

CHLORITE-CHLORITOID-GARNET EQUILIBRIA AND GEOTHERMOMETRY IN THE SANANDAJ-SIRJAN METAMORPHIC BELT, SOUTHERN IRAN*

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Abstract – Chloritoid is crystallised with chlorite, white mica and garnet in chlorite zone metapelites of the regional metamorphic rocks of the Sanandaj-Sirjan metamorphic belt in southern Iran. Chemistry of coexisting minerals is studied using microprobe analysis. Application of the chlorite-chloritoid geothermometry gives temperatures of 515°C and 557°C. The Chlorite-garnet Fe-Mg exchange geothermometer indicates temperatures between 442°C and 460°C for various pressures. A comparison of the results from two geothermometers, along with a study of mineral assemblages in the rocks show that the chlorite-chloritoid thermometer overestimates the temperature by about 70°C.

Keywords – Sanandaj-Sirjan metamorphic belt; metapelites; chlorite-chloritoid-garnet geothermometry

1. INTRODUCTION

Metapelites are important metamorphic rocks which are sensitive to the condition of metamorphism and can be used to estimate the pressure and temperature of metamorphism. Despite these characteristics, it is difficult to find low-grade metapelites (lower greenschist facies) possessing enough phases in equilibrium to have low-variance assemblages. Therefore, estimation of pressure and temperature of metamorphism in these rocks is difficult [1]. Some investigators have considered this problem and have attempted to calibrate useful geothermometers for low-grade rocks. The most important geothermometers for these types of rocks are chlorite-garnet (for garnet phyllites and garnet schists) and chlorite-chloritoid geothermometers. Chlorite-chloritoid- garnet and chlorite-chloritoid assemblages were found in metapelites of the Sanandaj-Sirjan belt in southern Iran. One calibration of a chlorite-chloritoid Fe-Mg exchange geothermometer and three different calibrations of a chlorite-garnet Fe-Mg exchange geothermometer were applied to metapelites of Sanandaj-Sirjan metamorphic rocks. A brief petrography of the studied rocks, mineral chemistry and mineral classification and geothermometry results are discussed in this paper.

2. GEOLOGY OF THE STUDY AREA

The study area is located 25 km east of Sirjan in southern Iran, within the Sanandaj-Sirjan metamorphic belt (Fig. 1). There is no radiometric age determination on the rocks and the exact age of the metamorphism is not clear. The sedimentary protoliths were turbiditic sandstone, carbonates and pelitic rocks, which are metamorphosed regionally up to amphibolite facies [2]. The outcrop of

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the pelitic rocks exceeds that of two other types. Minor magmatic activities generated basic igneous rocks, mainly dolerite. Regional metamorphism produced a variety of slates, phyllites, chlorite schists, actinolite schists, chloritoid schists, calc schists, marbles, mica schists, garnet schists and amphibolites [3].

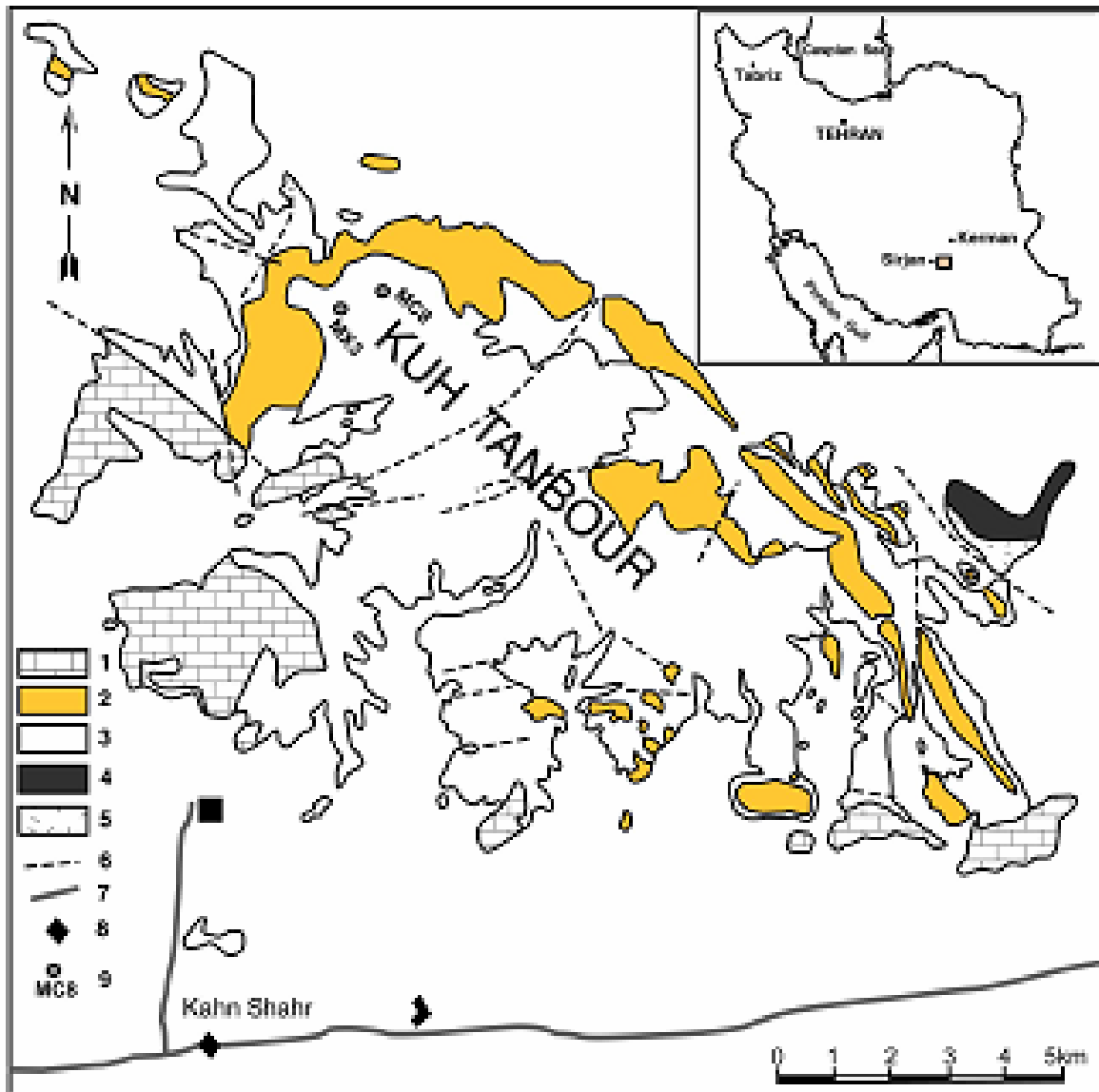


Fig. 1. Simplified geological map of the studied area. 1. Oligo-Miocene limestone; 2. Calcareous metapelites; 3. Metapelites and metabasites; 4. Ophiolitic rocks; 5. Cretaceous limestone; 6. Fault; 7. Road; 8. Village; 9. Sample locality

Based on microfossil studies, Mijalkovic and Saric [4] concluded a Lower Permian age for phyllites and slates. Upper Permian rocks are garnet-mica schist, metadolomite, amphibole schist and amphibolite [3]. A block of ophiolitic rocks and Cretaceous limestone are located close to the Palaeozoic metamorphic rocks by a strike-slip fault (Fig. 1). Unmetamorphosed limestone of Oligo-Miocene covers the metamorphic rocks disconformably in the southern part of the studied area.

3. PETROGRAPHY OF THE CHLORITOID-BEARING ROCKS

Chloritoid was found in two pelitic samples (MC8 and MX3) in the area studied. Sample MC8 is a fine-grained phyllite with well-developed crenulation cleavage. The rock is composed of fine-grained muscovite (Ms), chlorite (Chl), quartz (Qtz), opaque minerals (magnetite) and minor phases of titanite and zircon. Porphyroblasts of chloritoid (Ctd) up to 1.5 mm long have developed in the rocks. Chloritoid shows polysynthetic twinning and green pleochroism. Fig. 2a shows a back-scattered electron microscope image of the chloritoid crystals in the MC8 sample. Sample MX3 is a medium-grained pelitic schist containing porphyroblasts of chloritoid and garnet (Grt). The sample consists of muscovite, chlorite, quartz, opaque minerals (magnetite) and minor amounts of titanite and zircon. Chloritoid and garnet appear as porphyroblasts up to 4 mm long. Polygonal texture among quartz crystals and crenulation cleavage are developed in the rock. Fig. 2b shows a microscopic view of chloritoid and garnet in the MX3 sample.

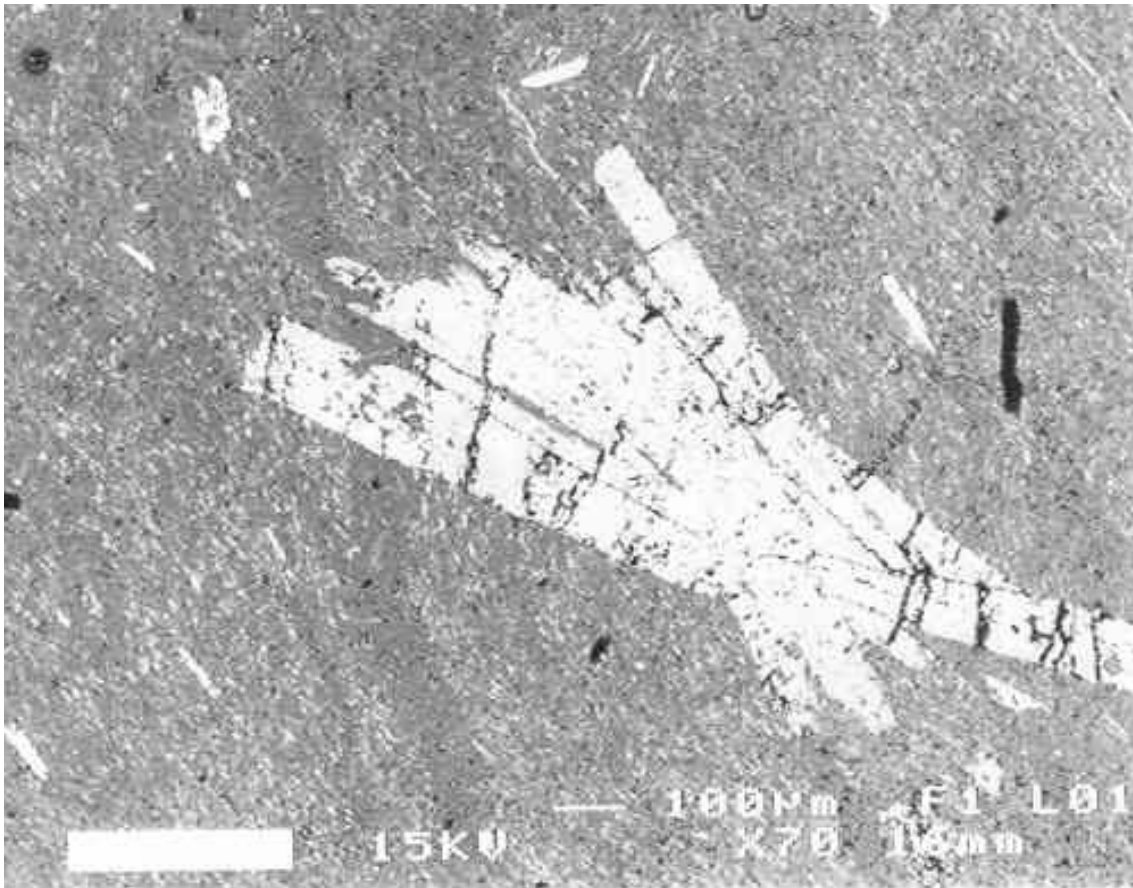


Fig. 2a. Back-scattered electron microscope view of the chloritoid crystals in the MC8 sample

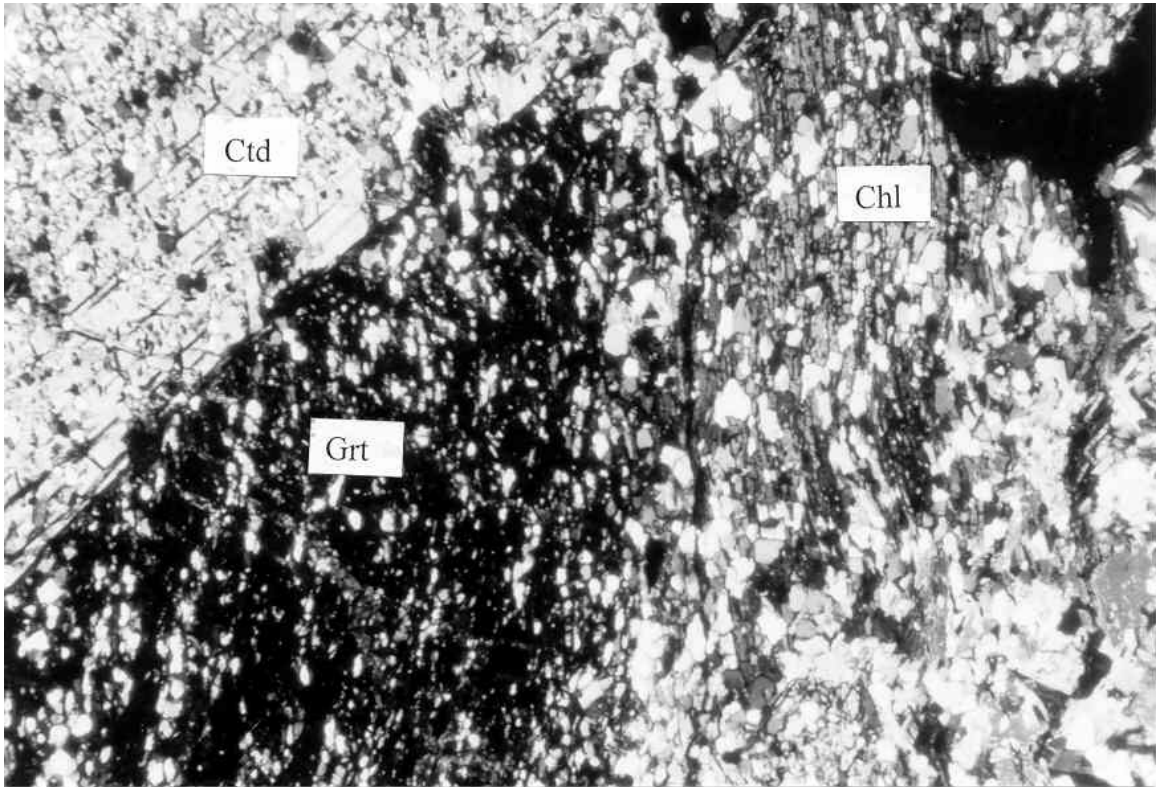
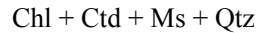
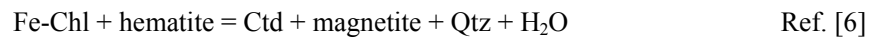


Fig. 2b. Photomicrograph of the MX3 sample illustrating garnet (Grt), chlorite (Chl) and chloritoid (Ctd). Field of view is 4.2 mm, XPL

The AFM minerals in MC8 and MX3 are as follows (abbreviations from [5]):



A schematic presentation of these minerals on an AFM diagram plotted from (Ms+Qtz+H₂O) can be found in Fig. 3. According to mineral assemblages, the following possible metamorphic reactions can be considered as reactions responsible for a generation of chloritoid and garnet in the rocks.



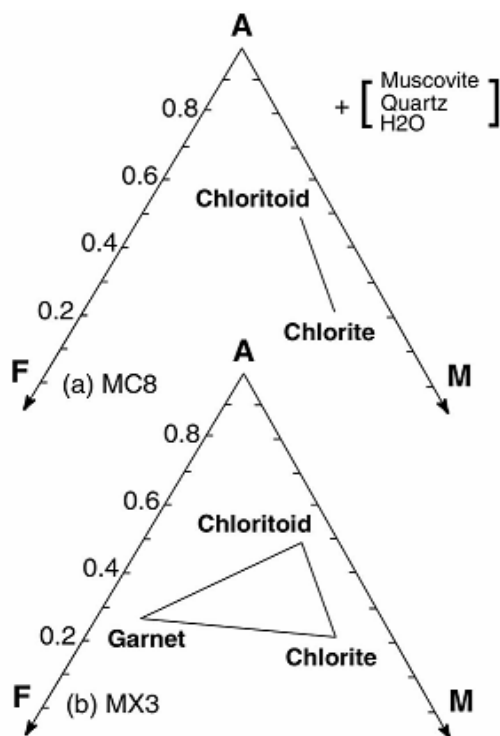


Fig. 3. Schematic presentation of the studied samples on AFM diagram plotted from Ms + Qtz + H₂O

a) Mineral chemistry

In order to identify the chemical composition of coexisting chlorite, chloritoid and garnet, and associated phases in the studied samples, minerals in two thin sections of the rocks were analysed for major elements using an electron microprobe. A modified Cambridge Instrument Geoscan microprobe at the Department of Earth Sciences in Manchester University was used for analysis. The machine is interfaced to an Oxford Instrument/Link Analytical QX-2000 energy dispersive X-ray spectrometer (EDS). Link System ZAF4/FLS software was used to convert X-ray spectra, obtained from the specimen, into chemical analyses. 15 kv electron beam acceleration voltage and 40 second acquisition time per analyses were applied. The detection limit of the machine is approximately 0.2 wt%.

A fine-grained phyllite sample (MC8) was also analysed by means of a JEOL JSM 6400 Scanning Electron Microscope (SEM) in the department of Earth Sciences, Manchester University. The results of microprobe and SEM analyses are almost identical.

b) Mineral chemistry of chlorite

Microprobe analyses of chlorite in the MX3 and MC8 samples are provided in Table 1. The number of cations is calculated on the basis of 28 oxygens. The oxide totals are between 84.32 and 87.64. The amount of Ti is between 0.00 and 0.03 atom per formula unit (apfu). The chlorites are Mn-free. Na varies from 0.06 to 0.25 apfu, and K from 0.00 to 0.07 apfu. Substitution of Al³⁺ for Si⁴⁺ is calculated using stoichiometric approach. Fig. 4 shows the classification of the studied chlorites. According to this figure, chlorites are of ripidolite to daphnite type. This figure also shows the Fe-rich nature of the chlorites.

Table 1. Microprobe analyses of chlorite in the studied samples.
The formula is calculated on the basis of 28 oxygens

	MX3						MC8					
SiO ₂	22.89	23.65	23.30	23.06	23.52	23.06	24.81	23.12	23.42	23.64	23.23	23.44
TiO ₂	0.11	0.04	0.05	0.13	0.08	0.17	0.00	0.00	0.00	0.00	0.15	0.00
Al ₂ O ₃	21.81	22.37	22.19	22.32	22.38	21.93	24.16	22.38	22.69	22.86	22.98	22.68
FeO	29.60	28.08	28.97	28.59	28.62	30.41	27.30	28.43	28.12	27.38	27.73	27.56
MnO	0.00	0.08	0.01	0.02	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	11.37	12.07	11.02	11.78	11.36	9.89	10.70	9.71	11.04	10.40	10.46	10.57
CaO	0.00	0.01	0.03	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	0.36	0.35	0.51	0.41	0.14	0.17	0.61	0.55	0.34	0.40	0.32	0.43
K ₂ O	0.07	0.08	0.04	0.06	0.00	0.01	0.26	0.13	0.08	0.21	0.00	0.00
Total	86.21	86.73	86.12	86.37	86.23	85.64	87.84	84.32	85.69	84.89	84.87	84.68
Si	5.05	5.12	5.13	5.06	5.15	5.14	5.26	5.15	5.13	5.21	5.13	5.18
Ti	0.02	0.01	0.01	0.02	0.01	0.03	0.00	0.00	0.00	0.00	0.03	0.00
Al	5.67	5.71	5.76	5.77	5.77	5.27	6.03	5.88	5.86	5.94	5.98	5.91
Fe	5.46	5.09	5.34	5.24	5.24	5.67	4.83	5.30	5.15	5.05	5.12	5.09
Mn	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	3.75	3.90	3.62	3.85	3.70	3.29	3.38	3.23	3.61	3.42	3.44	3.48
Ca	0.00	0.00	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.15	0.15	0.22	0.18	0.06	0.07	0.25	0.24	0.14	0.17	0.14	0.18
K	0.02	0.02	0.01	0.02	0.00	0.00	0.07	0.04	0.02	0.06	0.00	0.00

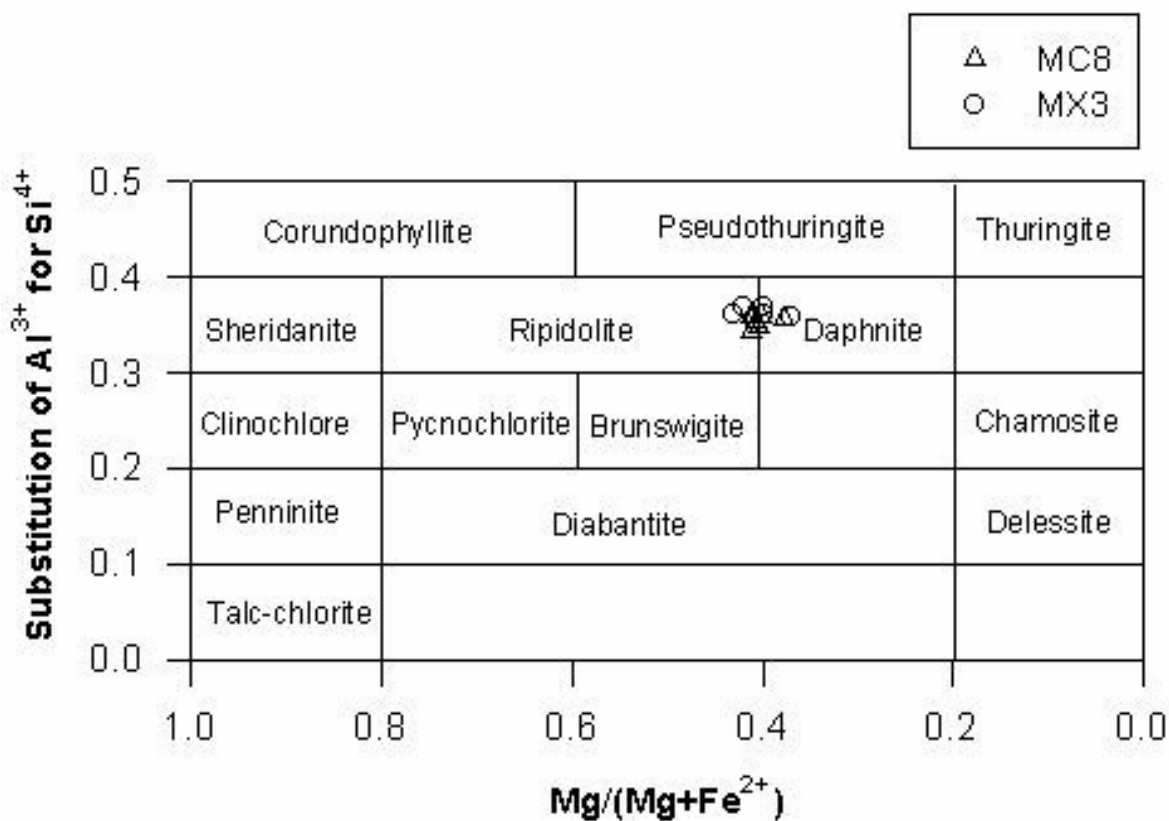


Fig. 4 Classification of the analysed chlorites using Al³⁺ substitution for Si⁴⁺ versus Mg/(Mg + Fe²⁺) diagram. Chlorites in both samples are ripidolite to daphnite in composition

c) Mineral chemistry of chloritoid

Table 2 includes the microprobe analyses of chloritoids in the studied samples. The number of cations is calculated on the basis of 12 oxygens. Oxide totals are between 90.38 and 92.63, which is a good sum for chloritoid. Ti is absent or occurs in very low amounts (0.01 apfu). Mn reaches to 0.02 apfu and there is appreciable Na in the studied chloritoids. Fe^{2+} and Fe^{3+} concentration was calculated on the charge balance and stoichiometric criteria [8]. Fig. 5 illustrates the composition of chloritoids on $\text{Al} + \text{Fe}^{3+}$, $\text{Fe}^{2+} + \text{Mn}$, Mg and Fe^{2+} , Mn, Mg triangular diagrams. According to the figure, Fe^{2+} occupies the cubic site (i.e. chloritoids are Fe-chloritoid).

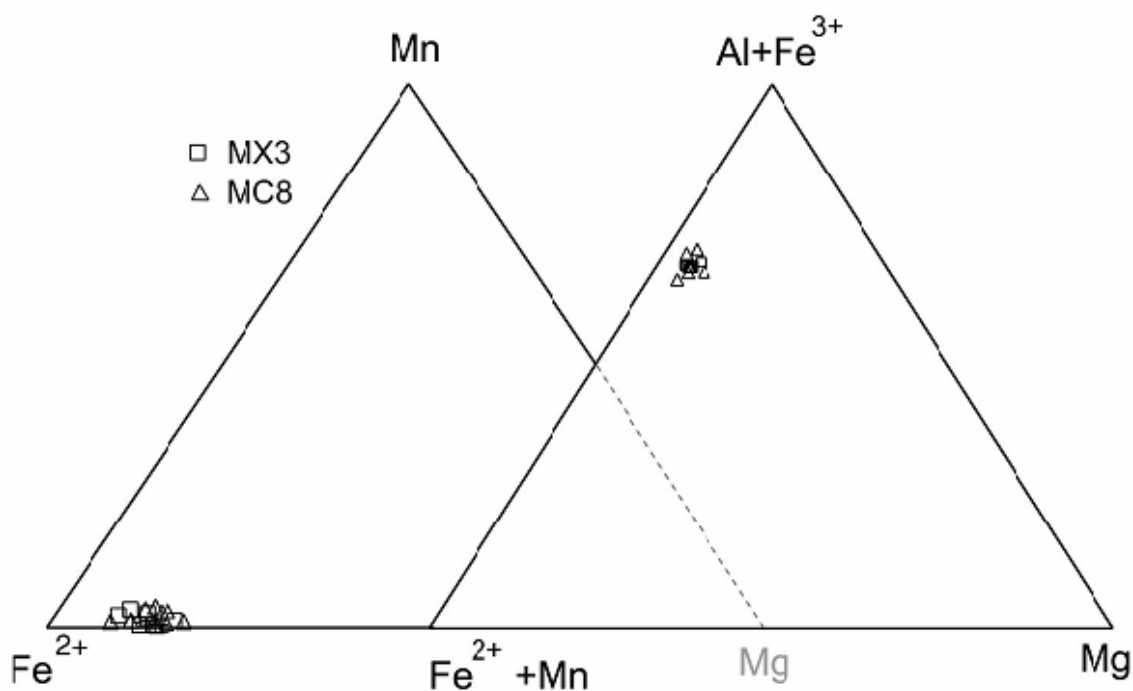


Fig. 5. Composition of the studied chloritoids plotted on the Mn, Fe^{2+} , Mg and $\text{Fe}^{2+} + \text{Mn}$, $\text{Al} + \text{Fe}^{3+}$, Mg triangular diagrams. Chloritoids are Fe-chloritoid

d) Mineral chemistry of garnet

Table 3 includes microprobe analyses of garnet in the MX3 sample. The formula of garnet is calculated on the basis of 12 oxygens. Oxide totals are between 100.14 and 101.71. Ti is not present or occurs in very low amounts. Fig. 6 shows the chemical composition of the analysed garnets on the Ca + Mn, Fe²⁺ and Mg triangular diagram. Fe²⁺ and Fe³⁺ contents of garnets were calculated using charge balance and stoichiometry criteria [8]. As this figure shows, the pyrope end-member is very low in the studied garnets, and they are almandine-rich with appreciable amounts of grossularite and spessartite.

Table 3. Microprobe analyses from garnet in the MX3 sample. The formula is calculated on the basis of 12 oxygens

SiO ₂	37.14	37.13	36.66	37.12	36.64	37.02	36.97
TiO ₂	0.10	0.19	0.11	0.03	0.07	0.12	0.16
Al ₂ O ₃	20.91	20.77	20.50	20.56	20.56	20.78	20.50
FeO	33.78	32.57	32.75	32.94	31.93	33.13	31.59
MnO	1.52	2.04	2.39	2.47	2.58	2.72	2.82
MgO	1.38	1.32	1.25	1.29	1.17	1.20	1.15
CaO	6.59	6.83	6.18	6.29	7.20	6.19	6.83
Na ₂ O	0.29	0.14	0.29	0.19	0.17	0.18	0.17
K ₂ O	0.00	0.00	0.01	0.02	0.00	0.01	0.00
Total	101.71	101.19	100.14	100.91	100.32	101.35	100.19
Si	2.96	2.97	2.97	2.99	2.96	2.97	2.98
Ti	0.00	0.01	0.01	0.00	0.00	0.01	0.01
Al	1.96	1.96	1.96	1.95	1.96	1.97	1.96
Fe	2.25	2.18	2.22	2.22	2.16	2.22	2.14
Mn	0.10	0.14	0.16	0.17	0.18	0.18	0.19
Mg	0.16	0.16	0.15	0.16	0.14	0.14	0.14
Ca	0.56	0.59	0.54	0.54	0.62	0.53	0.59
Na	0.05	0.02	0.04	0.03	0.03	0.03	0.03
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00

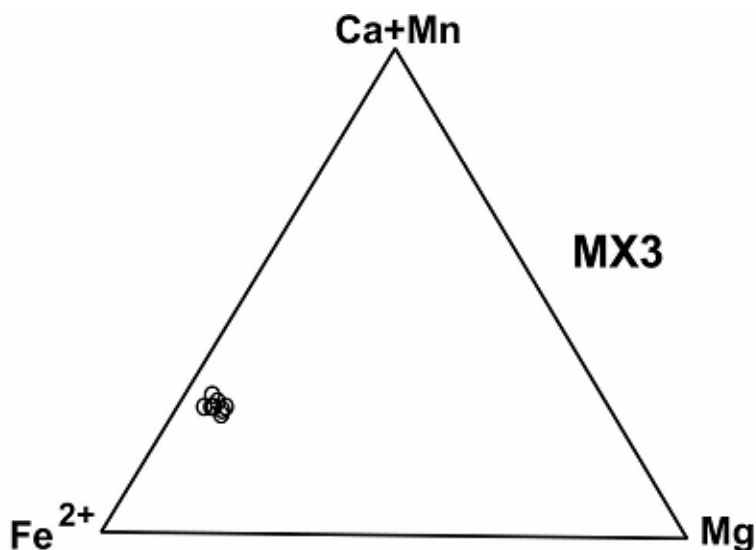


Fig. 6. Chemical composition of the analysed garnets in the MX3 sample plotted on Ca + Mn, Mg triangular diagram. Garnets are essentially almandine with significant grossularite and spessartite contents

e) Mineral chemistry of white mica

Microprobe analyses of white mica are provided in Table 4. The formula of mica is calculated on the basis of 22 oxygens. Oxide totals are between 93.01 and 93.85. Fe varies between 0.01 and 0.24 and Mg is between 0.09 and 0.18. Na varies from 0.19 to 0.56 apfu, indicating a considerable substitution of the paragonite end-member. Fig. 7 illustrates the classification of white micas in the SiO₂-Al₂O₃-FeO diagram. This figure shows that the studied white micas are essentially muscovite and the celadonite end-member is absent.

Table 4. Microprobe analyses of white mica in the studied samples.
Formula of mica is calculated on the basis of 22 oxygens

	MC8						MX3					
SiO ₂	45.77	45.64	45.36	45.75	45.23	45.64	45.86	45.23	45.81	45.75	45.11	45.16
TiO ₂	0.20	0.36	0.26	0.38	0.36	0.00	0.20	0.32	0.35	0.31	0.31	0.40
Al ₂ O ₃	36.47	34.98	35.34	35.20	35.59	36.49	36.51	34.63	34.55	34.12	35.03	34.80
FeO	1.12	0.95	1.02	1.29	1.00	1.05	1.33	2.07	1.39	1.64	1.42	1.53
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.09
MgO	0.60	0.68	0.62	0.53	0.45	0.75	0.51	0.85	0.80	0.65	0.52	0.88
CaO	0.00	0.00	0.14	0.00	0.00	0.00	0.00	0.06	0.01	0.05	0.06	0.07
Na ₂ O	0.99	1.81	1.94	1.83	1.72	1.93	1.41	1.10	0.73	1.15	1.14	1.26
K ₂ O	7.90	8.64	8.92	8.75	8.73	7.95	8.03	8.87	9.96	9.34	9.45	9.41
Total	93.05	93.06	93.60	93.73	93.08	93.81	93.85	93.13	93.60	93.01	93.07	93.6
Si	6.25	6.12	6.12	6.15	6.12	6.63	6.12	6.17	6.19	6.21	6.13	6.11
Ti	0.02	0.04	0.03	0.04	0.04	0.00	0.02	0.03	0.04	0.03	0.03	0.04
Al	5.62	5.54	5.62	5.58	5.67	6.25	5.74	5.49	5.50	5.46	5.61	5.55
Fe	0.12	0.11	0.12	0.15	0.11	0.13	0.15	0.24	0.01	0.19	0.16	0.17
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Mg	0.12	0.14	0.12	0.11	0.09	0.16	0.10	0.17	0.16	0.13	0.11	0.18
Ca	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01	0.01
Na	0.25	0.47	0.51	0.48	0.45	0.54	0.36	0.29	0.19	0.30	0.30	0.33
K	1.32	1.49	1.54	1.50	1.51	1.47	1.37	1.55	1.72	1.62	1.64	1.63

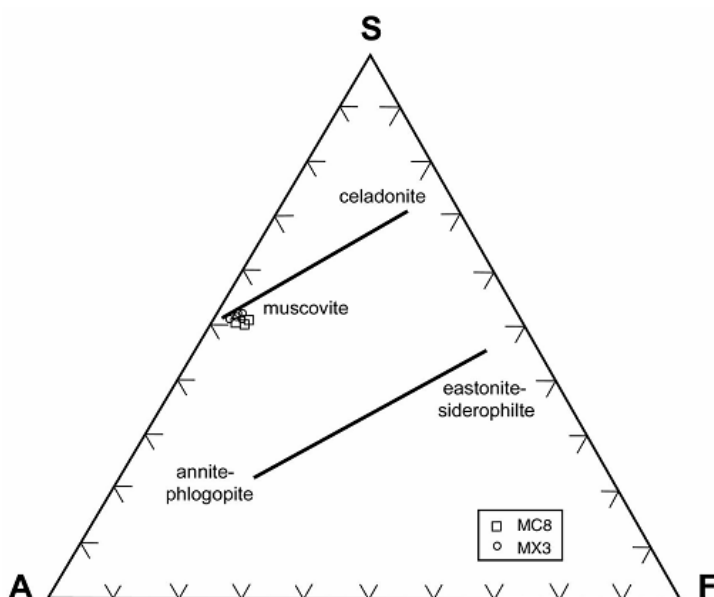
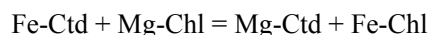


Fig. 7. Analysed white micas plotted on SAF diagram of [12]. All micas are muscovite

4. CHLORITE-CHLORITOID GEOTHERMOMETRY

The chlorite-chloritoid geothermometer has been applied to both samples studied. This thermometer is a Fe/Mg exchange thermometer. Partitioning of Fe-Mg between chloritoid and chlorite in equilibrium has been studied by Ashworth and Evirgen [10], Ghent *et al.* [11] and Vidal *et al.* [12]. These studies show that $K_D = (Fe/Mg)_{Ctd}/(Fe/Mg)_{Chl}$ decreases and tends toward unity with increasing equilibrium temperature. The chlorite-chloritoid pair is stable at greenschist to blueschist facies (~300-500° C) and Fe-Mg exchange reaction between both these minerals has a good potential as a geothermometer [12]. The partitioning coefficient (equilibrium coefficient) for reaction



can be written as:

$$\ln K = \ln \left\{ \frac{[(X_{Fe-Chl})^5 \cdot (X_{Mg-Ctd})^5]}{[(X_{Mg-Chl})^5 \cdot (X_{Fe-Ctd})^5]} \right\}$$

and

$$X_{Mg-Chl} = Mg / (Mg + Fe + Mn) \text{ in Chl}$$

$$X_{Fe-Chl} = Fe / (Mg + Fe + Mn) \text{ in Chl}$$

$$X_{Mg-Ctd} = Mg / (Mg + Fe + Mn) \text{ in Ctd}$$

$$X_{Fe-Ctd} = Fe / (Mg + Fe + Mn) \text{ in Ctd}$$

The equation for calculation of temperature suggested by Vidal *et al.* [12] is:

$$T (C^\circ) = [1977.7 / (\ln K_D + 0.971)] - 273.15$$

This thermometer is pressure independent and can therefore be used for greenschist rocks without information about the pressure of metamorphism.

Mole fractions of Mg and Fe in chlorites and chloritoids were calculated for the analysed samples and $\ln K$ was calculated using these data. The results are provided in Table 5. The geothermometer of Vidal *et al.* was then employed for temperature calculations. The calculated temperature for the MX3 sample is 515°C and the temperature for the MC8 sample is 557°C.

Table 5. Mole fraction of Mg and Fe ($1 - X_{Mg}$) in analysed chlorite and chloritoid.
N= number of analyses; M= mean and SD= standard deviation

	MX3		MC8	
Chl	Ctd	Chl	Ctd	
X_{Mg}	X_{Mg}	X_{Mg}	X_{Mg}	
0.41	0.12	0.41	0.13	
0.43	0.14	0.41	0.14	
0.40	0.12	0.39	0.14	
0.42	0.12	0.41	0.15	
0.41	0.13	0.41	0.13	
		0.40	0.14	
N=5 M= 0.43	N=5 M= 0.13	N= 6 M= 0.40	N= 6 M= 0.14	
SD = ± 0.02	SD = 0.01	SD = 0.01	SD = 0.01	

The following reaction can be written among mineral phases in the MX3 sample:



The position of the reaction curve on the PT grid was calculated using THERMOCALC software [13], assuming unit activity for all phases. Fig. 8 shows the reaction curve on the PT grid. As this figure illustrates, the reaction curve is not pressure sensitive and indicates a temperature of about 520°C, which is very close to the temperature calculated by the geothermometer of Vidal *et al.* [12]

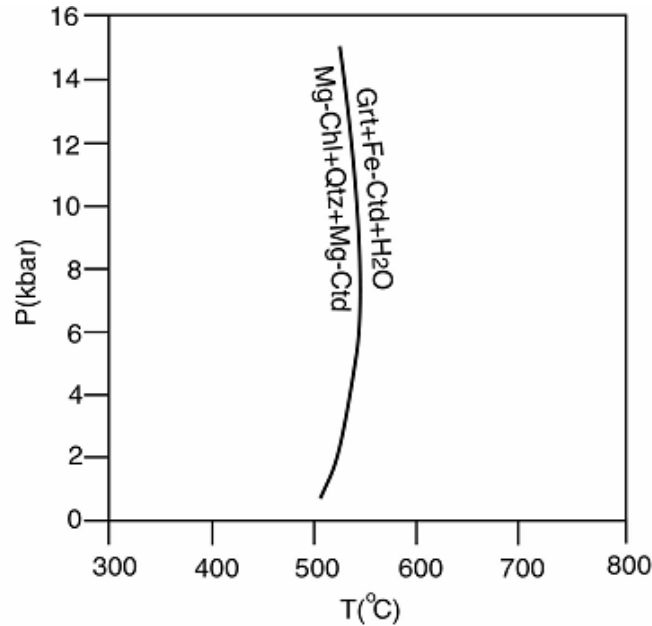


Fig. 8. Reaction curve for $\text{Mg-Chl} + \text{Qtz} + \text{Mg-Ctd} = \text{Grt} + \text{Fe-Ctd} + \text{H}_2\text{O}$ calculated by means of THERMOCALC software on PT grid, assuming unit activity for all phases. The reaction is a potential thermometer (almost parallel to P axis) and indicates a temperature of ca.530°C

5. CHLORITE-GARNET GEOTHERMOMETRY

Fe-Mg exchange between coexisting garnet and chlorite can be used as a thermometer. Partitioning coefficient of Mg and Fe between garnet and chlorite in thermodynamic equilibrium is studied by Albee [14]; Kamini [15]; Dickenson and Hewitt [16]; Ghent *et al.* [11] and Grambling [1].

The equation suggested by Dickenson and Hewitt [16] is as follows:

$$0 = 51906 - 7.541T = 0.438P + 15RT \ln K_D$$

T is temperature in °C, P is pressure in bars and R is gas constant.

The equation proposed by Ghent *et al.* [11] is:

$$T = (2109.92 + 0.00608P) / (0.6867 - \ln K_D)$$

The equation suggested by Grambling [1] is:

$$0 = 0.05P - 19.02T + 4607 \ln K_D + 24156$$

In the last two equations T is in °K

In all these equations K_D is:

$$K_D = \frac{[(\text{Mg}/\text{Fe})_{\text{Grt}}]}{[(\text{Mg}/\text{Fe})_{\text{Chl}}]}$$

These equations were used to calculate the temperature of the equilibrium of garnet and chlorite in the studied rocks. The results are summarised in the following table:

P kbar	T, Ghent, <i>et al.</i> , 1987	T, Grambling, 1990
4	442°C	450°C
6	446°C	456°C
8	450°C	460°C

Temperatures obtained from Dickenson and Hewitt's thermometer [16] are unrealistically low (~180°C) and are ignored here.

6. CONCLUSIONS AND DISCUSSION

Chlorite, chloritoid and garnet are in equilibrium in the studied samples. Chlorites are mainly ripidolite and daphnite and chloritoids are Fe-chloritoid. Garnets are slightly zoned and have a almandine-rich composition with appreciable amounts of spessartite and grossularite. White micas in equilibrium with other minerals are muscovite.

There are no suitable index minerals or thermometers in the studied samples except the Ctd-Chl and Chl-Grt thermometers. Application of these thermometers yields fairly close temperatures for regional metamorphism of the studied area within the chlorite zone, indicating a medium to high greenschist facies grade. Results of thermometry using Grt-Chl equilibria and Ctd-Chl equilibria are different. The Grt-Chl thermometer gives temperatures between 442°C & 460°C, but the Ctd-Chl thermometer gives temperatures between 515°C & 557°C. Dickenson and Hewitt's thermometer [16] gives unrealistically low temperatures. Considering the mineral assemblages and the nature of the rocks (phyllite and schist) it is probable that temperatures from the Grt-Chl thermometer are more realistic. The Ctd-Chl thermometer overestimates the temperature by about 70°C.

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