Zoning of chloritoid from kyanite-facies metapsammites, Alpi Apuane, Italy

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ABSTRACT

Chloritoid with significant Mg-Fe zoning occurs as lath-shaped porphyroblasts and as clusters of subradiating crystals in the Triassic Verrucano metapsammite (quartz + muscovite + chlorite + chloritoid ± kyanite) of the Massa Unit, Alpi Apuane. Two main types of chloritoid zoning profiles were found. The first type is characterised by gradual increase in Mg from core to rim of the porphyroblasts. In the second type the Mg content is constant from the core to the inner rim, but sharply decreases in the outer rim. Both types of zoning have been interpreted as the result of prograde growth during the Alpine metamorphism. The temperature, estimated using the chlorite-chloritoid thermometer, ranges from 467 to 560°C.

KEYWORDS: chloritoid, Mg-Fe zoning, chlorite, kyanite facies rocks, Alpi Apuane.

Introduction

Low-temperature kyanite facies metapsammites from the Massa Unit of the Alpi Apuane (Italy) commonly contain chloritoid porphyroblasts with significant Fe-Mg zoning. This paper describes two representative examples of Fe-Mg zoning of chloritoid in these rocks with the aim of gaining a better understanding of chloritoid zoning. To our knowledge, there are no examples in the literature of chloritoid zoning profiles from low-temperature kyanite-facies metapsammites.

The chloritoid rocks used in this study were collected from the Triassic Verrucano Formation of the Massa Unit, that forms the western part of the metamorphic core complex (Autochthon Unit and Massa Unit) of the Alpi Apuane. Two main tectonic phases were responsible for the metamorphism and deformation of the rocks of the Alpi Apuane (Carmignani and Kligfield, 1990). The metamorphic zonation of the Alpi Apuane is based on the regional distribution of pyrophyllite and kyanite in psammitic and pelitic rocks (Franceschelli et al., 1986a). Two metamorphic zones are recognised: pyrophyllite + quartz and kyanite + quartz in the Autochthon and Massa Units, respectively. Sporadic occurrence of

staurolite and pyrophyllite has been reported by Franceschelli et al. (1997) in the Massa Unit. The metamorphic history of these rocks can be summarised as follows (Carmignani and Kligfield, 1990; Franceschelli et al., 1997 and reference therein): initial burial and D_1 deformation (27 Ma) followed by an extensional D_2 phase (10–12 Ma); peak metamorphic conditions (P – 6–8 kbar and T – 420 to 500°C) between D_1 and D_2 deformations; subsequent uplift, with a high dP/dT ratio path and lastly nearly isobaric cooling to $P \approx 1.5$ kbar and $T \approx 120$°C.

Description of samples

Chloritoid-bearing metapsammites are schistose with a distinct porphyroblastic texture given by chloritoid poikiloblasts. Chloritoid typically crosscuts the S_1 schistosity and forms lath-shaped crystals or sub-radiating clusters. Sample 406 consists of quartz (30%) muscovite (25%) chloritoid (20%), chlorite (10%) kyanite (5%) and Fe and Ti oxides (10%). The chloritoid porphyroblasts (0.1–1.0 mm in size) preserve muscovite, rutile and magnetite inclusions. Epidote, tourmaline, apatite and zircon are accessory minerals. Sample 818 is made up of quartz (25%),

muscovite (30%), chloritoid (20%), chlorite (15%) and Fe and Ti oxides (10%). Chloritoid porphyroblasts (1−4 mm in size) contain abundant magnetite and rutile, quartz, muscovite, paragonite and chlorite (Fig. 1a,b) inclusions.

Mineral chemistry

The composition of chloritoid and chlorite (Tables 1 and 2) was determined on polished thin sections with an Edax-Energy Dispersive System attached to a Philips 515 SEM and following the procedure described by Franceschelli et al. (1986b).

(1) Chloritoid: The Al_{tot} ranges from 3.934 to 4.003 a.p.f.u. and the Fe^{3+} (<0.060 a.p.f.u) and
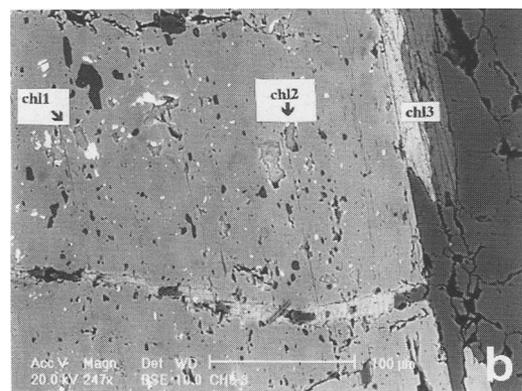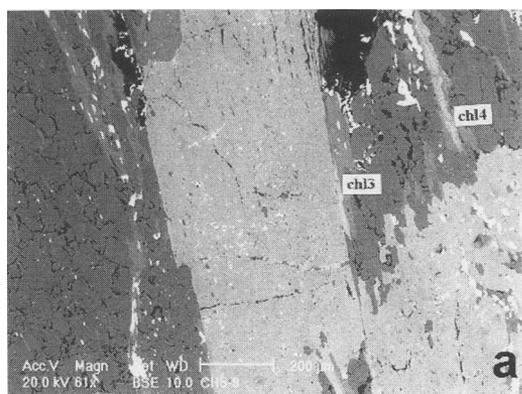
FIG. 1. (a) BSE image of a zoned chloritoid porphyroblast from the sample 818 with along the matrix chlorite: chl_3, and chl_4; (b) detail of chloritoid porphyroblast showing inclusion of chlorite in the core (chl_1) and in the rim (chl_2).

Mn (<0.053 a.p.f.u) contents are uniformly low. Representative zoning profiles for chloritoid from samples 406 and 818 are shown in Fig. 2. In sample 406 the Fe_{tot} content of chloritoid uniformly decreases from the core (1.610 a.p.f.u) to the inner rim (1.234 a.p.f.u.) and slightly increases in the outer rim. Mg gradually increases from the core (0.408 a.p.f.u.) to the inner rim (0.784 a.p.f.u.), and then gently decreases in the outer rim. In sample 818 the Fe_{tot} and Mg contents of chloritoid are quite constant from the core (Fe_{tot} = 1.675 a.p.f.u and Mg = 0.303 a.p.f.u.) to the inner rim; in the outer rim Mg abruptly decreases to 0.083 a.p.f.u and Fe_{tot} increases to 1.911 a.p.f.u.

(2) Chlorite: In sample 406 chlorite occurs only in the matrix. The composition of chlorite is homogeneous; X_{Mg} ($Mg/(Mg+Fe_{tot})$) is 0.755 and the Al^{VI} content 3.454 a.p.f.u.. In sample 818, chl_3 and chl_4 matrix chlorites (Fig. 1a) have X_{Mg} values of 0.154 and 0.177 and Al^{VI} contents of 3.349 and 3.287 a.p.f.u., respectively. The chlorite in the chloritoid core (chl_1) has an X_{Mg} value of 0.467 and an Al^{VI} content of 3.269 a.p.f.u, while in the chloritoid rim (chl_2) has an X_{Mg} value of 0.231 and an Al^{VI} content of 3.195 a.p.f.u.(Fig. 1b).

(3) Muscovite: This is a celadonite-poor muscovite and shows a clear deficiency in the interlayer cations (K+Na <1.85 a.p.f.u; Na/(Na+K) ratio $\approx$ 0.05). The Si content ranges from 6.14 to 6.31 a.p.f.u. The Mg+Fe sum range from 0.15 to 0.25 a.p.f.u..

(4) Kyanite: This is quite near its ideal composition. Fe and Mg show very limited ranges of 0.04 0.13 and 0.00 0.13 a.p.f.u., respectively.

(5) Paragonite: This was found only in sample 818 where it was included in the chloritoid. The following ranges of elements content (in a.p.f.u) were observed: Al: 3.87, Fe: 0.027, Na: 1.62, K: 0.16.

(6) Rutile: This is almost pure TiO_2 with very small amounts of Al and Fe.

(7) Magnetite: Total Fe as FeO: 86−90; TiO_2 up to 1.30.

(8) Ilmenite: Al up to 0.014 and Ti up to 1.04 (a.p.f.u), Ca and Mn are present in traces.

Discussion

Interpretation of chloritoid zoning

The composition of the chloritoid rim of sample 406 is apparently in equilibrium with chlorite

TABLE 1. Chemical composition of the chloritoid core, inner rim and outer rim for two representative samples of Triassic Verrucano rocks of the Massa Unit

Sample	406			818		
	cld_{core}	$cld_{inner\ rim}$	$cld_{outer\ rim}$	cld_{core}	$cld_{inner\ rim}$	$cld_{outer\ rim}$
SiO_2	25.67	26.59	26.79	25.74	25.79	25.31
Al_2O_3	42.60	43.98	44.35	42.85	43.18	43.01
FeO_{tot}	24.60	19.40	19.81	25.61	25.96	28.94
MnO	0.60	0.34	0.35	0.81	0.00	0.00
MgO	3.50	6.92	6.11	2.60	2.90	0.71
Total	96.97	97.23	97.41	97.61	98.33	97.97
Si	2.023	2.022	2.036	2.016	2.010	2.000
Al^{IV} (M2)	3.000	3.000	3.000	3.000	3.000	3.000
Al^{VI} (M1A)	0.934	0.943	0.972	0.955	0.967	1.003
Fe^{3+}	0.060	0.045	–	0.037	0.010	–
Fe^{2+}	1.550	1.189	1.259	1.638	1.651	1.911
Mn	0.039	0.021	0.022	0.053	–	–
Mg	0.408	0.784	0.692	0.303	0.337	0.083
Sum	1.997	1.994	1.973	1.996	1.998	1.994
$Mg/(Mg+Fe^{2+})$	0.208	0.397	0.354	0.156	0.169	0.042

The structural formula of chloritoid was calculated on the basis of 12 oxygens. Fe^{3+} was calculated following the procedure described by Chopin et al. (1992).

under kyanite facies metamorphic conditions. The $K_D^{cld/chl}$ value [(Fe^{2+}/Mg) cld/(Fe_{tot}/Mg) chl] for sample 406 is 5.62, a value similar to that reported for other chloritoid-chlorite pairs in rocks of similar metamorphic grade (Ashworth and Evirgen, 1984; Cruickshank and Ghent, 1978; Ghent et al., 1987). In spite of the coexistence of chloritoid (cld), chlorite (chl), kyanite (ky) and quartz (qtz), the Mg-Fe zoning profile from the core to the inner rim of the chloritoid in sample 406 cannot be produced by a growth zoning model in which kyanite, chlorite and chloritoid began to grow contemporaneously. In fact the end-member temperatures of equilibrium (1) cld + qtz = chl + ky + H_2O (Franceschelli et al., 1997) are $T_{Mg} < T_{Fe}$; in the case of prograde metamorphism, this means that the X_{Mg} value during chloritoid growth should progressively decrease, in contrast with the early chloritoid zoning profile of sample 406. The composition of chloritoid also depends on the a_{H_2O}, f_{O_2}, and P_{H_2O} variations and on possible coeval reactions, consuming Mg or Fe. In sample 406 a significant variation in a_{H_2O} and f_{O_2} during the growth of chloritoid must be ruled out because hydrated phases such as muscovite and chlorite, and f_{O_2} controlling phases, such as magnetite, occur within the chloritoid and as major phases in the matrix.

The influence of the dP/dT slope of reaction (1) and reaction (2) prl (pyrophyllite) + chl = 5 cld + 14 qtz + $3H_2O$ on the chloritoid composition is very small. X_{Mg} in chloritoid increases with increasing metamorphic temperature in the stability field of pyrophyllite,for any variations in pressure, because reaction (2) has a strong negative slope. In contrast, the decrease in X_{Mg} the stability field of kyanite should be very low, because the slope of reaction (1) is positive but flat (Vidal et al., 1992).

The zoning profile of chloritoid in sample 406 may be predicted if we assume that it began to grow in the pyrophyllite field and the composition of the chloritoid-chlorite pair was controlled by equilibrium (3) Fe-cld+Mg-chl = Mg-cld+ Fe-chl. When equilibrium (3) operated during prograde metamorphism in the pyrophyllite $P-T$ field, it produced an increase in X_{Mg} in the chloritoid (as observed in chloritoid 406 from the core to the

TABLE 2. Chemical composition of chlorite in two samples from the Triassic Verrucano of the Massa Unit

Sample	406	818			
	chl	chl_1	chl_2	chl_3	chl_4
SiO_2	27.25	25.18	23.60	22.49	22.55
Al_2O_3	27.11	24.39	22.77	23.66	22.96
FeO_{tot}	12.39	25.82	35.61	37.90	37.87
MnO	0.01	0.00	0.00	0.00	0.00
MgO	21.43	12.70	5.99	3.88	4.57
Total	88.19	88.09	88.01	87.93	87.98
Si	5.273	5.263	5.239	5.067	5.086
Al^{IV}	2.727	2.737	2.761	2.933	2.914
Al^{VI}	3.454	3.269	3.195	3.349	3.287
Fe_{tot}	2.004	4.511	6.608	7.139	7.140
Mn	–	–	–	–	–
Mg	6.176	3.954	1.981	1.302	1.535
Sum	11.650	11.734	11.784	11.790	11.962
$Mg/(Mg+Fe_{tot})$	0.755	0.467	0.231	0.154	0.177

Abbreviations for sample 818: chlorite enclosed in the chloritoid core (chl_1), chlorite enclosed in the outer rim (chl_2), chlorite in contact with chloritoid (chl_3) and in the matrix (chl_4).

inner rim). The zoning profile of chloritoid from the inner rim to the outer rim and the consequent decrease in X_{Mg} may be explained by assuming that the rocks crossed the pyrophyllite/kyanite $P-T$ boundary during the late growth stage of chloritoid and equilibrium (3) operated in the kyanite $P-T$ field. Since the compositional loop of the chloritoid and chlorite pair, controlled by equilibrium (1) in the kyanite P/T field, has a negative dX_{Mg}/dt slope, in contrast with that of the one loop in the pyrophyllite field (Franceschelli et al., 1997), both the increase in X_{Mg} from the core to the inner rim and the decrease in X_{Mg} from the inner rim to the outer rim should reflect an increase in metamorphic temperature. The discontinuity in the zoning profile could mark the entry of kyanite into the assemblage.

The chloritoid of sample 818 has the lowest X_{Mg} value (0.156) in the inner core, a rather constant X_{Mg} from the outer core to the inner rim, which then decreases towards the outer rim. According to Vidal et al. (1992), the low X_{Mg} in chloritoid and chlorite in sample 818 preclude a stable cld+chl+qtz+ky assemblage to form. The zoning from the outer core to the outer rim may

be produced during prograde metamorphism, considering that the composition of chloritoid and chlorite is controlled by the equilibrium (3). Detailed microprobe investigation of this sample suggests that the variation in chlorite composition was contemporaneous with the growth of chloritoid. The exact position of chlorite with respect to the Mg-Fe zoning profile of chloritoid is reported in Fig. 2. The chlorite included in the chloritoid core (chl_1) has a X_{Mg} value of 0.467 decreasing to 0.231(chl_2) in the inner rim and to 0.154 (chl_3) in the matrix in contact with chloritoid. The $K_D^{cld/chl}$ values for the chloritoid-chlorite pair are 4.7 in the core and 4.20 in the chloritoid outer rim in contact with chlorite (chl_3). The Mg-Fe zoning of chloritoid and the variation of chemical composition of chlorite in time may only be produced by equilibrium (3) during prograde metamorphism under $P-T$ conditions corresponding to the kyanite field.

P-T conditions

According to Vidal et al. (1998) the equilibrium constant of the exchange reaction (3) depends only on the Fe and Mg content of chlorite and
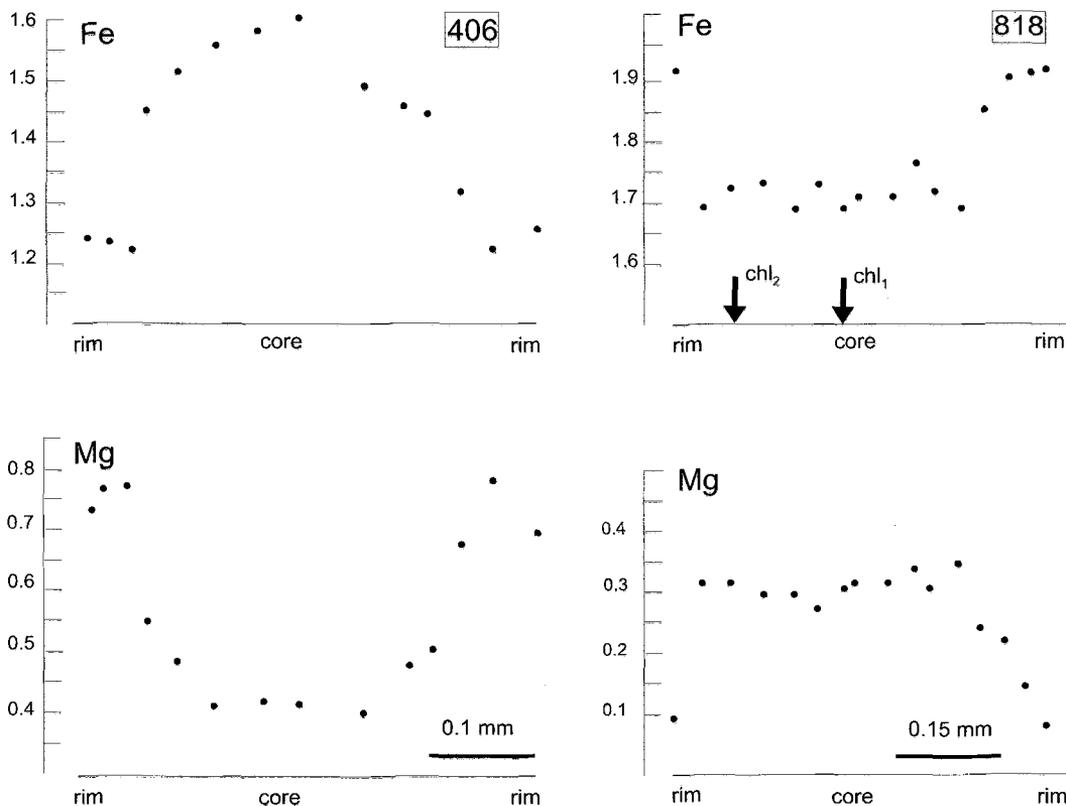
FIG. 2. Mg and Fe_{tot} (a.p.f.u) zoning profile across two representative samples from the Triassic Verrucano of the Massa Unit. In the zoning profile of sample 818 arrows indicate the position of chlorite (chl_1 and chl_2, Table 2) with respect to the Mg-Fe zoning profile of chloritoid.

chloritoid and at constant pressure varies linearly with $1/T$ from 300°C to about 600°C. On the basis of a compilation of literature data on the Mg-Fe composition of coexisting chlorite and chloritoid Vidal et al. (1998) gives the following empirical calibration:

$$\ln K_D^{cld/chl} = 2023.06/T(K) - 1.004232$$

In the sample 406, the composition of the chloritoid outer rim and matrix chlorite matches the composition predicted by Vidal et al. (1992) for cld+chl+ky assemblages at 8–9 kbar for 450–500°C. Moreover using the chlorite-chloritoid calibration of Vidal et al. (1998) we find a temperature of the 467°C. The temperature conditons of metamorphism in samples 406 are also constrained by the following reactions: prl + qtz = ky + H_2O, and chl + cld + qtz = alm (almandine) + H_2O that define the lower stability field of the kyanite+quartz pair and the upper stability field of chl+cld+qtz assemblage in the FeO-Al_2O_3-SiO_2-H_2O system. Both reactions, calculated by the database of Berman (1988), for a pressure range of 4–10 kbar, define a metamorphic temperature of ≈ 400–530°C.

In the samples, 818 the chloritoid-chlorite pair can be used to estimated the T condition during the growth of chloritoid. We find $T = 517$ for chloritoid core and chl_1 chlorite and $T = 560$ for chloritoid outer rim chl_3 chlorite. The LnKd chloritoid inner rim—chlorite (chl_2) is 0.45, leading to $T = 1115$°C. This indicated that chl_2 chlorite is not in equilibrium with the inner rim but is probably in equilibrium with a chloritoid composition between the inner rim and the outer rims of the right margin. This is sustained by the asymmetric zoning profile of the chloritoid (Fig. 2).

Other independent estimates of metamorphic temperatures have been made in pelitic rocks and marble in the studied area of the Massa Unit (Franceschelli et al., 1997; Cardaci, 1987). The magnesium contents of calcite coexisting with dolomite in the Massa Unit marbles suggest a temperature range from 430 to 520°C (Cardaci, 1987). The metamorphic pressure was estimated at about 6—8 kbar on the basis of a systematic study of the Si content of muscovite in pelitic and psammitic rocks (Franceschelli et al., 1986a, 1997).

Conclusions

The two examples of Mg-Fe zoning of chloritoid here described indicate that the chloritoid of the Massa Unit rocks grew during a prograde Alpine metamorphic stage. For sample 406, the zoning suggests that the chloritoid started to crystallise in the $P-T$ field of pyrophyllite and continued to develop in that of kyanite. Using the chlorite-chloritoid thermometer of Vidal et al. (1998), we determined a temperature of the 467°C for chloritoid rim and matrix chlorite. The Mg-Fe zoning of sample 818 suggests that the chloritoid growth entirely in the kyanite field. Metamorphic temperature, estimated using the chlorite-chloritoid thermometer range from $T = 517$°C for chloritoid core and chl_1 chlorite to $T = 560$°C for chloritoid outer rim and chl_3 chlorite.

Acknowledgements

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