Canadian Mineralogist
Vol. 16, pp. 365-373 (1978)

DI/TRIOCTAHEDRAL CHLORITE IN QUARTZ VEINS FROM THE ARDENNE, BELGIUM

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ABSTRACT

Chlorite flakes, particularly pure and very close to $(Al_3Mg_2)(Si_3Al)O_{10}(OH)_8$, occur in quartz veins crosscutting slates of low-grade metamorphism at the southeastern border of the Cambro-Tremadocian Stavelot Massif (Belgian Ardenne). It is a di/trioctahedral chlorite II*b* polytype; the cell parameters calculated from the diffractogram are: *a* 5.238, *b* 9.080, *c* 14.284 Å, β = 97°21′, *d* 001=14.16, *d* 060=1.513 Å. The optical data are: α 1.583, β 1.589, γ 1.601, (+) $2V_{obs}$ = 70°. The infrared spectra and DTA curves are rather typical of dioctahedral chlorites.

SOMMAIRE

Une chlorite en paillettes particulièrement pure et de composition chimique très proche de $(Al_3Mg_2)(Si_3Al)O_{10}(OH)_8$, s'observe dans les filons de quartz recoupant les phyllades légèrement métamorphiques du massif Cambro-trémadocien de Stavelot (Ardenne belge). Il s'agit d'une chlorite di/trioctaédrique, polytype II*b* dont le diffractogramme de poudre conduit aux paramètres de maille suivants: *a* 5.238, *b* 9.080, *c* 14.284 Å, β = 97°21′, *d* 001 = 14.16, *d* 060 = 1.513 Å. Les caractères optiques sont: α 1.583, β 1.589, γ 1.601, (+) $2V_{obs}$ = 70°. Le spectre infrarouge et la courbe ATD sont typiques de chlorites dioctaédriques.

INTRODUCTION

Recent systematic investigations of the contents of quartz veins of the Belgian Ardenne, mainly outcropping in the low-grade metamorphic zone of the southeastern border of the Stavelot Massif, have led to the discovery of phyllosilicates: pyrophyllite, Mg-rich chlorites, dickite and micas (Mélon *et al.* 1976). The remarkable abundance of di/trioctahedral chlorite, a new mineral species in Belgium, and the purity of its well-crystallized flakes in Ottré and Regné have encouraged a complete mineralogical investigation.

PREVIOUS OCCURENCES

Since Sudo and his collaborators found regular mixed-layer Al-rich chlorite-montmorillonite and inferred the existence of dioctahedral chlorite (Hayashi & Oinuma 1964), many occurrences of this mineral species have been reported from various parts of the world and from various types of deposit. For instance, dioctahedral chlorite has been found in hematite ores from the Tracy mine, Michigan (Bailey & Tyler 1960), in bauxites from Saint-Paul-de Fenouillet, East Pyrénées (Caillère *et al.* 1962), in pyrophyllite mines from Kamikita (Hayashi & Oinuma 1964, Itaya (Henmi & Yamamoto 1965) and Shinyo, Japan (Fujii *et al.* 1971), in soils from Alberni, B.C. (Brydon *et al.* 1961), in sediments from Plochingen, Württemberg (von Engelhardt *et al.* 1962), Colorado (Schultz 1963) and Cornberg, Hesse (Müller 1967), in hydrothermally altered tuffs of Permian age from Triberg (Müller 1961), in hydrothermally weathered arkose from Kaiserbachtal (Frenzel & Schembra 1965), in argillaceous altered rhyolitic rocks from Furutôbe, Japan (Tsukahara 1964), in hydrothermally altered spodumene and lepidolite from the Namivu pegmatite, Mozambique (Figueiredo Gomes 1967) and in a Sn-bearing quartz vein from Atondo, Zaïre (van Oosterwyck-Gastuche & Delien 1968).

Mineralogical properties in most reports are generally incomplete because the dioctahedral chlorite is fine-grained and mixed with other minerals. Various impurities are detected by X-ray diffraction and chemical analyses. Thermal properties are reported for impure material. Structural data have been published for a well-crystallized specimen from the Tracy mine (Eggleston & Bailey 1967), but Aleksandrova *et al.* (1973) have considered the coarse-grained dioctahedral chlorite described in Russia as a more valid specimen for a structural refinement. Drits & Lazarenko (1967) investigated such an Al-rich chlorite but did not publish a powder pattern.

CLASSIFICATION AND NOMENCLATURE

These minerals are commonly called dioctahedral chlorites in order to emphasize their higher Al content compared to trioctahedral chlorites. On the basis of the general formula $(Al, Fe^{3+})_{4-y}(Mg, Fe^{2+})_{\frac{x}{2}+\frac{3y}{2}}(Si_{4-x}Al_x)O_{10}(OH)_8$ proposed by Müller (1963), Sudo & Sato (1966) considered that the dioctahedral chlorite group is characterized by $4 \leqslant n \leqslant 5$ (n is the number of octahedral cations) and $0 \leqslant x + y \leqslant 2$. The trioctahedral chlorites have $5 < n \leqslant 6$ and $2 < x + y \leqslant 4$. Moreover, these authors distinguish in the first group (1) chlorites with a layer and an interlayer of dioctahedral nature, and (2) chlorites in which one of these layers is trioctahedral and the other dioctahedral. They suggest di/dioctahedral and di/tri-(or tri/di-) octahedral terms mainly characterized by n near 4 and $x + y$ near 0 and by n near 5 and $x + y$ near 2, respectively. Eggleston & Bailey (1967) added a third category to include imperfectly crystallized specimens similar to (1) or (2) but with incomplete and swelling interlayers.

The nomenclature of the dioctahedral chlorite subgroup is fraught with confusion and ambiguity. The pure dioctahedral mineral from Triberg $Al_{4.27}(Si_{3.2}Al_{0.8})O_{10}(OH)_8$ has been named *sudoite* (Müller 1963). This author has also extended the term to the dioctadedral chlorite group (thought to possess two dioctahedral sheets at that time). After the structural investigation of a di/trioctahedral chlorite $(Al_{2.7}Mg_{2.3})$ $Si_{3.3}Al_{0.7})$ $O_{10}(OH)_8$ from the Tracy mine, Eggleston & Bailey (1967) abandoned the idea of Müller and proposed the same name sudoite as a species name for a II*b* polytype of di/trioctahedral chlorite. This suggestion is generally followed in the literature, especially by Japanese authors. However, the conclusions of Müller (1963) and Eggleston & Bailey (1967) are conflicting, and have introduced confusion concerning mineralogical properties. The name *sudoite* is presently reserved for di/trioctahedral chlorite and the earlier name *donbassite,* given by Lazarenko in 1940 (*in* Drits & Lazarenko 1967) designates di/dioctahedral chlorite. Although that nomenclature broadens the meaning of sudoite (Eggleston & Bailey 1967), Strunz (1970) maintains the name sudoite as it was proposed by von Engelhardt *et al.* (1962).

As confusion still exists between the names sudoite and donbassite, the present writers have refrained from assigning a specific name to the mineral from the Ardenne in spite of its purity and the numerous data that characterize it.

MINERALOGICAL DESRIPTION

The Cambro-Tremadocian Stavelot Massif is mainly characterized by low-grade metamorphic shales and slates. In quarries, shales of upper Salmian age (Tremadocian) are commonly crosscut by several quartz veins containing interesting mineral associations; the occurrence of a colorless chlorite had been previously pointed out (Corin 1929, 1934).

Near Ottré village, a di/trioctahedral chlorite has been detected in a thick quartz vein. This chlorite is in close association with pyrophyllite, pistachio-green ottrelite, blue grains of andalusite and whitish fibres of altered davreuxite (Fransolet & Bourguignon 1976). The pale green mineral occurs in coarse-grained nests or pods. The basal cleavage provides flakes larger than 1mm with a pearly lustre. Specific gravity measurements (Berman balance) yield 2.68(3).

The same material has been collected from dumps of an old quarry near Regné in a hand specimen associated with quartz and hematite. The chlorite has a finer-grained texture than in Ottré but its color is identical and its specific gravity is 2.70(3).

CRYSTALLOGRAPHIC PROPERTIES

Powder method

In order to get a representative diffractogram of both chlorites, specimens were purified by careful handpicking from the richest zones embedded in quartz or pyrophyllite, then ground and immersed in a graduated cylinder filled with distilled water. After one hour, the mineral in suspension was filtered, and the sedimented flakes ground again. This operation was repeated until a sufficient amount of the chlorite was collected to fill an aluminum holder for X-ray diffraction. A small part of this fine-grained mineral was mixed with lead nitrate as an internal standard.

The X-ray analysis of the coarse fraction shows an identical diffractogram, free of pyrophyllite, kaolinite and quartz but with weaker and broader *hkl* reflections for the chlorite. The selected fraction and the coarser one were mixed for chemical analysis. The powder diffractograms were obtained with a diffractometer using monochromatized $FeK\alpha$ radiation, a $\frac{1}{2}°2\theta$/min scanning rate, and a set of 1°-2°-1° slits.

The complete powder data corrected with a $Pb(NO_3)_2$ internal standard ($a = 7.8568$Å), are presented in Table 1. The relative intensities are also provided from direct measurements on the diffractogram, except for the 001 and 002 whose intensities have been corrected according to Klug & Alexander (*in* Schoen 1962). Both powder patterns of the Belgian chlorites are similar and the common 060 value of 1.513 Å indicates their dioctahedral nature. There are no significant differences between our observed d values and those published by Eggleston & Bailey (1967) although these authors have ob-

TABLE 1. X-RAY POWDER DIFFRACTION DATA

	OTTRE			REGNE		
hkl	I/I_o	d_{obs}(Å)	d_{calc}(Å)	I/I_o	d_{obs}(Å)	d_{calc}(Å)
001	20	14.16	14.17	25	14.15	14.17
002	65	7.08	7.08	65	7.07	7.08
003	100	4.721	4.722	100	4.718	4.722
110	45	4.506	4.509	60	4.500	4.513
021				20	4.327	4.325
$11\bar{2}$	10	4.007	4.011	10	4.015	4.017
022				<5	3.829	3.823
004	60	3.541	3.542	70	3.541	3.542
023				<5	3.270	3.273
005	20	2.833	2.833	30	2.834	2.833
024				<5	2.787	2.793
130	<5	2.612	2.615	5	2.613	2.616
$20\bar{1}$			2.615			2.619
131	20	2.545	2.543	25	2.547	2.543
$20\bar{2}$			2.546			2.550
$13\bar{2}$	40	2.509	2.506	50	2.511	2.508
201	45	2.499	2.499	65	2.500	2.501
132	20	2.402	2.404	25	2.407	2.404
006	10	2.361	2.361	15	2.359	2.361
202	10	2.343	2.343	15	2.345	2.345
$22\bar{1}$	<5	2.264	2.266	<5	2.267	2.269
$20\bar{4}$	5	2.235	2.235			
133	5	2.228	2.228	10	2.228	2.228
203	<5	2.160	2.162			
042			2.162			
007	10	2.025	2.024	15	2.024	2.024
$13\bar{5}$	15	1.995	1.987	20	1.993	1.988
204	20	1.978	1.978	25	1.979	1.977
$20\bar{6}$	5	1.870	1.870	15	1.872	1.873
135				10	1.863	1.863
$13\bar{6}$	5	1.816	1.812	10	1.815	1.813
205	5	1.802	1.803	10	1.802	1.803
008	<5	1.771	1.771	<5	1.771	1.771
$20\bar{7}$	5	1.709	1.706	<5	1.710	1.708
$20\bar{8}$	10	1.559	1.559	15	1.560	1.561
137	10	1.549	1.553	15	1.550	1.553
060	25	1.513	1.513	30	1.513	1.514
$33\bar{1}$			1.512			1.514
$33\bar{3}$	<5	1.480	1.481	5	1.483	1.482
062			1.480			1.480
331	5	1.477	1.478	5	1.476	1.478
332	<5	1.439	1.438	<5	1.439	1.439
00.10	<5	1.417	1.417	<5	1.416	1.417

Diffractogram taken with monochromatized FeKα radiation and corrected with $Pb(NO_3)_2$ internal standard.

TABLE 2. CELL PARAMETERS

	OTTRE	REGNE
$\underline{a}$ (Å)	5.238(1)	5.245(3)
$\underline{b}$ (Å)	9.080(1)	9.083(3)
$\underline{c}$ (Å)	14.284(3)	14.288(5)
β	97°21'(2')	97°27'(2')
V (Å^3)	674(1)	675(1)
$\underline{d}$001 (Å)	14.16	14.15
$\underline{d}$060 (Å)	1.513	1.513
$S.G._{obs}$	2.68(3)	2.70(3)
$S.G._{calc}$	2.68	2.67

tained the pattern with a 114.6mm camera with Cu*Kα* radiation. The diffractometer used here with Fe*Kα* radiation allows a better resolution of some broad reflections.

The possibility of a regular mixed-layer dioctahedral chlorite–montmorillonite or an incompletely crystallized interlayer material has also been investigated. For both chlorites the 001 does not shift after ethylene glycol solvation and after heating at 550°C; values between 14.14 and 14.15 Å are systematically observed, and no 30 Å reflection is present. The dioctahedral chlorites are probably not interlayered with swelling material.

Cell parameters

Indexing of the two diffractometer patterns was initially based on the data of Eggleston & Bailey (1967) in space group *C*2/*m*. The calculation of cell parameters by a least-squares procedure (Cox 1967) yields the values quoted in Table 2. The cell parameters of the Ottré and Regné chlorites, the Tracy mine chlorite and the dioctahedral chlorite described by Drits & Lazarenko (1967) are similar. Morever, the *b* and 060 values are here definitely different from those characterizing Al-rich dioctahedral chlorite of Müller (1961, 1963). If the Tracy mine material is considered as a di/trioctahedral chlorite (Eggleston & Bailey 1967), the crystallographic properties of Ottré and Regné chlorites tend to indicate a di/trioctahedral structure as well.

Intensity method

In addition to the *b* value used to classify the Al-rich chlorites and to distinguish the dioctahedral from the di/trioctahedral (Eggleston & Bailey 1967), the relative intensities of the 00*l* spacing reflections are used to interpret the crystal chemistry of the sheet unit. By a comparison of the relative intensities of the first five 00*l* reflections of the two chlorites with the models provided by Sudo & Sato (1966), a similarity appears between Ottré and Regné chlorites and an idealized model for a di/trioctahedral chlorite in which only the silicate sheet is dioctahedral (Table 3). However such an observation needs some discretion, because the direct use of intensities as estimated on a diffractogram is not accurate. One observes in both cases even after corrections a rather low 001 intensity as compared to the 002, 003 and 004 (Table 1).

Our specimens have been X-rayed in a Debye-Scherrer camera. The relative intensity of the 00*l* reflections is modified and a still better agreement appears with the measured Tracy mine chlorite (Eggleston & Bailey 1967).

The intensities of the two powder patterns estimated on the diffractograms can be compared with the measured intensities from the

TABLE 3. CALCULATED AND OBSERVED 001 INTENSITIES.

001	Calculated* A	Calculated* B	Calculated* C	Observed Ot	Observed Rg
001	21	100	100	20	25
002	74	37	36	65	65
003	100	25	82	100	100
004	75	38	66	60	70
005	14	14	23	20	30

* Calculated intensities (following Sudo and Sato 1966): A. when the layer is dioctahedral; B. when only the hydroxyl interlayer is dioctahedral; C. when both layers are dioctahedral. Ot = Ottré; Rg = Regné.

powder pattern of Tracy mine chlorite and with the calculated *F* values for 20*l* reflections (Brown & Bailey 1962). The result of that comparison tends to demonstrate that the chlorites considered di/trioctahedral could correspond to a II *b*-layer polytype. Although a single-crystal technique is required (Brown & Bailey 1962), the presence of several very weak reflections with $k = 3n$, as in the Tracy-mine chlorite powder pattern and also in the Regné diffractogram, indicates a regular-layer stacking. The possibility of a regular-layer stacking and of a regular alternation of dioctahedral and trioctahedral sheets has to be considered with discretion. The technique here used is not suitable for such an investigation (Sudo & Sato 1966).

CRYSTAL CHEMISTRY

Chemical composition

The chemical analysis of the X-rayed specimens has been performed with 0.5g of carefully selected material, air-dried during 2 hours at 100°C. Ti, Al, Mn, Zn, Ni, Mg, Ca, Na, K and Li were obtained by atomic absorption with the Perkin Elmer 603 spectrophotometer. Si has been gravimetrically determined; the ferrous and ferric iron were distinguished by the colorimetric method of Wilson (1960); H_2O was determined by the Penfield method.

The results of the chemical analyses are shown in Table 4. It is difficult to compare most dioctahedral chlorites, because they are mixed with impurities such as quartz, carbonates, sulfates, pyrophyllite or hematite as identified by X-ray diffraction.

TABLE 4. CHEMICAL COMPOSITIONS

	OTTRE 1	OTTRE 2	OTTRE 3	REGNE 1	REGNE 2	REGNE 3	REGNE 4
SiO_2	33.00	33.06	6.02	32.71	32.82	5.97	33.58
Al_2O_3	35.69	35.74	7.67	36.04	36.16	7.75	37.98
Fe_2O_3	2.74	2.74	0.38	2.45	2.45	0.34	-
FeO	0.24	0.24	0.04	0.05	0.05	0.01	-
MnO	0.28	0.28	0.04	0.24	0.24	0.04	-
MgO	14.07	14.09	3.82	14.30	14.35	3.89	15.02
ZnO	0.05	-	-	0.09	-	-	-
NiO	0.09	-	-	0.04	-	-	-
CaO	n.d.	-	-	n.d.	-	-	-
Na_2O	<0.01	-	-	0.00*	-	-	-
K_2O	0.00*	-	-	0.00*	-	-	-
Li_2O	0.04	-	-	0.08	-	-	-
H_2O^+	13.83	13.85		13.88	13.93		13.42
Total	100.03	100.00		99.88	100.00		100.00
n			4.98			4.99	5
x + y			1.96			1.97	2
Al_d			1.85			1.85	2

1. Analyst J.M. Speetjens. n.d.: not detected;*<0.005%.
2. Analyses recalculated to 100%, without minor Zn, Ni, Li contents.
3. Numbers of cations on the basis of 56 cationic valences.
4. Theoretical composition for $(Al_3Mg_2)(Si_3Al)O_{10}(OH)_8$.

In chemical composition our chlorites are quite similar to the Beriozovsk chlorite (Drits & Lazarenko 1967). Because of their Al content, they are also comparable with the Kamikita mine material (Hayashi & Oinuma 1964); the MgO percentage is close to the content of the Kaiserbachtal mineral (Frenzel & Schembra 1965).

The structural formula

The concentrations of Ni, Co and Li indicated for the chemical compositions of both di/trioctahedral chlorites (Table 4) is neglected here. These minor elements are too low in concentration and do not represent any chemical particularity. However these elements will be meaningful in a further discussion dealing with the geochemical and genetic problem.

The structural formulae are established on the basis of 56 positive valences balancing 20 O^{2-} and 16 $(OH)^-$ in a monoclinic cell with $Z = 2$ (Table 4). This method has been chosen rather than to consider the whole of the 72 cationic charges because the infrared analysis has shown the presence of molecular H_2O. That excess of H_2O is not due to vermiculitic layers and is strongly absorbed on the sheet structure. Sudo & Sato (1966) have also mentioned such water in dioctahedral chlorites.

The following structural formula can be written for the Ottré chlorite: $(Al_{2.84}Mg_{1.91}Fe^{3+}_{0.19}Fe^{2+}_{0.02}Mn_{0.02})(Si_{3.01}Al_{0.99})O_{10}(OH)_8 \cdot 0.20\ H_2O$, its calculated density being 2.68 g.cm^{-3} without the assumed molecular water. The Regné chlorite, $(Al_{2.86}Mg_{1.94}Fe^{3+}_{0.17}Mn_{0.02})$ $(Si_{2.99}$

$Al_{1.01})O_{10}(OH)_8 \cdot 0.22H_2O$, has a calculated density of 2.67 g.cm^{-3}. These densities are in very good agreement with the measured values (Table 2).

Considering the general formula $(Al,Fe^{3+})_{4-y}$ $(Mg, Fe^{2+})_{\frac{x}{2}+\frac{3y}{2}}(Si_{4-x}Al_x)O_{10}(OH)_8$ proposed for Al-rich chlorites (Müller 1963, Sudo & Sato 1966), the crystallochemical formulae established above give for $x + y$, 1.96 and 1.97, and for n (octahedral population) 4.98 and 4.99, respectively. Oinuma *et al.* (1972) have also suggested the term Al_d indicating the difference between octahedral and tetrahedral Al in dioctahedral chlorite. The value for Al_d is 1.85 in both cases. All these supplementary data, employed in the classification proposed by Sudo & Sato (1966), Eggleston & Bailey (1967) and Oinuma *et al.* (1972), confirm the di/trioctahedral nature. Morever, these data are fairly noteworthy: $x + y$, n and Al_d are quite close to 2, 5 and 2, respectively. Both compositions are very similar and agree closely with an ideal formula $(Al_3Mg_2)(Si_3Al)O_{10}(OH)_8$, whose theoretical composition is given in Table 4.

The interest of the ideal composition mentioned above can be also emphasized in calling attention to its particular position in the system $MgO–Al_2O_3–SiO_2–H_2O$ commonly used in petrologic discussions (Fig. 1). Indeed, the abundant well-crystallized di/trioctahedral chlorite of Ardenne seems to constitute an important mineral in the genesis of quartz veins in that area and it could play a role in further investigations on experimental mineralogy of these assemblages.

Optical Properties

The following optical properties were obtained for the Ottré mineral. Because of the good basal {001} cleavage, it was practically impossible to measure γ. With the immersion method in oils and sodium light, $\alpha = 1.583(1)$ and $\beta = 1.589(1)$. The values correspond to $\beta - \alpha = 0.006$; the birefringence of (001) sections, measured with an Ehringhaus compensator, is 0.007. A measurement of the birefringence with the same compensator and with the U-stage yields $\gamma - \alpha = 0.018$ for sections parallel to the optic axial plane, which value allows us to deduce $\gamma = 1.601(5)$. $2V_{calc}$ of (+) 71° is in good agreement with $2V_{obs}$ (+) 70° ± 5° (Mallard method). In the optic axial plane, X lies within the (001) plane and Z is virtually perpendicular to the cleavage flake. The Regné di/trioctahedral chlorite, finer grained than the Ottré specimen, does not allow a complete op-

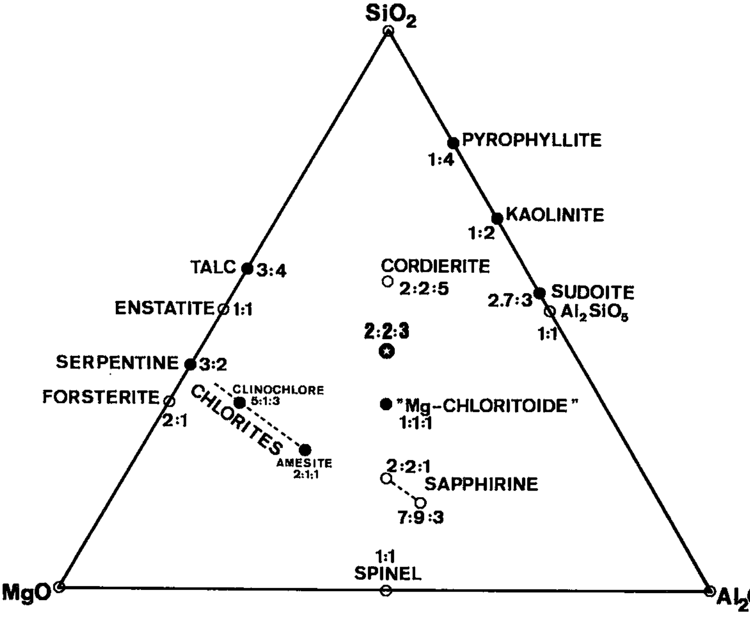

FIG. 1. The ideal composition of phases in the system $MgO–Al_2O_3–SiO_2–H_2O$ represented in a projection on the water-free triangular diagram. The full circles indicate hydrous phases, open circles correspond to anhydrous ones; the white star is the position of (Al_3Mg_2) $(Si_3Al)O_{10}(OH)_8$. The composition of sudoite is one of those reported by Müller (1963).

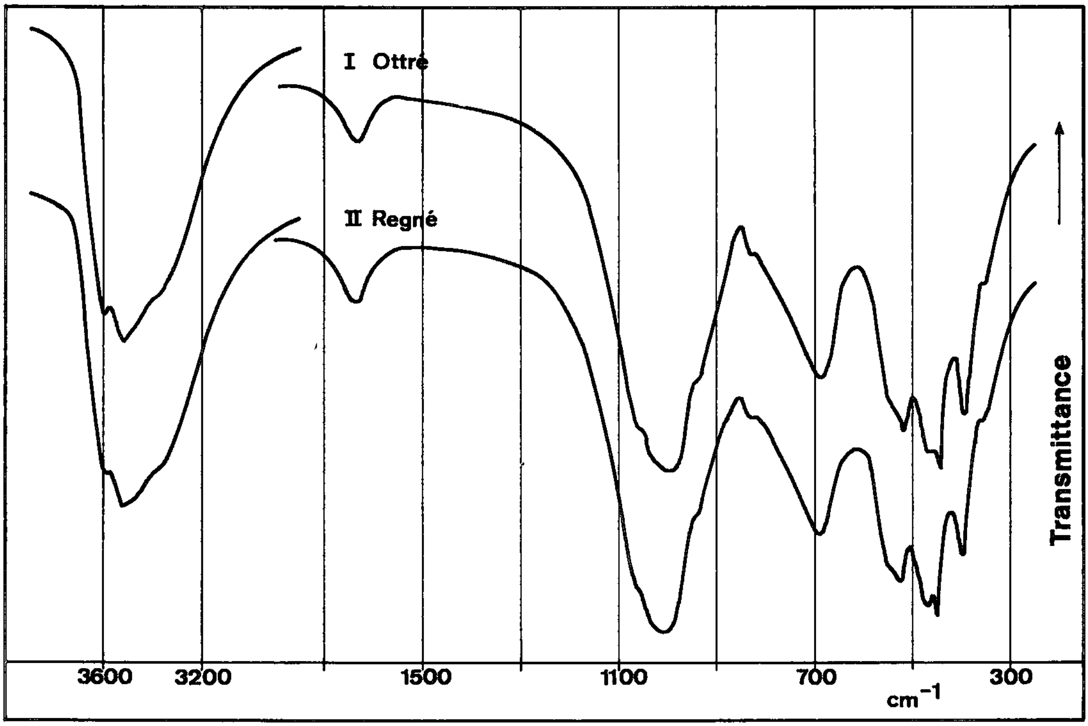

FIG. 2. Infrared absorption spectra of the Ottré and Regné di/trioctahedral chlorites.

TABLE 5. INFRARED ABSORPTION SPECTRA

OTTRE	REGNE	KAMIKITA*
350 sh	355 sh	
403	405	
453	453	
473	472	475
528	532	528
550 sh	552 sh	555
693 b	690 b	692
830 w	832 w	825
935 sh	940 sh	
1000 b	1000 b	1004
1060 sh	1060 sh	
1640 w	1640 w	
3375 b-sh	3400 b-sh	3340
3520	3525	3520
3600	3600	3620

Frequencies in cm^{-1}; sh = shoulder; b = broad; w = weak.
* Hayashi and Oinuma (1965,1967).

tical investigation, but presents the same optical characteristics, especially $\beta = 1.589(1)$ and $2V_{obs} = 70° \pm 5°$. Both are optically identical according to X-ray data and chemical composition.

It seems that the Ottré mineral is more similar to the Russian material. Although the Al/Mg ratio is quite comparable in Ottré, Regné and Beriozovsk chlorites, the refractive indices are very different. The number of optical measurements is very small and no obvious relationship can be observed between chemical content, low refractive indices and optically negative sign.

INFRARED ANALYSIS

The infrared absorption spectra were registered between 4000 and 250cm^{-1} with the Beckman IR–12 spectrophotometer. The pressed-disk technique has been used for the preparation of the two samples: 3mg chlorite were carefully ground and mixed with 0.6g KBr. The infrared spectra (Fig. 2) are similar to the di/trioctahedral chlorite of Kamikita mine (Hayashi & Oinuma 1964). The wavenumbers are listed in Table 5.

The shape of the 4000-3200cm^{-1} region (Fig. 2) and the absorption in the domain of OH$^-$ stretching vibrations, are completely different

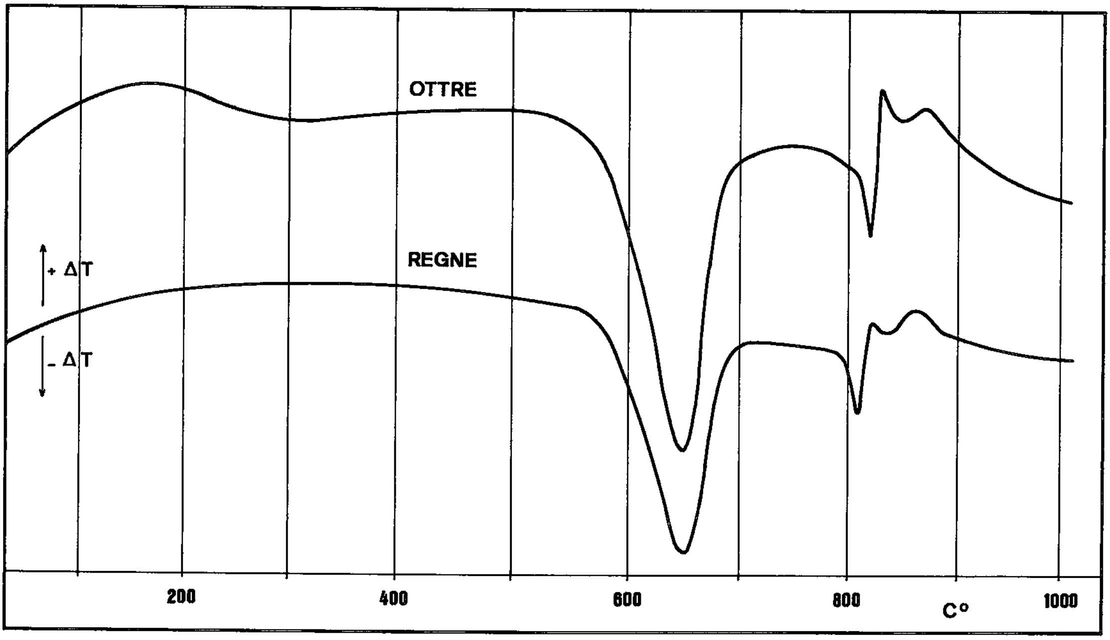

FIG. 3. DTA curves of the Ottré and Regné di/trioctahedral chlorites.

from those observed for trioctahedral chlorite, and typical of dioctahedral chlorites (Hayashi & Oinuma 1967). Our minerals present a distinct shoulder at 3375-3380cm^{-1} whereas the Kamikita chlorite is characterized by a band at 3340cm^{-1} (Hayashi & Oinuma 1967).

The weak absorption band at 1640cm^{-1} obviously corresponds to the bending vibrations of H_2O. It probably indicates the presence of hygroscopic water strongly maintained in the sheet texture as in the case of fraipontite (Fransolet & Bourguignon 1975).

The very large and intense band at 1000cm^{-1} and its weak shoulder at 1060cm^{-1} are mainly due to Si–O stretching vibrations. Their shape suggests the presence of Al in the tetrahedral site (Lyon & Tuddenham 1960). Its frequency indicates a high Al to Fe+Mg ratio (Hayashi & Oinuma 1967). The weak shoulder that clearly appears at about 935cm^{-1} can probably be attributed to a H–O–Al motion (Stubičan & Roy 1961).

According to the previous observations (Stubičan & Roy 1961; Hayashi & Oinuma 1965), the spectra (Fig. 2) show a weak absorption band at 830cm^{-1} assigned to Si–O–Al vibration and a very broad and intense one at 693cm^{-1} due to a Si–O vibration. As for the specimen from Kamikita mine, no band can be observed near 730cm^{-1} because it is probably too weak and screened by the asymmetric aspect of the 693cm^{-1} band. The high value of this absorption emphasizes the abundance of Al.

The wavenumber of the frequency near 550cm^{-1} has a tendency to increase with an increasing amount of octahedral Al (Hayashi & Oinuma 1965). Considering the data published by these authors, the relationship between the frequency 550cm^{-1} and the amount of octahedral Al is rather tenuous. This relationship is only established with a poorly defined band of the spectra. In Figure 2, smooth shoulders only appear around 550cm^{-1} an dthese data do not allow a satisfactory estimation of the Al content in octahedral position.

THERMAL BEHAVIOR

Thermal analysis

The DTA curves (Fig. 3) obtained at a heating rate of 10°C/min in air show an important endothermic peak at 650°C and a weaker one at 810°C. They correspond to different weight losses on the TGA curves: the strongest one appears between 500° and 650°C and the last one, extremely weak and not always perceptible, between 750° and 850°C. They represent a total loss of about 13% and must correspond to dehydration. Two dehydroxylation reactions start at about 550° and 780°C, respectively. The weak exothermic peak at 860°C may be accompanied by another, sharper and asymmetrical one at 830°C.

The DTA curves are rather similar to those of other dioctahedral chlorites reported in the literature, especially by Fujii *et al.* (1971) who described a di/trioctahedral material with II*b* one-layer type. The exothermic peak appears here at a lower temperature than for those recorded in the literature. In fact, this doublet at 830°–860°C also characterizes the mineral from Saint-Paul-de-Fenouillet (Caillère *et al.* 1962) and from Namivu (Figueiredo Gomes 1967).

Dioctahedral chlorites with a higher Al content seem to have an earlier endothermic reaction than the di/trioctahedral chlorites richer in Mg. This hypothesis tends to confirm the suggestion of Caillère & Hénin (1960), who consider that the beginning of the dehydroxylation in the octahedral sheets depends on the cations in the usual trioctahedral chlorites. The more Al in both layers, the lower the temperature of this phenomenon. From the thermal behavior of our chlorites, the beginning of two dehydroxylations occurring at 550° and at 780°C tends to show that Mg is present in the hydroxyl interlayer rather than in the silicate sheet, in which all the octahedral positions are occupied by Al. As with Caillère & Hénin (1960), this assumption needs further structural refinements before inferring that in our chlorites the Mg and Al cations are so perfectly distributed.

X-RAY INVESTIGATION OF THERMAL BREAKDOWN PRODUCTS

A static heating for two hours in a porcelain crucible gives the following evolution of the specimens: at 500°C, the mineral is unchanged; at 550°C, the 001 reflection is enhanced and its spacing is slightly contracted to 14.12 Å; at 700°C, all the reflections collapse except for 001 at 14.10 Å whose intensity strongly increases; between 825° and 900°C, the complete disappearance of reflections shows that all phases are amorphous; at 1000°C, spinel is produced; at 1100°C, spinel continues to grow whereas sapphirine slowly appears; at 1200°C, the complete powder pattern of sapphirine can be recognized and an additional product, a metastable quartz-type phase (Schreyer & Schairer 1961) is also present. At that temperature, as the *d* values for spinel are practically identical to the strongest lines of sapphirine, the presence of the former mineral is doubtful.

If the formation of a spinel phase is obvious when Mg, accompanied by minor Fe, is available, the production of sapphirine and a high-quartz solid solution both at 1200°C has never been reported in thermal investigations of such chlorites. Schreyer & Schairer (1961) detected that metastable high-quartz solid solution in the system $MgO–Al_2O_3–SiO_2$. The mixture of sapphirine and a high-quartz solid solution at 1200°C is certainly of some importance in the experimental analysis of that system and because, without a chemical analysis, an examination of the breakdown phases can help to identify dioctahedral chlorites (Bailey & Tyler 1960).

The thermal response of 001 spacing reflection at 550°C shows no vermiculitic reaction and is of strictly chloritic character. The temperature of the dehydroxylation tends to demonstrate a di/trioctahedral nature as far as the hypothesis of Caillère & Hénin (1960) is reliable, *i.e.*, all the octahedral positions of the silicate layer would be occupied by Al.

GENETIC PROBLEM

A complete investigation of mineral assemblages observed in the quartz veins from Ardenne will allow us to establish the conditions of formation. Occurrences of well-developed di/trioctahedral chlorite with a II*b*-layer type among these associations are noteworthy for such further genetic discussion. One can now report that the II*b* polytypes are considered as hydrothermal in origin (Bailey & Tyler 1960; Hayashi & Oinuma 1964; Frenzel & Schembra 1965). This general idea appears to be in good agreement with the sparse data on the mineralogy of these quartz veins.

ACKNOWLEDGMENTS

The authors are indebted to Professor P. Tarte (Université de Liège) who recorded infrared spectra, and to Professor W. Schreyer (Ruhr-Universität Bochum) who critically read the manuscript. Thanks are extended to Mr. A. Egeroff for Russian translations.

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Received February 1978; revised manuscript accepted May 1978.