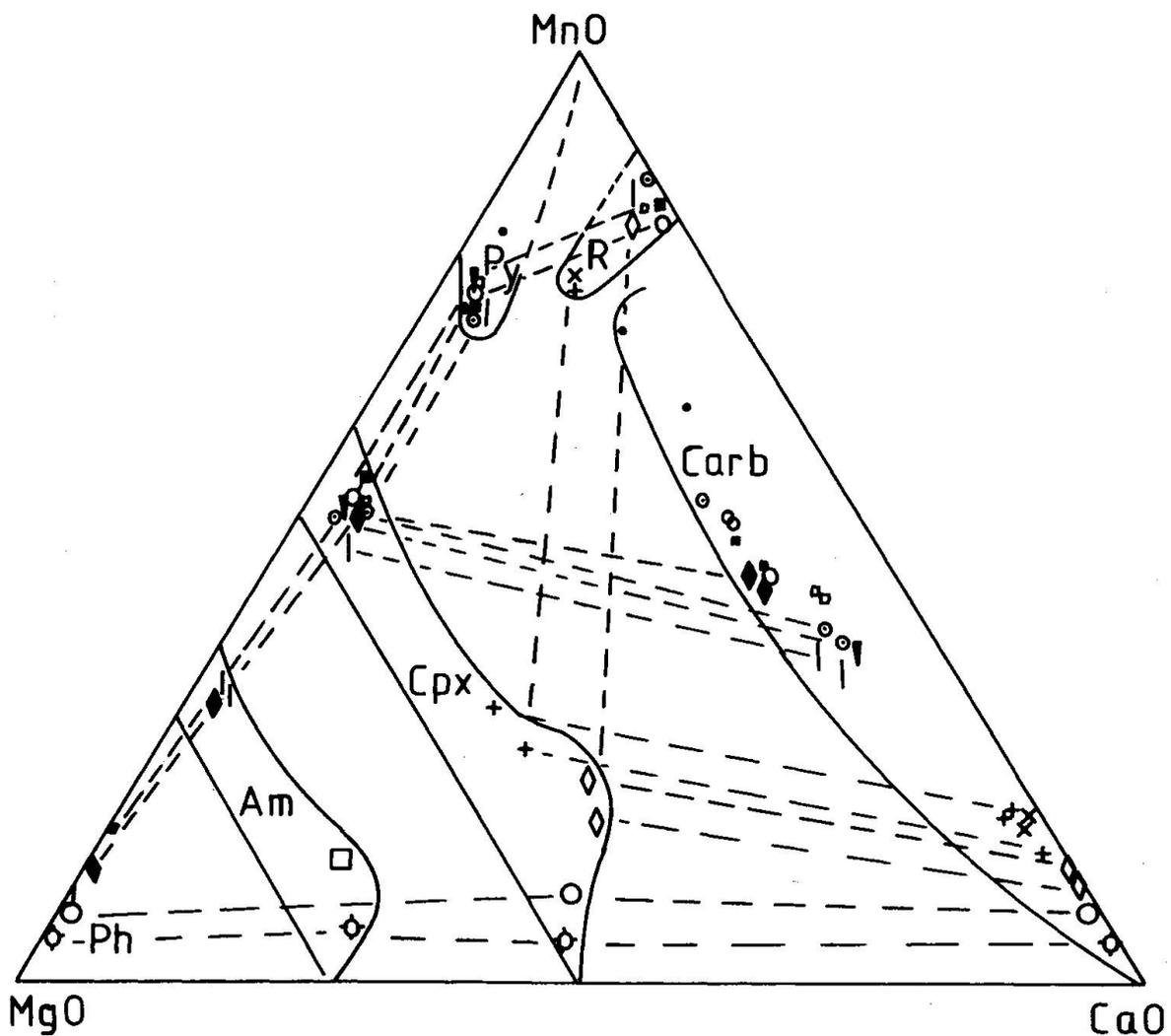


Fig. 1 Coexisting mineral solid solutions at Buritirama. The triangle defines a projection from the CaO-MnO-MgO-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> space. Tie-lines of coexisting minerals are indicated and also the probable composition ranges. Mineral data from Table 1, 2 and PETERS et al. (1977). Py = Pyroxmangite, Rh = Rhodonite, Carb = Carbonate, Cpx = Clinopyroxene (Diopside-Kanoite), Am = Amphibole (Tremolite-Tirodite), Ph = Mn-Phlogopite. Mineral parageneses are indicated by same symbols.

Table 1 Chemical Compositions of coexisting Minerals from Buritirama. Full chemical analyses in weight%, CaO, MgO, MnO values in mol.%. Numbers indicate sample nr., all samples from the same locality.

	(10)				(11)				(8)				(14)						
	Cc	diops	biot		Cc	diops	biot	garnet	Cc	kan	biot	garnet	Cc	rhod	pxm	biot	garnet		
K <sub>2</sub> O	-	-	10.6	-	-	-	10.2	-	-	-	9.2	-	-	-	-	10.5	-		
CaO	56.6	25.0	-	10.6	54.8	23.0	-	10.6	26.1	1.72	1.35	-	28.5	7.0	2.03	-	2.84		
MgO	1.14	17.9	24.9	3.3	0.49	16.7	21.7	3.3	3.8	15.6	20.8	23.8	3.1	0.38	7.4	24.8	0.84		
Al <sub>2</sub> O <sub>3</sub>	-	0.52	15.6	20.8	-	0.53	15.2	20.8	-	0.10	0.24	13.6	-	-	-	12.3	18.4		
TiO <sub>2</sub>	-	-	0.54	-	-	-	1.08	-	-	-	-	1.25	0.3	-	-	0.71	0.2		
SiO <sub>2</sub>	-	56.1	40.7	39.5	-	55.2	40.4	39.5	-	52.3	55.9	41.4	38.1	-	49.6	42.4	37.8		
MnO	0.45	0.2	0.01	21.2	2.53	2.46	1.27	21.2	22.5	28.8	16.4	3.1	36.5	-	41.2	3.8	36.8		
FeO	0.10	0.95	2.88	4.2	0.09	1.87	5.4	4.2	0.44	1.8	1.94	2.27	1.02	0.07	0.32	1.68	3.0		
NiO	-	-	0.05	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
CaO	0.963	0.492	-	-	0.951	0.463	-	-	0.527	0.036	0.030	-	-	0.570	0.163	0.045	-		
MgO	0.027	0.490	0.939	-	0.107	0.468	0.853	-	0.107	0.456	0.646	0.887	-	0.086	0.012	0.228	0.888		
MnO	0.006	0.003	-	-	0.035	0.040	0.030	-	0.359	0.478	0.289	0.065	-	0.343	0.822	0.721	0.077		
FeO	0.001	0.015	0.061	-	0.001	0.030	0.118	-	0.007	0.03	0.033	0.047	-	0.001	0.002	0.005	0.034		
	(5)				(12)				(13)				(6)						
	Cc	diops	trem		Cc	kan	biot	garnet	Cc	kan	pxm	rh	biot	garnet	Cc	kan	rhod	pxm	biot
K <sub>2</sub> O	-	-	-	-	-	-	10.4	-	-	-	-	-	10.6	-	-	-	-	-	10.1
CaO	53.8	22.7	12.1	2.32	23.0	1.43	-	2.32	23.0	1.39	1.08	6.4	-	2.88	17.7	1.06	5.8	1.37	-
MgO	0.47	14.7	20.0	1.29	5.0	16.5	24.1	1.29	4.3	15.6	20.4	0.29	24.2	1.66	4.9	16.0	0.17	8.0	23.6
Al <sub>2</sub> O <sub>3</sub>	-	0.38	0.9	18.3	-	-	13.9	18.3	-	0.05	-	-	13.7	19.4	-	0.14	-	-	13.1
TiO <sub>2</sub>	-	-	-	-	-	-	1.07	-	-	-	-	-	0.75	0.54	-	-	-	-	0.9
SiO <sub>2</sub>	-	53.8	57.6	37.0	-	52.0	41.8	37.0	-	51.6	55.6	49.0	42.6	37.1	-	49.7	47.9	49.9	39.7
MnO	4.7	4.3	3.0	37.0	26.6	30.3	4.7	37.0	26.6	30.3	20.8	41.6	3.9	36.3	29.8	30.8	45.0	40.7	5.2
FeO	0.24	3.7	5.1	3.6	0.08	0.21	2.48	3.6	0.09	0.4	0.13	0.28	2.21	2.45	0.02	0.22	0.15	0.19	1.79
NiO	-	-	-	-	-	-	-	-	-	0.04	-	-	-	-	-	-	-	-	-
CaO	0.917	0.451	-	-	0.459	0.03	-	-	0.459	0.029	0.023	0.036	-	-	0.368	0.0221	0.139	0.030	-
MgO	0.012	0.406	-	-	0.119	0.473	0.856	-	0.119	0.458	0.617	0.219	0.009	0.875	0.142	0.465	0.006	0.248	0.856
MnO	0.064	0.066	-	-	0.431	0.493	0.094	-	0.420	0.506	0.357	0.740	0.837	0.080	0.490	0.509	0.852	0.718	0.107
FeO	-	-	-	-	0.001	0.003	0.049	-	0.001	0.006	0.002	0.005	0.003	0.045	0.000	0.003	0.002	0.003	0.036

quartz, K-feldspar, ore-minerals and all minor phases have not been considered in the discussion and the MgO-MnO-CaO triangle is, therefore, a projection of the  $K_2O-Al_2O_3-CaO-MnO-SiO_2-MgO-CO_2-H_2O$  space. Iron is generally very low (< 3 mol.%) in all carbonates and silicates except phlogopite and will not be considered.

### Mineral solid solutions

Starting from the CaO-MgO base line of the CaO-MgO-MnO triangle of Fig. 1, one encounters Ca-carbonate, diopsidic clinopyroxene, tremolitic amphibole and phlogopite, all mineral phases well known in impure dolomitic marbles (RICE, 1977). Initially, the addition of MnO does not alter the mineral assemblages as long as this new component is distributed among the coexisting phases. Only at higher concentrations of manganese and saturation of the parageneses, pyroxenoids like rhodonite and/or pyroxmangite are formed. Under the given metamorphic conditions, the five solid solutions (Ca,Mg,Mn)-carbonates, (Ca,Mg,Mn)-clinopyroxenes, (Ca,Mg,Mn)-amphiboles, (Mg,Mn)-micas and (Ca,Mg,Mn)-pyroxenoids are the dominant mineral phases. Each one of these solid solutions and their respective behaviour will be treated below.

### CARBONATES

The phase relations of carbonates as noted by PETERS et al. (1977) have been more closely constrained by newer and additional data, but the general trend is confirmed in the present study. The carbonate solid solution starts with almost pure calcite and the amount of  $MgCO_3$  is positively correlated with the  $MnCO_3/CaCO_3$  ratio. Normal powder X-ray diffraction investigations of carbonates approaching kutnahorite composition  $CaMn(CO_3)_2$  do not reveal ordering peaks implying  $R\bar{3}c$  structures. The carbonate solid solution is truncated by the appearance of pyroxenoids at the MnO-rich part. Two miscibility gaps are indicated, one at  $X_{MnCO_3} \sim 70\%$  with two carbonates coexisting in the same specimen and one between about 80 and 64 mol.%  $CaCO_3$  as implied by the lack of compositions in this interval. The presence of these two miscibility gaps is confirmed by a comparison of the experimental ternary phase relations at 500°C, 550°C and 600°C in the system  $CaCO_3-MgCO_3-MnCO_3$  (GOLDSMITH and GRAF, 1960) with the range of compositions at Buritirama as shown in Fig. 2. The miscibility gap on the calcic side confirms the estimation of about 550°C as peak temperature of metamorphism (PETERS et al., 1977).

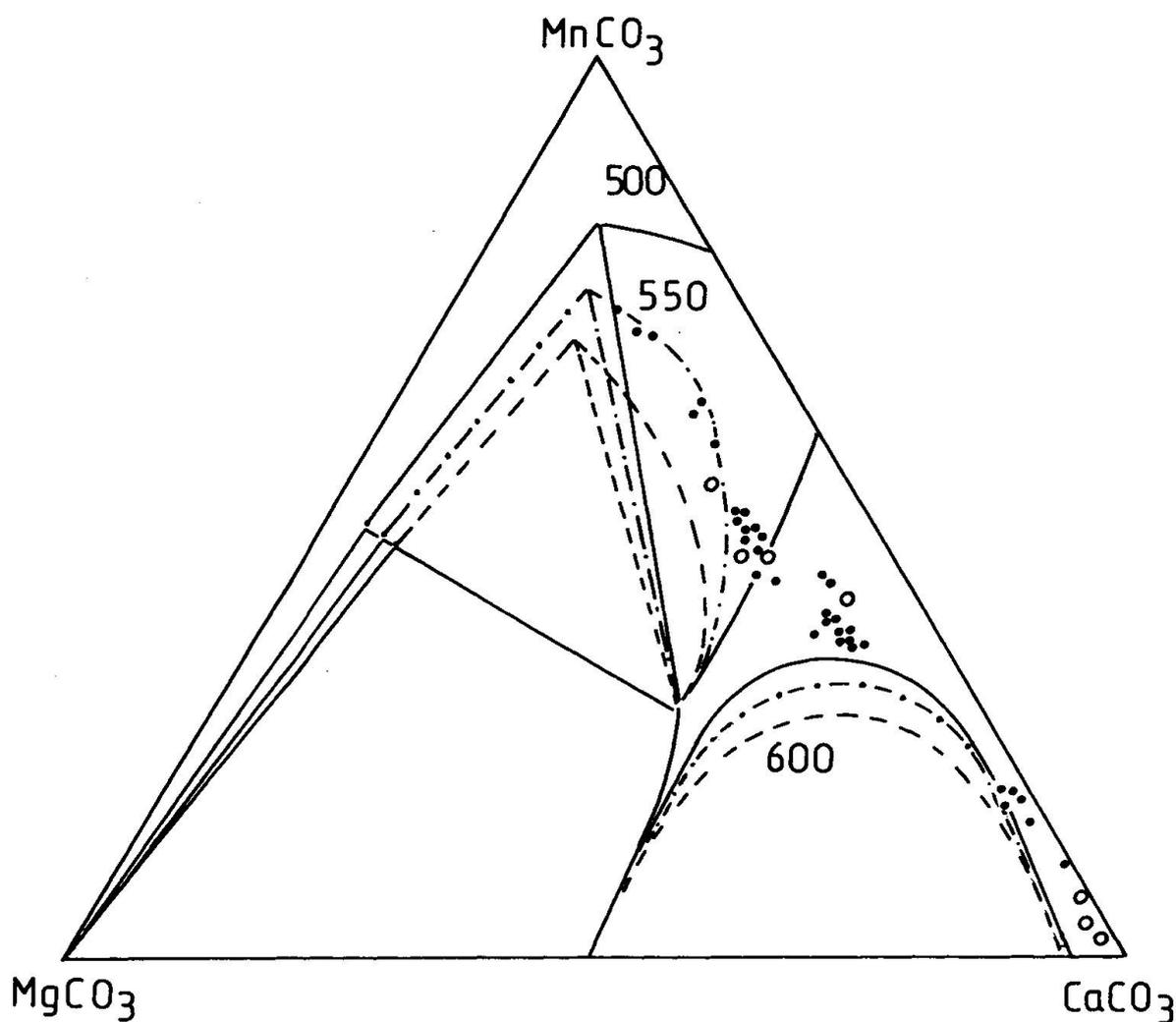


Fig. 2 Composition of Carbonates at Buritirama. Under the prevailing metamorphic conditions they form nearly a continuous solid solution series. The experimental results for 500, 550 and 600°C, 10 kb of GOLDSMITH and GRAF (1960) are indicated. ○ Data of this study, ● from PETERS et al. (1977).

#### CLINOPYROXENES

As shown by BROWN et al. (1980) and GORDON et al. (1981), two types of monoclinic pyroxenes exist in systems containing MnO-CaO-MgO. The phase  $\text{CaMgSi}_2\text{O}_6$ , diopside has the space group  $C 2/c$  at all temperatures. Johannsenite  $\text{CaMnSi}_2\text{O}_6$  on the CaO-MnO side with space group  $C 2/c$  transforms at higher temperatures to bustamite (ANGEL, 1984). The MgO-MnO side is characterised by kanoite  $\text{MnMgSi}_2\text{O}_6$  with space group  $P 2/c$  at temperatures lower than about 325°C (GORDON et al., op.cit.) and  $C 2/c$  above this temperature. Besides these natural phases, AKIMOTO and SYONO (1972) showed the presence of  $\text{Mn}_2\text{Si}_2\text{O}_6$  at high pressures with  $P 2/c$  and, finally, clinoenstatite and orthoenstatite,  $Pbca$  the latter and  $P 2/c$  the former at the  $\text{Mg}_2\text{Si}_2\text{O}_6$  point. The latter clinopyroxenes are not stable at Buritirama and will be ignored. The presence

of these compositional end members will give rise to interesting solid solution behaviour as discussed by GORDON et al. (op.cit.). The present work is concentrated on the substitution mechanism of MnO in diopsidic clinopyroxene and Fig. 1 shows at low MnO-concentrations the substitution of Ca by Mn in the M(1) site only of diopside. At higher concentrations of MnO, above about 5 mol.%, Mn enters at near 1:1 ratio the two sites M(1) and M(2) of diopside till about 25 mol.%. At still higher concentrations, Mn replaces again Ca in M(1) site only. This behaviour of changing the substitution mechanism cannot be explained by solid solution of kanoite and diopside alone as interpreted by GORDON et al. (op.cit.), because such relations involve only the M(1) site. A substitution mechanism involving the three end members  $\text{MnMgSi}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ - $\text{CaMnSi}_2\text{O}_6$  (LINDSTRÖM and WEILL, 1978) is much more likely to explain the observed chemical relations. In the absence of experimental data, the present data make isostructural and non-isostructural miscibility gaps in (Ca,Mn,Mg)-clinopyroxenes very likely in accordance with the system  $\text{CaO-MgO-FeO-SiO}_2$ . The suspected presence of kanoite  $\text{MnMgSi}_2\text{O}_6$  at Buritirama (BROWN et al., 1980) has been confirmed by X-ray diffraction and Fig. 1 shows kanoite coexisting with carbonates, pyroxenoids, amphiboles and Mn-phlogopite.

The compositional range of kanoite is much more restricted than the one of diopside. Not more than about 4 mol.% Ca is found at the prevailing conditions. The substitution of Mn in the M(2) site of kanoite is also quite restricted to about 6 mol.% in excess of the stoichiometric composition. GORDON et al. (op.cit.) imply a much higher solid solution of kanoite and diopside at temperatures in the range found at Buritirama, whereby kanoite is isostructural with diopside. This problem awaits further experimental work.

#### AMPHIBOLES

The amphiboles investigated in this study belong to the monoclinic amphiboles tremolite and tirodite (LEAKE, 1978). Phase relations between these two types of amphiboles may be similar to the relations between calcic amphiboles and cummingtonites and the miscibility gap between these can be explained by a compositional discontinuity in the occupancy of the M(4) site due to size difference of the substituting ions. In case of tremolite-tirodite, higher mutual solubilities may be expected than in case of tremolite-cummingtonite due to the intermediate size of the Mn-ion. ISHIDA (1985) indeed describes coexisting manganese actinolites and tirodites from Japanese manganese ore deposits of varying degrees of metamorphism and shows a narrowing of the miscibility gap at higher temperatures. Coexisting amphiboles have not been found at Buritirama. This fact can be explained by the lack of suitable chemical composition at

this locality produced by the miscibility gap on the calcic side of the carbonate solid solution series.

Contrary to earlier interpretations (PETERS et al., 1977), the amphiboles investigated in the present work belong to the mineral parageneses as shown in Fig. 1 and are not the product of hydrothermal alteration. Monoclinic tirodite is very well stable at the metamorphic conditions of Buritirama as shown by the work of HUEBNER (1986) and DASGUPTA et al. (1985). The former work shows the stable coexistence of tirodite, kanoite and pyroxenoid (pyroxmangite) at about 500 to 550 °C in accordance with the phase relations shown in Fig. 1.

The substitution mechanism of Mn for Ca in tremolite changes in a similar way as shown above for clinopyroxene. Although the number of analyses is more restricted than in case of monoclinic pyroxenes, Fig. 1 indicates an initial Mg by Mn substitution with constant Ca pointing to a hypothetical end member  $\text{Ca}_2\text{Mn}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ . This mechanism gives way to a Ca-Mn substitution above about 10 mol. % Mn leading ultimately to the  $\text{Mn}_2(\text{Mn},\text{Mg})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  composition.

#### Mg-Mn-MICAS

The analysed micas, although sometimes called manganophyllite, may be in the present case called more properly Mn-phlogopites. They show a quite restricted solubility of manganese under the present metamorphic conditions. PETERS et al. (1977) discuss the crystallochemistry of these phases in detail.

#### PYROXENOIDS

In the present study the two types of pyroxenoids, pyroxmangite and rhodonite, have been investigated. As discussed by PETERS et al. (1977), their composition correlates with the Ca-Mg-Mn ratio of the coexisting carbonates with pyroxmangite forming at higher and rhodonite at lower  $X_{\text{Mn}}$ . The compositional field of rhodonite, although in quite a narrow range of  $X_{\text{Ca}}$  between 0.13–0.16, shows a larger spread in  $X_{\text{Mg}}$  as is shown in Fig. 1. The composition of the most magnesian rhodonites approaches the one discussed by PEACOR et al. (1978), the magnesia-poorest have  $X_{\text{Mn}} = 0.003$  and they are always coexisting with pyroxmangite. These phases are quite low in Ca, but — when coexisting with kanoite — high in Mg ( $X_{\text{Mg}} = 0.15\text{--}0.25$ ).

Three samples showed coexisting rhodonite and pyroxmangite, partially as intergrowths, but more often in separate phases displaying granoblastic texture. The tie-lines of the latter are indicated in Fig. 3 and define the mutual solubilities of Ca and Mg in the respective phases. Submicroscopic intergrowths of

pyroxmangite and rhodonite and, likewise, intergrowths between tirodite and rhodonite could be observed. These are only resolved by high magnification under the electron beam and care has to be taken to exclude such intergrowths from the construction of tie-lines. Table 2 lists some analytical results of tirodite-rhodonite intergrowths.

Table 2 Chemical compositions of some rhodonite-tirodite submicroscopic intergrowths along a traverse (in weight-%).

	rh (1)	rh (2)	rh (3)	rh (4)	tir	rh (5)	tir	rh (6)	rh (7)
CaO	6.1	5.5	3.3	3.2	0.84	4.1	0.82	5.9	6.2
MgO	0.3	0.68	1.68	1.48	21.8	2.83	20.9	0.31	0.33
MnO	45.0	45.7	46.4	47.0	19.7	44.9	19.7	45.1	45.6
FeO	0.10	0.12	0.13	0.08	0.16	0.17	0.10	0.1	0.07
SiO <sub>2</sub>	47.6	47.3	47.4	47.2	56.1	48.5	54.3	47.5	47.8

Mg-rich rhodonites are also found at this locality (PETERS et al., 1977), but not in coexistence with pyroxmangite. Possible reactions involving rhodonite, kanoite and Ca-Mn-Mg-carbonates are indicated by PEACOR et al. (1978). The actual P, T,  $f_{H_2O}$  and compositional conditions leading to such assemblages are not yet known and await experimental work.

#### Miscibility Gap Rhodonite-Pyroxmangite

The coexisting pairs of pyroxmangite and rhodonite, Table 3, define the tie-lines for the prevailing metamorphic conditions at Buritirama. As shown in Fig. 3 and listed in Table 3, the Mg-content (0.6–1.2 mol.%) is very low, the Ca-content about 16 mol.% in rhodonite. Coexisting pyroxmangite has about 25 mol.% Mg and about 3 to 4 mol.% Ca. The data in Fig. 3 suggest a preferred substitution of Mg in pyroxmangite, while Ca is preferably distributed into rhodonite. The Mg-content of these pyroxmangites from Buritirama appears the highest one noted for natural phases (DEER et al., 1978).

Comparing the length and compositional inclination of these tie-lines in the CaO-MgO-MnO triangle with those shown by WINTER et al. (1981), PEACOR et al. (1978), CHOPIN (1978), BROWN et al. (1980) and PETERS et al. (1978), the pyroxenoid pairs from Buritirama define the largest compositional gap and, likewise, a totally different inclination angle between the base-line and Mn-Ca side-line of all occurrences cited.

Table 3 Coexisting rhodonite-pyroxmangite pairs (weight-% and mol.%)

	(13)		(14)		(6)	
	rhod	pxm	rhod	pxm	rhod	pxm
CaO	6.4	1.68	7.0	1.94	5.8	1.37
MgO	0.29	7.4	0.38	7.7	0.17	8.0
MnO	45.0	40.6	44.5	40.6	45.0	40.7
FeO	0.15	0.24	0.10	0.25	0.15	0.19
SiO <sub>2</sub>	47.2	49.2	48.6	50.2	47.9	49.9
CaSiO <sub>3</sub>	0.15	0.04	0.16	0.04	0.13	0.03
MgSiO <sub>3</sub>	0.01	0.23	0.01	0.24	0.0	0.25
MnSiO <sub>3</sub>	0.84	0.73	0.82	0.71	0.86	0.72
FeSiO <sub>3</sub>	0.0	0.0	0.0	0.0	0.0	0.0

samples (13) and (6) have kanoite coexisting.

The coexistence of pyroxmangite, rhodonite and kanoite as shown in Fig. 3 by the same symbols for each rock specimen defines the highest solubility of Mg in rhodonite and pyroxmangite under the given P-T conditions. For pyroxmangite the Mg-value is high indeed, but rhodonite shows very low Mg-contents. If all cited occurrences of the assemblage rhodonite-pyroxmangite are equilibrium phase associations, the miscibility gap between both minerals appears to be a rather complicated function of the prevailing P-T-X-conditions. Although quantitative conclusions from the data cannot be derived, as shown by WINTER et al. (1981), the experimental work by MARESCH and MOTTANA (1976), IWABUCHI and HARIYA (1985), HUEBNER (1986), ABRECHT and PETERS (1975), MOMOI (1968) and ITO (1972) shows  $dt/dX_{Mg}$  for the coexistence being positive but  $dt/dX_{Ca}$  negative at constant pressure. At constant temperature, however,  $dP/dX_{Mg}$  is negative (IWABUCHI and HARIYA, 1985) for both phases in agreement with results from SIMON (1978) in the system  $MnSiO_3$ - $FeSiO_3$ . Increasing pressure decreases the solubility of Mg in both, but the amount of Ca will increase as concluded from data given by ABRECHT and PETERS (1980). The steep T-X and P-X slopes make the system quite sensitive for small changes in bulk composition determining the occurrence of one or the coexistence of both phases.

The fact that Mg and Ca may occupy several sites of the structures of pyroxmangite and rhodonite (OHASHI and FINGER, 1975) will complicate the tracing of the phase boundaries due to partial ordering of the ions with concomitant energetic effects and solubilities as a function of partial order. The latter may explain diverging results of experimental work listed above and may even hinder a comparison of data from different localities metamorphosed under iden-

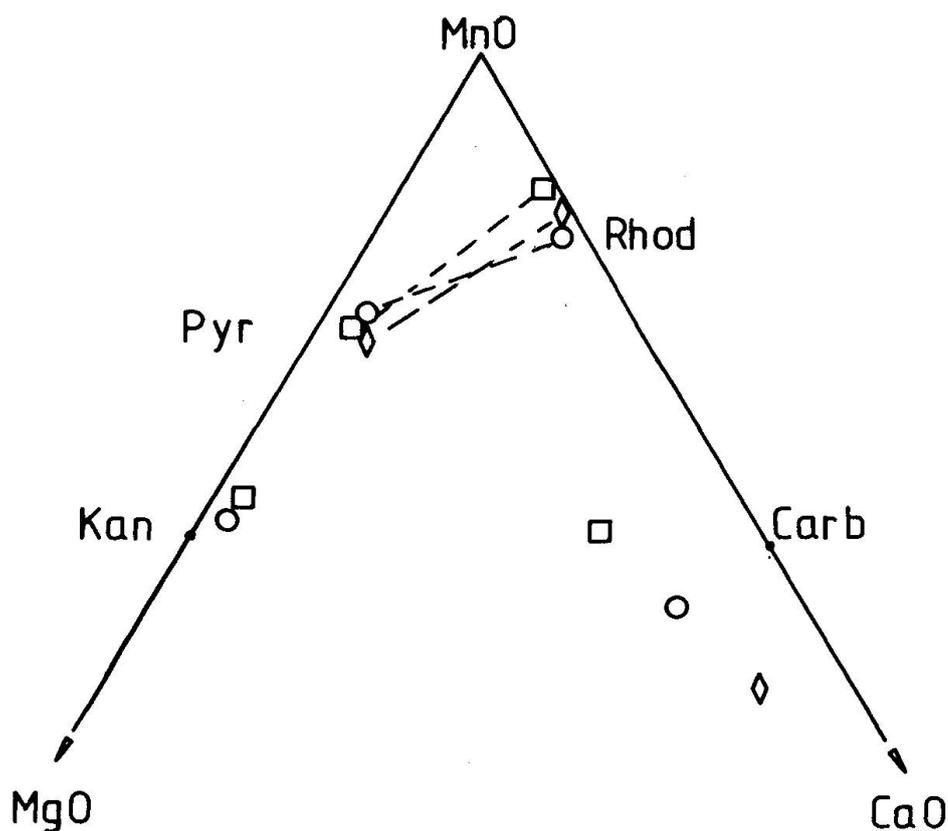


Fig. 3 Tie-lines of coexisting rhodonite and pyroxmangite at Buritirama.  $\circ$  and  $\square$  coexisting with kanoite and a Mg-rich Ca-Mn carbonate.

$\diamond$   $X_{\text{MgCO}_3} = 0.08$  in carbonate, no kanoite coexisting. Metamorphic conditions about 550°C, 3 kb total pressure. Projection from the CaO-MnO-MgO-SiO<sub>2</sub>-CO<sub>2</sub> space. Pyr = Pyroxmangite, Rhod = Rhodonite, Carb = Carbonate, Kan = Kanoite. Data from Table 3.

Points at Kan and Carb indicate 50 mol.% MgO and CaO respectively.

tical pressure and temperature conditions without due consideration of the effect of partial order.

#### Chemical constraints on phase relations

The phase relations as depicted in Fig. 1 imply a quite clearcut sequence of mineral solid solutions by the addition of MnO to the phases of the system CaO-MgO-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O. The regularity of the tie-lines suggests equilibration between the coexisting phases. At low concentration, Mn will be equally distributed between coexisting calcite, diopside, tremolite and phlogopite with tie-lines parallel to the CaO-MgO base. Increasing Mn-contents show a slight change in the tie-lines between carbonate, pyroxene and, possibly, amphibole, due to preferential incorporation of Mn into the silicate phases. In case of continuous solid solution in the amphibole and clinopyroxene phase, no new mineral is formed, in case of miscibility gaps two coexisting

phases may appear (ISHIDA, 1985; GORDON et al., 1980; BROWN et al., 1980). Only if these silicatic phases are saturated by Mn, rhodonite and/or pyroxmangite appear, depending on the bulk CaO-MgO-MnO relation. For the given conditions at Buritirama, the sequence kanoite-rhodonite, kanoite-rhodonite-pyroxmangite, kanoite-pyroxmangite and pyroxmangite-rhodonite or both phases alone appears to depend furthermore strongly on the MgO-content of the coexisting carbonate. The critical Mg-content seems to be about 10 mol.% as shown by the three cases of coexisting pyroxenoids given in Table 3. In two cases with about 11 mol.% MgCO<sub>3</sub> in the carbonate, kanoite is coexisting, but is not present at about 8 mol.% MgCO<sub>3</sub>. This may be one of the reasons why PETERS et al. (1977), WINTER et al. (1981) and CHOPIN (1978) do not report the occurrence of kanoite, although the metamorphic conditions are the same (PETERS et al., *op. cit.*) or alike the present ones (WINTER et al., *op. cit.*). The compositions of the carbonates given by these authors show only low MgCO<sub>3</sub> contents of about 3 to 8 mol.%, indicating a bulk rock composition poorer in MgO for the given mineral assemblage than at Buritirama.

The correlation of these mineral sequences with rock bulk composition cannot be done yet due to lack of sufficient chemical and mineralogical data. On the other hand, theoretical considerations, discussed below, may make such a project of little value. Up to now too little is known about natural phase relations of silicates at much lower metamorphic conditions to define all the reactions leading to the observed assemblage.

Furthermore, the role of additional phases, and especially of spessartite as one important controlling factor for the CaO-MnO-MgO ratios must finally be mentioned. This phase appears at rather low P-T-X<sub>CO<sub>2</sub></sub> conditions as shown by VALARELLI et al. (1980) and may be regarded as a sink for Al<sub>2</sub>O<sub>3</sub> and especially for MnO. The projection points of spessartites in the CaO-MgO-MnO triangle are restricted to the MnO-rich part seldom showing more than about 10 mol.% CaO and even less MgO (PETERS et al., 1977). This means that quite a high amount of MnO of the whole rock composition will form garnet if Al<sub>2</sub>O<sub>3</sub> is present and will not be able to participate in other reactions leading to Mn-silicates containing CaO and MgO. One extreme case is the formation of the assemblage spessartite-quartz only, very frequently found already in very low to low grade metamorphosed Mn-bearing sequences with initial bulk compositions of rhodochrosite and clay minerals as inferred from gradations into rhodochrosite-bearing rocks at Buritirama. Furthermore, at low temperatures, the carbonates in the system CaCO<sub>3</sub>-MgCO<sub>3</sub>-MnCO<sub>3</sub> show a quite complicated phase diagram with some two-phase and three-phase fields as shown in Fig. 2, which will lead to discontinuous reactions in the presence of quartz. It now depends strongly on the relative values of the enthalpies of reactions and Gibb's free energies of these mixed carbonates which may or may not, at given P-T-conditions, lead to the formation of silicate phases such as pyroxenes, pyroxe-

noids and amphiboles in certain compositional ranges. Fig. 2 and Fig. 1 show that the projection points of the silicates in the CaO–MgO–MnO triangle mirror the phase relations of the carbonatic system.

Rhodonite and pyroxmangite occupy the former rhodochrosite composition range (Mn-rich), kanoite and the clinopyroxenes are distributed along the former compositional line of dolomitic phases (Ca,Mn) (Mn,Mg) (CO<sub>3</sub>)<sub>2</sub>. These relations are clearly implied by a comparison of Figs. 1 and 2. Specific reactions leading to the observed assemblages cannot be deduced from the data displayed in this work. To achieve this, more field evidences from manganese deposits of lower metamorphic grade are needed. These will ultimately lead to a complete picture of possible reactions and phase associations.

#### Acknowledgement

This work benefitted from a critical review by J. Abrecht, Basel. Financial support from the Schweizerische Nationalfonds is gratefully acknowledged as well as the research leave from the Institute of Geosciences, University of São Paulo to one of the authors (R. S-G).

#### Appendix

The chemical compositions of the mineral phases were determined with an ARL electron microprobe of the type SEMQ, equipped with 6 spectrometres. The following technical conditions were used: 18 kV acceleration voltage, a sample current of 30 nA for silicates and between 10 and 20 nA for carbonates. The beam size was varied in case of carbonates to avoid decarbonatisation. For all analyses, natural minerals have been used as standards.

The automated electron microprobe corrected the rough data for background, deadtime and instrumental drift. For the calculation of the constituent oxides the Bence-Albee approach has been used. Care was taken to analyse minerals in contact with each other and to search for possible intergrowths with high magnification of the backscattered electron images.

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