

MANGANOAN CUMMINGTONITE FROM SAKARSANAHALLI, KOLAR DISTRICT

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ABSTRACT

Manganoan cummingtonite from the carbonate horizons of Sakarsanahalli is unique in containing 2.45 Mn^{2+} per formula unit. The manganese content of this mineral is the highest that has been reported so far. It has a Mg:Mn:Fe ratio of 49:42:9. The unit cell dimensions are $a = 9.598 \text{ \AA}$, $b = 18.072 \text{ \AA}$, $c = 5.266 \text{ \AA}$, $\beta = 103^\circ 44'$. The β -angle corresponds to a value between that of tremolite and cummingtonite, with a smaller c -value. This can only be attributed to the enrichment of Mn^{2+} in the M_4 site with a possible 8-coordination as against the normal 6-coordination.

IT is generally believed that manganese content in the monoclinic iron-magnesium amphiboles $(\text{Mg, Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ (cummingtonite-grunerite series) will not exceed 2 atoms per formula. This originates from the expectation that the larger divalent cations preferentially occupy the M_4 sites in the crystal structure, whereas the smaller cations fill in the various $Y(M_1, M_2, M_3)$ positions, all the sites having distorted octahedral coordination¹. Contrary to this view, a unique amphibole containing 2.45 atoms per formula (20.0% by wt. MnO) has been collected from Sakarsanahalli, Kolar District (Lat. $12^\circ 48'$; Long. $78^\circ 13'$). The amphibole occurs in the metamorphosed "silicate-carbonate" horizon of an abandoned manganese limestone quarry, west of the village. The quarry is a part of the complex rock exposures occurring as isolated small rises within the granites and gneisses of the south-west margin of Kolar Schist belt. The chief rock types of the complex are: carbonates (Mn — calcite + Mn — dolomite + amphiboles), ferruginous schists (quartz + haematite + magnetite + anthophyllite + talc), metapelites (cordierite + sillimanite + muscovite + quartz), pyroxenites (diopside + garnet + calcic amphiboles + clinozoisite + quartz) and amphibolites (hornblende + plagioclase + quartz). Manganese is a common substituent to varying degree in pyroxenes, garnets, and amphiboles. Tremolite and cummingtonite are the normal constituents of the carbonate rock.

Manganoan cummingtonite occurs as tufted acicular fibres along the localised shear planes in the carbonate rocks. The fibres could easily be handpicked and the sample thus obtained is treated with dilute hydrochloric acid. Microscopic examination reveals that the phase purity is over 99%. The amphibole is pale glistening white to light brown in colour. Most of the crystals are in the form of fine fibres (asbestiform). However, long slender transparent crystals can often be seen which show acicular and prismatic habits (Fig. 1). They

are non-pleochroic and show lamellar twinning parallel to c -axis. The extinction angle varies from 15° to 18° . The biaxial needles are optically negative. The optical properties are given in Table I, which corresponds to the manganoan cummingtonite reported by Jaffe *et al.*². Except by chemical means, it is often difficult to conclusively identify this mineral. It may be mistaken for tremolite asbestos which has optical properties similar to manganoan cummingtonite.



FIG. 1. Manganoan cummingtonite, Sakarsanahalli, Magnification, $\times 25$.

CHEMISTRY

The carbonates, the cummingtonite and the coexisting tremolites are analysed by wet chemical methods. Cations are estimated complexometrically; water and carbon dioxide by gas effluent analysis. No fluorine is detected in the sample (Tables I and II). The analytical data show that the amphibole under consideration is manganoan cummingtonite with the formula $(\text{Mg}_{2.9}\text{Mn}_{2.5}\text{Fe}^{2+}_{0.8}\text{Ca}_{0.3}\text{Al}_{0.5})\text{Si}_{7.00}\text{O}_{21.8}(\text{OH})_{2.1}$. According to Jaffe *et al.*², the monoclinic Mg-Mn-Fe amphibole containing 50 or above mole per cent Mg is to be called cummingtonite even though the manganese substituted mineral is optically negative. The Mg:Mn:Fe²⁺ is 49:42:9 for the present cum-

TABLE I
Chemical composition of amphiboles

	Manganooan Cumming- tonite	Manganooan Actinolite I	Manganooan Actinolite II
SiO ₂	55.14	50.11	54.74
TiO	0.03	0.28	0.49
Al ₂ O ₃	2.85	1.24	3.57
Fe ₂ O ₃	0.08	1.71	0.94
FeO	4.52	13.82	7.48
MnO	20.03	6.30	9.61
MgO	13.25	11.67	9.40
CaO	2.02	12.32	10.62
Na ₂ O	0.21	0.56	0.87
K ₂ O	0.05	0.07	0.20
H ₂ O ⁺	2.17	1.83	1.98
H ₂ O ⁻	0.04	0.06	0.15
Total	100.27	99.97	100.05
a	1.629	1.647	1.638
β	1.649	1.663	1.652
γ	1.652	1.669	1.661
2V	75°	74°	84°
ZΛc	17°	16°	20°
D	3.26	3.19	3.17
Number of cations on the basis of 24 (0) atoms			
Si	7.989	7.565	7.966
Al	0.011	0.221	0.034
Al	0.476		0.578
Ti	0.000	0.032	0.054
Fe ³⁺	0.009	0.194	0.103
Fe ²⁺	0.549	1.745	0.930
Mn	2.462	0.806	1.156
Mg	2.867	2.626	2.039
Ca	0.315	1.996	1.658
Na	0.059	0.164	0.245
K	0.011	0.014	0.037
(OH)	2.103	1.845	1.924

TABLE II
Chemical composition of carbonates

	Kutno- horite (1)	Manganooan Calcite (2)	No. of cations; Basis 6 (0) atoms (1)	(2)
FeO	0.28	1.55	Fe 0.008	0.044
MnO	24.30	14.40	Mn 0.715	0.411
MgO	4.12	5.80	Mg 0.213	0.291
CaO	29.35	34.72	Ca 1.093	1.253
CO	41.90	43.55	C 1.986	2.001
H ₂ O ⁺	0.13	0.11		
	100.08	100.13		
e	1.525	1.495	a, Å 4.84	4.89
w	1.713	1.683	c, Å 16.27	16.58
D	3.13	2.92		

ingtonite. Manganese substituted cummingtonite-grunerites are known by names like tirodite^{3,4} (5 to 10 wt% MnO and minimum FeO) and danne-morite^{5,6} (7.4% MnO and 24 wt% FeO). Jaffe *et al.*² have reported a manganooan cummingtonite with 2.28 Mn²⁺ per formula unit. This analysis is doubted because of the spessartite inclusion in the sample and that the analysis is carried out spectrographically. Klein⁷ has analysed three cummingtonites containing 2.02, 1.74 and 1.63 atoms of Mn²⁺ per formula. He has concluded that naturally occurring members of the cummingtonite-grunerite series vary from 35–100 mole % of Fe₇Si₈O₂₂(OH)₂ and 0–34 mole% of Mn₇Si₈O₂₂(OH)₂ components. The composition of manganooan cummingtonite from Sakarsanahalli exceeds this limit for manganese. Al₂O₃ and CaO contents in this amphibole are also more than the normal range encountered in cummingtonites. However, the Z-position is nearly filled by Si. The CaO content of 2.02 wt% (0.32 atoms per formula) indicates that Ca is more soluble in manganooan than Mn-poor cummingtonite.

The reason for such a higher concentration of manganese in this amphibole is the Mn-rich environment under which it is formed. This is indicated by the manganese content in the associated carbonates (Table II). They are, in general, (Ca, Mn, Mg) CO₃ with MnO content varying from 12 to 25 wt%, corresponding to manganooan calcite to kutnohorite compositions. This is further shown by the manganese content in the coexisting tremolite with 0.81 and 1.16 atoms per formula. In tremolites, Mn²⁺ substitutes for Fe²⁺ in the Y-positions since the bigger calcium ions occupy the M₄ sites.

POWDER DIFFRACTION PATTERN

Powder diffraction pattern for the manganooan cummingtonite is obtained with a Philips camera of 114.6 mm diameter, using Cr K_α-radiation (V-filtered) from a Rich-Seifert X-ray unit. In order to obtain the weak reflections, the film is exposed for 48 hours. Measurements are made to an accuracy of 0.05 mm and the film shrinkage is found to be lower than this. The 0 12 0 reflection is used to get the *b* value while 310, 061 and 20 $\bar{2}$ reflections are used to extract *a* sin β, *c* sin β, and β values. This results in the following cell dimensions: *a* = 9.598 Å, *b* = 18.072 Å, *c* = 5.266 Å, β = 103° 44'. The cell volume is 887.2 Å³ and a calculated density of 3.34 g/cc. The measured density is 3.26 g/cc. Using the cell parameters, the observed reflections in the powder diffraction pattern are indexed (Table III). The agreement between calculated and the observed *d*-spacing indicates the accuracy of the cell parameters. β-value is intermediate between cumming-

TABLE III

X-ray powder diffraction data of manganoan cummingtonite

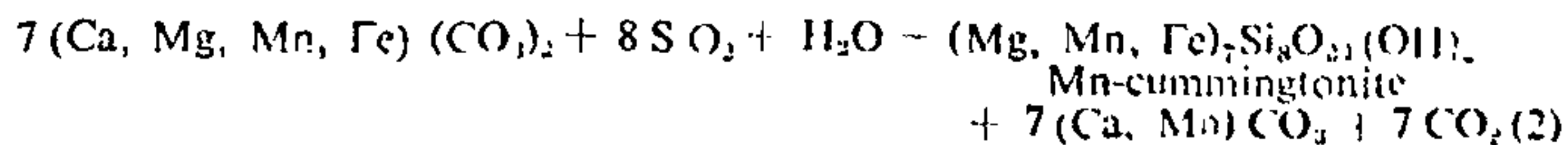
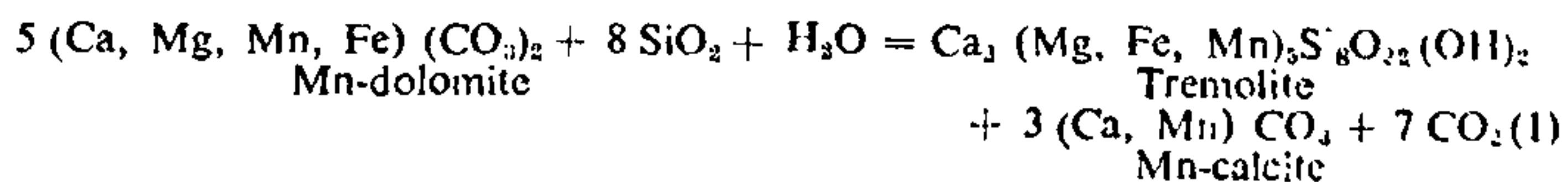
$a = 9.598 \text{ \AA}$, $b = 18.072 \text{ \AA}$, $c = 5.266 \text{ \AA}$ ($\pm 0.005 \text{ \AA}$),
 $\beta = 103^\circ 44'$, $V = 887.2 \text{ \AA}^3$, $Z=2$, sp.-group, $C_{2/m}$

$d(\text{\AA})$	hkl	Inten- sity	$d(\text{\AA})$	hkl	Inten- sity
9.02	020	50	1.855	510	10
8.28	110	75	1.782	530	3
4.512	040	3	1.698	37 $\bar{2}$	5
4.140	220	10	1.684	55 $\bar{1}$	3
3.384	131	5	1.640	461	50
3.241	240	50	1.617	1 11 0	30
3.059	310	100	1.554	600	15
2.932	221	5	1.505	0 12 0	20
2.761	330	10	1.495	60 $\bar{2}$	8
2.712	151	25	1.452	3 11 0	5
2.595	061	10	1.431	4 10 $\bar{1}$	3
2.508	20 $\bar{2}$	8	1.409	66 $\bar{1}$	90
2.352	350	5	1.357	512	5
2.293	17 $\bar{1}$	15	1.343	1 11 2	8
2.265	42 $\bar{1}$	10	1.338	66 $\bar{2}$	3
2.191	24 $\bar{2}$	3	1.298	0 12 2	5
2.160	261	15	1.290	0 14 0	10
2.047	202	5	1.281	751	5
2.008	351	5	1.207	602	3
1.959	281	8	1.185	5 11 $\bar{2}$	10

tonite (102°) and tremolite (105°). The smaller b - and c -values of the manganoan cummingtonite are nearer to that of tremolite. The a -axis, however, remains unchanged. The linear plots of $a \sin \beta$ and of b -values against composition in the Fe-Mg series will not hold good for the Mg-Mn-Fe ternary cummingtonites. The intensity ratios of the observed reflections also are at variance from those of Mn-free cummingtonite.

DISCUSSION

In the silicate-carbonate horizons, tremolite and cummingtonite are formed by the reaction of manganoan dolomite with silica impurities during metamorphism as per the reactions:



The Ca/Mg+Mn+Fe ratio in the dolomite is more than that of tremolite and that of cummingtonite. Therefore manganoan calcite becomes a product. The coexisting carbonates have all the characteristics of high temperature variety and are crystalline. Cummingtonite and tremolite thus formed will incorporate considerable amounts of

manganese, the extent of which is limited by the crystal chemistry of the silicates.

In the amphibole structure, bigger Ca-ions occupy the M_4 sites with an eight-coordination while the smaller cations show preference to M_1 , M_2 and M_3 sites which have distorted octahedral coordination. This results in the tremolite and hornblende structures⁸. On the other hand, in cummingtonite, all the four sites, M_1 to M_4 have distorted octahedral coordination. The dual coordination of M_4 sites in clinoamphiboles is possible due to the noncoplanar configuration of the oxygens forming the bases in the silicate double chains. The $(\text{Si}_4\text{O}_{11})$ chains can be bent about the (001) axis, modifying the nature of their stacking. Accordingly, the β adopts extreme values. The M_4 sites can thus acquire any coordination between six and eight. In the Mg-Fe-Mn cummingtonite, containing more than two Mn²⁺ per formula, can have manganese filling in the M_1 or M_3 sites, over and above the M_4 occupancy. In such cases, Mn²⁺ in the M_4 site gains eight-coordination, with a higher ionic radius (1.01 Å for the high-spin state)⁹, the silicate chains suitably modify and the structure approaches that of tremolite. This accounts for the closer similarity in physical properties of manganoan cummingtonite and tremolite and so also the cell parameters. Besides, Ca has higher solubility in Mn-cummingtonite than in Mn-free variety which supports the above conclusion. However, due to crystal field effects, the solid solubility between Mn-cummingtonite and tremolite can be expected to be limited.

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