MANGANESE-BEARING SILICATE MINERALS FROM METAMORPHOSED MANGANESE FORMATIONS OF INDIA. III TIRODITE

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ABSTRACT

Tirodite, the yellow manganiferous amphibole, described first by DUNN & ROY [1938] from metamorphosed manganese formations at Tirodi, Madhya Pradesh, India, has been studied in detail. Earlier workers related this mineral either to richterite or to cummingtonite. Determination of optical properties, X-ray powder data and interpretation of chemical analyses of the mineral from different localities indicate that the composition of tirodite (MnO 2.84 to 13.83%) varies fairly widely within the complete chemical series between tremolite and richterite. The tirodites were found either in an alkali-rich environment in pegmatites which assimilated part of the manganese formation they cut across, or in manganese silicate rocks themselves that have been subjected to soda-metasomatism.

INTRODUCTION

Tirodite, a manganiferous amphibole, with characteristic straw-yellow body colour, was first named and described from the metamorphosed manganese formations of the Precambrian Sausar Group at Tirodi mine, Balaghat District, Madhya Pradesh, India by DUNN & ROY [1938]. The mineral has, since then, been described from metamorphosed manganese formations from different areas in the States of Madhya Pradesh, Maharashtra, Gujarat and Orissa, India. [BABU & NAYAK, 1961; ROY & MITRA, 1964; ROY, 1966; ROY & PURKAIT, 1968; GHOSE *et al.* 1974].

DUNN & ROY [1938] originally suggested that tirodite approaches richterite in composition. BILGRAMI [1955] and BABU & NAYAK [1961] corroborated the above conclusion. ZWANN & VAN DER PLAS [1958] suggested that tirodite is a transitional member between tremolite and richterite but they also pointed out that X-ray data indicate a composition in the glaucophane-crossite group. SEGELER [1961] and KLEIN [1964] related tirodite to manganoan cummingtonite. TRÖGER [1961] concluded from published analyses of tirodite that it must be classified between kupfferite and Na—Ca amphiboles. ROY & PURKAIT [1968] showed that the composition of tirodite from Gowari Wadhona, Madhya Pradesh, occurring at the contact of manganese silicate rocks (gondite) and pegmatites, can be calculated in terms of cummingtonite, tremolite and glaucophane molecules but if the manganese is considered to be restricted entirely to the X site, the composition clearly approaches that of the richterite-tremolite series. GHOSE *et al.* [1974] very recently showed the presence of magnesio-richterite and magnesio-riebeckite as exsolved phases constituting the tirodite sample (from Tirodi) they studied.

MODE OF OCCURRENCE AND PARAGENESIS

Tirodite is fairly well distributed in regionally metamorphosed manganese silicate rocks (gondite) and in pegmatite veins invading the manganese formation in different parts of the Precambrian manganese ore belts of Madhya Pradesh and Maharashtra (Sausar Group) and Orissa (Gangpur Group). The mineral occurs in gondites of both greenschist and amphibolite facies and has also been found in contact metamorphosed manganese silicate rocks (kodurite) of pyroxene-hornfels facies at Jothvad, Gujarat, India [ROY, 1966]. The mineral assemblages from different areas in which tirodite is present, are shown in Table 1.

TABLE 1

Metamorphic grade	Locality	Host Rock	Mineral Assemblage
Greenschist facies	Dongri Buzurg, Maharashtra	Gondite	Tr-Sp-Mp-Br-Qz
Amphibolite facies	Chikla, Maharashtra	Gondite	Tr-Sp-Rh-Ap-Pl-Br-Qz
do	Tirodi, Madhya Pradesh	Gondite	Tr-Sp-Rh-Pl-Qz
		Gondite	Tr-Sp-Mp-Ap-Br-Qz
		Pegmatite	Tr-Bp-Mc-Qz
do	Ramdongri, Maharashtra	Gondite	Tr-Sp-Rh-Br-Jb-Qz
do	Netra, Madhya Pradesh	Gondite	Tr-Sp-Ap-Br-Qz
		Gondite	Tr-Sp-Bp-Rh-Ap-Qz
		Pegmatite	Tr-Bp-Mp-Mc-Qz
do	Gowari Wadhona, Madhya Pradesh	Pegmatite	Tr-Md-Ct-Br-Qz
		Pegmatite	Tr-Pl-Mc-Ct-Qz
Pyroxene-hornfels facies	Jothvad, Gujarat	Kodurite	Tr-Span-Rh-Bp-Mc-Ap-Qz
		Kodurite	Tr-Span-Bp-Ap-Mc-Mp-Qz

Tr- Tirodite, Sp- Spessartite, Span- Spessartite-andradite, Qz- Quartz, Bp- Brown manganiferous pyroxene, Mp- Manganophyllite, Rh- Rhodonite, Pl- Plagioclase, Mc- Microcline, Br- Braunite, Jb- Jacobsite, Ap- Apatite, Ct- Calcite, Md- Manganoan diopside.

In gondites of different metamorphic grades, tirodite is generally present as fine to coarse needles and blades. It occurs in the interstitital spaces of spessartite and rhodonite and also cuts across rhodonite and replaces brown manganiferous pyroxene (aegirine-augite; ROY, 1971) and manganoan diopside along and across cleavage. The mineral is more widespread in pegmatites at the contact of gondite and manganese orebodies and assumes very large dimensions (upto 10.5 long crystals reported, ROY, 1966). The tirodites, by and large, occur in association with rhodonite and brown manganiferous pyroxene and very rarely, if at all, accompanies blanfordite. The affinity of brown manganiferous pyroxene (manganiferous aegirine-augite) to tirodite has already been pointed out by ROY [1971].

Chemical Composition and Optical Properties of Tirodite

	1	2	3	4	5	6	7	8	9	10
SiO_2	53.25	53.26	53.26	54.88	53.03	54.88	54.54	54.78	51.84	55.08
Al_2O_3	2.31	2.25	1.25	3.04	1.77	2.37	1.50	3.10	4.08	1.17
TiO_2	0.79	0.78	—	0.05	0.75	1.10	0.75	TR	TR	0.17
Fe_2O_3	1.71	2.60	2.63	3.69	11.25	5.67	8.93	1.90	3.28	3.96
FeO	1.62	1.12	1.06	0.62	TR	TR	TR	1.01	TR	3.17
MgO	28.42	29.16	31.26	20.81	16.84	17.33	17.11	17.02	16.71	17.52
MnO	4.66	6.24	8.25	5.36	2.84	10.14	7.77	13.21	13.43	10.52
CaO	3.42	1.10	1.11	8.28	4.17	3.34	3.11	6.17	8.01	3.32
Na_2O	1.125	1.39	1.56	2.09	5.02	3.14	4.84	0.83	1.14	2.65
K_2O	0.06	0.09	0.07	0.48	1.03	0.42	1.08	0.05	0.24	0.74
H_2O^+ H_2O^-	[2.04	[1.87	[0.05	1.13 0.08	0.40 3.25	0.70 0.12	0.38 0.14	1.76 0.16	1.10 0.18	1.32 0.14
F	—	—	—	—	0.08	0.34	0.07	0.41	0.21	0.11
	99.63	99.86	100.50	100.51	100.42	99.55	100.19	100.40	100.22	99.87
O≡F	—	—	—	—	0.03	0.14	0.03	0.17	0.09	0.05
TOTAL	99.63	99.86	100.50	100.51	100.39	99.41	100.19	100.23	100.13	99.82
100 Mg:(Mg+ $Fe^{2+}+Fe^{3+}$+Mn)	86.72	84.31	81.53	80.12	69.79	66.67	65.72	65.33	64.25	64.25
					Σ(O, OH, F)=24					
Si	7.29	7.38	7.56	7.71	7.85	7.95	7.91	7.84	7.57	7.96
Al	0.52	[0.62 0.04	0.21	[0.29 0.20	[0.15 0.16	[0.05 0.36	[0.09 0.17	[0.16 0.36	[0.43 0.27	[0.04 0.16
Ti	0.16	0.08	—	0.01	0.08	0.11	0.08	—	—	0.02
Fe^{3+}	0.18	0.27	0.27	0.39	1.25	0.62	0.97	0.21	0.36	0.43
Fe^{2+}	0.18	0.12	0.12	0.07	—	—	—	0.12	—	0.38
Mg	5.88	6.02	6.05	4.39	3.72	3.74	3.70	3.63	3.63	3.78
Mn	0.54	0.73	0.98	0.63	0.36	[0.17 1.08	[0.08 0.88	[0.68 0.92	[0.74 0.92	[0.23 1.06
Ca	0.51	0.16	0.15	1.25	0.66	0.52	0.48	0.95	[1.08 0.18	0.51
Na	0.32	0.37	0.41	[0.12 0.46	[0.98 0.46	[0.40 0.48	[0.64 0.72	[0.13 0.10	0.32	[0.43 0.32
K	0.00	0.01	0.01	0.08	0.19	0.08	0.20	0.01	0.04	0.13
OH	1.86	1.72	0.00	1.13	0.39	0.68	0.37	1.68	1.07	1.27
F	—	—	—	—	0.07	0.15	0.03	0.18	0.10	0.05
ΣZ	7.81	8.00	7.77	8.00	8.00	8.00	8.00	8.00	8.00	8.00
ΣY	6.40	6.53	6.44	5.06	5.21	5.00	5.00	5.00	5.00	5.00
ΣX	1.37	1.27	1.55	2.00	2.00	2.00	2.00	2.00	2.00	2.00
ΣA	0.00	0.00	0.00	0.54	0.65	0.56	0.92	0.11	0.54	0.45
							OPTICAL PROPERTIES			
α	1.629	1.629	1.629*	1.617	1.627*	1.632*	1.628*	1.626*	1.630*	1.631*
β	—	—	1.639*	1.631	—	—	—	—	—	—
γ	1.650	1.650	1.650*	1.637	1.649*	1.652*	1.650*	1.648*	1.651*	1.650*
α	—	—	Colourless to pale yellow	Pale Yellow	Colourless	Very pale Yellow	Colourless	Pale Buff	Pale yellow	Colourless
β	—	—	—	Pale Yellow	Pale Yellow	Pale Yellow	Pale Yellow	Buff	Yellow	Pale Yellow
γ	—	—	Pale yellow to straw yellow	Straw yellow	Yellow	Straw Yellow	Pale yellow with greenish tinge	Yellowish Brown	Yellow with brownish and greenish tinge	Pale yellow with greenish tinge
γ:[001]	18°	17°	21°	—	22°	20°	24°	23°	22°	20°
$2V_x$	41°	37°	88°	68°	80°	78°	66°	82°	80°	78°
Analyst:	S. A. Bilgrami	R. K. Phillips	P. C. Roy	S. K. Babu	P. B. Gupta	B. P. Gupta	B. P. Gupta	B. P. Gupta	B. P. Gupta	B. P. Gupta

* ±0.002

1. Tirodite, Tirodi, Madhya Pradesh [Bilgrami, 1955]
2. Tirodite, Chikla, Maharashtra [Bilgrami, 1955]
3. Tirodite, Tirodi, Madhya Pradesh [Dunn & Roy, 1938]
4. Richterite (Tirodite), Miragpur, Madhya Pradesh [Babu & Nayak, 1961]
5. Tirodite, Sitapatore, Madhya Pradesh [Roy, 1966]
6. Tirodite, Ramdongri, Maharashtra [Present study]
7. Tirodite, Gowari Wadhona, Madhya Pradesh [Roy & Purkait, 1968]
8. Tirodite, Gara, Madhya Pradesh [Present study]
9. Tirodite, Mansar, Maharashtra [Present study]
10. Tirodite, Dongri Buzurg, Maharashtra [Present study].

CHEMICAL COMPOSITION, OPTICAL PROPERTIES AND X-RAY DATA OF TIRODITE

The chemical composition and optical properties of tirodite cocurring in metamorphosed manganese formations in different localities of Madhya Pradesh and Maharashtra (Sausar Group) have been compiled in Table 2. The X-ray powder data of tirodite (Analysis No. 6., Table 2) from Ramdongri, Maharashtra are given in Table 3.

DISCUSSION

Survey of earlier literature shows that the mineral tirodite has been considered to be related to either richterite [DUNN & ROY, 1938; BILGRAMI, 19555, BABU & NAYAK, 1961] or cummingtonite [SEGELER, 1961; KLEIN, 1964]. Intermediate composition between the two (Kupfferite$_{50}$ Calcium-edenite$_{30}$ Richterite$_{20}$) has also been suggested by TRÖGER [1961]. The manganoan cummingtonites described from different areas so far, are pale greyish to light green in hand specimens and colourless to nonpleochroic pale green in thin section in plane polarized light [JAFFE *et al.* 1961; CHAKRABORTY, 1963; KLEIN, 1964], whereas the tirodites are invariably straw yellow to brownish yellow in hand specimens and distinctly pleochroic in shades of yellow in thin sections. The refractive indices of tirodite (α 1.617—1.632, γ 1.637—1.652; Table 2) are much lower than those of cummingtonites and are well within the range of the richterite-tremolite series, though lower R. I. values for manganoan cummingtonites have been reported. The 100 $Mg/(Mg+Fe^{2+}+Fe^{3+}+Mn)$ values for tirodite are in higher range (86.72 to 64.25) than in cummingtonites (67.7 to 33.8; DEER, HOWIE & ZUSSMAN, 1963, pp. 236—237) and approach those for richterite-tremolite series (99.8 to 66.8; DEER, HOWIE & ZUSSMAN, 1963, pp. 354—355). The Fe_2O_3, CaO and Na_2O contents of tirodites, though variable (Fe_2O_3 — 1.91 to 11.25, CaO — 1.10 to 8.28, Na_2O — 0.83 to 5.02; Table 2), in general, approach the range for richterite-tremolite and are much higher for cummingtonite. Also the FeO content of tirodite is negligible compared to the high FeO content of cummingtonite.

TABLE 3

X-ray Powder Data for Tirodite from Ramdongri, Maharashtra
Cu/Ni Radiation

d (Å)	I	*d*(Å)	I	*d* (Å)	I
8.44	8B	2.944	5	1.653	5
4.82	1	2.723	10	1.587	4
4.456	3	2.55	6B	1.512	4B
3.84	W	2.302	6B	1.435	5
3.415	7	2.175	6B	1.378	4
3.245	4	2.039	4B	1.344	4
3.112	7	1.88	W8	1.289	5B

For these alkali-rich amphiboles, with a general formula of $AX_2Y_5Z_8O_{22}(O, OH, F, Cl)_2$, the allocation of Mn in either *X* or *Y* site is important. In most cases, there is too much of manganese to be allocated wholely to *Y* site and a part most certainly occupies the X position. The proportion between the amount of Mn in X and Y sites is variable (PHILLIPS & LAYTON, 1964). In the X site, Mn apparently replaces Ca.

In analyses nos. 1, 2, 3, 4, 5 (Table 2) the Y site is oversubscribed (>5.00) without considering Mn at all and in analyses 6, 7, 8, 9, 10, Mn is divided between X and Y sites with the larger part invariably in the X site. Thus, in all probability, Mn largely replaces Ca in preference to (Mg, Fe^{2+}) in tirodite.

When the analyses of tirodite in Table 2 were recalculated to the basic formula of amphiboles, with Na representing all cations in A site, Ca representing Ca+Mn in X site, Mg representing Mg+Mn and Al representing Al+Fe^{3+}+Ti in Y site [PHILLIPS & LAYTON, 1964, p. 1107], analyses nos. 1, 2, 3, 4, 8, 9 & 10 indicate a composition approaching that of tremolite with some sodium and analyses nos. 5, 6 & 7 approach richterite composition (varying from Na_2Ca to $NaCa_{1.5}$ atoms per formula unit; SUNDIUS, 1946). It, therefore, indicates that the tirodites correspond to mànganoan tremolite-richterite, with the composition varying fairly widely within the complete chemical series between tremolite and richterite.

Very recently GHOSE *et al.* [1974] have shown by electron microprobe analysis, electron microscopy and single crystal X-ray diffraction that tirodite from Tirodi show magnesio-richterite and magnesio-riebeckite as two exsolved phases, indicating a miscibility gap between the two. They stated that the bulk composition of tirodite approaches that of magnesio-richterite (with only small magnesio-riebeckite) on the basis of extremal composition determined in clear patches in tirodite by electron microprobe analysis. None of the analyses of bulk tirodite samples (clean one-phase samples subject to the resolution of polarising microscope) presented in Table 2 approaches the composition of magnesio-richterite ($Na_2Mg_6Si_8O_{22}(OH)_2$) which was known [before GHOSE *et al.* 1974] only as a synthetic phase. However, analyses nos. 5 and 7 approach a composition intermediate between richterite and magnesio-richterite as synthesized by CHRISTOPHE-MICHEL-LEVY [1957].

As already stated, tirodite is found to occur largely in the pegmatite veins at their contact with manganese silicate rocks or manganese orebodies. It is also found in the regionally and contact metamorphosed manganese silicate rocks (gondite and kodurite, respectively) themselves. It is evident that the tirodites were formed in the pegmatites in an alkali-rich environment and the manganese was derived from the host rocks by assimilation. In the gondites and kodurites the tirodites were formed by soda metasomatism during the emplacement of the pegmatites.

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