

# INTERPRETATION OF CHEMICAL COMPOSITION AND X-RAY DIFFRACTION PATTERNS OF CHLORITES

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**Abstract:** All crystallochemical classifications of chlorites published so far use conventional boundaries for contents of individual cations in chlorite structure. This article deals with a way of chlorite chemistry interpretation which is based on the determination of isomorphous series whose theoretical end-members are defined. It is a general approach based on vector representation of chlorite chemistry proposed by Wiewióra and Weiss (1990). This fact allows to transform trioctahedral as well as dioctahedral chlorites into a common basis. In the submitted paper, the principal classification criterion to interpret chlorite chemistry is the composition of octahedral sheets. The paper's second part deals with the effect of chlorite chemistry and polytypism on their X-ray diffraction pattern. Calculated diffraction patterns of chlorites of different chemical compositions have made it possible to derive diagrams which in turn allowed to estimate total contents of heavy atoms (e.g. Fe) in the structure and their distribution between octahedral sheets of 2:1 layers and interlayers. The estimation is based on the intensity of basal diffractions 002, 004 and 001, 003.

**Key words:** chlorites, crystallochemical classification, X-ray diffraction analysis, polytypism.

## Introduction

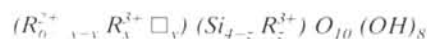
According to a recommendation of the AIPEA Nomenclature Commission (Bailey et al., 1980), chlorites are phyllosilicates whose structure contains 2 : 1 layers (two tetrahedral and one octahedral sheet) mutually separated by interlayer (hydroxide) sheets. The 2 : 1 layer plus interlayer sheet form a 2 : 2 layer whose thickness is approximately equal to 1.4 nm and the above layer is sometimes termed chlorite layer. The interlayer sheet consists of octahedra where the central cations are coordinated by OH-groups. Therefore, the chlorite structures contain two octahedral sheets. Positions of octahedral cations in chlorites being occupied by a wide range of isomorphous-substituting elements such as Fe, Mg, Al, etc. This fact makes any crystallochemical classification of chlorites difficult.

Crystallochemical classifications were proposed by a number of authors, e. g. OrceI et al. (1950), Serdyuchenko (1953), Hey (1954), Brindley and Gillery (1956), Melka (1957), Lapham (1958), Foster (1962) and Fleischer (1971). All these works use arbitrary subdivisions of chlorites and employ numerous special mineralogical names. A new concept of trioctahedral chlorite classification was put forward by Bayliss (1975) who proposed that chlorites should be classified according to their dominant divalent octahedral cations. This concept has also been accepted by the AIPEA

Nomenclature Commission which, at the same time, recommended not to use chemical composition of tetrahedral sheets nor distribution of octahedral cations between the 2 : 1 layer and interlayer for classification purposes (Bailey et al., 1980). The commission recommends to modify the basic names of the end-members of trioctahedral chlorites by adjectives indicating important octahedral cations rather than to form a number of special mineralogical names. The classification of dioctahedral chlorites has not so far been complexly resolved.

## Chemical composition of chlorites

If we assume the general crystallochemical formula of chlorites



then chlorite chemistry may be represented by a vector diagram after Wiewióra and Weiss (1990) which is shown in Fig. 1. General principles of the construction of vector diagrams illustrating phyllosilicate chemistry are described by Wiewióra (1990). A concrete representation of chemical composition (Fig. 1) in the plane  $R^{2+} - R^{3+} - \square - R^{3+(IV)}$  allows to jointly illustrate both trioctahedral and dioctahedral chlorites. In this respect, however, we have to note that the

division of chlorites into dioctahedral and trioctahedral subgroups is more complicated than e.g. that of micas (Wiewióra, 1990) because chlorites contain two octahedral sheets. That is the reason why chlorite division into subgroups has to be appropriately modified.

If we define the composition of the trioctahedral sheet as  $R_{2.5-3.0} \square_{0.5-0.0}$  ( $R$  = sum of octahedral cations) and that of the dioctahedral sheet as  $R_{2.0-2.5} \square_{1.0-0.5}$ , then three chlorite subgroups can be established on the basis of the proportion of occupied and unoccupied positions in their octahedral sheets:

- 1 - tri-trioctahedral chlorites containing  $R_{5.0-6.0} \square_{1.0-0.0}$ ,
- 2 - tri-dioctahedral and di-trioctahedral chlorites containing  $R_{4.5-5.5} \square_{1.5-0.5}$ ,
- 3 - di-dioctahedral chlorites containing  $R_{4.0-5.0} \square_{2.0-1.0}$ .

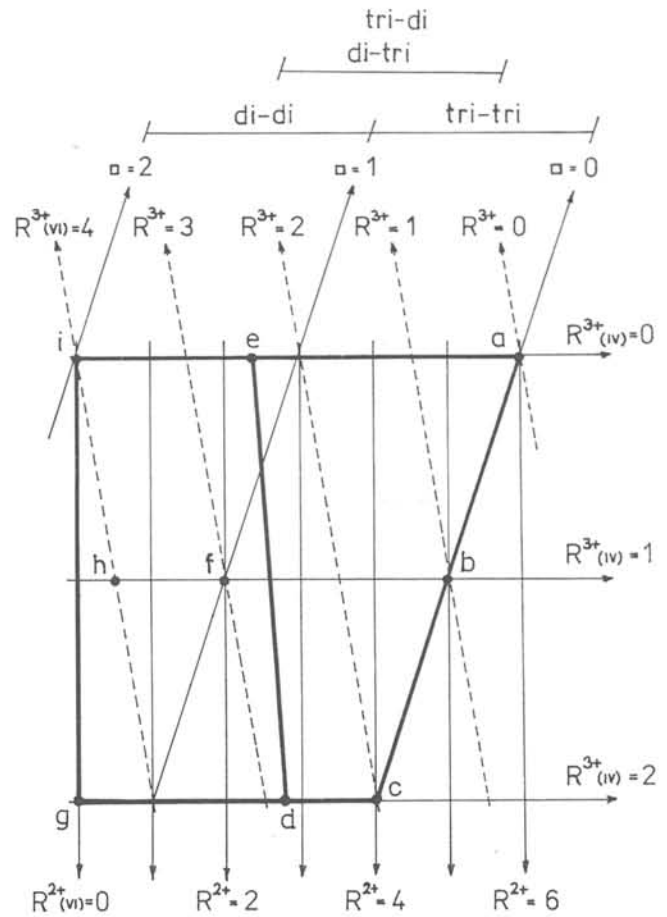
In the above names, the first prefix marks the octahedral sheet of the 2 : 1 layer and the second one the octahedral sheet of the interlayer. Taking into account all these subgroups, overall composition of the octahedral sheets suggests that the intervals in which octahedral positions are occupied by cations overlap each other. If we lack additional information on the distribution of cations within the structure, the chlorite cannot be assigned to the above-mentioned subgroups on the basis of its crystallochemical formula, unless the composition of octahedral sheets is represented by  $R_{5.5-6.0} \square_{0.5-0.0}$  (such chlorites belong to tri-trioctahedral ones) and  $R_{4.0-4.5} \square_{2.0-1.5}$  (these belong to di-dioctahedral chlorites).

The vector representation of chlorite chemistry shown in Fig. 1 makes it possible to illustrate not only chlorites of the three above-mentioned subgroups but also significant end-members as theoretical points so it is no longer necessary to establish arbitrary boundaries for individual chlorite types. Chlorite nomenclature can therefore be focused on the determination of the isomorphous series involving the studied chlorite and/or on the determination of its position within this isomorphous series. Selection of the series as well as identification of the position within this series should be based on dominant octahedral cations. According to the general vector representation in Fig. 1, chlorites can be divided into two large group. The first one comprises chlorites with the dominant divalent cations in octahedra ( $R^{2+} > R^{3+}$ ), which can be illustrated in the field defined by the points (a), (b), (c), (d), and (e) in Fig. 1. The second group involves chlorites with the dominant trivalent cations ( $R^{3+} > R^{2+}$ ) falling into the field defined by the points (e), (d), (i), and (g). Taking into consideration concrete cations, we may define theoretical end-members of isomorphous series in each of the cation representations. An analysis of numerous published chlorite formulae (e.g. Foster, 1962; Bailey and Lister, 1989) has revealed that the end-members can be best derived from the points (b), (f), and (h) in Fig. 1. This fact is consistent with end-members of trioctahedral chlorites established by Bayliss (1975) as well as Wiewióra and Weiss (1990).

End-members of chlorite series illustrated in the cation representation  $Mg-Al^{(VI)}-\square-Al^{(IV)}$  can be defined as follows:

- |                  |   |
|------------------|---|
| clinochlore..... | $(Mg_5Al)(Si_3Al)O_{10}(OH)_8$                    |
| sudoite.....     | $(Al_3Mg_2\square)(Si_3Al)O_{10}(OH)_8$           |
| donbassite.....  | $(Al_4Mg_{0.5}\square_{1.5})(Si_3Al)O_{10}(OH)_8$ |

These are three structurally different chlorites falling into various subgroups, i.e. clinochlore belongs among tri-trio-



**Fig. 1.** General representation of chlorite chemical composition based on the octahedral cations  $R^{2+}$ ,  $R^{3+}$ , tetrahedral cations  $R^{3+(IV)}$  and vacancy in octahedral positions (marked by  $\square$ ).

Field confined by thick line represents theoretically possible chemistry of chlorites. Explanations to isoline descriptions:  $R^{3+(VI)} = 4$  represents four trivalent octahedral cations and  $R^{3+(IV)} = 1$  represents one trivalent tetrahedral cations, etc. Points designated by letters represent the following general chemical composition of chlorites:

- a -  $(R_6^{2+})(R_4^{3+})O_{10}(OH)_8$ ;
- b -  $(R_2^{2+}R_1^{3+})(R_4^{3+}R_1^{3+})O_{10}(OH)_8$ ;
- c -  $(R_4^{2+}R_2^{3+})(R_2^{3+}R_2^{3+})O_{10}(OH)_8$ ;
- d -  $(R_{2.5}^{2+}R_{2.5}^{3+}\square_{0.4})(R_2^{3+}R_2^{3+})O_{10}(OH)_8$ ;
- e -  $(R_2^{2+}R_{2.4}^{3+}\square_{1.2})(R_4^{3+})O_{10}(OH)_8$ ;
- f -  $(R_2^{2+}R_1^{3+}\square_1)(R_3^{3+}R_1^{3+})O_{10}(OH)_8$ ;
- g -  $(R_{1.5}^{2+}\square_{1.3})(R_2^{3+}R_2^{3+})O_{10}(OH)_8$ ;
- h -  $(R_{0.5}^{2+}R_1^{3+}\square_{1.5})(R_3^{3+}R_1^{3+})O_{10}(OH)_8$ ;
- i -  $(R_4^{3+}\square_2)(R_4^{3+})O_{10}(OH)_8$ .

tahedral chlorites, sudoite among di-trioctahedral chlorites, whereas donbassite is assigned into di-dioctahedral chlorites.

The following end-members of chlorite series can be defined relative to the points (b), (f) and (h) in the cation representation  $Fe^{2+}-Al^{(VI)}-\square-Al^{(IV)}$ :

- |                      |  |
|----------------------|--|
| chamosite.....       | $(Fe_5^{2+}Al)(Si_3Al)O_{10}(OH)_8$                    |
| ferrosudoite.....    | $(Al_3Fe_2^{2+}\square)(Si_3Al)O_{10}(OH)_8$           |
| ferrodonbassite..... | $(Al_4Fe_{0.5}^{2+}\square_{1.5})(Si_3Al)O_{10}(OH)_8$ |

In this case, introduction of a special mineralogical name is justified only for the chamosite. The other names have been derived from the end-members defined in the preceding cation representation by the addition of the prefix ferro-.

No special name should be applied in the cation representation  $Mg-Fe^{3+}-\square-Al^{(IV)}$ , and its theoretical end-members can be derived from clinocllore, sudoite as well as donbassite by the prefix ferri-.

Considering two cation representations  $Mg-Al^{(VI)}-\square-Al^{(IV)}$  and  $Fe^{2+}-Al^{(VI)}-\square-Al^{(IV)}$  and a possible isomorphous replacement  $Mg \rightleftharpoons Fe^{2+}$ , we may set up a three-dimensional graph, as is shown in Fig. 2. Similar graph illustrating possible isomorphous replacement  $Al^{(VI)} \rightleftharpoons Fe^{3+}$  is given in Fig. 3. The individual isomorphous series and their proposed end-members are clearly visible in the above figures. Any isomorphous series can be similarly illustrated, however, the determination of the series being a key problem in this crystallochemical chlorite classification. In addition to introduction of further names of end-members is questionable, because of natural occurrences of chlorites of different chemical composition. Bayliss (1975) recommends introduction of new names such as nimate for Ni-dominant chlorite  $(Ni_5Al)(Si_3Al)O_{10}(OH)_8$  which can be illustrated in the cation representation  $Ni-Al^{(VI)}-\square-Al^{(IV)}$  and pennantite for  $Mn^{2+}$ -dominant chlorite whose formula is  $(Mn_5Al)(Si_3Al)O_{10}(OH)_8$ .

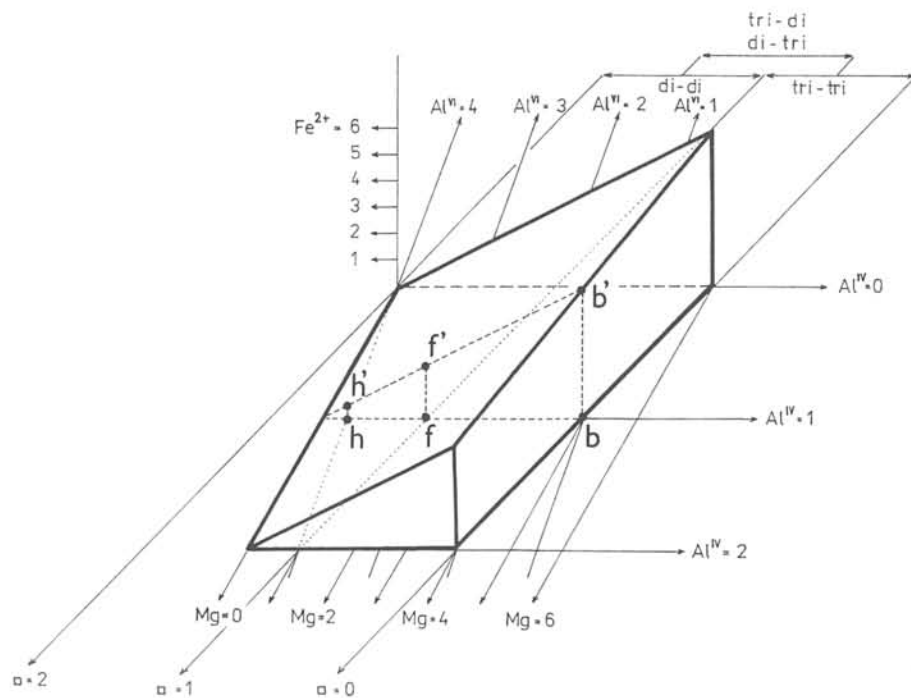
If we know the crystallochemical formula of the investigated chlorite, its name can be specified using the following points:

(a) Determination of the general type of the chlorite

studied according to the sum of divalent ( $R^{2+}$ ) or trivalent ( $R^{3+}$ ) octahedral cations. The first type involves  $R^{3+}$ -dominant chlorites, whereas the second includes  $R^{2+}$ -dominant ones. For the determination of the general type we may make use of the representation shown in Fig. 1, however, in practice it is more convenient to employ a diagram given in Fig. 4. For the sake of better illustration, Fig. 4b shows analyses of 154 chlorites, their crystallochemical formulae being after Foster (1962), as well as analyses of 5 chlorites whose structures were refined by various authors.

(b) Determination of the main isomorphous series. This is based on the previously identified general types of the chlorite concerned. The main isomorphous series can be specified by means of two dominant divalent (first type where  $R^{2+} > R^{3+}$ ) or trivalent (second type where  $R^{3+} > R^{2+}$ ) octahedral cations. The name of the studied chlorite should be determined with regard the end-members of the main isomorphous series. Dominant divalent (first type) or trivalent (second type) cation thus determines the basic name of the chlorite corresponding to the end-member of the main isomorphous series. This basic name can be modified by an adjective indicating the second dominant cation (divalent in the first type, trivalent in the second type). Also in this case, chlorite composition can be graphically illustrated by means of a diagrams, as have been proposed for the main isomorphous series clinocllore-chamosite (of the first type) in Fig. 5.

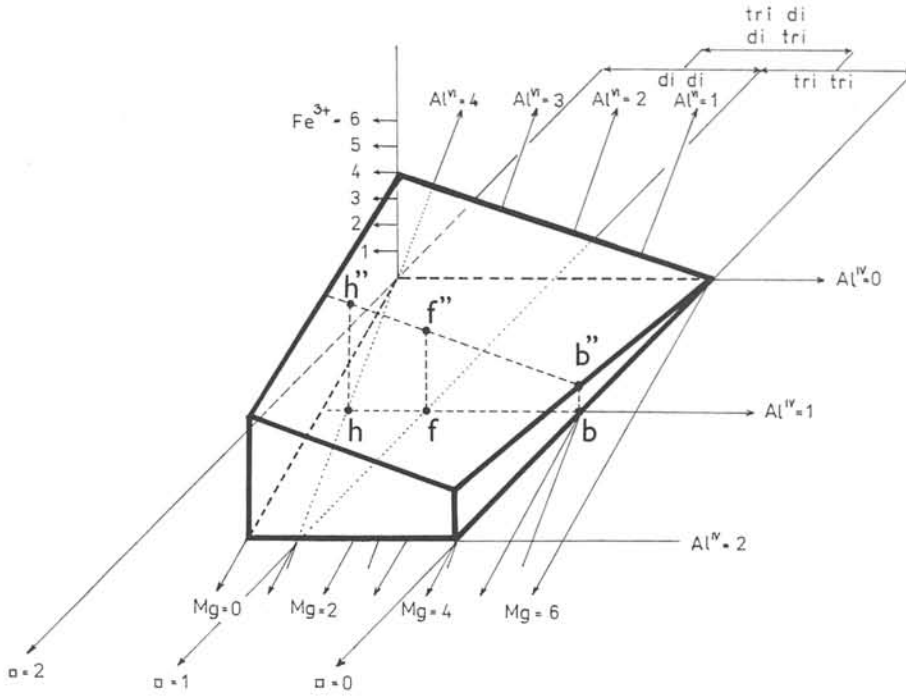
(c) Determination of subordinate isomorphous series. First type chlorites are sometimes affected by significant isomorphous replacement taking place also (or exclusively) among trivalent cations, whereas in the second-type chlorites



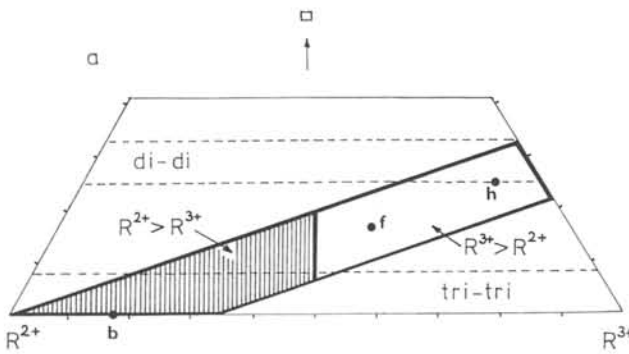
**Fig. 2.** Cation representation  $Mg-Fe^{2+}-Al^{(VI)}-\square-Al^{(IV)}$  of the chlorite chemistry expressing possible isomorphous replacement  $Mg \rightleftharpoons Fe^{2+}$ . Isomorphous series in this representation are marked by letters corresponding to Fig. 1 in the following way:  
 b - b' = isomorphous series whose end-members are represented by clinocllore b and chamosite b';  
 f - f' = isomorphous series whose end-members are represented by sudoite f and ferrosudoite f';  
 h - h' = isomorphous series whose end-members are represented by donbassite h and ferrodonbassite h'.

the replacement takes place among divalent cations. In this case, subordinate isomorphous series can be determined in more detail by means of two important cations (trivalent in the first type and divalent in the second type of chlorites). The subordinate isomorphous series is also marked (if necessary) by an adjective added to the chlorite's basic name reflecting its predominant cation.

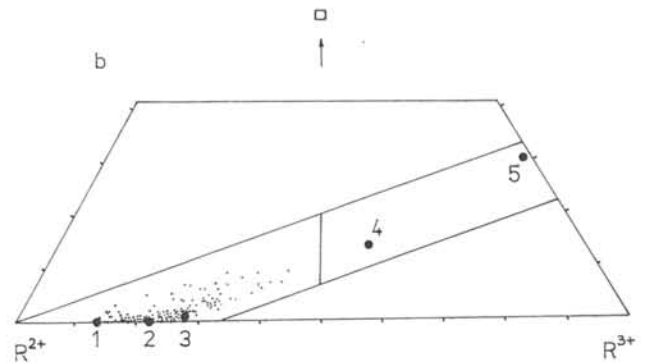
(d) Closer specification of chlorite position in the isomorphous series using a schematic formula. To express chlorite chemistry, a schematic formula of two octahedral sheets composed of three or four identifiers can be used. The first two of them (always present) represent percentage of the two cations defining the main isomorphous series, whereas the third identifier (present only if necessary) reflects



**Fig. 3.** Cation representation  $Mg-Al^{(VI)}-Fe^{3+}-\square-Al^{(IV)}$  of the chlorite chemistry expressing possible isomorphous replacement  $Al^{(VI)} \rightleftharpoons Fe^{3+}$ . Isomorphous series in this representation are marked by letters corresponding to Fig. 1 in the following way:  
 b - b'' = isomorphous series whose end-members are represented by clinocllore b and ferriclinocllore b'';  
 f - f'' = isomorphous series whose end-members are represented by sudoite f and ferrisudoite f'';  
 h - h'' = isomorphous series whose end-members are represented by donbassite h and ferridonbassite h''.



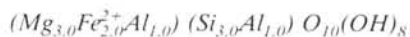
**Fig. 4a.** Part of a triangular diagram illustrating chlorite chemistry relative to contents of divalent ( $R^{2+}$ ), trivalent ( $R^{3+}$ ) octahedral cations and octahedral vacancy  $\square$ . Field confined by thick line was derived from general representation shown in Fig. 1 and so were positions of points b, f, and h marking projections of isomorphous series end-members. Shaded area represents chlorites in which divalent cations prevail over trivalent ones in octahedra. In contrast, unshaded area represents chlorites with dominant trivalent cations.



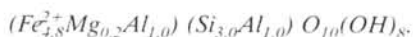
**Fig. 4b.** Part of a triangular diagram from (a) supplemented by chemical compositions of octahedral sheets of 154 chlorites published by Foster (1962), Joswig et al. (1980) (No.1), Rule and Bailey (1987) (No.2), Shirozu and Bailey (1965) (No.3), Alexandrova et al. (1973) (No.4) and Alexandrova et al. (1972) (No.5). Numbered points mark chlorites whose structures were refined by the above authors.

percentage of the dominant cation of the subordinate isomorphous series. The fourth identifier gives percentage of the remaining octahedral cations (including vacancy) and in the following text it will be marked by X.

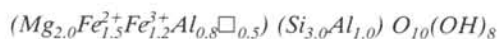
Examples:



First type, main series: clinochlore-chamosite, name: ferrous clinochlore, schematic formula:  $Mg_{50}Fe_{33}^{2+}X_{17}$ .



First type, main series: clinochlore-chamosite, name: chamosite, schematic formula:  $Mg_3Fe_{80}^{2+}X_{17}$ .



First type, main series: clinochlore-chamosite, subordinate series: clinochlore-ferriclinochlore, name: ferrous-ferric clinochlore, schematic formula:  $Mg_{33}Fe_{25}^{2+}Fe_{20}^{3+}X_{22}$ .

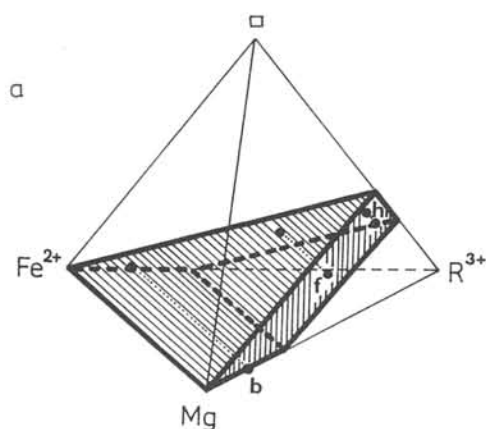


Fig. 5a. Tetrahedron allowing to illustrate chemical composition of chlorite octahedral sheets with regard to  $Mg \rightleftharpoons Fe^{2+}$  substitution. Shaded area was derived from the field confined by thick line in Fig. 1.

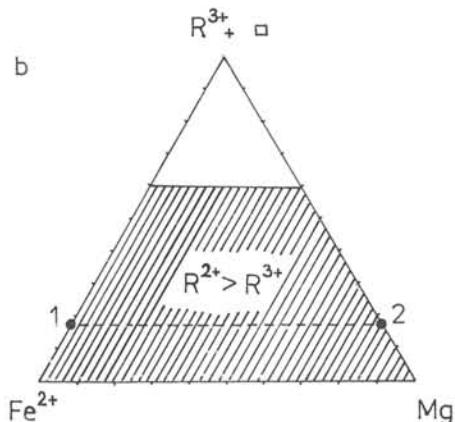


Fig. 5b. A way to illustrate  $Mg \rightleftharpoons Fe^{2+}$  substitution in chlorite octahedral sheets in a triangular diagram. Shaded area marks chlorites of the first type, in the octahedra of which divalent cations prevail over trivalent ones. 1 = clinochlore, 2 = chamosite.

$(Al_{2,0}Fe_{1,0}^{3+}Fe_{1,2}^{2+}Mg_{0,8}\square_{1,0})(Si_{3,0}Al_{1,0})O_{10}(OH)_8$   
 Second type, main series: sudoite-ferrisudoite, subordinate series: sudoite-ferrosudoite, name: ferric-ferrous sudoite, schematic formula:  $Al_{33}Fe_{17}^{3+}Fe_{20}^{2+}X_{30}$ .

Sometimes, the determination of the isomorphous series would be insignificant because of cations capable of isomorphous replacement. This means that chemistry of the studied chlorite equals or is very similar to that of an end-member such as  $(Mg_5Al_1)(Si_3Al_1)O_{10}(OH)_8$ , which is clinochlore that can be schematically expressed  $Mg_{83}Fe_{0}^{2+}X_{17}$ . In some instances, however, contents of an element representing the subordinate isomorphous series, in our case Al, are increased. For example, the following situation may occur:



Such chlorite is clinochlore with an increased proportion of the subordinate cation, i. e. Al. Its name can be derived from the basic one by adding an adjective according to the same principles as those concerning the main and subordinate isomorphous series. In this case the chlorite's name is aluminium clinochlore and its schematized formula can be expressed as  $Mg_{58}Fe_{0}^{2+}Al_{33}X_9$  thus emphasizing the increased Al content.

Specification of the chlorite's position within the isomorphous series is closely related to the question when the basic name must or should be modified by an adjective, i.e. what content of the second dominant cation justifies application of the adjective. The usage of such adjectives may be arbitrary and no strict boundaries must be set up. We recommend, however, the basic name should be formed within the main isomorphous series according to the dominant cation and the adjective should express the second cation if its content exceeds 20 % of the dominant cation. In this respect, some selected examples of real crystallochemical formulae of chlorites belonging to clinochlore-chamosite series are given:

$(Mg_{4,57}Fe_{0,10}^{2+}Fe_{0,30}^{3+}Al_{1,00}\square_{0,03})(Si_{2,80}Al_{1,20})O_{10}(OH)_8$   
 name: clinochlore, schematic formula:  $Mg_{76}Fe_{27}^{2+}X_{22}$

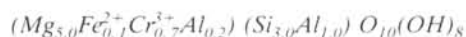
$(Mg_{3,01}Fe_{1,59}^{2+}Fe_{0,14}^{3+}Mn_{0,05}Al_{1,19}\square_{0,02})(Si_{2,69}Al_{1,31})O_{10}(OH)_8$   
 name: ferrous clinochlore, schematic formula:  $Mg_{50}Fe_{27}^{2+}X_{23}$

$(Mg_{2,02}Fe_{2,31}^{2+}Fe_{0,22}^{3+}Al_{1,16}Ti_{0,02}\square_{0,28})(Si_{3,13}Al_{0,87})O_{10}(OH)_8$   
 name: magnesium chamosite, schematic formula:  $Mg_{34}Fe_{39}^{2+}X_{27}$

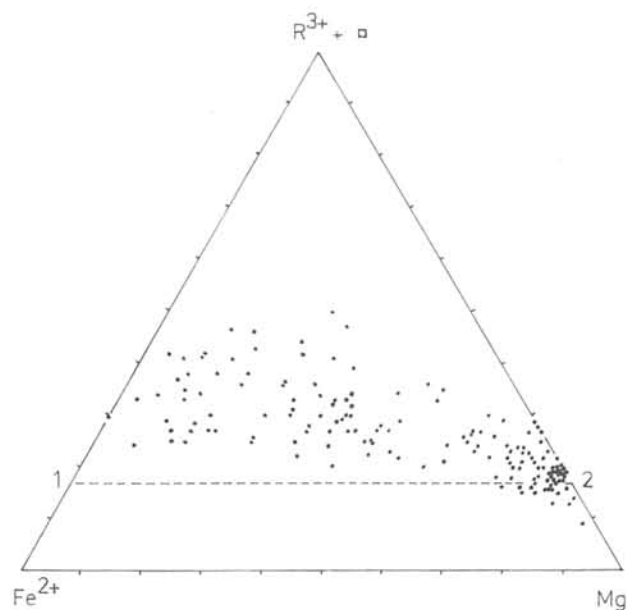
$(Mg_{0,31}Fe_{3,58}^{2+}Fe_{0,80}^{3+}Al_{1,04}Ti_{0,02}\square_{0,19})(Si_{2,51}Al_{1,49})O_{10}(OH)_8$   
 name: chamosite, schematic formula:  $Mg_6Fe_{60}^{2+}X_{34}$ .

As already mentioned, three-dimensional graphs of cation representation, examples of which are given in Figs. 2 and 3, may be successfully applied to derive the main as well as subordinate isomorphous series. Both these graphs show end-members of the illustrated isomorphous series. "Sudoite-type" chlorites in the graphs have not been designated by special names with respect to their ferrous and ferric iron contents, but their names have been derived from sudoite by the prefixes ferro- and ferri-. The same approach has been employed for theoretical "donbassite-type" end-members. Problems frequently arise in designating Cr-bearing chlorites. These were designated by special names, even in cases when

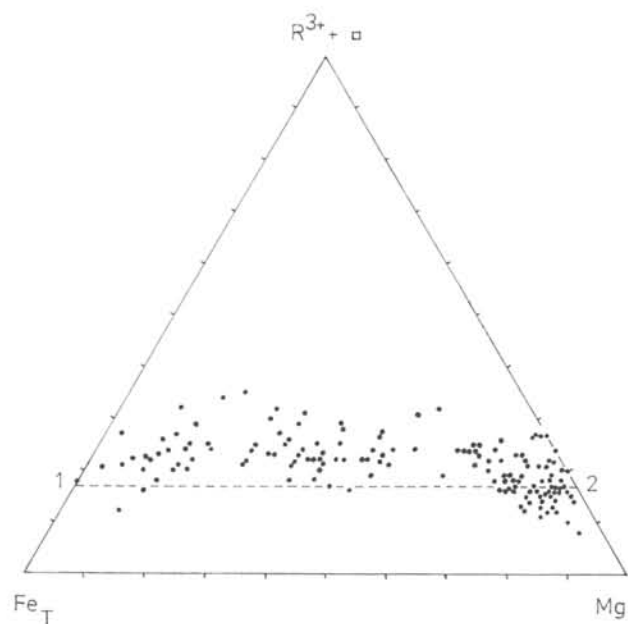
the Cr content in octahedral positions was very low (e.g. Lapham, 1958). This fact contradicts our classification and therefore such cases should not be solved by the application of special names, but better only an adjective should be added to the basic name. This can be illustrated by a chlorite described by Brown and Bailey (1963):



which belongs to the main clinochlore-chamosite series.



**Fig. 6.** Triangular diagram from Fig. 5b supplemented by chemical composition of octahedral sheets of 174 chlorites (154 of those published by Foster, 1962 and 20 by the author of this article). 1 = clinochlore, 2 = chamosite.



**Fig. 7.** Triangular diagram from Fig. 6 supplemented by chemical composition of octahedral sheets of 174 chlorites, the only difference being that  $Fe_T$  includes  $Fe^{2+}$  as well as  $Fe^{3+}$ .

Among subordinate cations, Cr prevails over Al and therefore this chlorite should be termed chromium clinochlore, its schematic formula being  $Mg_{8.3}Fe_{2.7}^{2+}Cr_{1.2}X_3$ . Applying the concept proposed by us, a special name (e.g. kämererite) should be used to denominate "sudoite-type" chlorite whose composition  $(Cr_{3.3}^{3+}Mg_{2.7})_3(Si_3Al)O_{10}(OH)_8$  corresponds to a theoretical end-member. In essence, this problem closely resembles that one which has already been discussed and is related to the assignation of chlorites with  $Fe^{3+}$ -rich octahedra. By the determination of  $Fe^{2+}$  and  $Fe^{3+}$  contents there arises a problem of the  $Fe^{3+}$  origin (the analysis can be influenced by admixtures e.g. those of iron oxides in the whole sample). Furthermore,  $Fe^{2+}$  and  $Fe^{3+}$  contents cannot be distinguished from one another by frequently used up-to-date analytical methods (e.g. microprobe). The analysis of natural chlorites (including 154 results published by Foster, 1962 along with 20 results by the author of this article) falling into the clinochlore-chamosite series indicates that the average  $Fe^{3+}$  content is  $0.30 \pm 0.29$  and that of  $Al^{VI}$  amounts to  $1.14 \pm 0.26$ . In contrast,  $Mg \rightleftharpoons Fe^{2+}$  replacement is very widespread. If the results of the above-mentioned analyses are graphically plotted (Fig. 6 and 7), we can see that in the first case, which deals with  $Fe^{2+}$  and Mg in the role of dominant cations, dispersion of the points is much greater compared to the case when the dominant cations are represented by total Fe and Mg. Understandably, this fact does not justify unequivocal conclusions that ferrous and ferric iron were not correctly distinguished in the chlorite samples, but it is at least a reason to speculate about the problem. Moreover, it is noteworthy that by more than 90 % of the studied samples, chlorite name will not change if we consider total Fe ( $Fe_T$ ) instead of  $Fe^{2+}$  and  $Fe^{3+}$  and at the same time if we respect principles of the proposed classification.

#### X-ray diffraction pattern of chlorites

The most important factors complicating X-ray diffraction identification of natural chlorites include also considerable variability in their chemical composition as well as different stacking of layers, i.e. their polytypism. Distribution of diffraction intensities is influenced by the presence and distribution of "heavy" atoms such as Fe and Cr as well as by the stacking of layers.

An analysis of calculated diffraction patterns corresponding to seventeen different models of tri-trioctahedral chlorites which differ from one to another in the degree of  $Mg \rightleftharpoons Fe$  replacement and in Fe distribution in the octahedral positions M1, M2, M3 within 2 : 1 layers as well as interlayer octahedral positions Mi1, Mi2, Mi3 (Tab. 1) has revealed the following facts concerning changes in the intensity of individual diffraction types:

(a) 001, 201 types of diffractions with even 1 and 131 type of diffractions with odd l.

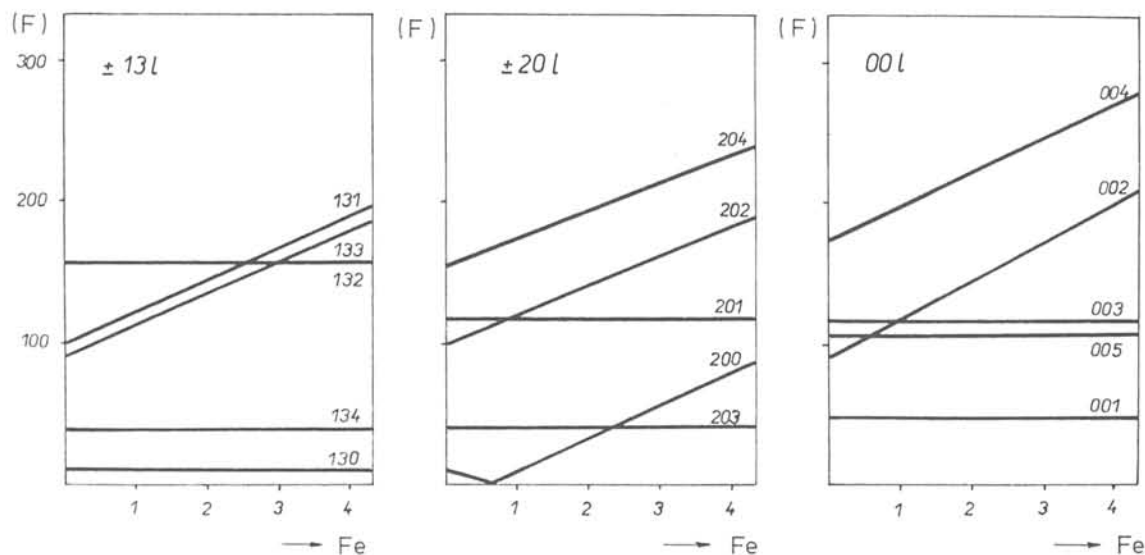
Their intensities change only with increasing total Fe content in the octahedra. No matter how is Fe distributed in the octahedral positions M1, M2, M3 or Mi1, Mi2, Mi3. For example, if there are two chlorites with equal total Fe contents in their octahedral sheets, the above diffraction intensities are also equal regardless of the fact that Fe occupies octahedra in the 2 : 1 layer or interlayer, i.e. scattering power of octahedral cations is  $f(M) < f(Mi)$  or  $f(M) > f(Mi)$ , respectively.

**Table 1.** Octahedral composition of models of trioctahedral chlorites  $(Mg, Fe, Al)_6 (Si_{2.6}Al_{1.4}) O_{10}(OH)_8$  and corresponding calculated absolute intensities of basal diffractions I (00l) for powder diffraction. The intensities are given in electron units multiplied by 100, without correction for absorption.

Model	Octahedral sheet in 2 : 1 layer (M)	Octahedral sheet in interlayer (Mi)	Octahedral sheets	Absolute powder intensities					I <sub>1</sub> <sup>1)</sup>	I <sub>2</sub> <sup>2)</sup>
				001	002	003	004	005		
CH-1	Mg <sub>2.3</sub> Al <sub>0.7</sub>	Mg <sub>2.3</sub> Al <sub>0.7</sub>	Mg <sub>4.6</sub> Al <sub>1.4</sub>	606	539	420	491	114	1.10	1.44
CH-2	Mg <sub>2.0</sub> Fe <sub>0.3</sub> Al <sub>0.7</sub>	Mg <sub>2.0</sub> Fe <sub>0.3</sub> Al <sub>0.7</sub>	Mg <sub>4.0</sub> Fe <sub>0.6</sub> Al <sub>1.4</sub>	605	753	419	580	114	1.30	1.44
CH-3	Mg <sub>2.0</sub> Fe <sub>0.3</sub> Al <sub>0.7</sub>	Mg <sub>1.0</sub> Fe <sub>0.7</sub> Al <sub>0.7</sub>	Mg <sub>3.6</sub> Fe <sub>1.0</sub> Al <sub>1.4</sub>	298	919	519	643	89	1.43	0.57
CH-4	Mg <sub>1.6</sub> Fe <sub>0.7</sub> Al <sub>0.7</sub>	Mg <sub>2.0</sub> Fe <sub>0.3</sub> Al <sub>0.7</sub>	Mg <sub>3.6</sub> Fe <sub>1.0</sub> Al <sub>1.4</sub>	996	898	324	628	137	1.11	3.07
CH-5	Mg <sub>1.3</sub> Fe <sub>1.0</sub> Al <sub>0.7</sub>	Mg <sub>1.3</sub> Fe <sub>1.0</sub> Al <sub>0.7</sub>	Mg <sub>2.6</sub> Fe <sub>2.0</sub> Al <sub>1.4</sub>	591	1369	410	797	111	1.72	1.44
CH-6	Mg <sub>2.3</sub> Al <sub>0.7</sub>	Mg <sub>0.3</sub> Fe <sub>2.0</sub> Al <sub>0.7</sub>	Mg <sub>2.6</sub> Fe <sub>2.0</sub> Al <sub>1.4</sub>	21	1369	857	797	34	1.72	0.02
CH-7	Mg <sub>0.3</sub> Fe <sub>2.0</sub> Al <sub>0.7</sub>	Mg <sub>2.3</sub> Al <sub>0.7</sub>	Mg <sub>2.6</sub> Fe <sub>2.0</sub> Al <sub>1.4</sub>	2836	1369	126	797	232	1.72	22.51
CH-8	Mg <sub>1.8</sub> Fe <sub>0.5</sub> Al <sub>0.7</sub>	Mg <sub>0.8</sub> Fe <sub>1.5</sub> Al <sub>0.7</sub>	Mg <sub>2.6</sub> Fe <sub>2.0</sub> Al <sub>1.4</sub>	99	1404	627	817	68	1.72	0.16
CH-9	Mg <sub>0.8</sub> Fe <sub>1.5</sub> Al <sub>0.7</sub>	Mg <sub>1.8</sub> Fe <sub>0.5</sub> Al <sub>0.7</sub>	Mg <sub>2.6</sub> Fe <sub>2.0</sub> Al <sub>1.4</sub>	1502	1371	248	797	166	1.72	6.06
CH-10	Fe <sub>3.0</sub>	Mg <sub>2.3</sub> Al <sub>0.7</sub>	Mg <sub>2.3</sub> Fe <sub>3.0</sub> Al <sub>0.7</sub>	4490	1910	48	980	307	1.95	93.50
CH-11	Mg <sub>2.3</sub> Al <sub>0.7</sub>	Fe <sub>3.0</sub>	Mg <sub>2.3</sub> Fe <sub>3.0</sub> Al <sub>0.7</sub>	346	1960	1155	1003	13	1.95	0.30
CH-12	Mg <sub>1.8</sub> Fe <sub>0.5</sub> Al <sub>0.7</sub>	Mg <sub>0.3</sub> Fe <sub>2.5</sub> Al <sub>0.2</sub>	Mg <sub>2.1</sub> Fe <sub>3.0</sub> Al <sub>0.9</sub>	17	1964	868	1006	36	1.95	0.02
CH-13	Mg <sub>0.5</sub> Fe <sub>1.8</sub> Al <sub>0.7</sub>	Mg <sub>0.5</sub> Fe <sub>1.8</sub> Al <sub>0.7</sub>	Mg <sub>1.0</sub> Fe <sub>3.6</sub> Al <sub>1.4</sub>	579	2345	402	1107	109	2.12	1.44
CH-14	Mg <sub>0.5</sub> Fe <sub>2.0</sub> Al <sub>0.5</sub>	Mg <sub>0.8</sub> Fe <sub>1.4</sub> Al <sub>0.8</sub>	Mg <sub>1.4</sub> Fe <sub>3.4</sub> Al <sub>1.3</sub>	1047	2173	302	1052	139	2.07	3.47
CH-15	M1 = Fe <sub>1.0</sub> M2+M3=Mg <sub>1.3</sub> Al <sub>0.7</sub>	Mi1 = M1 Mi2 = M2 Mi3 = M3	Mg <sub>2.6</sub> Fe <sub>2.0</sub> Al <sub>1.4</sub>	590	1370	410	797	111	1.72	1.44
CH-16	M = Mg <sub>2.3</sub> Al <sub>0.7</sub> M2 = M3 = M1	Mi1 = Fe <sub>1.0</sub> Mi' = Mg <sub>1.3</sub> Al <sub>0.7</sub> Mi3 + Mi2 = Mi'	Mg <sub>3.6</sub> Fe <sub>1.0</sub> Al <sub>1.4</sub>	97	898	613	628	67	1.43	0.16
CH-17	M1 = Fe <sub>1.0</sub> M' = Mg <sub>1.3</sub> Al <sub>0.7</sub> M3 + M2 = M'	Mi = Mg <sub>2.3</sub> Al <sub>0.7</sub> Mi1 = Mi2 = Mi3	Mg <sub>3.6</sub> Fe <sub>1.0</sub> Al <sub>1.4</sub>	1540	921	254	643	170	1.43	6.06

<sup>1)</sup> I<sub>1</sub> = I (002)/I (004), where I (002) and I (004) are intensities of 002 and 004 diffractions, respectively.

<sup>2)</sup> I<sub>2</sub> = I (001)/I (003).



**Fig. 8.** Changes of (F) (structure factor) as a function of total iron (atoms) content in the octahedra of homioctahedral chlorites for selected 00l, 20l and 13l diffractions. The indexing refers to the 1M unit cell.

Changes in the intensity of these diffractions relative to total Fe contents in the structure of homioctahedral chlorites (all positions in their octahedral sheets are occupied by the same cations) are shown in Fig. 8 for  $f(M) = f(Mi)$ .

(b) 00l, 20l types of diffractions with odd l and 13 l type of diffractions with even l.

The intensity of such diffractions changes only if Fe is unequally distributed between M and Mi positions, e.i. if

$f(M) \neq f(Mi)$ . On the contrary, if  $f(M) = f(Mi)$ , as is shown in Fig. 8, the intensity of these diffractions is not influenced by total Fe content in the structure. Similarly, the intensities are independent from Fe distribution between the individual octahedral positions M1, M2, M3 or Mi1, Mi2, Mi3 within each octahedral sheet, but depend only on differences in scattering power of all atoms in the 2 : 1 layer octahedral sheet and all atoms in the interlayer octahedral sheet.

(c) 021 type of diffractions.

The intensity of such diffractions is only depend on Fe distribution between the individual octahedral positions M1,

M2, M3 in the 2 : 1 layer and Mi1, Mi2, Mi3 in the interlayer octahedral sheet. If the chlorite structure is homooctahedral, the intensity of these diffractions is independent from total Fe content in the structure and is also independent from Fe distribution between M and Mi.

The problem how to estimate the total content of heavy atoms (predominantly Fe) in the structure of tri-trioctahedral chlorites on the basis of their X-ray diffraction patterns was solved largely by the study of intensity changes in selected basal diffractions (e.g. Brown, 1955; Petruk, 1964; Oinuma et al., 1973 and Bailey, 1972). The submitted work deals with

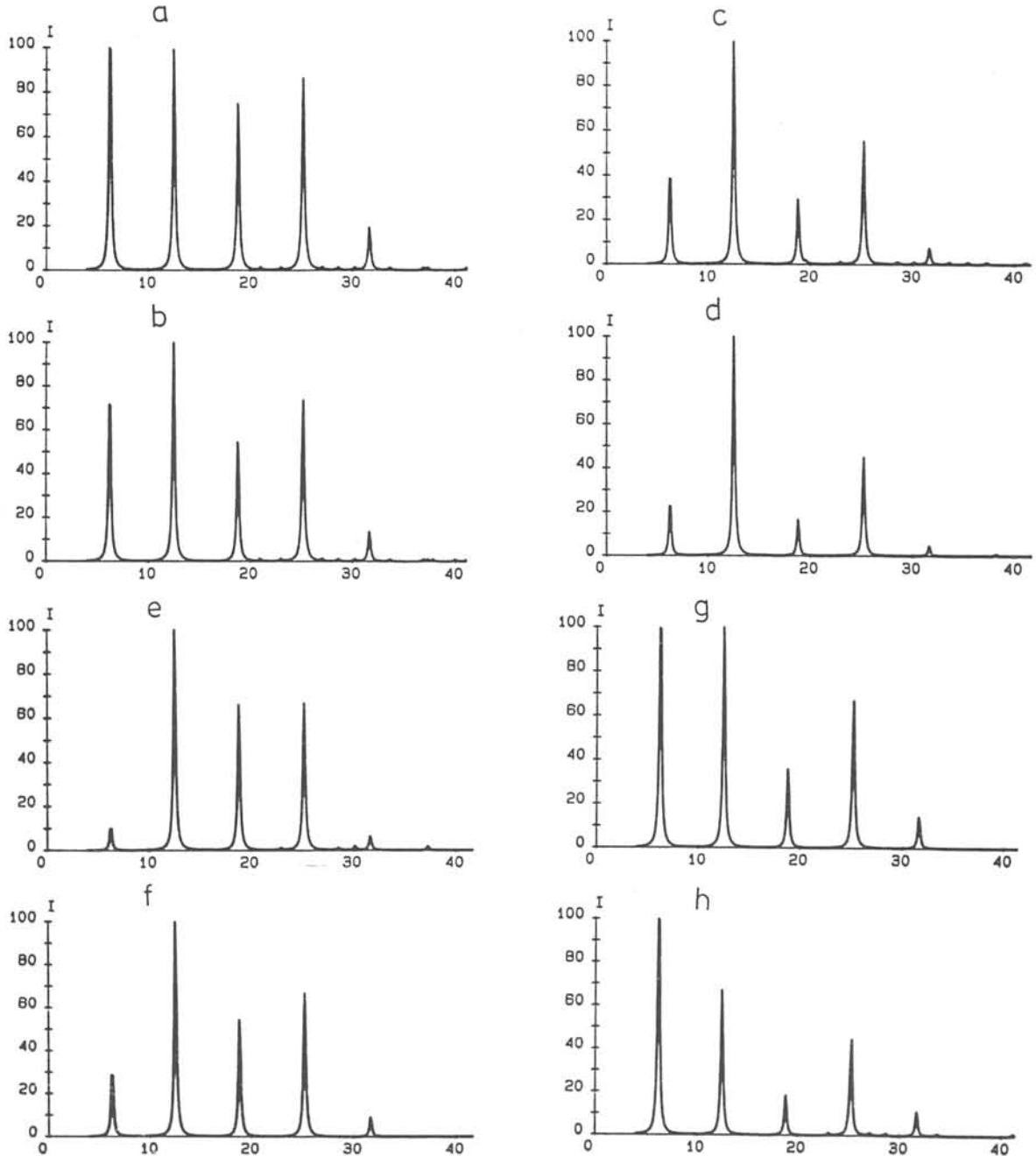


Fig. 9. Calculated powder diffraction patterns ( $\text{CuK}\alpha$  radiation) containing only basal diffractions 001 to 005 corresponding to different octahedral composition models of chlorites belonging to clinocllore-chamosite series given in Tab. 1: a) CH-1; b) CH-2; c) CH-15; d) CH-13; e) CH-16; f) CH-3; g) CH-4; h) CH-17.

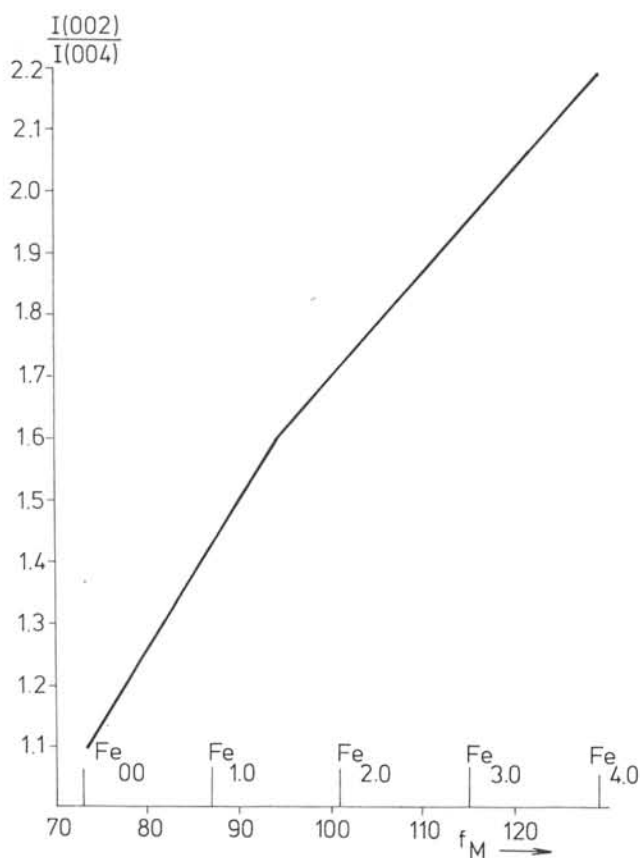


this problem from the point of view of calculated powder diffraction patterns corresponding to individual models of chlorite chemistry given in Tab. 1. To calculate the patterns, we have used the DIFK program (Weiss and Krajiček, 1979). The atomic coordinates serving as input data are taken from Joswig et al. (1980) and occupations of individual atomic positions were derived from crystallochemical formulae of chlorite models given in Tab. 1. The fact that the intensity of basal diffractions varies substantially with chlorite chemistry is illustrated in Fig. 9. Shown parts of diffraction powder patterns contain only basal diffractions and correspond to highly-oriented samples which are analysed by diffractometer with the standard arrangement. In such cases, intensity changes in basal diffractions 00l are due to:

\* change in total Fe content in the structure which is responsible for variations in the intensity of 00l diffractions with even l.

\* change in Fe distribution between M and Mi which in turn causes variations in the intensity of 00l diffractions with odd l.

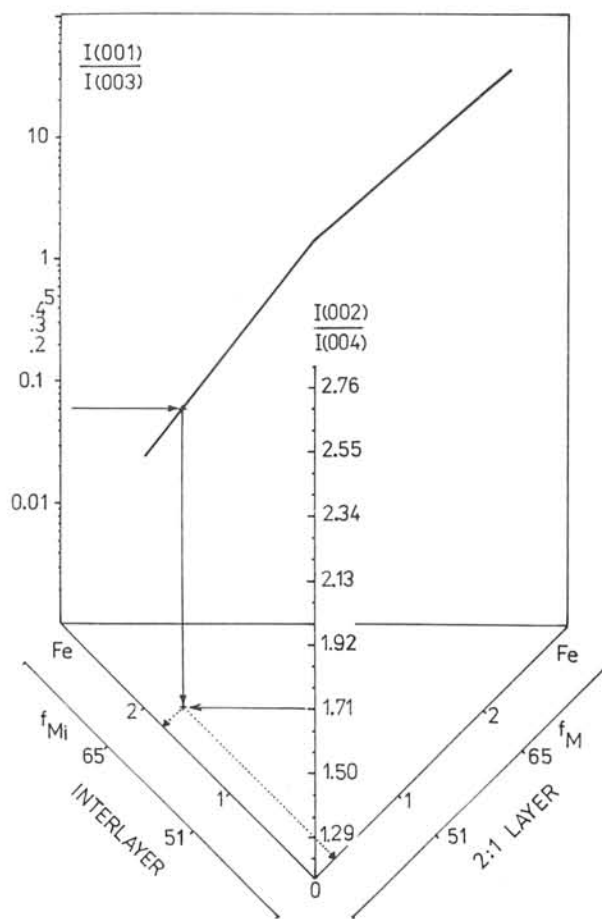
The above calculations have enabled us to work out a technique for the estimation of total Fe content in the octahedral sheets based on changes in 002/004 intensity ratio. Using the above ratio of the intensities of selected basal diffractions and graph given in Fig. 10 we can estimate the



**Fig. 10.** Ratio of powder intensities  $I(002)/I(004)$  plotted against the total number of iron atoms in octahedral positions; the alternate scale on the horizontal axis shows the scattering power  $f(M)$  of octahedral cations (unionized atoms are assumed). The intensities are derived from calculated powder diffraction patterns for different octahedral compositions of chlorites belonging to clinocllore-chamosite series given in Tab. 1.

total scattering power of all octahedral cations in the chlorite structure (it is expressed as  $f(M)$  and equals to  $f(M) + f(M_i)$ ). Considering another ratio of intensity of diffractions, i.e. 001/003 ratio, we may then estimate the possible asymmetry between scattering power of atoms in octahedra of the 2 : 1 layer ( $f(M)$ ) and the interlayer ( $f(M_i)$ ). A combination of these relationships has resulted in a diagram which allows, on the basis of the above-mentioned intensity ratios, to estimate total content of heavy atoms (e.g. Fe in our case) in the studied chlorite as well as their distribution between M and  $M_i$  (Fig. 11). It is our duty to notify possible users of these graphs that they can be applied exclusively to tri-octahedral chlorites.

We have so far dealt with basal diffractions intensity distribution. Such distribution is unaffected by different stacking sequence of layer in chlorite structure, i.e. polytypism. Different kinds of stacking sequence of layers, however, cause considerable changes in the intensity distribution of non-basal diffractions which can be observed on powder diffraction patterns, particularly 20l, 13l, 02l and 11l diffractions. With regard to the complexity of the problems



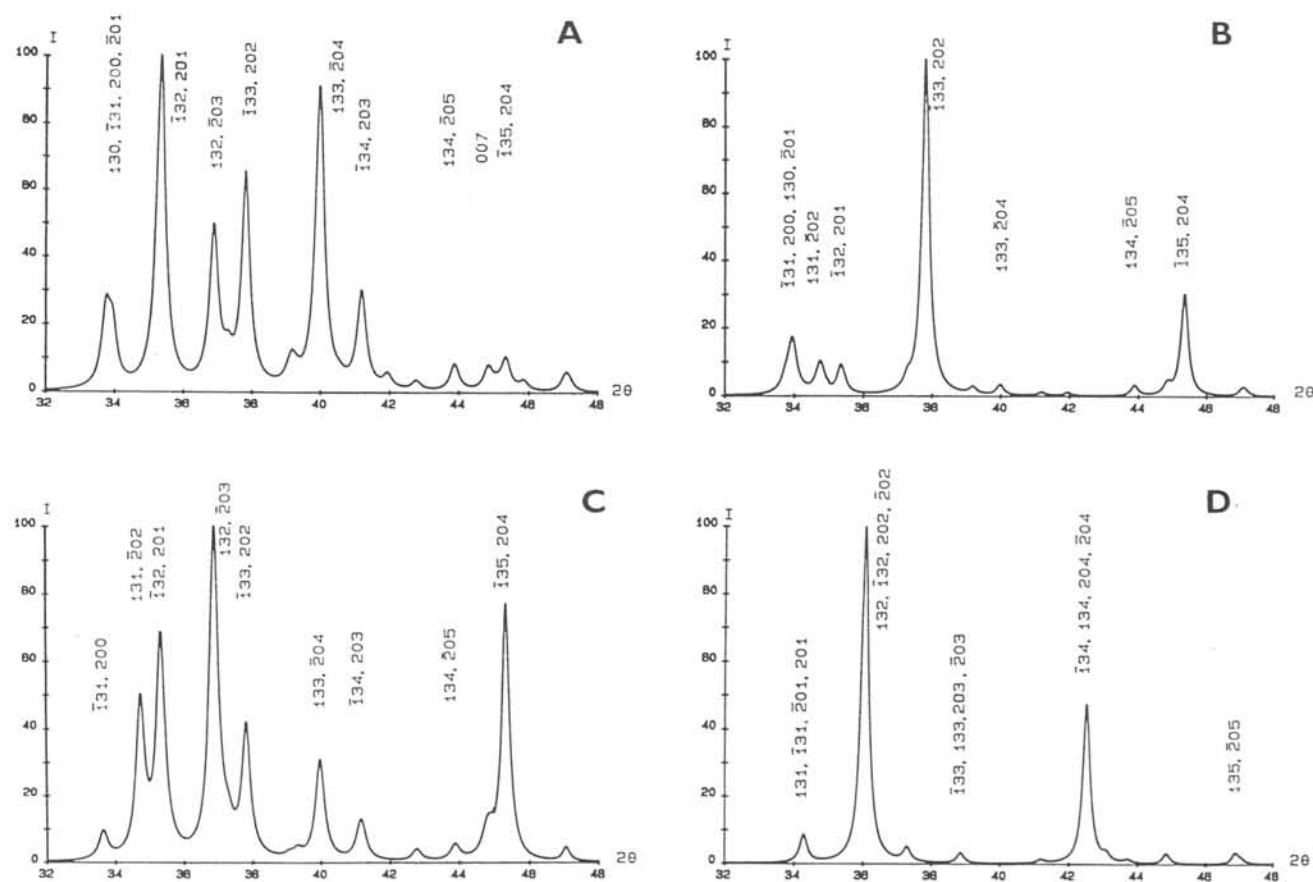
**Fig. 11.** Diagram for the estimation of the iron content and/or scattering power of octahedral cations  $f(M)$  (in the 2 : 1 layer),  $f(M_i)$  (in the interlayer) and their distribution in the respective octahedral sheets from intensity ratios  $I(001)/I(003)$  and  $I(002)/I(004)$ . The ratios are based on calculated diffraction patterns for different octahedral composition of chlorites belonging to clinocllore-chamosite series (Tab. 1).

concerning chlorite polytypism we are not going to describe all details related to it. We just mention some basic informations which can be useful for a mineralogist analysing chlorites by powder diffraction. For a more complex study, some special publications given by Đurovič et al. (1983), Weiss and Đurovič (1983) and Bailey (1988) are recommended.

According to classification of the MDO (maximum degree of order) polytypes of chlorites, i.e. those which are most widespread in the nature, a concrete polytype can be identified, if we know its 20l (13l) and 02l diffractions intensity distribution. Diffractions of the first type (20l, 13l) are sharp and characteristic for all polytypes belonging to a given subgroup of polytypes, the so called subfamily. Among chlorite polytypes there are four different subfamilies designated A, B, C and D. Diffractions of the second type (02l) are usually weaker and, if there is some randomness in stacking of layers, may be diffuse or even assume the form of continuous streaks. These diffractions are characteristic for all polytypes belonging to another group which is termed MDO group (designated I, II, III, etc.). Among homooctahedral chlorite polytypes there are eight different MDO groups. Thanks to this, the individual MDO polytype may be identified if the subfamily and MDO group are determined, i.e. if we are able to recognize the intensity distributions of 20l (13l) and 02l diffractions.

As mentioned above, diffractions of the second type are usually diffuse and therefore the identification of MDO groups is very problematic. On the contrary, the identification of subfamilies is realistic if powder methods are used. To identify a subfamily by means of powder diffraction, it is advisable to employ the diagnostic part of the pattern between  $32$  and  $46^\circ 2\theta$  ( $\text{CuK}\alpha$ ) which contains mutually overlapping 20l and 13l diffractions. Fig. 12 shows calculated diagnostic parts of powder patterns corresponding to subfamilies A, B, C, and D of clinocllore. The variability in chlorite chemistry is also reflected in polytype identification and therefore there take place changes in intensity distribution of diffractions which serve us to identify the subfamily. For the sake of comparison, Fig. 13 shows the diagnostic parts of powder patterns corresponding to subfamilies of magnesium chamosite. Groups of chlorite polytypes similar to subfamilies were described by Brown and Bailey (1962) who designated them IIa (subfamily A), Ia (subfamily B), IIb (subfamily C) and Ib (subfamily D). In literature, however, there occur frequent faults because some authors write e.g. of IIb polytype of clinocllore. In fact, it is not a polytype but whole group of possible polytypes.

Finally, it is appropriate to mention some relationships concerning natural occurrences of various subfamilies of chlorite polytypes. The investigated set totalled 375 chlorite samples (316 of which were identified by Brown and Bailey,



**Fig. 12.** Diagnostic section of calculated powder diffraction patterns of MDO polytypes of homooctahedral clinocllore suitable for identification of A, B, C, and D subfamilies.

The indexing refers to the 1M unit cell. Idealized symmetry of chlorite structures are assumed in calculation. Conditions: diffractometer,  $\text{CuK}\alpha$  radiation, sample with random orientation of particles, intensities are normalized to the strongest diffraction in the diagnostic section.

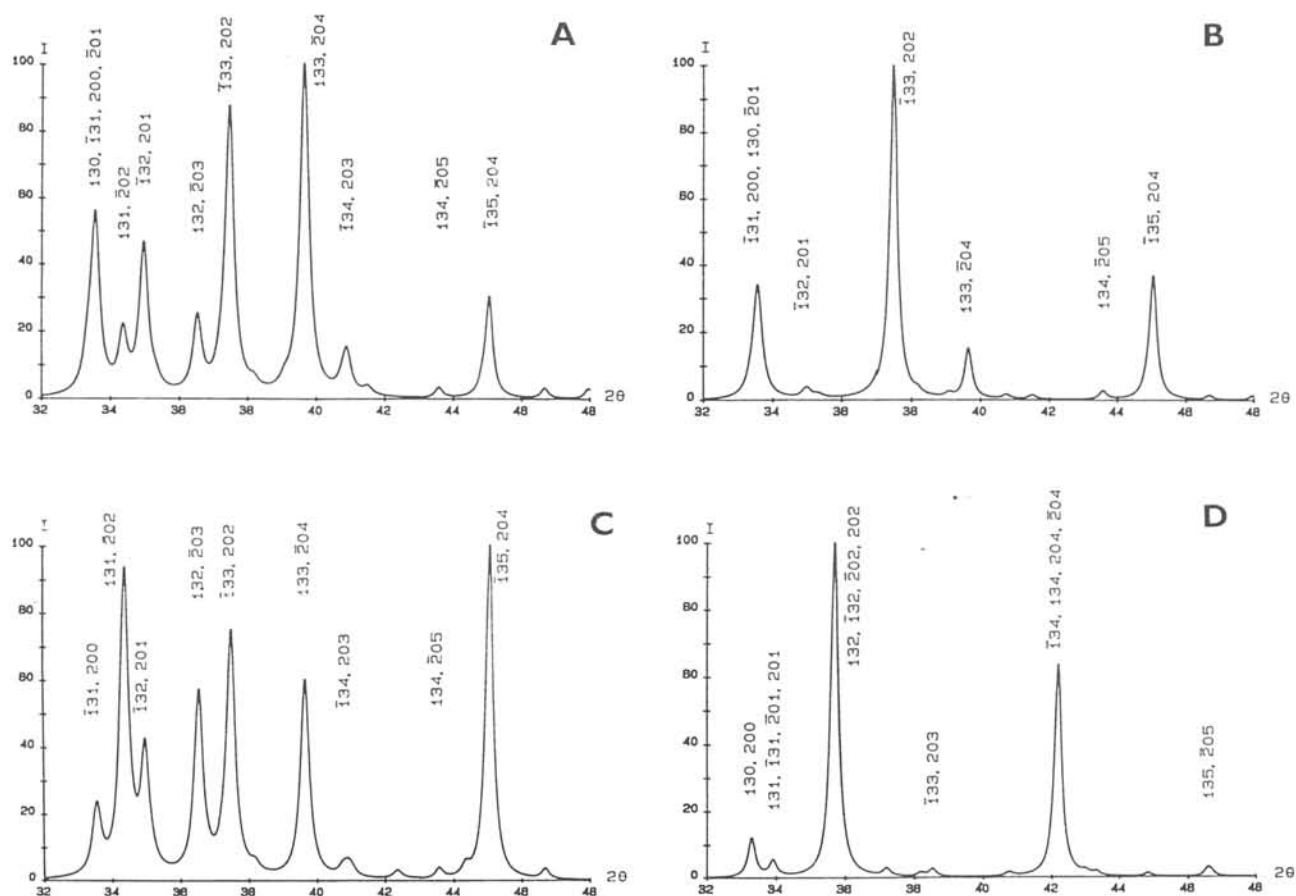


Fig. 13. Diagnostic section of calculated powder diffraction patterns of MDO polytypes of homoctahedral magnesium chamosite ( $\text{Mg}_{15}\text{Fe}_{62}^{2+}\text{X}_{23}$ ) suitable for identification of A, B, C, and D subfamilies. The indexing refers to the 1M unit cell. Conditions of calculations are specified in Fig. 12.

1962: 39 by Hayes, 1970; and 20 by the author). Of this number, 93 % samples could have been assigned into one of the subfamilies derived on the basis of MDO polytypes (Đurovič et al., 1983). Of these 349 chlorite samples, 78 % belong to the subfamily C, 17 % to the subfamily D and 5 % to the subfamily B. The subfamily A was not identified.

Translated by L. Böhmer

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