*The Canadian Mineralogist*
Vol. 36, pp. 713-726 (1998)

# NEW DATA ON METAMORPHIC CHLORITE AS A PETROGENETIC INDICATOR MINERAL, WITH SPECIAL REGARD TO GREENSCHIST-FACIES ROCKS

ANTONELLA ZANE[1] AND RAFFAELE SASSI

*Dipartimento di Mineralogia e Petrologia dell'Università di Padova, C.so Garibaldi 37, I-35137 Padova, Italy*

CHARLES V. GUIDOTTI

*Department of Geological Sciences, University of Maine, Orono, Maine 04469, U.S.A.*

## ABSTRACT

For rock-forming minerals, the extent and the behavior of solid solution are understandable only if considered in the context of a rigorous petrological framework, as has been shown repeatedly in the metamorphic petrology literature. Herein, we present a study of the composition of trioctahedral chlorites, with special focus on non-limiting mineral assemblages in rocks of low metamorphic grade. The goal has been to discern and understand any systematic changes of chlorite composition due to changing T, P, and bulk-rock composition. The three main compositional variations shown by the metamorphic chlorite in this study include the ratio Fe/Mg, the extent of Tschermak substitution, and deviation from trioctahedral toward dioctahedral chlorite. Our database includes 2619 chlorite compositions, of which 450 are selected from literature covering the temperature range subgreenschist – amphibolite facies, and 2169 are newly determined compositions from greenschist-facies rocks. All samples used are classified according to metamorphic grade, pressure, and bulk-rock composition, thereby establishing groups and subgroups of analytical data. These data are plotted on diagrams aimed at enabling one to discern more specifically how bulk-rock composition, temperature and pressure affect the three main compositional variations of chlorite from typical metamorphic rocks. Each of these parameters controls chlorite composition to some extent, but the control by the bulk-rock chemistry is clearly dominant. Commonly, it largely obscures the systematic compositional changes caused by temperature and pressure. Thus, despite numerous attempts, it is evident that chlorite composition by itself is non-viable for geothermobarometric purposes in the case of the non-limiting assemblages typical of the greenschist facies. Attempts to use chlorite from such assemblages for geothermobarometry should be restricted solely to approaches involving cation exchange with some coexisting phase(s).

*Keywords*: chlorite, electron-microprobe data, low-grade metamorphism, compositional variation, geothermobarometry.

## SOMMAIRE

On peut parvenir à comprendre l'étendue et le comportement des séries de solution solide parmi les minéraux des roches seulement dans un contexte rigoureusement défini du point de vue pétrologique, comme celà a maintes fois été prouvé dans la littérature sur la pétrologie métamorphique. Nous présentons ici les résultats d'une étude sur la composition des chlorites trioctaédriques, portant en particulier sur les assemblages non limitatifs équilibrés à faible degré de métamorphisme. Le but de notre étude était de discerner et de comprendre les changements systématiques de la composition de la chlorite dus aux variables T, P, et la composition globale des roches. Les trois variables compositionnelles de la chlorite métamorphique sont le rapport Fe/Mg, l'étendue de la substitution dite de Tschermak, et l'écart de la stoechiométrie trioctaédrique vers les pôles dioctaédriques. Notre banque de données compte 2619 compositions de chlorite, dont 450 sont tirées de la littérature sur l'intervalle de température représentatif du faciès inférieur aux schistes verts jusqu'au faciès amphibolite, et 2169 ont été déterminées récemment dans le contexte de notre travail sur les roches du faciès schistes-verts. Tous les assemblages ont été classés selon intensité du métamorphisme, pression et composition globale des roches, ce qui a mené à des groupes et des sous-groupes de données analytiques. Ces données ont été reportées sur des diagrammes conçus pour faire ressortir clairement l'influence de la composition globale des roches, la température et la pression sur les trois variables compositionnelles de la chlorite typique des roches métamorphiques. Chacun de ces paramètres exerce un contrôle jusqu'à un certain point, mais l'influence de la composition globale d'une roche est prédominante. Des plusieurs cas, c'est ce paramètre qui domine, et obscurcit, par ce fait même, l'influence systématique de la température et de la pression. Malgré plusieurs tentatives, il semble

---

[1] *E-mail address*: anto@dmp.unipd.it

évident que la composition de la chlorite, par elle-même, est insuffisante pour applications géothermobarométriques dans le cas des assemblages non limitatifs typiques du faciès schistes-verts. On devrait limiter toute tentative d'extraire de la chlorite des notions géothermobarométriques aux seules considérations d'échanges de cations avec certaines des phases coexistantes.

(Traduit par la Rédaction)

*Mots-clés*: chlorite, données de microsonde électronique, métamorphisme de faible intensité, variation en composition, géothermobarométrie.

## INTRODUCTION

Chlorite is widespread in metamorphic rocks, except those containing upper-amphibolite and granulite-facies assemblages. Although its stability field is relatively well known, the petrological meaning of its compositional variations is still poorly understood, despite the significant contribution on this topic by Laird (1988). Among the numerous studies on metamorphic chlorites, the data and interpretations of Guidotti *et al.* (1991) are noteworthy, because they show that significant changes in the composition of chlorite occur within low-pressure greenschist- to amphibolite-facies metapelites.

In this paper, we present an overview of the composition of metamorphic chlorites, based on a large database (2619 analyses). Our aim is to outline the compositional changes of metamorphic chlorites as related to the main extensive and intensive variables, over the whole P–T field of metamorphism, but the primary focus is on chlorites from non-limiting greenschist-facies assemblages. Because the number of phases is lower than the number of components for such assemblages, it is well known that the composition of chlorite in them will be a function of both intensive and extensive variables. However, the relative effects of these variables are so poorly known at present that it is unclear if they can be differentiated at all. For some metamorphic minerals, it is possible to recognize and use for geothermobarometry the effects of T and P on mineral composition, even in the case of non-limiting assemblages [*e.g.* for muscovite, Guidotti & Sassi (1976, 1998) and Sassi *et al.* (1994)].

Previous attempts to use the composition of chlorite alone for geothermometric purposes were recently reviewed by De Caritat *et al.* (1993), Jiang *et al.* (1994) and Essene & Peacor (1995). De Caritat *et al.* (1993) compared three geothermometric methods based on the chemistry of chlorite-group minerals formed in hydrothermal and geothermal systems (Cathelineau & Nieva 1985, Cathelineau 1988, Walshe 1986) and sedimentary basins (Hutcheon 1990), and concluded that none of these thermometers gives reliable results over a wide range of physicochemical conditions of crystallization. Jiang *et al.* (1994) considered the particular case of geothermometry based on the proportion of $^{IV}$Al and vacancies in the octahedral site in subgreenschist-facies chlorites, and considered it unwarranted owing to the probability of mixed-layering occurring between chlorite and other sheet silicates in low-grade metamorphic rocks. Essene & Peacor (1995) considered the thermometric implication of the Al content of chlorite and proposed six reactions that constrain Al content as a function of specific mineral assemblages; they pointed out that "contrary to the implications of chlorite thermometry as it is usually applied, different specific assemblages will drive the Al content of chlorite in different directions with increasing grade". In their opinion, the lack of reliable activity–composition relations for chlorite solid-solutions experimentally calibrated in the appropriate T range makes the application of any reaction speculative.

### *Crystal chemistry of chlorite-group minerals*

Readers are referred to Bailey (1988) and references therein for a full review of the structure of chlorite. Briefly, chlorite consists of a regular interlayering of a 2:1 layer $R_6Z_8O_{20}(OH)_4$ (formerly called the "talc-like layer"), and an interlayer sheet $R_6(OH)_{12}$ (formerly called the "brucite-like sheet"), where $R$ represents Mg, $Fe^{2+}$, Al and $Fe^{3+}$ (occasionally Cr, Mn, V, Ni, Cu, Zn, Ti, Li), and $Z$ stands for Si, partially replaced by Al (occasionally by $Fe^{3+}$, $B^{3+}$, $Zn^{2+}$, $Be^{2+}$).

Because of the variety of chemical substitutions, vacancies, *etc.*, the general formula of chlorite may be written as follows (Wiewióra & Weiss 1990):

$$^{VI}(R^{2+}_{u}\,R^{3+}_{y}\square_{z})^{IV}(Si_{8-x}Al_{x})O_{20}(OH)_{16}$$

where: $R^{2+}$ is mainly $Mg^{2+}$, $Fe^{2+}$, $R^{3+}$ is mainly $Al^{3+}$, $Fe^{3+}$, $\square$ represents octahedral vacancies [as defined in Bailey (1988), *i.e.*, vacancies in the octahedrally coordinated sites]. In the above formula, $z = (y - x)/2$; $u + y + z = 12$.

Three main substitutions occur in chlorite: (i) the Tschermak substitution (*TK*), (ii) the "dioctahedral" substitution (*AM*), and (iii) the $FeMg_{-1}$ substitution (*FM*). Because they are controlled by physical and chemical environment conditions, their chemical meaning is briefly explained below, but without a discussion of their full implications regarding charge balance and vacancies.

### *The Tschermak substitution*

The *Tschermak substitution* involves the following substitutions: $^{IV}Al^{VI}AlSi_{-1}Mg_{-1}$, $^{IV}AlCr^{3+}Si_{-1}Mg_{-1}$ and $^{IV}Al_2Ti^{4+}Si_{-2}Mg_{-1}$.

The second one is important only in ultramafic rocks and some metabasic rocks, and the third substitution generally is unimportant. The nature of the *TK* substitution is shown graphically in Figure 1. Data points at the origin have no *TK* substitution, and points lying along the arrow have increasing extents of *TK* as distance from the origin increases.

### *The "dioctahedral" substitution*

The *"dioctahedral" substitution* $Al_2Mg_{-3}$ produces one vacancy in the sheets of octahedra. Its occurrence and extent may also be evaluated in Figure 1, by the distance from the *TK* arrow. Specifically, (1) data points lying on the *TK* arrow represent chlorite in which no *AM* substitution occurs; (2) data points plotting above the arrow (vacancy field: $\Delta = {}^{IV}Al - ({}^{VI}Al + 2Ti + Cr) < 0$) represent chlorite compositions in which Al, Cr or $^{VI}Ti$ replaces $R^{2+}$ without a concomitant replacement of Si by $^{IV}Al$, *i.e.*, chlorite compositions in which the *AM* substitution occurs, with the distance from the *TK* arrow being a measure of its importance.

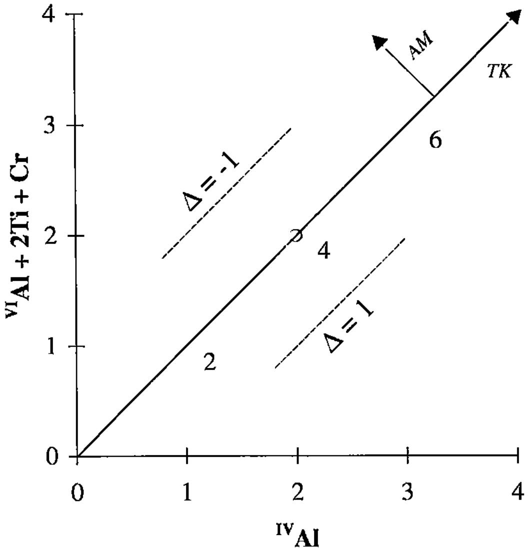


FIG. 1. A summary of the essential features of the Tschermak and the dioctahedral substitutions. The progression of numbers on the long arrow shows the increasing extent of *TK* substitution. The short arrow points toward increasing *AM* extent of substitution. $\Delta = {}^{IV}Al - ({}^{VI}Al + 2Ti + Cr)$. The open circle indicates the position of the end-members clinochlore – chamosite.

Data points plotting below the arrow ($\Delta > 0$) indicate incorporation of trivalent cations $R^{3+}$ not considered in the *TK* substitutions (*e.g.*, $Fe^{3+} \Leftrightarrow Al$) as necessary for charge balance. In such a case, the *AM* substitution is not involved.

The proportion of *vacancies* occurring in the octahedrally coordinated sites may be calculated by subtracting $\Sigma^{VI}(R^{2+} + R^{3+} + R^{4+})$ from the full theoretical octahedral occupancy [*i.e.*, 12 *apfu* (atoms per formula unit) calculated on a 28-oxygen basis]. The role of vacancies in chlorite, as well as in other hydrous silicates, was discussed by Dyar *et al.* (1993). They showed that 1) chlorite commonly has a lower content of $H^+$ (and hence OH) than that expected from stoichiometry, and 2) the amount of $H^+$ deficiency in them can be explained by $R^{3+}$ and $R^{4+}$ replacing $R^{2+}$ [excluding substitutions related to the balance of $^{IV}(R^{3+})$]. Hence, they concluded that this mechanism accounts for the great majority of $R^{3+}$ and $R^{4+}$ incorporation (apart from the Tschermak substitution), thus reducing or eliminating the need to invoke vacancies for charge balance. To the extent that their conclusion is valid, it suggests that many of the vacancies inferred for chlorite formulas, and hence much of the *AM* substitution, may be an artifact due to lack of direct data for $H_2O$.

The *occurrence of Fe*$^{3+}$ as a primary component of chlorite has commonly been suggested since the work of Foster (1962), but for many years its presence was attributed to "secondary oxidation". Suggested calculations for indirect estimation of its *minimum* amount from electron-microprobe data by means of the stoichiometry criteria have been proposed by Walshe (1986) and Jacobson (1989), but such calculations are notoriously inaccurate. The importance of direct measurements of $Fe^{3+}$ and $H^+$ in hydrous silicates was emphasized by Dyar *et al.* (1993), who demonstrated that $H^+$ contents in these minerals are petrologically controlled, and relatable to the deprotonation (or "oxysubstitution") reaction $H^+_{mineral} + (Fe,Mg)^{2+}_{mineral}$ $(Fe^{3+}, Al^{3+}, Cr^{3+}, Ti^{4+})_{mineral} + [H_2]_{gas}$, which is also a dehydration reaction. The samples of chlorite studied by Dyar *et al.* (1993) have $H_2O$ contents (8.80–10.41 wt%) that are systematically lower than the ideal stoichiometric value (12 wt%). Nevertheless, in contrast to micas (*e.g.*, Guidotti & Dyar 1991, Guidotti *et al.* 1994), chlorite-group minerals formed in various conditions of $f(O_2)$ have low $Fe^{3+}$ contents, typically less than 15% of $Fe_{tot}$ (Dyar *et al.* 1992). In particular, $Fe^{3+}$ ranges between 6 and 13% of $Fe_{tot}$ in chlorite that coexists with garnet and ilmenite within Al-, Ti-, Si-saturated metapelites, and is close to 10 ± 5% of $Fe_{tot}$ in chlorite coexisting with hematite + pyrite + epidote in hydrothermal veins. Thus the content of $Fe^{3+}$ in rock-forming chlorites is strongly controlled by crystallochemical constraints rather than by $f(O_2)$ conditions (Dyar *et al.* 1992, Nelson & Guggenheim 1993), and it is never abundant.

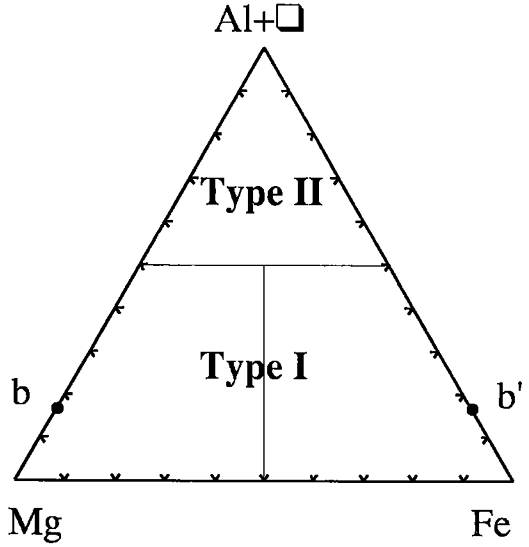


FIG. 2. Classification diagram for rock-forming chlorites according to Zane & Weiss (1998). The points for some end-members, as defined by Wiewióra & Weiss (1990), are also shown: b: clinochlore, b': chamosite. ☐: vacancies. With few exceptions, samples of Mg-dominant chlorite and Fe-dominant chlorite plot in the appropriate subfields of type-I chlorite.

### *The FeMg$_{-1}$ substitution*

The *FeMg$_{-1}$ substitution* (*FM* for short) is also very important in metamorphic chlorites. Its extent covers the full range between $Mg^{2+}$ and $Fe^{2+}$ end-members.

Several systems of *chlorite classification* have been proposed in past decades. One of the still most commonly used is that of Hey (1954), although new systems were proposed later (Bailey 1980, Wiewióra & Weiss 1990, Weiss 1991). These classifications were designed to cover chlorites from all types of parageneses.

More recently, Zane & Weiss (1998) proposed a very simple, practical procedure of classification, which was specifically designed to provide rigorously defined names for rock-forming chlorites, based solely on results of electron-microprobe analyses (EMPA) (in which iron contents are given only as $Fe_{tot}$). A triangular compositional diagram (Fig. 2) and a flowchart are linked to this classification procedure.

In conjunction with Hey's diagram (see below), this triangular diagram is very useful in showing the main petrologically controlled changes in composition of metamorphic chlorites. Hence, both are used extensively below, in addition to the *TK*, *AM*, and *FM* plots.

## METHODS OF STUDY

The approach used in the present study includes: 1) detailed examination of the literature, in order to collect the largest possible number of chemical data obtainable for chlorite from well-defined petrological settings; 2) collection of new samples from a range of bulk compositions within various greenschist-facies terranes; these new analyses were planned in order to get a new dataset produced in the same laboratory; 3) petrographic analyses of the new samples; 4) electron-microprobe analyses and formula calculations; 5) data processing and plotting. Each of these aspects is discussed briefly below.

(1) Of the 555 chemically analyzed chlorites initially collected from the literature [part of which were included in the review of Laird (1988)], a significant number (105) was not used for the following reasons: a) ambiguous or insufficient petrological data concerning P, T estimates; b) chemical compositions clearly indicating a mixture of minerals, such as interlayered sheet silicates; c) chemical analyses deviating from a set of chemical constraints chosen as a quality grid (see below).

(2) In collecting new samples, an attempt was made to obtain rocks formed over the widest possible range of pressures and bulk compositions within the greenschist facies. However, this goal was only partially achieved, because of the scarcity of samples from high-pressure terranes.

(3) The detailed petrographic analyses were aimed at selecting suitable sites for EMPA in addition to gaining standard petrographic insights (*i.e.*, mineral assemblages and compatibilities, texture, crystallization – deformation relationships).

(4) The EMPA included a preliminary stage to identify the most suitable analytical conditions. After several trial runs, these were established at: 15 kV, 15 nA, t = 20 s, $\phi = 1$ µm. The very small size of the electron beam is directly related to the fine grain-size of chlorite grains in the analyzed samples. Chlorite formulas were then calculated from the EMPA results on the basis of 28 atoms of oxygen (anhydrous basis). No corrections were applied for $Fe^{3+}$, as it is typically low (Dyar *et al.* 1992); this fact was also ascertained by means of a few Mössbauer analyses (G. Pedrazzi, University of Parma).

(5) All chemical compositions were then screened through a quality-control grid. Chemical data from the literature were screened using the criteria proposed by Foster (1962), but a more selective quality-control grid was used for the new analytical data, all of which fit the constraints listed below [the corresponding values proposed by Foster (1962) are given in parentheses]: Na + K + Ca lower than 0.1 *apfu* (0.5 wt. %), total

occupancy of octahedrally coordinated cations in the range 11.7 – 12.1 *apfu* (10.9 – 12.1 *apfu*), and Si ranging between 5.00 and 5.65 *apfu* (4.68 – 6.90 *apfu*).

The above compositional constraints make up a quality-control grid to be used as a reference for evaluating EMPA results for metamorphic chlorites, at least for greenschist-facies rocks.

Several chlorite grains from greenschist-facies rocks were also studied by transmission electron microscopy (TEM), in order to test for submicroscopic interlayering with other phases. The TEM images (M. Mellini, University of Siena) revealed a good degree of crystallinity and lack of significant interlayering in all the samples studied, as also confirmed by diffraction patterns and results of analytical electron microscopy (AEM) analyses.

## THE DATABASE AND PETROGRAPHY OF THE SAMPLE POPULATION

The database consists of results of 2619 electron-microprobe analyses, of which 450 were selected from the literature and 2169 are new. The data from the literature pertain to chlorite from various metamorphic grades, whereas the new data all pertain to chlorite from low metamorphic grades, mainly from non-limiting greenschist-facies assemblages (*i.e.* those in which number of phases is lower than number of components). The new analyses were carried out on 238 representative grains. A copy of the database can be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario, Canada K1A 0S2.

The chlorite compositions were arranged according to bulk-rock composition, T and P, respectively. Three groups of bulk-rock compositions were first established, namely metapelites, metabasic rocks and felsic rocks. Further subdivisions were then made according to T and P, as shown in Table 1, which also indicates the number of chlorite compositions in each group and subgroup.

For these subdivisions, the following criteria were adopted: a) subgroups of low (LP), medium (MP) and high (HP) pressure were established on the basis of the occurrence of andalusite, kyanite and glaucophane, respectively, in the rocks of appropriate grade and bulk composition belonging to the same rock sequence. Alternatively, for the data taken from the literature, this LP, MP, HP classification was based on the geobarometric estimates reported. b) Subgroups of very low temperature (VLT), low temperature (LT) and medium temperature (MT) correspond to the subgreenschist, greenschist and amphibolite facies, respectively.

TABLE 1. CHLORITE COMPOSITIONS IN GROUPS AND SUBGROUPS MAKING UP THE DATABASE

| | LITERATURE DATA | | | | | | | | NEW DATA | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | VLT | LT | MT | LP | MP | HP | N.D. | LIT | LP | MP | HP | LTn | Total |
| Metapelites | 7 LP<br>-<br>1 HP | 51 LP<br>34 MP<br>27 HP | 82 LP<br>47 MP<br>9 HP | 140 | 81 | 37 | 9 | **267** | 698 | 242 | 168 | **1108** | **1375** |
| *Subtotal* | *8* | *112* | *138* | *140* | *81* | *37* | *9* | *267* | *698* | *242* | 168 | *1108* | *1375* |
| Metabasic rocks | 71 LP<br>-<br>22 HP | 27 LP<br>1 MP<br>25 HP | 1 LP<br>19 MP<br>- | 99 | 20 | 47 | 6 | **172** | 463 | 181 | 32 | **676** | **848** |
| *Subtotal* | *93* | *53* | *20* | *99* | *20* | *47* | *6* | *172* | *463* | *181* | 32 | *676* | *848* |
| Felsic rocks | -<br>-<br>- | 7 LP<br>4 MP<br>- | -<br>-<br>- | 7 | 4 | - | - | **11** | 385 | - | - | **385** | **396** |
| *Subtotal* | - | *11* | - | *7* | *4* | - | - | *11* | *385* | - | - | *385* | *396* |
| *Total* | *101* | *176* | *158* | *246* | *105* | *84* | | ***450*** | *1546* | *423* | 200 | ***2169*** | ***TOT 2619*** |
| Low pressure (LP) | 78 | 85 | 83 | | | | | **246** | | | | **1546** | **1792** |
| Medium pressure (MP) | - | 39 | 66 | | | | | **105** | | | | **423** | **528** |
| High pressure (HP) | 23 | 52 | 9 | | | | | **84** | | | | **200** | **284** |
| *Total* | *101* | *176* | *158* | | | | | ***435**** | | | | ***2169*** | ***TOT 2604**** |

* This number is lower than the total (TOT), because it was impossible to assign a specific physical condition to a few analyses from the literature (see column "N.D."). VLT means "very low temperature", LT and MT "low temperature" and "medium temperature" respectively. LTn includes "chlorite zone", "biotite zone" and "garnet zone". LP, MP, HP refer to low, medium, high pressure respectively. N.D. = Specific physical conditions unknown.

## INFLUENCE OF BULK-ROCK COMPOSITION ON CHLORITE COMPOSITION

An initial evaluation of the importance of the influence of bulk-rock composition on chlorite composition was made on the whole population of samples, *i.e.*, disregarding the P, T aspects of the samples. This type of evaluation is certainly very rough, but it is useful in understanding whether the effects of the composition of the system in which chlorite crystallizes are significant, and whether or not they dominate over the effects of the intensive variables.

Figures 3a, b, and c, referring to metapelites, metabasic rocks and felsic rocks, respectively, show the location of the chlorite data-points in the triangular diagram of Zane & Weiss (1998) (Fig. 2), and how the field of highest density of points reflects the changing bulk-rock composition. These plots indicate that: (i) common metamorphic chlorite is type-I chlorite according to the nomenclature of Zane & Weiss (1998), *i.e.*, $X_{Mg} + X_{Fetot} \geq X_{VIAl} + X_{\square}$ (where $X$ is the atomic fraction per formula unit); (ii) chlorites from metapelites cover a wide compositional range, from the fields of Fe-dominant chlorites to that of Mg-dominant chlorites (Fig. 3a); (iii) chlorites from metabasic rocks are mostly Mg-dominant (Fig. 3b), whereas those from felsic rocks are Fe-dominant chlorites, with only a few exceptions (Fig. 3c); (iv) the $X_{VIAl} + X_{\square}$ contents also change, although only slightly, in response to bulk-rock composition: the highest $X_{VIAl} + X_{\square}$ values are common in chlorites from metapelites (m = 24.59, s = 1.06, where m represents the average value and s, the standard deviation); intermediate and low $X_{VIAl} + X_{\square}$ values prevail in chlorites from metabasic rocks (m = 21.65, s = 1.14) and from felsic rocks (m = 22.69, s = 1.58).

### *TK and AM substitutions*

Each of the three diagrams in Figures 4a, b, and c shows the rectangular area into which all 2619 data-points fall in the $^{VI}Al + 2\,Ti + Cr$ *versus* $^{IV}Al$ diagram (excluding 18 scattered points *i.e.*, 0.69% of the whole population). The intercepts of the arrow with the short sides of the rectangular field represent, for the data set used, the lowest and highest values, respectively, of the *TK* substitution. The long sides reflect the limit for the range of *AM* substitution.

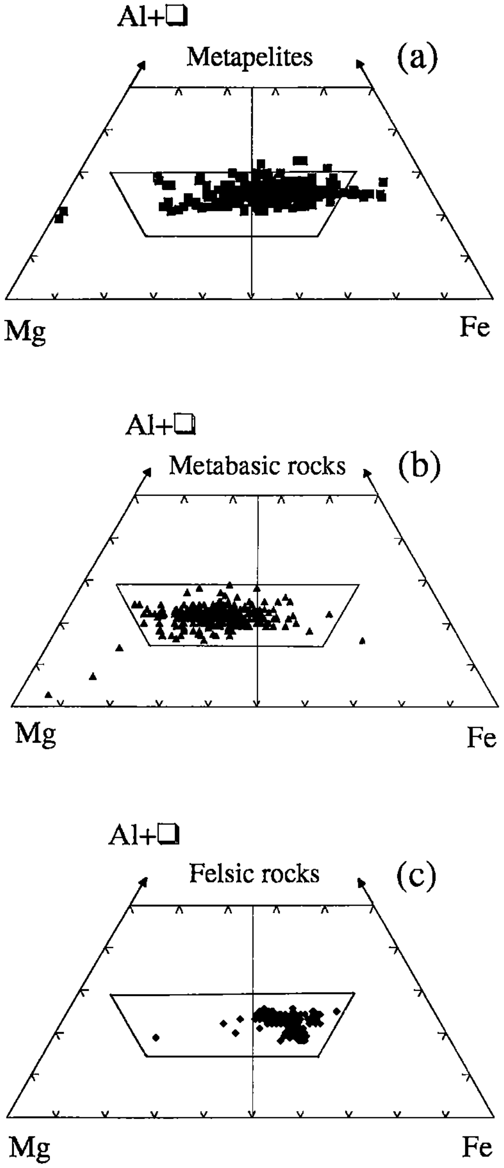


FIG. 3. Plots of chlorite compositions from various bulk-rock compositions using the classification diagram of Figure 2: (a) chlorite from metapelites, (b) chlorite from metabasic rocks, and (c) chlorite from felsic rocks. The trapezoidal contour shown for reference confines the area within which 99% of the whole population (*i.e.*, 2604 chlorite compositions out of 2619) falls.

In general, the locations of data points show that: (i) the extent of *TK* substitution is important in each case, and is higher than that occurring in the end-members clinochlore – chamosite, which on the axes of these diagrams, lies at x = y = 2 (open circle in Figure 5); (ii) the degree of *AM* substitution is also significant for a large number of data points, with most values lying in the so-called "vacancy field", *i.e.* where $\Delta = {}^{IV}Al - ({}^{VI}Al + 2Ti + Cr) < 0$. However, recalling the conclusion of Dyar *et al.* (1993), noted above, these values showing $\Delta < 0$ may be an artifact due to the lack of data on $H_2O$ in the EMPA datasets.

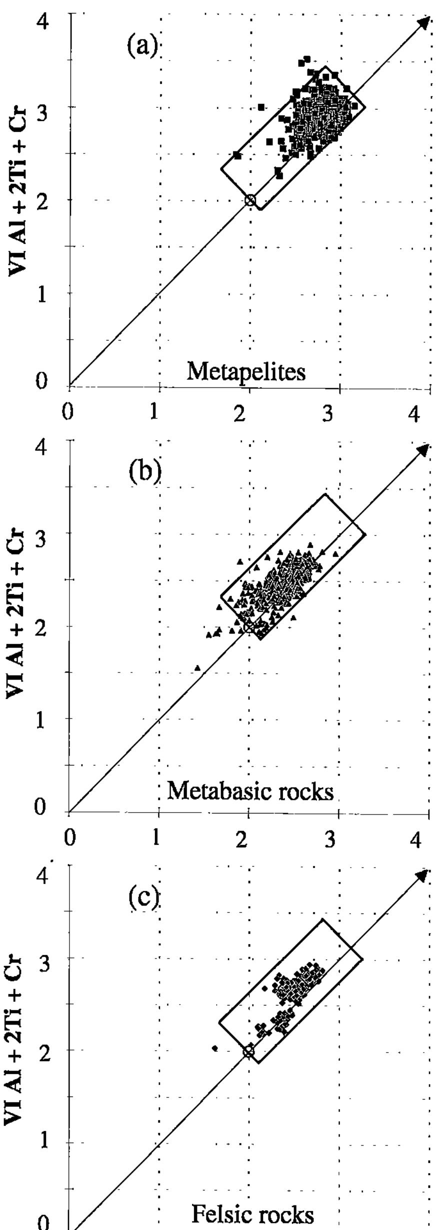


FIG. 4. Plots of chlorite compositions from various bulk-rock compositions using the classification diagram of Figure 1: (a) chlorite from metapelites, (b) chlorite from metabasic rocks, and (c) chlorite from felsic rocks. The rectangular contour shown for reference confines the area within which 99% of the whole population (*i.e.*, 2604 chlorite compositions out of 2619) falls. The open circle indicates the position of the end-members clinochlore – chamosite. Data-points lying at $^{IV}Al > 3$ belong to the data set taken from literature.

It is worth pointing out that the density of points decreases more or less gradually toward high values of $\Delta < 0$ (*i.e.*, those above the arrow), and the distribution field is more sharply defined in the field of $\Delta > 0$ (*i.e.*, below the arrow), displaying some kind of boundary at *ca.* $\Delta \simeq 0.25$. The area below the $y = -0.25 + x$ line seems to be a "forbidden zone" for metamorphic chlorites, probably due to crystallochemical constraints such as charge balance (*e.g.*, Dyar *et al.* 1992, Nelson & Guggenheim 1993). This difference in the behavior of the distribution of points in the two Δ fields may provide some confirmation on the assertion of Dyar *et al.* (1992, 1993) regarding the possibility of a crystallochemical control and the claim that vacancies are an artifact.

With regard to the extents to which metamorphic chlorites from different bulk-rock compositions display differing *TK* and *AM* substitutions, visual comparison among the three diagrams of Figure 4 shows that: (i) the extent of *AM* substitution does not differ significantly in the three chlorite subgroups, being only slightly higher for the metapelites; (ii) the extent of *TK* substitution in chlorites changes significantly from metapelites ($x + y$ ranges from 5 to 6.25) to metabasic rocks ($x + y$ ranges from 4 to 5.5, but less than 5.25 for 88% of data-points). Chlorites from felsic rocks are more or less intermediate between the chlorites from the other two rock types ($x + y$ ranges from 4.5 to 5.75, but greater than 5 in 82% of data-points, and never exceeds 6). The gap shown in Figure 4c may be related to the low number of samples; moreover, the cloud of data-points at lower *TK* values pertains to retrograde chlorites.

### *$Fe^{2+}Mg_{-1}$ substitution*

Figures 5a, b, and c show: (i) the rectangular area in which 98.7% of the 2619 data-points fall on the Mg *versus* $Fe^{2+}$ diagram; most data plot in a narrow belt between 8.70 and 10 *apfu* for $\Sigma(Mg + Fe^{2+})$; (ii) the regression line of all data-points is $y = -1.0966x + 9.6156$ (with $R = 0.9817$; $n = 2619$), which deviates, although only slightly, from the 1:1, $y = x$ line that would reflect solely an *FM* substitution. This slight deviation may be due to *AM* substitution or occurrence of $Fe^{3+}$.

In general, the distribution fields for the data-points in Figure 5 show that the *FM* substitution occurs continuously over a very wide range. The extent of this substitution in chlorites from different bulk-rock compositions varies as follows: (i) the very wide Mg/Fe range detected in the whole population of chlorites is mainly due to chlorites from metapelites, in which Mg/Fe ranges from 3.5 to 0.14; (ii) Mg/Fe in chlorites from metabasic rocks is uniformly greater or equal to 0.66, and in the great majority of cases (91% of the 811 data-points), it is greater than 1; (iii) this ratio is less than 1 for chlorites from felsic rocks (if four scattered data-points are disregarded).

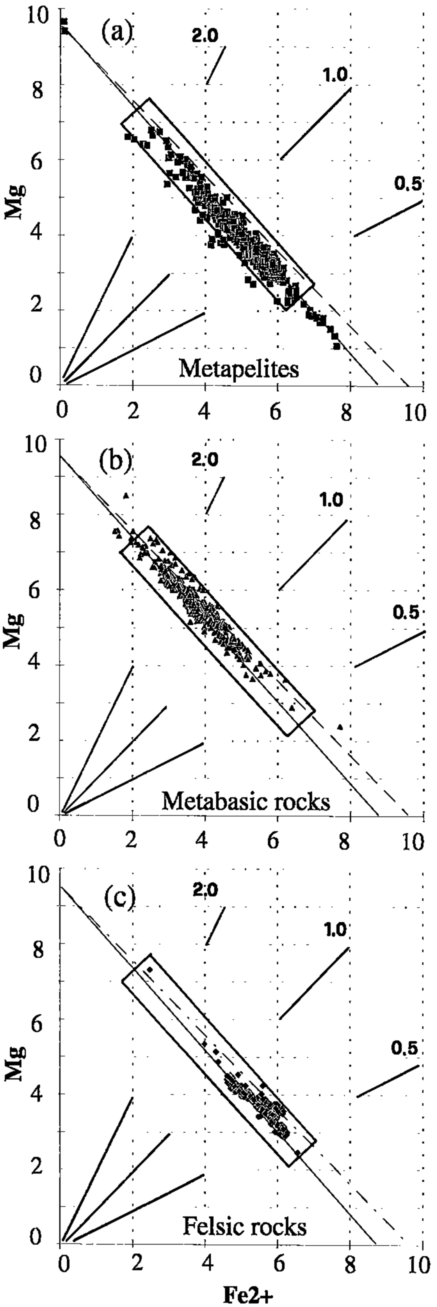


FIG. 5. Plots of chlorite compositions from various bulk-rock compositions in the $FeMg_{-1}$ diagram: (a) chlorite from metapelites, (b) chlorite from metabasic rocks, and (c) chlorite from felsic rocks. The rectangular contour defines the area within which 99% of the whole population (*i.e.*, 2585 chlorite compositions out of 2619) falls. Solid line: best-fit line of the whole population; dashed line: Fe + Mg = 9.6. Radial lines corresponding to Mg/Fe of 2, 1 and 0.5 are shown for references.

Furthermore, (Mg + Fe) is slightly higher in the chlorites from metabasic rocks and felsic rocks than in those from metapelites. This fact reflects higher *TK* substitution in the latter chlorites, *i.e.* more Al-rich bulk compositions.

Systematic patterns are also clearly present if the data are plotted on the diagram proposed by Hey (1954), as shown in Figures 6a, b, c, d. These plots show that metamorphic chlorites mainly fall in the field of ripidolite, partly in the field of pycnochlorite and, to a lesser extent, in that of brunsvingite. In particular: (i) chlorites from metapelites are primarily ripidolite (Fig. 6b); furthermore, they cover almost completely the whole ripidolite field in terms of the range of both Si content and also of $Fe_{tot}/(Fe + Mg)$, although the lowest and highest $Fe_{tot}/(Fe + Mg)$ values for ripidolite are less common; (ii) with a very few exceptions, the most distinctive feature of chlorites from metabasic rocks is that they plot in a belt characterized by relatively low $Fe_{tot}/(Fe + Mg)$ values (mostly <0.5), within the fields of ripidolite and pycnochlorite (Fig. 6c); (iii) this contrasts with the majority of chlorites from felsic rocks, which are ripidolite, and show a relativly narrow range of intermediate $Fe_{tot}/(Fe + Mg)$ values. Intermediate values of $Fe_{tot}/(Fe + Mg)$ seem to be the most important feature of chlorites from felsic rocks, because it also affects the few chlorites from felsic rocks that fall outside the ripidolite field due to their high Si contents (Fig. 6d).

In summary, the data presented above show consistently and clearly the manner in which the composition of metamorphic chlorites from non-limiting assemblages is strongly controlled by bulk-rock composition. This control was also shown clearly by comparing chlorites from the three different bulk-compositions but crystallized under differing sets of T and P conditions. The numerous relevant sets of diagrams are not shown here for sake of brevity, and can be found in Zane (1995).

## INFLUENCE OF TEMPERATURE AND PRESSURE ON CHLORITE COMPOSITION

### *Temperature*

The effect of T on chlorite chemistry was tested by comparing on standard diagrams the distribution of chlorite data-points for each rock type at different metamorphic grades. Of the numerous diagrams plotted in Zane (1995), only the most significant ones are shown below. They show the data points concerning the amphibolite facies taken from the literature (Table 1, column MT) compared to a contour defined by the data for greenschist facies (Table 1, column LTn in the right-hand part).

For metapelites and metabasic rocks, Figure 7 shows how the distribution of data-points for chlorites from non-limiting assemblages changes with increasing

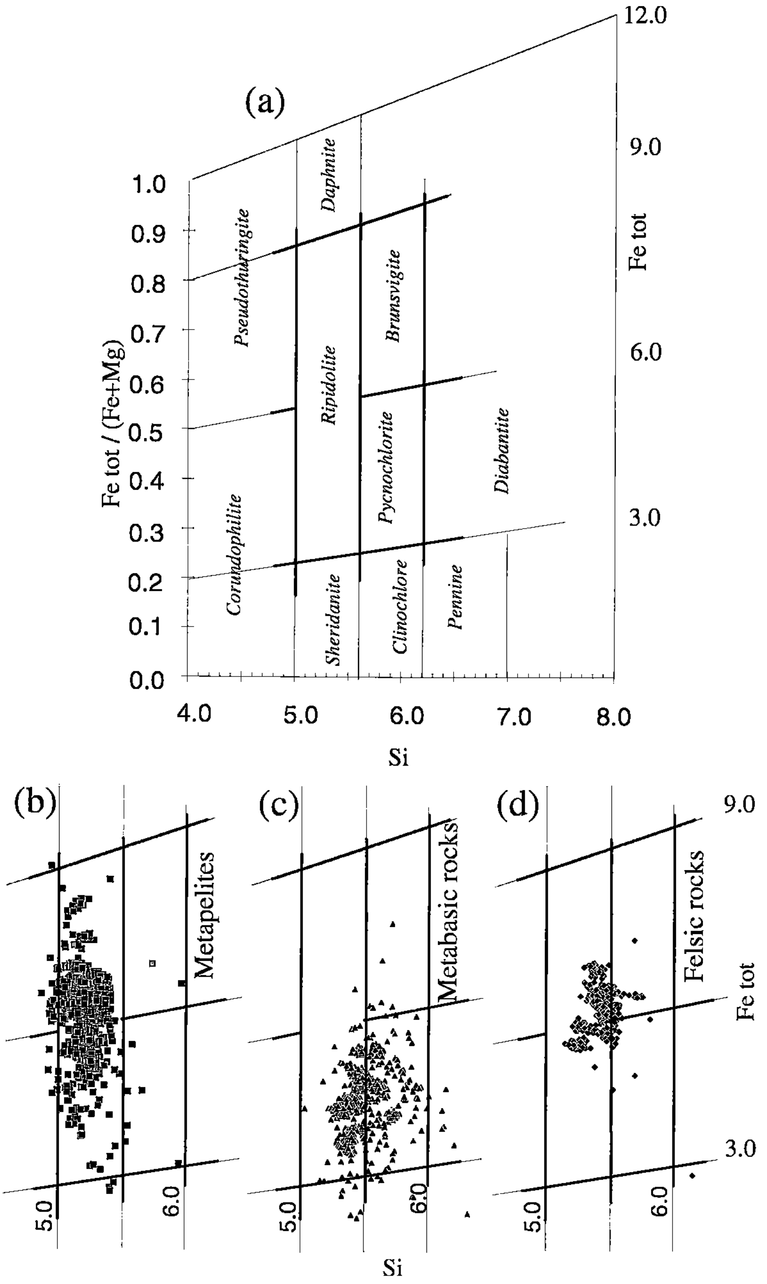


FIG. 6. Top: Classification diagram according to Hey (1954). In (a), the darkened lines include the portions shown in plots b, c, d. Bottom: plots of chlorites from different bulk-rock compositions: (b) chlorite from metapelites, (c) chlorite from metabasic rocks, and (d) chlorite from felsic rocks.

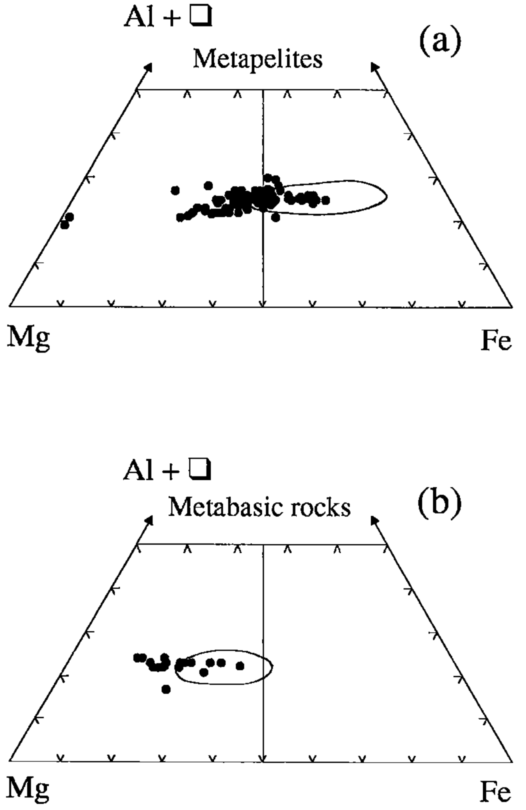


FIG. 7. Plots of chlorite compositions from metapelites (a) and metabasic rocks (b) of different metamorphic grade. Data points: amphibolite-facies chlorites. Contour: area in which greenschist-facies chlorites fall.

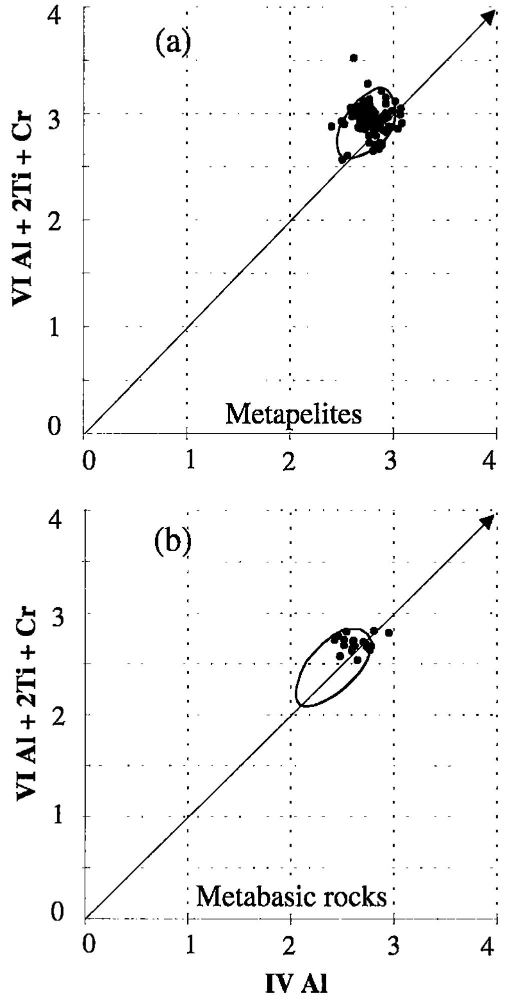


FIG. 8. *TK* plots of chlorite compositions from metapelites (a) and metabasic rocks (b) of different metamorphic grade. Data points: amphibolite-facies chlorites. Contour: area in which greenschist-facies chlorites fall.

metamorphic grade. In particular, *in the metapelites*, chlorites crystallized under greenschist-facies conditions (Fig. 7a: contour) are Fe-dominant chlorite, if a few data (2.8% of a total of 1108) are disregarded. With increasing metamorphic grade, the boundary between Fe-dominant and Mg-dominant chlorite is approached and then crossed. Most chlorites from amphibolite-facies metapelites (Fig. 7a: dots) are Mg-dominant chlorites or plot near the boundary. This change reflects the fact that, for increasing T, chlorite can occur in the non-limiting assemblage chlorite + biotite only for Mg-rich metapelitic bulk-compositions, because Mg-enriched chlorite and biotite are produced by the continuous reactions that occur in the limiting assemblages (*i.e.*, those with number of phases equal to number of components, so that compositions of phases are a function of the intensive variables). Guidotti *et al.* (1991) discussed the controls on chlorite composition in lower and middle amphibolite-facies metapelites, with reference to the limiting assemblages garnet + chlorite + biotite and staurolite + chlorite + biotite, respectively.

*In the metabasic rocks* (Fig. 7b), although all chlorites are Mg-dominant owing to bulk-composition constraints, a similar increase in Mg/Fe occurs with increasing metamorphic grade. In rocks bearing greenschist-facies assemblages (Fig. 7b, contour), the value 100 Fe/[Fe + Mg + (Al + □)] is higher than 25 in most chlorites, whereas it is lower than 25 in most chlorites of the amphibolite facies (Fig. 7b, dots). A further difference between the two

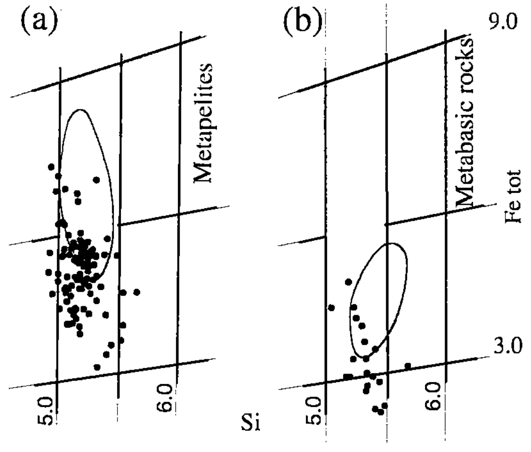


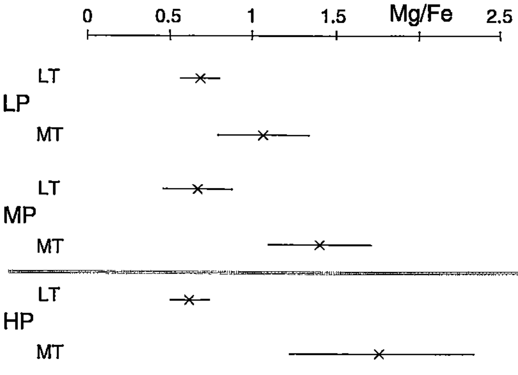
FIG. 9. Hey (1954) classification plots of chlorite compositions from metapelites (a) and metabasic rocks (b) of different metamorphic grade. Data points: amphibolite-facies chlorites. *Contour*: area in which greenschist-facies chlorites fall.

subgroups of chlorite plotted in Figure 7b is a decrease of the scatter in the range of Al + □ with increasing metamorphic grade.

Figures 8 and 9 are particularly useful for a better understanding of the changing composition of chlorite with increasing T: on these plots, the contoured field shows greenschist-facies chlorite, whereas the points are amphibolite-facies chlorite. Figures 8a, b show that if chlorites from non-limiting assemblages are considered, the extent of both *TK* and *AM* substitutions seems to be unaffected by increasing metamorphic grade in metapelites (Fig. 8a). This probably reflects the fact that for a large fraction of the metapelitic samples, the non-limiting assemblage consists of the phases chlorite + biotite + muscovite. From an AFM projection of this assemblage (see Guidotti *et al.* 1991), it is evident that $FeMg_{-1}$ substitution in such chlorites can vary widely, but *TK* and *AM* will be fixed for a given set of P, T conditions. In metabasic rocks, the average *TK* value is somewhat higher at higher T (Fig. 8b).

This control is also clear as shown in Figures 9a, b for chlorites from metapelites and metabasic rocks. As expected from the *TK* diagram of Figure 8b, Figure 9b suggests that grade exerts some control on chlorite Si contents, with Si decreasing somewhat with increasing T. For metabasic rocks, chlorites from greenschist facies (contour) cluster on both sides of the boundary between the fields of pycnochlorite and ripidolite, but those from the amphibolite facies mostly fall at moderately high Si values of the ripidolite and partly in the sheridanite field. In every case, Fe/(Fe + Mg) remains constrained at low values for chlorites from metabasic rocks, owing to bulk-rock compositional constraints and Mg-enrichment of chlorite as grade increases. It is worth noting that chlorite data-points from subgreenschist-facies (not shown in the plots but widely scattered in all cases) mainly fall in the ripidolite field for metapelites, and in the pycnochlorite field for metabasic rocks. Thus, their location is roughly consistent with the above outlined prograde compositional trends.

For metapelites, the compositional behavior outlined above, shown by the whole data-set for Mg/Fe, is also consistent with those samples detected from subpopulations of data points related to different ranges of pressure of metamorphism (Fig. 10).



| | | *n* | min | max | *n* tot |
|---|---|---|---|---|---|
| LP | LT | 741 | 0.25 | 1.00 | 749 |
| | MT | 82 | 0.45 | 1.88 | 82 |
| MP | LT | 270 | 0.47 | 1.16 | 276 |
| | MT | 28 | 0.91 | 2.01 | 31 |
| HP | LT | 188 | 0.49 | 1.20 | 195 |
| | MT | 7 | 0.90 | 2.46 | 9 |

FIG. 10. Schematic representation of Mg/Fe values in chlorites from LP, MP, HP metapelites of different metamorphic grade (LT, MT). Cross: mean value; total error-bar: 2 standard deviations.

In conclusion, the effects of temperature on the chemistry of metamorphic chlorites from non-limiting assemblages are clearly discernible, but those due to bulk-rock composition are clearly dominant. Moreover, as noted above, scatter in the data-points was found to be very large in the subgreenschist-facies chlorites. This is because chemical equilibrium is commonly not attained in very-low grade rocks (Essene & Peacor 1995), particularly in low-strain conditions.

### *Pressure*

The effects of P on chlorite chemistry were tested by visual inspection of the distribution of data-points for each subpopulation formed at different metamorphic P. A further evaluation was also carried out by considering separately the subgroups of different metamorphic grade (subgreenschist facies, greenschist facies, amphibolite facies), but the statistical weight (*i.e.*, number of data-points) of some subgroups is very low.

No new plots are presented in this section because they either show overlapping fields of distribution related to different pressures of metamorphism or, in some cases only ill-defined trends for increasing pressure. For chlorites from metapelites, these ill-defined trends for increasing P include a decrease in the *TK* substitution and thus a concomitant increase in ($Fe^{2+}$ + Mg) content. This sum is, in most cases, less than 9 *apfu* in LP rocks, and lies below the best-fit line $y = -1.0217x + 9.1517$ calculated from MP and HP data ($R$ = 0.9840; $n$ = 537). No reportable trends were detected from metabasic rocks and felsic rocks.

Thus for chlorites from non-limiting assemblages, subtle controls on their composition by pressure may be expected, but they are clearly of lesser importance than those due to T and especially bulk-rock composition.

### *General trends*

These temperature and pressure effects are sketched as qualitative general patterns on Figures 11a, b, and c. The effects of P and especially T are clearly discernible, notwithstanding the high phase-rule variance due to the low number of phases coexisting with chlorite. Our results confirm quite well most of the trends previously suggested by Laird (1988). The particular value of this confirmation is related to the size and nature of our database, which (i) is very much larger, and (ii) mostly consists of a uniform data-set obtained in the same laboratory and with the same conditions of analysis.

## CONCLUDING REMARKS

Several attempts to use the chemical composition of chlorite alone as a geothermometer in hydrothermal zones and greenschist- plus subgreenschist-facies rocks are reported in the literature, and give conflicting messages with regard to the viability of this approach. On the other hand, Guidotti *et al.* (1991) showed that, for limiting assemblages, the composition of chlorite alone could serve as a monitor of T quite unambiguously.

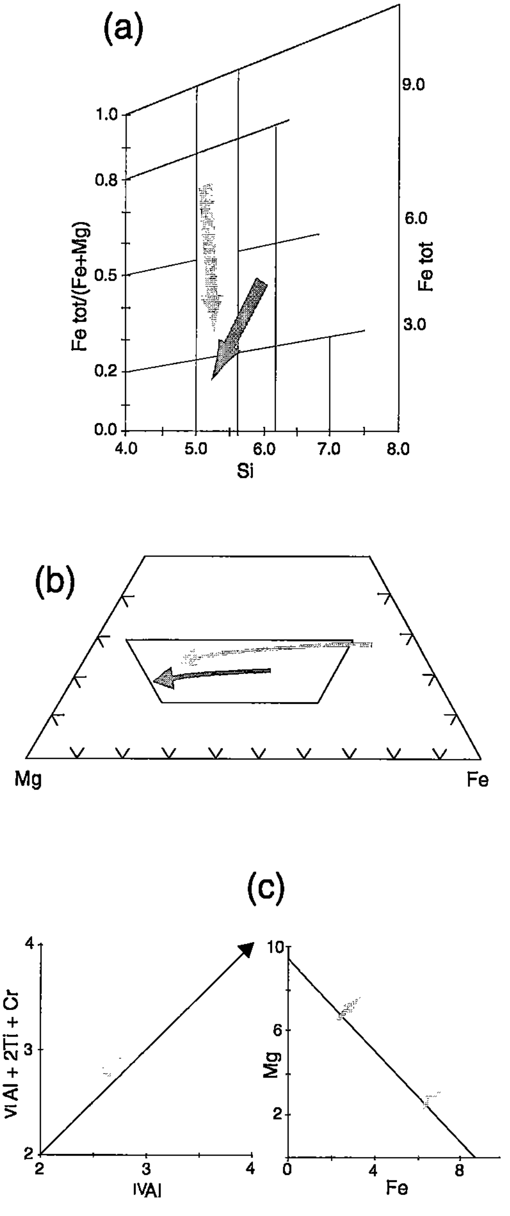


FIG. 11. Trends of compositional variation in chlorite with increasing metamorphic grade (a, b) in metapelites (light grey arrow) and in the metabasic rocks (dark grey arrow) and with increasing pressure in metapelites (c).

The numerous diagrams shown above and the discussion thereof, clearly indicate the manner and extent to which the chemical composition of metamorphic chlorite from non-limiting assemblages is controlled by *(i)* bulk-rock chemistry, *(ii)* T and *(iii)* P. Nonetheless, the effect of rock chemistry is clearly dominant, both with regard to the hand-specimen scale and, as determined by Sassi & Zane (1997) for low metamorphic grades, also at smaller scale, *i.e.*, with regard to the composition of the microsystem within which the given chlorite flake crystallized.

This study clearly demonstrates that for non-limiting assemblages, the effect of bulk-rock composition on chlorite chemistry is so great that it should discourage attempts to establish geothermobarometers based on chlorite composition alone. Any geothermobarometers involving chlorite in non-limiting assemblages should be based on specific cation-exchange reactions with other phases (*e.g.*, Powell & Evans 1983, Dickenson & Hewitt 1986).

## ACKNOWLEDGEMENTS

We thank F.P. Sassi for critically reviewing the manuscript. M. Mellini and G. Pedrazzi are also thanked for assistance in some analytical work, respectively TEM and Mössbauer analyses. A.Z. is greatful to G.M. Molin for his extensive help during the development of her Ph.D. thesis. C. Viti is thanked for her assistance with TEM, and R. Carampin for his assistance with the electron microprobe. Finally, the suggestions of R. Offler and W.E. Trzcienski, Jr., who reviewed this paper, are very much appreciated. Financial support was provided by MURST, CNR and University of Padova.

## REFERENCES

BAILEY, S.W. (1980): Summary of recommendation of AIPEA Nomenclature Committee. *Clays Clay Minerals* **15**, 85-93.

________ (1988): Chlorites: structures and crystal chemistry. *In* Hydrous Phyllosilicates (Exclusive of Micas) (S.W. Bailey, ed.). *Rev. Mineral.* **19**, 347-403.

CATHELINEAU, M. (1988): Cation site occupancy in chlorites and illites as a function of temperature. *Clay Mineral.* **23**, 471-485.

________ & NIEVA, D. (1985): A chlorite solid solution geothermometer. The Los Azufres (Mexico) geothermal system. *Contrib. Mineral. Petrol.* **91**, 235-244.

DE CARITAT, P., HUTCHEON, I. & WALSHE, J.L. (1993): Chlorite geothermometry. A review. *Clays Clay Minerals* **41**, 219-223.

DICKENSON, M.P.& HEWITT, D.A. (1986): A garnet–chlorite geothermometer. *Geol. Soc. Am., Abstr. Programs* **18**, 584.

DYAR, M.D., GUIDOTTI, C.V., HARPER, G.D., MCKIBBEN, M.A. & SACCOCIA, P.J. (1992): Controls on ferric iron in chlorite. *Geol. Soc. Am., Abstr. Programs* **24**, 130.

________, ________, HOLDAWAY, M.J. & COLUCCI, M. (1993): Nonstoichiometric hydrogen contents in common rock-forming hydroxyl silicates. *Geochim. Cosmochim. Acta* **57**, 2913-2918.

ESSENE, E.J & PEACOR, D.R. (1995): Clay mineral thermometry – a critical perspective. *Clays Clay Minerals* **43**, 540-553.

FOSTER, M.D. (1962): Interpretation of the composition and a classification of the chlorites. *U.S. Geol. Surv., Prof. Pap.* **414-A**, 1-33.

GUIDOTTI, C.V. & DYAR, M.D. (1991): Ferric iron in metamorphic biotite and its petrologic and crystallochemical implications. *Am. Mineral.* **76**, 161-175.

________ & SASSI, F.P. (1976): Muscovite as a petrogenetic indicator mineral in pelitic schists. *Neues Jahrb. Mineral., Abh.* **127**, 97-142.

________ & ________ (1998): Petrogenetic significance of Na–K white mica mineralogy: recent advances for metamorphic rocks. *Eur. J. Mineral.* (in press).

________, TEICHMANN, F. & HENRY, D.J. (1991): Chlorite-bearing polymetamorphic metapelites in the Rangeley area, Maine: evidence for equilibrium assemblages. *Am. Mineral.* **76**, 867-879.

________, YATES, M.G., DYAR, M.D. & TAYLOR, M.E. (1994): Petrogenetic implications of the $Fe^{3+}$ content of muscovite in pelitic schists. *Am. Mineral.* **79**, 793-795.

HEY, M.H. (1954): A new review of the chlorites. *Mineral. Mag.* **30**, 277-292.

HUTCHEON, I. (1990): Clay–carbonate reactions in the Venture area, Scotia Shelf, Nova Scotia, Canada. *In* Fluid–Mineral Interactions: a Tribute to H.P. Eugster (R.J. Spencer and I.-Ming Chou, eds.). *Geochem. Soc., Spec. Publ.* **2**, 199-212.

JACOBSON, C.E. (1989): Estimation of $Fe^{3+}$ from electron-microprobe analyses: observations on calcic amphibole and chlorite. *J. Metamorphic Geol.* **7**, 507-513.

JIANG, WEI-TEH, PEACOR, D.R. & BUSECK, P.R. (1994): Chlorite geothermometry? Contamination and apparent octahedral vacancies. *Clays Clay Minerals* **42**, 593-605.

LAIRD, J. (1988): Chlorites: metamorphic petrology. *In* Hydrous Phyllosilicates (Exclusive of Micas) (S.W. Bailey, ed.). *Rev. Mineral.* **19**, 405-453.

NELSON, D.O. & GUGGENHEIM, S. (1993): Inferred limitations to the oxidation of Fe in chlorite: a high-temperature single-crystal X-ray study. *Am. Mineral.* **78**, 1197-1207.

POWELL, R. & EVANS, J.A. (1983): A new geobarometer for the assemblage biotite – muscovite – chlorite – quartz. *J. Metamorphic Geol.* **1**, 331-336.

SASSI, F.P., GUIDOTTI, C.V., BLENCOE, J.G. & SASSI, R. (1994): The paragonite–muscovite solvus: new results. *Per. Mineral.* **63**, 169-178.

SASSI, R. & ZANE, A. (1997): On the compositional variability of metamorphic chlorites as an effect of the micro-site chemistry. *Rend. Fis. Accad. Lincei* **9**, **8**, 77-93.

WALSHE, J.L. (1986): A six-component chlorite solid solution model and the conditions of chlorite formation in hydrothermal and geothermal systems. *Econ. Geol.* **81**, 681-703.

WEISS, Z. (1991): Interpretation of chemical composition and X-ray diffraction patterns of chlorites. *Geologica Carpathica* **42**(2), 93-104.

WIEWIÓRA, A. & WEISS, Z. (1990): Crystallochemical classifications of phyllosilicates based on the unified system of projection of chemical composition. II. The chlorite group. *Clay Mineral.* **25**, 83-92.

ZANE, A. (1995): *Variazioni compositive nelle cloriti di basso grado metamorfico.* Tesi di dottorato, Università di Padova, Padova, Italy.

________ & WEISS, Z. (1998): A procedure for classification of rock-forming chlorites based on microprobe data. *Rend. Fis. Accad. Lincei* **9**, **9**, 51-56.

*Received October 24, 1997, revised manuscript accepted March 29, 1998.*