

Manganese-rich calcic amphiboles of the tremolite–ferro-actinolite series

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Abstract

Amphiboles of the tremolite–ferro-actinolite series from the Bergslagen district in central Sweden have between 0 and 46% of their $M1$ – $M3$ sites occupied by Mn. These amphiboles are divided into two groups; (1) a group characterised by $Mn (M1-M3) > (Mg \text{ or } Fe) (M1-M3)$, and (2) a group with much lower contents of Mn ($M1$ – $M3$), showing the following chemical characteristics: (a) Mn ($M1$ – $M3$) never exceeds Fe ($M1$ – $M3$); (b) in Mg-rich members of the group [$Mg (M1-M3) > (Mn \text{ or } Fe) (M1-M3)$], the highest amounts of Mn ($M1$ – $M3$) occur in amphiboles with about 2.20 Mg ($M1$ – $M3$) per formula unit (pfu); in Fe-rich members of the group $Fe [(M1-M3) > (Mg \text{ or } Mn) (M1-M3)]$ high amounts of Mn ($M1$ – $M3$) [$> 0.4 Mn (M1-M3)$] pfu only occur in amphiboles with $> 3.40 Fe (M1-M3)$ pfu; (d) the lowest amounts of Mn ($M1$ – $M3$) occur in amphiboles with $Mg (M1-M3) = Fe (M1-M3)$.

Mn ($M4$) increases with increasing amounts of Mn ($M1$ – $M3$), indicating that solid solution towards the tirodite–dannemorite series is enhanced by incorporation of Mn ($M1$ – $M3$).

KEYWORDS: amphibole, tremolite, actinolite, Bergslagen, Sweden.

Introduction

THIS paper presents the mineral chemistry of some amphiboles of the tremolite–ferro-actinolite series with between 0 and 46% of their $M1$ – $M3$ sites occupied by Mn. The amphiboles are from various localities in the Bergslagen district of central Sweden. A literature survey showed that the amphiboles presented in this paper include those with the highest Mn-contents that have been reported to date. The range of Mn-substitution for Mg and Fe in the $M1$ – $M3$ sites and the distribution of Mn over the $M1$ – $M3$ and $M4$ -sites of these amphiboles will be discussed.

Analytical procedures

Electron microprobe analyses were made with a Cambridge Instrument Company Microscan 9, operated at acceleration potentials of 15 and 20 kV and sample currents of 25 and 40 nA. Raw data were corrected with the Mark 9 on-line ZAF program. Standards used were diopside (Ca, Si), rhodonite (Mn), fayalite (Fe), forsterite (Mg),

jadeite (Na) and corundum (Al). Counting times (sec) and analytical precision (2σ) are presented by Damman (1989a). Cations in the amphiboles were calculated on the anhydrous basis of 23 oxygen, assuming total iron as FeO.

The amphiboles investigated have $> 7.8 Si$, $< 0.2 Al^{IV}$, $< 0.1 Al^{VI}$, $< 0.01 Ti$ and $< 0.03 Zn$ per formula unit (pfu). In the calculations, total tetrahedral $Si + Al$ were constrained to equal 8. Several amphibole analyses show a total of slightly more than 7 cationic charges in the $M1$ – $M4$ sites. Forcing these analyses to 7 (Robinson *et al.*, 1982) requires that some Fe^{3+} and some Na ($M4$) should be present in these amphiboles. The following site-occupancy scheme is used in recalculating the microprobe analyses of all amphiboles (Robinson *et al.*, 1982):

T-site: add Si, then Al to sum to 8.00.

C-sites ($M1, M2, M3$): add left-over Al, then Fe^{3+} , Mg^{2+} , Fe^{2+} , Zn^{2+} and Mn^{2+} in this order to sum to five.

B-site ($M4$): add left-over Mn^{2+} , then Ca^{2+} , then Na^{1+} in this order to sum to 2.

A-site: add left-over Na and K.

Description of sample localities

The Gåsborn area, West Bergslagen, central Sweden. The skarns occurring of the Gåsborn area were formed by three successive processes (Damman, 1989b; Damman and Kieft, 1990): (I) deposition of exhalative-sedimentary iron-ore bearing marbles, volcanics and cherts; (II) intrusion of a synvolcanic, high-level granite and contact metamorphic formation of calc-silicate- and manganese-silicate reaction skarns in the exhalites; (III) formation of metasomatic infiltration skarns by reaction of marbles and reaction skarns with fluids released from the granite.

In Mn-rich lithologies from the Gåsborn area (Damman, 1989b) tremolite and actinolite only occur in metasomatic infiltration skarns, where they form colourless to pale green, up to 600 μm long crystals, accompanied by hornblende, biotite, rhodochrosite and helvite. In some samples analysed these minerals contain relict garnet, rhodonite, clinopyroxene and tephroite, suggesting that they were formed by replacement of the latter minerals. In other samples they are inclusion-free, suggesting that they were formed directly out of the manganeseiferous sediments.

In Mn-poor marbles from the Gåsborn area (Damman and Kieft, 1990) tremolite occurs in calc-silicate bands and reaction skarns as pale green, up to 5 mm long crystals that replace phlogopite, diopside, forsterite, clinohumite and chondrodite. In metasomatic infiltration skarns actinolite occurs as thin, pale green to dark green rims around potassium hastingsite (Damman and Kieft, 1990).

The Älvängen-Vikern area (Hellingwerf *et al.*, 1988). In the Älvängen-Vikern area exhalative-sedimentary sphalerite ores contain thin bedding parallel bands of actinolite and ferro-actinolite, cummingtonite, garnet, biotite, tourmaline and sulfides (Hellingwerf *et al.*, 1988).

In brecciated marbles that occur stratigraphically below the sphalerite ores, actinolite crystals protrude from the rim of marble fragments into a surrounding matrix.

The Stollberg Fe-Pb-Zn-Mn-(Ag) deposit (Ripa, 1988; Beetsma, 1990). The Stollberg deposit was formed similarly as the Gåsborn deposits, by three successive processes (Beetsma, 1990): (I) deposition of exhalative-sedimentary manganeseiferous iron-ore bearing marbles, volcanics and cherts; (II) prograde formation of reaction skarns and calc(manganese)-silicate bands; (III) retrograde formation of sulfide-bearing metasomatic infiltration skarns.

In the reaction skarns and calc(manganese)-silicate bands up to 400 μm large colourless to

palegreen poikiloblasts of tremolite and actinolite replace diopside and forsterite (Beetsma, 1990); in the metasomatic infiltration skarns actinolite and ferro-actinolite occur in large aggregates, intergrown with phlogopite, allanite and several sulfides. In some samples these minerals contain relict clinopyroxene, garnet and Mn-rich olivine inclusions (Beetsma, 1990), suggesting that they were formed by replacement of the latter minerals. In other samples they are inclusion-free, suggesting that they were formed directly out of the manganeseiferous sediments.

The Ösjoberg-Sirsjöberg iron-ore horizon (Baker, 1985). In the Ösjoberg-Sirsjöberg iron-ore horizon tremolite and actinolite occur in schistose zones, together with talc and chlorite, that occur between the iron-ores and the surrounding metavolcanics (Baker, 1985).

Mineralogy and mineral chemistry

Calcic amphiboles from the Gåsborn area. Actinolite from the Gåsborn area Mn-skarns shows a wide range of compositions (Table 1). Very Mn-rich actinolite occurs in thin veinlets, enclosed by a less Mn-rich actinolite. Only two such veinlets have been observed, up to 20 μm wide, and several hundred μm long (Fig. 1a-d). On electron microprobe back-scatter (Fig. 1a and c) and Mn-K α X-rays images (Fig. 1b and d) the very Mn-rich actinolite appears as bands, showing sharp boundaries towards the less Mn-rich actinolite. The very Mn-rich actinolite (Fig. 2; analyses 1 and 2, Table 1; Analyses 1-3, Table 2) shows limited composition variation (MnO 17.3-20.11 wt.%; FeO 5.97-7.44 wt.%; MgO 7.90-9.40 wt.%) and forms a small cluster on the Mn-rich side of the line Mn=Mg in Fig. 2; the less Mn-rich actinolite (Fig. 2; analyses 3 and 4, Table 1) shows a somewhat larger compositional variation (MnO 5.14-6.51 wt.%; FeO 14.56-19.45 wt.%; MgO 8.08-12.21 wt.%). The very Mn-rich actinolites are slightly more mottled and show optical orientations different from that of the surrounding less Mn-rich actinolite. This texture suggests that the very Mn-rich actinolite has replaced the less Mn-rich actinolite along fractures in the latter.

Several of the actinolites in the Gåsborn Mn-silicate skarns show Mn-rich cores and/or bands (Analyses 5 and 6, Table 1; Fig. 1e and f; Fig. 2) surrounded by a relatively Mn-poor rim (Analyses 7 and 8, Table 1; Fig. 2). Cores and rims can not be optically distinguished from one another, but they are clearly recognisable on electron microprobe back-scatter and Mn-K α X-ray images (Fig. 1e and f). Sharp and gradual

Table 1 Microprobe analyses of tremolite-ferro-actinolites from Bergslagen

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	w12	unk	taa	taa	a'	tb	c	d	trd	aa	apa	afi	trem	ab	ferr	ab2	H	DA	KN
SiO ₂	52.64	52.06	53.06	54.01	52.50	52.63	54.68	53.63	57.60	54.40	52.00	51.20	56.72	53.97	51.24	50.64	49.10	49.93	50.15
Al ₂ O ₃	0.06	0.11	0.00	0.04	0.45	0.37	0.96	1.13	0.97	0.84	0.28	0.14	0.78	0.56	1.17	0.35	0.48	0.24	0.19
FeO	6.93	6.09	15.02	13.35	10.66	10.77	8.32	8.31	4.93	13.50	25.20	29.00	3.57	13.51	26.32	28.06	30.67	25.64	26.18
MnO	19.19	19.46	5.22	5.11	10.63	11.06	4.73	4.76	0.25	0.16	1.59	2.08	1.40	2.60	0.91	4.14	2.48	8.45	8.40
MgO	8.00	8.25	11.48	11.73	10.33	9.71	16.32	16.28	21.50	15.30	6.15	3.21	21.48	13.59	6.21	3.34	2.10	2.13	2.03
ZnO	0.00	0.06	0.04	0.19	0.15	0.14	0.10	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CeO	10.85	10.40	11.60	11.72	11.50	11.54	11.39	11.56	13.10	12.70	12.20	12.00	12.03	12.20	12.25	11.63	11.51	11.04	11.07
Na ₂ O	0.05	0.14	0.00	0.14	0.22	0.18	0.74	0.68	0.06	0.10	0.04	0.00	0.19	0.07	0.14	0.11	0.02	0.04	0.06
K ₂ O	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.07	0.05	0.03	0.02	0.00	0.00	0.00
Total	97.72	96.57	96.42	96.13	96.44	96.40	97.24	96.42	97.57	97.00	97.46	97.63	96.24	96.55	98.27	98.29	96.36	97.47	98.05
Si	8.00	8.00	8.00	8.00	7.96	7.99	7.89	7.85	7.94	7.91	8.00	8.00	7.94	7.99	7.87	7.95	7.91	7.98	7.98
Aliv	0.00	0.00	0.00	0.00	0.04	0.01	0.11	0.15	0.06	0.09	0.00	0.00	0.06	0.01	0.13	0.05	0.09	0.02	0.02
Alvi	0.01	0.02	0.00	0.04	0.04	0.06	0.05	0.05	0.10	0.05	0.05	0.03	0.07	0.10	0.08	0.02	0.00	0.03	0.02
Fe ³⁺	0.03	0.04	0.00	0.06	0.00	0.03	0.00	0.00	0.08	0.00	0.00	0.00	0.02	0.00	0.00	0.04	0.04	0.00	0.00
Fe ²⁺	0.86	0.75	1.89	1.66	1.35	1.35	1.00	1.02	0.38	1.64	3.25	3.84	0.40	1.66	3.38	3.64	4.11	3.42	3.48
Mn	2.48	2.54	0.67	0.66	1.37	1.42	0.58	0.58	0.03	0.02	0.21	0.30	0.17	0.33	0.12	0.55	0.34	1.14	1.13
Mg	1.82	1.89	2.57	2.61	2.33	2.20	3.51	3.52	4.41	3.30	1.41	0.77	4.48	2.96	1.42	0.78	0.51	0.51	0.48
Zn	0.00	0.01	0.00	0.02	0.02	0.02	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ce	1.78	1.71	1.87	1.90	1.87	1.88	1.76	1.79	1.93	1.98	2.00	2.00	1.81	1.92	2.00	1.96	1.99	1.89	1.89
Na	0.02	0.04	0.00	0.04	0.06	0.05	0.21	0.19	0.02	0.03	0.01	0.00	0.05	0.02	0.04	0.03	0.01	0.01	0.02
K	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00
Total	15.00	15.00	15.00	15.00	15.04	15.01	15.12	15.16	14.95	15.01	14.95	14.95	14.99	15.00	15.05	15.02	15.00	15.00	15.02

boundaries between the cores and rims have been observed, even in the same crystal (Fig. 1e and f). Most frequently unzoned actinolites occur, showing wide variations in composition (Fig. 2). The highest Mn-content in the *M1-M3* sites of actino-

lites in this cluster is represented by the point $Mg_{44}Mn_{28}Fe_{28}$ (Analysis 6, Table 1; Analysis 4, Table 2).

Calc-silicate reaction skarns and metasomatic infiltration skarns from the Gåsborn contain

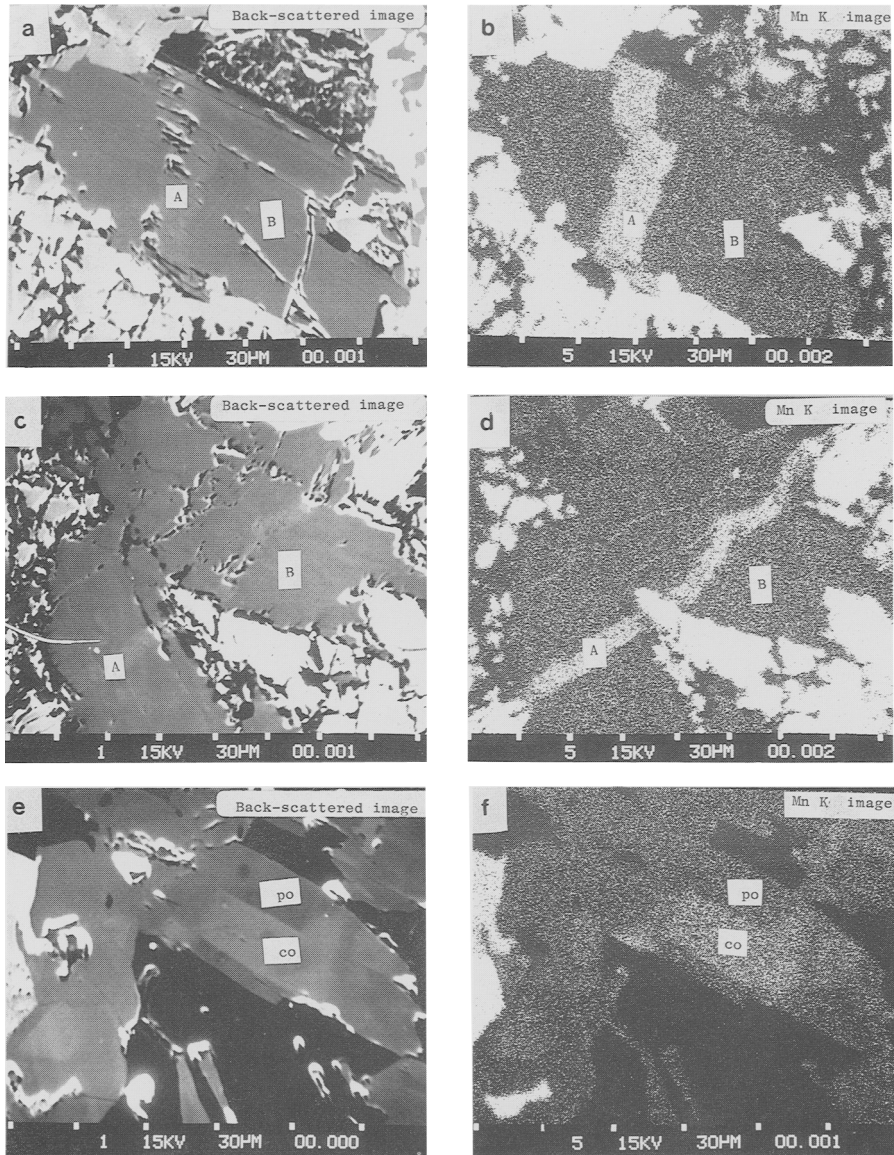
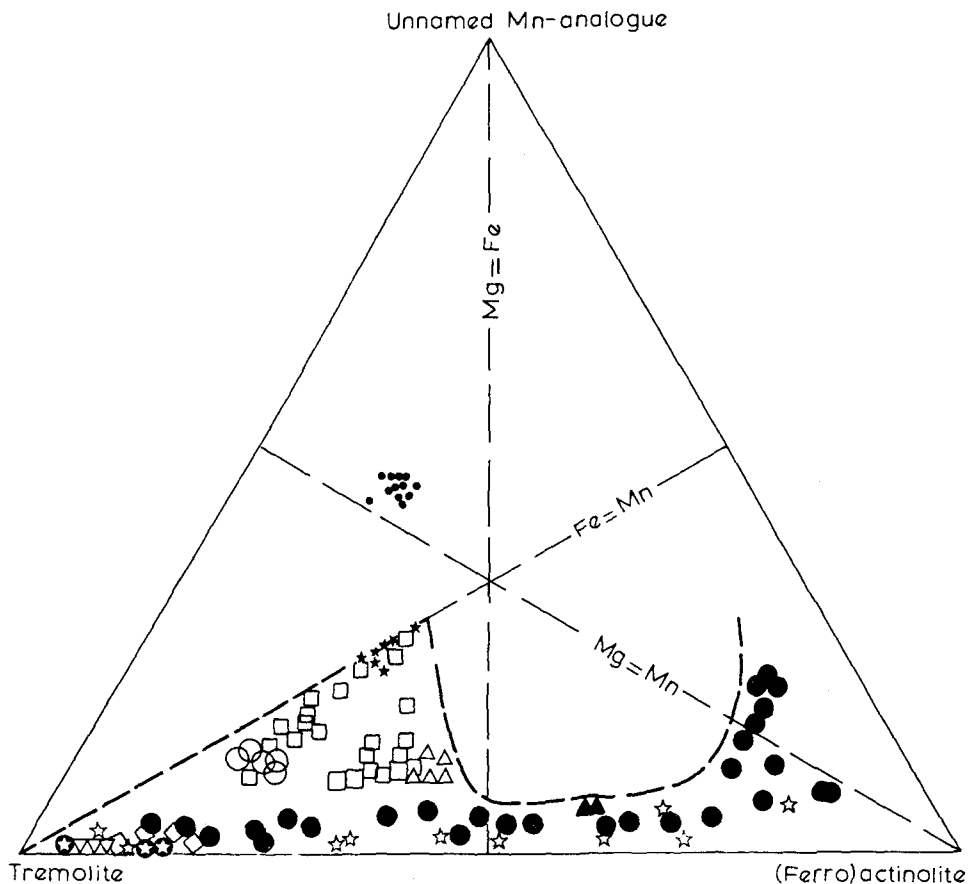


FIG. 1(a-f). (a and c) Electron microprobe back-scattered X-ray images, showing veinlets of very Mn-rich actinolite (A) in a less Mn-rich actinolite (B). (b and d) Mn-K α images of the amphiboles depicted in Fig. 1a and c; the very Mn-rich actinolites (A) show sharp boundaries towards the enclosing less Mn-rich (B) ones. (d and e) Electron microprobe back-scattered X-ray and Mn-K α of zoned actinolite, showing a Mn-rich core (co) and a Mn-poor (po) rim. Boundaries between core and rim are sharp (left hand side of the crystal) or gradual (right hand side of the crystal). All pictures have the same size; bar (Fig. 1a) = 30 μ m.



Sample localities

Gåsborn area

- -very Mn-rich actinolite from Mn-silicate skarns
- △ -less Mn-rich actinolite surrounding very Mn-rich actinolite
- ★ -cores of zoned actinolites from Mn-silicate skarns
- -rims of zoned actinolites from Mn-silicate skarns
- -unzoned actinolites from Mn-silicate skarns
- ▽ -tremolite from calc-silicate reaction skarns
- ▲ -actinolite from calc-silicate metasomatic infiltration skarns

Other localities

- ☆ -actinolite and ferro-actinolite from the Älvängen-Vikern area
- ◇ -tremolite and actinolite from the Stollberg reaction skarns
- -actinolite and ferro-actinolite from the Stollberg metasomatic infiltration skarns
- ⊛ -actinolite from the Osjöberg-Sirsjöberg iron-ores

FIG. 2. Distribution of Mg, Fe and Mn in the M1-M3 sites of tremolite-ferro-actinolite amphiboles. ---- = Inferred maximal extent to which Mg, Fe and Mn can be incorporated in tremolite-ferro-actinolite under the P, T conditions described in this paper.

either tremolite (Fig. 2) with $X_{Mg} [= Mg/(Mg + Fe^{2+} + Fe^{3+} + Mn)]$ 0.91-0.93; $X_{Fe} [= Fe^{2+}/$

$(Mg + Fe^{2+} + Fe^{3+} + Mn)]$ 0.06-0.08; $X_{Mn} [= Mn/(Mg + Fe^{2+} + Fe^{3+} + Mn)]$ 0.01-0.03 or

actinolite (Fig. 2) with $X_{Mg} = 0.36-0.38$; $X_{Fe} = 0.57-0.59$; $X_{Mn} = 0.05-0.06$).

Actinolite and ferro-actinolite from the Älvlång-Vikern area (Hellingwerf *et al.*, 1988; Analyses 9-12, Table 1; Fig. 2) vary from actinolite ($X_{Mg} = 0.88$) to ferro-actinolite ($X_{Fe} = 0.80$), with only a low Mn-content ($X_{Mn} < 0.06$).

In the Stollberg Fe-Pb-Zn-Mn-(Ag) deposit (Ripa, 1988; Beetsma, 1990), the calc-silicate bands and reaction skarns contain tremolite-actinolite with $X_{Mg} > 0.75$ (Fig. 2); the metasomatic infiltration skarns contain Mg-rich actinolites to ferro-actinolites (Beetsma, 1990; Analyses 13-19, Table 2; Fig. 2; Analyses 5-9, Table 2) with high Mn-contents in some ferro-actinolites clustering near the point $Mg_{10}Fe_{68}Mn_{22}$.

Calcic amphiboles from the Ösjoberg-Sirsjöberg iron-ores (Baker, 1985) vary in composition from tremolite (Fig. 2) to ferro-actinolitic hornblende.

Interpretation of results

The composition of metamorphic amphiboles is controlled by the temperature (T) and pressure (P) of metamorphism, the bulk chemistry of reacting rocks, minerals and hydrothermal fluids, and the amphibole's own crystal-chemical limitations.

The tremolite-ferro-actinolite amphiboles

under discussion were formed under similar metamorphic facies conditions at roughly the same pressures (1-3 kbar) and temperatures (400-500°C) (Table 3), suggesting that other parameters than P and T have controlled their compositional variation.

The bulk rock chemistry is important in those cases where the amphiboles formed by metamorphic reaction between carbonates and quartz, such as in the case of the Mn-poor marbles from the Gäsborn area (Damman and Kieft, 1990) and the Ösjoberg-Sirsjöberg iron-ores (Baker, 1985). In these rocks the formation of Mn-poor tremolites (Fig. 2) reflects the composition of the reacting carbonates, i.e. calcite and dolomite, with only minor other components (Table 3; Magnusson, 1930; Geyer and Magnusson, 1944; Damman, 1989b).

In reaction skarns from the Stollberg area the Fe, Mg and Mn contents of tremolite-actinolite (Fig. 2) are similar to that of diopside and forsterite (Beetsma, 1990), suggesting that the composition of the tremolite-actinolite is controlled by the minerals it replaces.

The Älvlång-Vikern exhalites (Hellingwerf *et al.*, 1988) are Mn-poor rocks with varying Fe/Mg ratios (Table 3), and contain Mn-poor actinolite-ferro-actinolite (Fig. 2) with a wide range of Fe- and Mg-contents, suggesting that their chemistry is controlled by the bulk chemistry of the rocks in which they are formed.

Table 2 Site occupancies in calcic amphiboles discussed in this paper

	T				M1-M2-M3				M4				A	
	Si	Al ^{IV}	Al ^{VI}	Fe ²⁺	Mg	Fe ²⁺	Zn	Mn	Mn	Ca	Na	Na	K	
WL2	8.00	0.00	0.01	0.03	1.82	0.86	0.00	2.28	0.20	1.78	0.02	0.00	0.00	
UNK	8.00	0.00	0.02	0.04	1.89	0.75	0.01	2.29	0.25	1.71	0.04	0.00	0.00	
TTD	8.00	0.00	0.00	0.00	2.15	0.77	0.00	2.08	0.29	1.71	0.00	0.00	0.00	
TB	7.99	0.01	0.06	0.03	2.20	1.35	0.02	1.34	0.08	1.86	0.04	0.01	0.00	
5983AH	7.93	0.07	0.04	0.03	2.40	2.36	0.00	0.17	0.04	1.94	0.02	0.00	0.01	
5983AI	7.89	0.11	0.04	0.09	2.31	2.39	0.04	0.11	0.07	1.91	0.02	0.02	0.01	
6136AB	7.94	0.06	0.00	0.09	0.73	3.17	0.00	0.71	0.06	1.92	0.02	0.01	0.00	
6136KN	7.98	0.02	0.02	0.00	0.48	3.48	0.00	1.02	0.11	1.89	0.00	0.02	0.00	
6136DA	7.98	0.02	0.03	0.00	0.51	3.42	0.00	1.31	0.10	1.89	0.01	0.00	0.00	

Table 3 P, T conditions during the formation of tremolite-ferro-actinolite discussed in this paper, and bulk chemical compositions of rocks in which they were formed.

Locality	P	T	Whole rock composition
Mn-poor marbles from the Gäsborn area	1kbar	app.500°C	Calcite-dolomite mixtures; <1 wt.% MnO.
Mn-silicate skarns from the Gäsborn area	1kbar	app.500°C	16-30 wt.% MnO; 16-20 wt.% Fe ₂ O ₃ ; 0.20-2.00 wt.% MgO.
Ösjoberg-Sirsjöberg		Greenschist facies conditions	Calcite-dolomite mixtures; <0.6 wt.% MnO.
The Älvlång-Vikern area		Greenschist facies conditions	0.23-2.17 wt.% MnO; 4.6-28.0 wt.% Fe ₂ O ₃ ; 1.5-9.7 wt.% MgO
Marbles from Stollberg area	3kbar	app.500°C	
Mn-silicate skarns from the Stollberg area	3kbar	app.500°C	6-12 wt.% MnO; 15-30 wt.% Fe ₂ O ₃ .

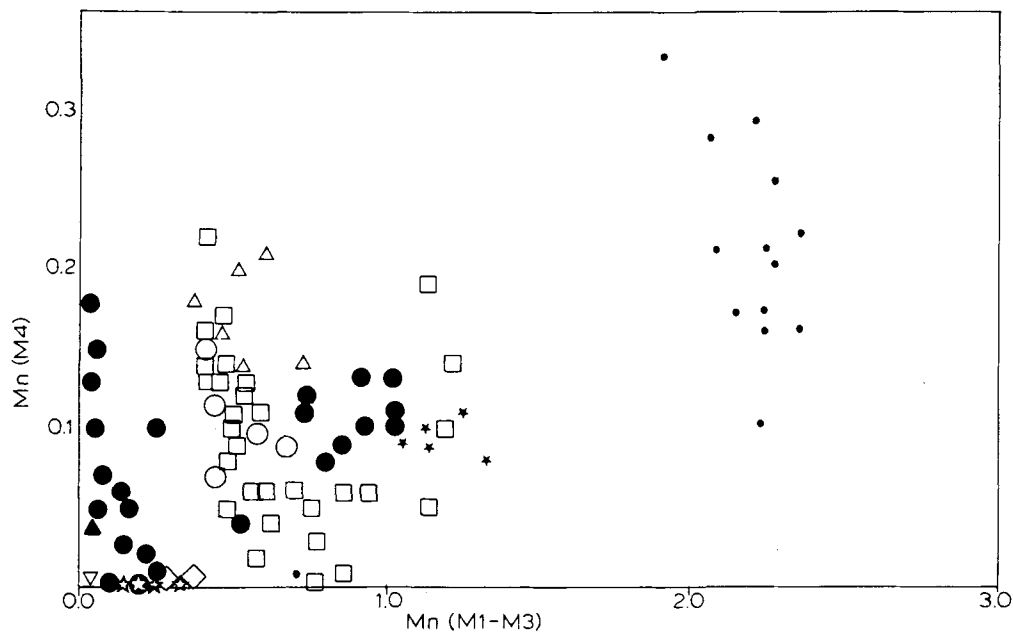


FIG. 3. Mn (*M1-M3*) vs. Mn (*M4*) in tremolite-ferro-actinolite described in this paper. Symbols as in Fig. 2.

In Mn-silicate metasomatic infiltration skarns from the Gåsborn (Damman, 1989*b*; Fig. 2) and the Stollberg areas (Beetsma, 1990; Fig. 2) actinolite and ferro-actinolite were formed by replacement of the manganeseiferous sediment and by replacement of garnet, clinopyroxene, rhodochrosite, knebelite and tephroite. These reactions take place under influence of an Fe-rich, Mg- and Mn-poor hydrothermal fluid (Damman, 1989*b*; Beetsma, 1990). The composition of the latter rocks and minerals (Table 3; Damman, 1989*b*; Beetsma, 1990) is very different from that of actinolite and ferro-actinolite, indicating that the composition of actinolite and ferro-actinolite in this case is not controlled by that of the rocks and minerals they replace. The Fe-rich hydrothermal fluid may account for the Fe-richness of some ferro-actinolites from the Stollberg area that occur on the extreme right-hand side of Fig. 2, but it can not explain many of the other amphibole compositions presented in Fig. 2. These compositions cannot be attributed to variations in *P* and *T* or the chemistry of the reacting rocks and minerals (see above) either. This suggests that these compositions are most likely controlled by the crystal-chemical limitations of the amphiboles. In other words, the analyses covering the lower half of Fig. 2 are believed to represent the maximum possible variation of Mg, Mn and Fe (*M1-M3*) in tremolite-ferro-actinolite that are

formed under the *P, T* conditions described in this paper.

A similar type of reasoning can be applied to the gap between the extremely Mn-rich and the less Mn-rich actinolites on the left-hand side of Fig. 2. The extremely Mn-rich actinolites occurring above the gap are formed as replacement products after less Mn-rich actinolite occurring below the gap, but the boundary between these two groups of amphiboles is sharp (Fig. 1), and there is a large gap in chemical composition between them (Fig. 2). This suggests that amphiboles with compositions falling in the empty space between the lines $Fe=Mn$ and $Mg=Mn$ on the left-hand side of Fig. 2 cannot be formed under the prevailing conditions either.

Unfortunately, from the data presented in this paper nothing can be concluded about the maximum possible amount of Mn in extremely Mn-rich actinolite (Fig. 2) and nothing can be concluded about the maximum possible amount of Mn in ferro-actinolite (? , Fig. 2).

Fig. 3. presents the relationship between Mn (*M1-M3*) and Mn (*M4*) in the tremolite-ferro-actinolites. There is a wide range of Mn (*M4*) contents at any amount of Mn (*M1-M3*). It is interesting to note that amphiboles with higher Mn (*M1-M3*) contain higher Mn (*M4*) than amphiboles with lower amounts of Mn (*M1-M3*). This suggests that an increase in Mn (*M1-M3*) in

tremolite-ferro-actinolite increases the extent to which these amphiboles can form a solid-solution series with amphiboles of the tirodite-dannemorite series.

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