# Cr-rich Mg-chloritoid, a first record in high-pressure metagabbros from Monviso (Cottian Alps), Italy

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## Abstract

Metamorphosed troctolite cumulates occur interbedded with Mg-rich metagabbros in the Monviso ophiolitic massif; they have developed chloritoid, omphacite, talc and garnet during the eclogitic stage of the Eo-alpine metamorphism. The lack of penetrative deformation in the rocks has made it possible to recognize different microstructural sites of chloritoid growth, in which the chloritoid composition may vary widely and is controlled by the specific inherited chemical domain.

The chloritoid compositions are unusually rich in Cr and Mg with large variations in  $Fe^{2+}/Mg$  and Cr/Al<sup>VI</sup> ratio. The Cr/Al ratio in chloritoid is linked to both the Cr value of the primary minerals (i.e. Cr-rich spinels, Cr-end-members in the clinopyroxenes) and a limited redistribution of Cr during metamorphism. The  $Fe^{2+}/Mg$  ratio, while being partly affected by bulk composition of the host rocks, also varies between different microstructural sites; the highest ratio is recorded in coronas between clinopyroxene and plagioclase, lower values occurring in coronas between plagioclase and olivine.

KEYWORDS: chloritoid, meta-troctolites, metagabbros, Monviso massif.

## Introduction

THE Monviso ophiolitic massif represents a section of the Ligurian-Piedmontese Oceanic Basin lithosphere and constitutes the most complete metamorphic ophiolite section in the Western Alps (for references on Alpine metamorphic ophiolites see: Bearth, 1974; Dal Piaz and Ernst, 1978; Caby *et al.*, 1978; Messiga *et al.*, 1983; Messiga, 1986, and bibliography therein).

As already pointed out in previous papers (Lombardo *et al.*, 1978, 1980), the original lithologic sequence of the massif is still well preserved despite the polyphase alpine metamorphic overprinting. Particularly, the intrusive section of gabbroic rocks often shows a primary magmatic layering with repeated alternations of ultramafic cumulates, Mggabbros, Fe-gabbros and Fe-diorites (Costa Ticino series, Passo Gallarino complex and Lago Superiore metagabbros).

Alpine eclogite facies metamorphism in basic rocks is represented, as a general rule, by the

Mineralogical Magazine, December 1987, Vol. 51, pp. 681–687 © Copyright the Mineralogical Society

association of Na-clinopyroxene (chloromelanite) + garnet  $\pm$  Na-amphibole in Fe-rich metagabbros and metabasalts, and by the association of Na-clinopyroxene (omphacite) + garnet + zoisite + talc  $\pm$ Na-amphibole in Mg-rich metagabbros.

At the base of the sequence, cumulitic metatroctolites have been found interbedded with Mgrich metagabbros. Their unusual concentrations of MgO and Al<sub>2</sub>O<sub>3</sub> allowed crystallization of unusual mineral parageneses. On the outcrop, these rocks appear as elongated, dark-stained, emerald green bodies; they developed chloritoid, omphacite, talc and garnet parageneses during the eclogitic stage. A complete survey of such parageneses from a petrologic view-point has been deferred to future studies. The purpose of this paper is the chemical characterization of the chloritoids occurring in the rocks, as they appear to be unusually rich in Cr and Mg with significant variations in  $Fe^{2+}/Mg$  and  $Cr/Al^{VI}$ ratios which relate to the microstructural site of origin.

# **Primary lithologies**

The bulk chemical analysis of the sample MOE 11B is considered representative of the metatroctolite compositions studied: SiO<sub>2</sub> 45.07, Al<sub>2</sub>O<sub>3</sub> 21.12, Fe<sub>2</sub>O<sub>3</sub> 1.43, FeO 3.11, MgO 12.99, CaO 9.93, Na<sub>2</sub>O 3.19, Cr<sub>2</sub>O<sub>3</sub> 0.04, H<sub>2</sub>O 3.24% (compare with the chemical data on the Northern Apennines ophiolites; Serri, 1980). Mineral and textural relics show that the analysed rocks can be referred to clinopyroxene- and spinel-bearing troctolites with slight, but significant, differences between the various lithotypes. Clinopyroxene and spinel are still present as relics, but neither olivine nor plagioclase were preserved. In some cases, textural relationships suggest that orthopyroxene may have occurred; if so, it is now replaced by a mineral assemblage (talc + chloritoid) similar to the olivine pseudomorphs. It is therefore impossible to state unequivocally whether primary orthopyroxene was present and how abundant it was.

The following original parageneses can be reconstructed, for each sample, from their pseudomorphs: (1) plagioclase + olivine (and/or orthopyroxene) + Cr-rich-spinel and rare clinopyroxene (MOE 11A); (2) plagioclase + clinopyroxene + Cr-rich-spinel and rare olivine (and/or orthopyroxene) (MOE 11B); and (3) plagioclase + olivine (and/or orthopyroxene) + clinopyroxene + Cr-rich-spinel (MOE 12). The latter sample corresponds to a contact between lithotypes (1) and (2) and is characterized by a higher Cr-rich spinel content.

During the high-pressure metamorphic event, talc, garnet and omphacite grew, in addition to smaller quantities of tremolitic amphibole and chlorite, and constitute the most typical mineralogical association found with chloritoid.

# Metamorphic textures

The investigated samples contain the following metamorphic mineral assemblages:

MOE 11A: talc, chloritoid, omphacite; MOE 11B: chloritoid, omphacite, garnet, talc; MOE 12: talc, omphacite, chloritoid, garnet.

The distribution of metamorphic minerals in the rocks is controlled by microstructural sites, characterized by specific chemistry.

It is still possible to recognize the shape of the magmatic minerals, although they are partly or completely replaced. The metamorphic assemblages developed in the different types of pseudomorphs can be summarized as follows:

(1) in pseudomorphs after olivine (and/or orthopyroxene)—talc in large crystals, sometimes in addition to tremolitic amphibole; (2) in pseudomorphs after clinopyroxene—large neoblastic omphacite bodies having elongated shape and decussate texture, together with small idioblastic chloritoid grains;

(3) in pseudomorphs after plagioclase—large neoblastic omphacite crystals and fine-grained omphacite aggregates can be frequently found associated with rare garnet and talc in the outer parts of pseudomorphs close to the contact with mafic minerals whereas in the internal part of pseudomorphs, chloritoid and fine omphacite aggregates occur;

(4) in Cr-rich spinel pseudomorphs—Mg-Cr chloritoid, rutile and ores; as a rule, they are filled with numerous small ore grains and fine chloritoid aggregates.

Another distinctive aspect of the metamorphic textures is the occurrence of coronas along the contacts between former mafic minerals and plagioclase. The coronas are characterized by more complex mineral associations than pseudomorphs because chemical exchanges occurred at mineral boundaries during metamorphism in the eclogite facies.

The coronas between clinopyroxene and plagioclase and between olivine (and/or orthopyroxene) and plagioclase are both characterized by chloritoid + omphacite + talc + garnet. Cr-chloritoid and Cr-omphacite characterize coronas between the original sites of Cr-spinel and plagioclase.

Together these observations allow us to define six sites in the samples where chloritoid occur:

site A: in pseudomorphs after Cr-rich spinel, associated with oxides;

site B: in pseudomorphs after primary clinopyroxene, associated with omphacite;

site C: in pseudomorphs after plagioclase, associated with talc and omphacite;

site D: in olivine (and/or orthopyroxene)-plagioclase coronas, associated with talc, omphacite and sometimes garnet;

site E: in clinopyroxene-plagioclase coronas, associated with garnet, omphacite and sometimes talc;

site F: in Cr-rich spinel-plagioclase coronas, associated with garnet, omphacite and sometimes talc.

Chloritoid has been analysed in each of these sites.

#### Chloritoid composition

Analyses have been carried out with a Camebax Microprobe using oxides and natural ores as



FIGS. 1 and 2. FIG. 1 (*left*). Cr-Al<sup>VI</sup> plot for chloritoids in different chemical domains: • site A; ■ site B; ▲ site C; ▲ site D; □ site E; • site F. FIG. 2 (*right*). Fe<sup>2+</sup>-Mg plot for chloritoids in different chemical domains (same symbols as in Fig. 1).

standards. Atomic proportions have been calculated based on 12 oxygens and  $Fe^{2+}$  has been evaluated by the stoichiometric relation:

$$Fe^{3+} = 6 - (Al_{tot} + Si + Cr).$$

Figs. 1 and 2 show all these analyses whereas only representative analyses are reported in Tables 1, 2, and 3. As shown in Figs. 1 and 2, a fair negative correlation exists between Cr and Al<sup>VI</sup> and between  $Fe^{2+}$  and Mg. In terms of atoms per formula unit, Cr ranges between 0.01 and 0.60 and Mg between 0.66 and 1.72. Considering that the chloritoid structure (Brindley and Harrison, 1952; Hanscom, 1975; Fyfe et al., 1968; Ribbe, 1980) consists of tetrahedral layers of SiO<sub>4</sub>, octahedral layers of AlO<sub>6</sub> (L1 corundum type) and octahedral layers of  $R2 + AlO_2(OH)_4$  (L2 brucite type), the Fe-Mg substitution of Cr-Al<sup>vi</sup> is assumed to occur only in the octahedral layers L2; the substitution seems more complex, since it may occur in both octahedral layers L1 and L2. In terms of atoms per formula unit the investigated chloritoids show negligible values of Mn (max. 0.013), Ca (max. 0.008), Na (max. 0.008) and Ti (max. 0.003).

The chloritoid compositions relate to the host rock composition, as well as to the microstructural

site in which they occur. The  $Fe^{2+}/Mg$  ratio relates to both these factors, whereas the Cr/Al<sup>VI</sup> ratio is linked to the specific microstructural site. Thus a higher  $Fe^{2+}/Mg$  (mean value = 0.27) ratio can be observed in the chloritoids of the sample MOE 11B (FeO/MgO<sub>rock</sub> = 0.24) and a lower one (mean value = 0.20) in the sample MOE 11A (FeO/ MgO<sub>rock</sub> = 0.08), whereas the chloritoids in the sample MOE 12, which represents the transition between the two previous lithotypes, have an intermediate  $Fe^{2+}/Mg$  ratio (mean value = 0.21).

In any single sample, however, chloritoid compositions show significant  $Fe^{2+}/Mg$  ratio variations and these are related to the microstructural site. For instance, the chloritoids of sample MOE 11B have the highest variation in their composition; the  $Fe^{2+}/Mg$  ratio has high values for the chloritoids in site E, and a very wide range (0.16-0.54), while chloritoids in site F have a more limited range (0.29-0.44). More restrictive ranges and intermediate ratio values characterize the chloritoids in site C (0.20-0.23) and site B (0.19-0.22), while the chloritoids in site A have the lowest ratio values (0.16-0.19).

As far as microstructural sites are concerned, the chloritoids from site A have the highest Cr and Mg

		A		D		
	5-3	5-1	17	2	16	6-159
Si02	26.23	26.89	26.90	26.72	26.71	26.98
TiO2	0.06	0.03	0.00	0.00	0.00	0.00
A1203	37.82	42.80	43.53	40.95	43.53	42.16
Cr203	8.47	2.47	1.20	4.54	1.54	3.54
Fe0 <sup>+</sup>	4.99	5.51	7.30	5.26	6.05	5.84
MnO	0.00	0.02	0.08	0.04	0.04	0.08
MgO	14.43	14.47	13.35	14.74	14.28	14.70
CaO	0.00	0.02	0.02	0.02	0.01	0.00
Na 0	0.00	0.02	0.00	0.00	0.00	0.00
тот.	92.00	92.23	92.38	92.27	92.16	93.30
Si	2.029	2.034	2.039	2.034	2.021	2.029
Ti	0.003	0.002	0.000	0.000	0.000	0.000
Al <sup>iv</sup>	0.000	0.000	0.000	0.000	0.000	0.000
Al <sup>Vi</sup>	3.448	3.817	3.890	3.673	3.882	3.737
Cr	0.518	0.148	0.072	0.273	0.092	0,211
Fe <sup>3+</sup>	0.034	0.035	0.038	0.054	0.026	0.052
Fe <sup>2+</sup>	D.289	0.314	0.424	0.281	0.357	0.315
Mn	0.000	0.001	0.005	0.003	0.003	0.005
Mg	1.663	1.631	1.509	1.673	1.610	1.647
CaO	0.000	0.001	0.000	0.002	0.001	0.003
Na	0.000	0.002	0.000	0.000	0.000	0.000
TOT.	7.985	7.984	7.979	7.994	7.991	7.998
Fe/Mg	0.17	0.19	0.28	0.17	0.22	0.16

TABLE 1. Representative analyses of chloritoids from sample MOE 11A; A, C and D indicate the different chemical domains;  $Fe0^*=$  Fe0 total.

TABLE 2. Representative analyses of chloritoids from sample MOE 11B; A, B, C, E and F indicate the different chemical domains;  $FeO^* = FeO$  total.

	<u>A</u>		В		с		E				F
	2~9	26	49	50	23	24	42	44	55	35	28
SiO2	26.07	26.17	27.19	27.22	26.84	26.06	26.95	26.73	27.32	26.97	26.86
TiO2	0.03	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01
A1203	35.06	36.85	44.84	44.31	44.20	44.40	43.48	43.85	44.82	43.30	42.99
Cr203	9.64	9.48	0.06	0.18	0.39	0.36	0.11	0.09	0.24	0.41	2.34
Fe0 <sup>+</sup>	4.80	4.90	6.34	5.93	6.58	6.10	11.21	9.16	5.95	10.31	7.61
MnO	0.04	0.06	0.05	0.02	0.03	0.03	0.20	0.12	0.00	0.16	0.09
MgO	14.54	14.44	14.25	14.51	14.13	14.56	10.62	12.25	14.75	11.43	13.49
CaO	0.01	0.03	0.02	0.02	0.00	0.02	0.11	0.14	0.02	0.30	0.03
Na <sub>2</sub> 0	0.00	0.02	0.00	0.00	0.00	0.00	0.06	0.06	0.00	0.13	0.01
TOT.	90.19	91.95	92.76	92.19	92.17	91.53	92.74	92.40	93.11	93.03	93.43
Si	2.067	2.033	2.035	2.046	2.028	2.031	2.067	2.039	2.034	2.058	2.026
Ti	0.002	0.000	0.008	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001
Aliv	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Al <sup>Vi</sup>	3.277	3.374	3.955	3.925	3.934	3.928	3.930	3.942	3.933	3.894	3.821
Cr	0.604	0.582	0.004	0.011	0.023	0.021	0.007	0.006	0.014	0.025	0.139
Fe <sup>3+</sup>	0.119	0.044	0.042	0.064	0.043	0.051	0.064	0.053	0.053	0.081	0.040
Fe <sup>2+</sup>	0.199	0.274	0.355	0.309	0.373	0.332	0.656	0.532	0.317	0.577	0.440
Mn	0.003	0.004	0.003	0.002	0.002	0.002	0.013	0.008	0.000	0.010	0.006
Mg	1.718	1.672	1.589	1.626	1.590	1.629	1.214	1.392	1.637	0.658	1.516
Ca	0.001	0.002	0.002	0.002	0.000	0.001	0.009	0.011	0.002	0.024	0.002
Na	0.000	0.003	0.000	0.001	0.000	0.000	0.009	0.009	0.001	0.019	0.001
TOT.	7.990	7.991	7,985	7.986	7.993	7.994	7.969	7.991	7.991	7.990	7.995
Fe/Mg	0.12	0.16	0.22	0.19	0.23	0.20	0.54	0.38	0.19	0.44	0.29

#### Cr- AND Mg-RICH CHLORITOID

	A		с		D			E		F	
	2-2	2-7	1-1	1-3	13	36	5-7	3-5	3-6	2-6	2-16
Si02	26.09	26.41	26.81	26.80	26.75	27.49	26.72	26.76	26.78	26,90	26.70
TiO2	0.04	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
A1203	37.17	40.06	43.60	43.22	45.35	45.25	44.18	43.84	43.82	43.26	42.86
Cr203	9.60	5.96	1.32	1.41	0.46	0.03	0.04	1.14	1.00	1.75	1.88
Fe0 <sup>+</sup>	4.76	5.33	5.75	5.99	5.75	6.51	7.26	5.63	5.88	5.55	5.75
MnO	0.00	0.02	0.04	0.01	0.01	0.05	0.07	0.01	0.02	0.01	0.02
MgO	14.60	14.35	14.52	14.29	14.86	14.30	13.39	14.53	14.40	14.61	14.33
CaO	0.00	0.01	0.00	0.02	0.00	0.03	0.02	0.01	0.00	0.02	0.02
Na 0	0.00	0.01	0.00	0.01	0.02	0.01	0.01	0.00	0.01	0.00	0.00
TOT.	92.26	92.17	92.06	91.75	93.20	93.69	91.69	91.92	91.91	92.11	91.56
Si	2.019	2.023	2.025	2.035	1.991	2.038	2.033	2.022	2.025	2.032	2.032
TI	0.003	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Al <sup>iv</sup>	0.000	0.000	0.000	0.000	0.009	0.000	0.000	0.000	0.000	0.000	0.000
Al <sup>Vi</sup>	3.390	3.618	3.884	3.869	3.969	3.953	3.963	3.907	3.908	3.853	3.847
Cr	0.587	0.361	0.079	0.084	0.027	0.003	0.003	0.068	0.060	0.105	0.113
Fe <sup>3+</sup>	0.023	0.021	0.037	0.047	0.004	0.044	0.034	0.025	0.032	0.042	0.040
Fe <sup>2+</sup>	0.285	0.320	0.327	0.333	0.354	0.360	0.428	0.331	0.340	0.309	0,326
Mn	0.000	0.001	0.003	0.001	0.000	0.003	0.004	0.001	0.001	0.001	0.001
Mg	1.683	1.638	1.635	1.617	1.648	1.580	1.518	1.636	1.623	1.644	1.627
Ca	0.000	0.001	0.000	0.001	0.000	0.002	0.001	0.000	0.000	0.001	0.002
Na	0.000	0.001	0.000	0.001	0.001	0.002	0.002	0.000	0.001	0.000	0.000
TOT.	7.990	7.986	7.992	7.988	8.008	7.990	7.986	7.991	7.992	7.988	7.988
Fe/Mg	0.17	0.20	0.20	0.21	0.21	0.23	0.28	0.20	0.21	0.19	0.20

TABLE 3. Representative analyses of chloritoids from sample MOE 12; A, C, D, E and F indicate the different chemical domains;  $FeO^* = FeO$  total.

content (see Figs 3 and 4). Furthermore, as shown in Fig. 3, the Cr distribution is not homogeneous. Its content is high and variable in the crystals formed inside the spinel pseudomorphs but decreases rapidly in the crystals formed in the outside rim of the spinel, due to the  $A1^{VI}/Cr$  substitution. It should also be pointed out that in this microstructural site the  $Fe^{2+}-Mg$  substitution is high.

As shown in Figs. 1 and 2, idioblastic chloritoid crystals in site B exhibit smaller Cr and Mg variations than site A. The highest  $Fe^{2+}/Mg$  ratios occur when chloritoid is associated with omphacite. In site C, the chloritoid shows a wide variation in composition especially as far as Cr-Al<sup>VI</sup> substitution is concerned, and this must be due to a non-homogeneous Cr redistribution during metamorphism as neither Cr, Fe or Mg were present in this site before metamorphism. Fig. 4 is particularly significant: along the profile of a large crystal of chloritoid, Cr-Al<sup>VI</sup> substitution has a random character, while towards the boundary the  $Fe^{2+}$ -Mg substitution decreases symmetrically.

In the coronas, the chloritoids do not show wide compositional variations but they are clearly linked to the primary minerals from which they derive. In site D the chloritoid may be associated with different minerals according to the host rock composition; in sample MOE 11A (analysis 6-159), it occurs with omphacite and talc and has a  $Fe^{2+}/Mg$  ratio of 0.16, whereas in sample MOE 12 (analyses 5-7, 13, and 36) it coexists with talc and garnet and has a higher ratio (0.21-0.28).

Chloritoid compositions in site E, in sample MOE 11B, show that the highest  $Fe^{2+}/Mg$  ratio in the chloritoid is achieved when it is associated with garnet, omphacite and talc, along the coronas between primary clinopyroxenes and plagioclases.

## Discussion

The results show that compositions of chloritoids are significantly linked both to the host rock composition and to the site of growth. The latter variation can be illustrated in terms of  $Cr/Al^{VI}$  and  $Fe^{2+}/Mg$  variations (Table 4).

The Cr/Al<sup>VI</sup> ratio decreases from pseudomorphs on primary Cr-rich spinel (site A) through plagioclase-spinel coronas (site F) and pseudomorphs on plagioclase (site C) to pseudomorphs on primary clinopyroxene (site B), while for sites D and E such



FIGS. 3 and 4. FIG. 3 (*left*). Compositional zoning of chloritoids from pseudomorphs after Cr-rich spinel (site A) and corona between Cr-rich spinel and plagioclase (site F). Sample MOE 12. FIG. 4 (*right*). Compositional zoning of chloritoids associated with omphacite in pseudomorphs after plagioclase (site C). Sample MOE 11A.

				A		В			
Chemica domains	L Cr-ctd	Cr-omp	ctd	omp	gnt	tc	ores	Cr	Mg
A	x	(x)					x	0.60 - 0.21	1,72 - 1,63
В			x	x			(x)	0,06 - 0,00	1.65 - 1.59
С			x	x		x		0,39 - 0,00	1.67 - 1.51
D			x	x	(x)	x		0,21 - 0,00	1.65 - 1.52
E			x	x	x	(x)	(x)	0.07 - 0.01	1.64 - 1.21
F	x	x		_		-		0.40 - 0.03	1.68 - 1.30

TABLE 4. Coexisting minerals and critical compositional factors for different chemical domains of the investigated metatroctolites; parentheses indicate minerals only occasionally present.

ctd = chloritoid; omp = omphacite; gnt = garnet; tc = talc.

ratios are practically zero. The Cr content is therefore affected both by the Cr value of the primary minerals and by a limited redistribution of Cr during metamorphism (e.g. the presence of abundant though inhomogeneous Cr in chloritoid from plagioclase pseudomorphs).

The Fe<sup>2+</sup>/Mg ratio, while being affected by the bulk composition of the system, is also significantly linked to different microstructural sites. The highest ratio is recorded in the coronas between clinopyroxenes and plagioclases, lower values occurring in coronas between plagioclase and olivine. Commonly, Fe<sup>2+</sup>/Mg appears to vary with Cr/Al<sup>VI</sup>.

Chloritoid compositions unusually rich in Cr are linked to the presence of Cr-rich spinels in the original protolith, as already highlighted by Mevel and Kienast (1980). Cr redistribution during Alpine metamorphism is very slight, since high-pressure, low-temperature metamorphism does not result in chemical homogenization of the rock.

Although the chloritoid parageneses in metamorphosed gabbros of the Alps have been studied previously (Bearth, 1963; Chinner *et al.*, 1973; Kienast, 1982), in this case, the lack of penetrative deformations has made it possible to recognize different microstructural sites related to original minerals, and to demonstrate how the large range in chloritoid composition is constrained by specific inherited chemical domains.

## Acknowledgements

The manuscript has benefited from discussion with C. Chopin, C. Mevel and G. B. Piccardo.

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[Revised manuscript received 13 November 1986]