In memory of Max H. Hey

Katoite, a new member of the $Ca_3Al_2(SiO_4)_3$-$Ca_3Al_2(OH)_{12}$ series and a new nomenclature for the hydrogrossular group of minerals

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Abstract. — The new mineral katoite, $Ca_3Al_2(SiO_4)(OH)_8$, occurs in Pietramassa near Montalto di Castro (Viterbo, Italy), associated with many other hydrated calcium silicates and aluminates in the vugs of a phonolite which effused through argillaceous marls of Pliocene age. Microprobe and TG analyses yielded the empirical formula $Ca_{2.96}(Al_{1.85}Mg_{0.01})(Si_{0.69}S_{0.11})O_{2.93}(OH)_{9.07}$; X-ray study showed it to be cubic, $Ia3d$ with a 12.358(2) Å. Physical properties (thermal behaviour, refractive index, infrared spectrum, and X-ray powder diffraction) are consistent with its chemical composition and with its pertinence to the solid solution series $Ca_3Al_2Si_3O_{12}$ (grossular) and $Ca_3Al_2(OH)_{12}$ (synthetic phase) with an approximate content of 27 % of the former and 73 % of the latter. This makes it the first natural compound of the series with a grossular content lower than 50 % and confirms the existence, also in nature, of a complete series with a $SiO_4 \rightleftharpoons (OH)_4$ isomorphous replacement within the grossular structure. By analogy with other isomorphous mineral series, two names, hibschite and katoite, are appropriate to represent the two solid solution fields with more and less than 50 % Si in the tetrahedra, respectively. The name hydrogrossular remains applicable as a group name for members of the whole series with an appreciable OH content but otherwise undetermined $SiO_4/(OH)_4$ ratio. The paragenetic sequence found in nature and laboratory experiments reported in earlier literature, indicate for katoite a crystallization temperature of approximately 300 °C with a relatively high water vapour pressure and a limited Si supply.

Key words : katoite, new mineral, hibschite, plazolite, hydrogrossular, nomenclature.

La katoïte, un nouveau membre de la série $Ca_3Al_2(SiO_4)_3$-$Ca_3Al_2(OH)_{12}$ et une nouvelle nomenclature du groupe de l'hydrogrossulaire.

Résumé. — La katoïte $Ca_3Al_2(SiO_4)(OH)_8$ est un nouveau minéral trouvé en association avec plusieurs silicates et aluminates hydratés de calcium dans les cavités d'une phonolite mise en place dans des marnes argileuses d'âge Pliocène à Pietramassa près de Montalto di Castro (Viterbo, Italie). Analysé par microsonde électronique et par thermogravimétrie, il donne la formule empirique suivante : $Ca_{2.96}(Al_{1.85}Mg_{0.01})(Si_{0.69}S_{0.11})O_{2.93}(OH)_{9.07}$; l'étude par diffraction des rayons X montre une maille cubique dans le groupe spatial $Ia3d$ avec a 12,358(2) Å. Les propriétés physiques (comportement thermique, indice de réfraction, spectre IR, et diagramme de poudre) sont en accord avec sa composition chimique et son appartenance à une solution solide entre $Ca_3Al_2Si_3O_{12}$ (grossulaire) et $Ca_3Al_2(OH)_{12}$ (phase synthétique) avec un pourcentage d'environ 27 % du premier et 73 % du second. La katoïte est donc le premier composé naturel de la série où le pourcentage de grossulaire est inférieur à 50 %, et qui confirme l'existence, dans la nature, d'une série complète où il y a isomorphisme $SiO_4 \rightleftharpoons (OH)_4$ dans la structure cristalline du grossulaire. Par analogie avec d'autres séries de minéraux isomorphes, deux noms, hibschite et katoïte, sont appropriés pour représenter les deux champs de solution solide avec respectivement plus et moins de 50 % de silicium. Le nom hydrogrossulaire, toujours applicable comme un nom de groupe, désigne tous les membres de la série avec un contenu appréciable de OH mais avec un rapport $SiO_4/(OH)_4$ non spécifié. La séquence paragénétique et les résultats de synthèse dans la littérature indiquent, pour la katoïte, une température de cristallisation proche de 300 °C, avec une pression relativement haute de vapeur d'eau et une disponibilité limitée en silicium.

Mots-clés : katoïte, nouveau minéral, hibschite, plazolite, hydrogrossulaire, nomenclature.

INTRODUCTION AND HISTORICAL OUTLINE

Six names are currently used for minerals with compositions between $Ca_3Al_2(SiO_4)_3$ (grossular) and $Ca_3Al_2(OH)_{12}$ (synthetic phase) ; *hibschite, plazolite, grossularoid, hydrogarnet, garnetoid* and *hydrogrossular*.

The name *hibschite* was introduced by Cornu (1906) for a new silicate mineral occurring as

minute octahedral colourless isotropic crystals containing dodecahedral garnet nuclei in xenolithic marl inclusions in a phonolite at Marianská Hora (= Marienberg), near Ústí nad Labem (= Aussig), Bohemia. Cornu was unable to separate the hibschite outer shell from the garnet core and obtained a rather poor chemical analysis by subtracting the composition of the cores, which were analyzed separately, from that of the bulk sample. The chemical composition thus derived ($CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) was identical to that of lawsonite, with which a comparison of physical properties was also given. In the same work, Cornu also reported the occurrence of hibschite from Aubenas (France) for a sample previously referred to by Lacroix (1893) as garnet. Another occurrence of hibschite was reported by Cornu (1907) at Madstein, Bohemia, for which no composition was given.

Foshag (1920) introduced the name *plazolite* for a mineral occurring as very small colourless dodecahedral crystals in a metamorphosed limestone at Crestmore, Riverside County, California, for which he obtained the chemical formula $3CaO \cdot Al_2O_3 \cdot 2(SiO_2, CO_2) \cdot 2H_2O$. He considered the mineral related to sodalite, whereas Winchell (1933) suggested its relationship to the ugrandite series of garnets. Pabst (1937), in his crystal structure determination of plazolite from Crestmore, excluded the CO_2 content from the chemical formula proposed by Foshag and proposed the new formula $3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. The structure of plazolite was found to be analogous to that of grossular, the lattice constant (12.16 Å) being slightly larger. Belyankin and Petrov (1939) described a characteristic paragenesis of hibschite from Nikortzminda, Georgia, similar to that mentioned by Cornu (1906) and debated as to the validity of the chemical formula accepted for this mineral as proposed by Cornu. Shortly thereafter the same authors (1941a) analyzed concentrates of Nikortzminda hibschite and proposed the ideal formula $3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. They concluded that hibschite "is simply grossularite in which one molecule of SiO_2 is replaced by two molecules of H_2O". In the same year Belyankin and Petrov (1941b), by comparing hibschite from Nikortzminda with plazolite from Crestmore, concluded that the two minerals "are very much alike in their properties" and, probably being unaware of Pabst's (1937) conclusions, stated that they differ chemically "only by a small and

rather variable CO_2 content" in the latter. They concluded that "hibschite and plazolite are both members of the same mineral group" which they proposed to name *grossularoid* "because of its close relationship to grossularite". Incidentally, they reported another locality for "grossularoid" in the Lopan gorge, Southern Osetia, Transcaucasia. Pabst (1942), on the basis of optical and X-ray examinations, demonstrated the close analogies existing among hibschite from the type locality (Marienberg), plazolite from Crestmore, and grossular, thereby confirming the close similarity between hibschite and plazolite and their pertinence to the grossular group of minerals as previously suggested by Belyankin and Petrov (1941b).

Some time earlier Flint *et al.* (1941) synthesized, by hydrothermal treatment of glasses of appropriate composition, various phases with the garnet structure and compositions intermediate between $3CaO \cdot Al_2O_3 \cdot 3SiO_2$ (grossular) and $3CaO \cdot Al_2O_3 \cdot 6H_2O$. Their X-ray studies confirmed the existence of a complete isomorphous series between these two end members, $3SiO_2$ being interchangeable with $6H_2O$. Furthermore they considered plazolite a natural intermediate member of this series which they proposed to collectively name *hydrogarnets*.

A year later McConnell (1942), discussing the analogies among griphite (a phosphate), plazolite, and berzeliite (an arsenate), proposed the term *garnetoid* to describe minerals with structures analogous to garnet, including all hydrogarnets. Griphite was actually found (Rinaldi, 1978) not to be closely related to garnets, however a clear indication came from McConnell's work that $(OH)_4$ groups could isomorphically replace SiO_4 tetrahedra within the garnet structure. This hypothesis was confirmed 21 years later (Cohen-Addad *et al.*, 1964) with the determination of the H positions in cubic $Ca_3Al_2(OH)_{12}$ with a garnet structure.

Hutton (1943) reported the chemical analysis of a garnet-like mineral from New Zealand with a composition between $Ca_3Al_2(SiO_4)_3$ (grossular) and $Ca_3Al_2Si_2O_8(OH)_4$ (hibschite = plazolite) and proposed the name *hydrogrossulars* for all minerals with chemical formulae between grossular and hibschite.

Since Hutton's proposal, the term hydrogrossular has been generally accepted to describe

new occurrences of hydrogarnets of the grossular type, except by Nalivkina (1960) and Nikolic & Zaric (1972) who used the name hibschite to describe minerals from Bug River, USSR, and Bezovica, Yugoslavia, respectively. Hydrogrossular occurrences have been reported from Eulamina, Australia (Miles, 1950) ; King Island, Tasmania (Scott, 1951) ; Ayrshire, England (Bloxam, 1964) ; Tokatoka, New Zealand (Mason, 1957) ; the Bushveld complex, Transvaal (Hall, 1925 ; Tilley, 1957 ; Frankel, 1959) ; Clear Creek, California (Coleman, 1961) ; Pastoki, Pakistan (Bilgrami and Howie, 1960) ; and the Hatrurim formation, Israel (Gross, 1977). Zabinski (1966) critically reviewed all earlier occurrences, except that reported by Nalivkina (1960), on the basis of a thorough reexamination by means of microscopic, X-ray, thermal, and infrared analyses. He noted that some of the occurrences previously reported as typical hydrogrossulars (Transvaal, Eulamina) are heterogeneous as they contain dispersed vesuvianite, others (some varieties of South African ''jade'') contain two microcrystalline garnet phases, grossular and hydrogrossular. He also gave a detailed account on the terminology in use.

Recently Basso *et al.* (1983) refined the crystal structure of plazolite from Crestmore reporting a composition, obtained by microprobe analysis, very similar to that reported, for the same sample, by Pabst (1942) as obtained from Foshag's (1920) analysis no. 3 after substraction of the CO_2 due to admixture. These authors do not make any mention of this last work by Pabst and declare unreliable both their own microprobe analysis (although without reporting the experimental conditions) and that reported by Pabst (1937) in favour of a chemical composition calculated from the chemical formula obtained from the structure refinement alone. The composition thus derived differs from that proposed by Pabst (1942) and from that obtained by microprobe analysis, for a distinctly lower Si content. In the lack of substantial reasons for doubting the validity of both the wet method and the microprobe results and in view of their good agreement, we assumed the latter as the most representative for plazolite from Crestmore.

Table I lists, in increasing order of total Fe, all compositions, and corresponding atomic ratios, reported to date for hibschite (except that reported by Nikolic & Zaric, 1972 ; unreliable because of xonotlite admixture), plazolite, and various minerals described as hydrogrossulars ; physical parameters, when available, are also reported. In view of the well established isomorphism between grossular and all other minerals of this group, we also reported the percentage of the grossular end-member (hereafter indicated as Gr%) for each sample. These percentages, when reported on a linear diagram such as that of figure 1, show a concentration of all compositions so far reported in the literature within the left-hand field of the diagram, corresponding to more than 50 % of the tetrahedral sites occupied by Si (Gr% > 50).

In the present work we report the finding of a natural member of this group with a composition that plots well within the right-hand field of the diagram corresponding to much less than 50 % of the tetrahedral sites occupied by Si (Gr% < 50). As in a continuous mineral series it is the custom to use two different names indicating the two end-members as well as the corresponding intermediate members within 50 % of one or the other (as for example the olivine group), this finding has prompted our proposals for a new mineral and mineral name as well as a definition of the nomenclature for the whole group. All proposals have been approved by the appropriate commissions of the International Mineralogical Association ; details are given in the discussion section. The new mineral has been named katoite in honour of Akira Kato of the National Science Museum, Tokyo, in recognition of his dedicated activity to minerals and mineralogy and also this mineral being the last one to be approved during Dr. Kato's long and productive chairmanship of the IMA Commission on New Minerals and Mineral Names.

The holotype material of katoite is deposited with no. 25529 in the mineral collection of the ''Museo Civico di Storia Naturale'', Milan, Italy.

MINERALOGICAL DESCRIPTION OF KATOITE

Occurrence and paragenesis

Katoite has so far been identified only in a few samples collected at the Campomorto

Sample	1	2	3	4	5	6	7	8	9	10	11
SiO_2	25.71	27.30	25.35	37.60	34.59	34.46	34.48	36.55	27.57	37.28	32.95
Al_2O_3	25.27	23.97	23.44	22.25	20.81	21.25	19.87	23.44	18.52	23.11	17.78
TiO_2	–	–	–	0.10	0.15	0.14	0.03	0.12	0.67	0.06	0.86
Cr_2O_3	–	–	–	0.10	–	0.01	–	0.25	–	–	–
P_2O_5	–	–	–	0.05	–	–	–	–	–	–	–
Fe_2O_3	–	0.30	0.31	0.50	0.99	0.97	0.61	1.27	3.70	5.26	6.78
FeO	–	–	–	0.55	0.29	0.32	0.85	0.52	0.15	0.73	–
MnO	–	0.19	–	tr.	0.05	0.18	0.02	0.04	0.08	–	–
MgO	–	2.01	0.52	tr.	1.20	1.13	2.07	0.79	2.13	4.12	1.25
CaO	39.75	37.00	39.67	38.40	36.13	36.46	37.40	36.06	38.39	37.44	35.42
Na_2O	–	–	–	–	0.01	0.05	0.02	–	–	n.d.	0.27
K_2O	–	–	–	–	–	–	0.01	–	–	n.d.	0.35
SO_3	–	–	–	–	–	–	–	–	–	.–	–
H_2O^-	–	0.20	10.71	0.20	0.36	0.65	0.23	–	0.29	0.44	–
H_2O^+	9.27	9.20		1.20	4.91	4.47	4.65	1.16	8.55	1.37	4.55
Tot.	100.00	100.17	100.00	100.95	99.49	100.09	100.24	100.20	100.05	99.81	100.21
Si	1.82	1.91	1.77	2.79	2.51	2.49	2.51	2.73	1.98	2.73	2.45
Al	2.11	1.98	1.93	1.95	1.78	1.81	1.70	2.06	1.57	2.00	1.55
Ti	–	–	–	0.01	0.01	0.01	tr.	0.01	0.04	tr.	0.05
Cr	–	–	–	0.01	–	tr.	–	0.01	–	–	–
P	–	–	–	tr.	–	–	–	–	–	–	–
Fe^{3+}	–	0.02	0.02	0.03	0.05	0.05	0.03	0.07	0.20	0.29	0.38
Fe^{2+}	–	–	–	0.03	0.02	0.02	0.05	0.03	0.01	0.04	–
Mn	–	0.01	–	–	tr.	0.01	tr.	tr.	tr.	–	–
Mg	–	0.21	0.05	–	0.13	0.12	0.22	0.09	0.23	0.45	0.14
Ca	3.01	2.77	2.97	3.05	2.80	2.82	2.91	2.89	2.96	2.16	2.82
Na	–	–	–	–	tr.	0.01	tr.	–	–	n.d.	0.04
K	–	–	–	–	–	–	tr.	–	–	n.d.	0.03
H^+	4.37	4.39	5.00	0.69	2.55	2.47	2.37	0.58	4.24	0.88	2.24
O	12	12	12	12	12	12	12	12	12	12	12
Gr%	60.67	63.67	59.00	93.00	83.67	83.00	83.67	91.00	66.00	91.00	81.67
a(Å)	12.16*	12.02	12.174	–	12.08	11.90	–	11.859	–	12.03	12.30
n	1.675	1.677	–	–	1.683 1.712	1.675 1.705	1.7021	1.728	1.681	1.663 1.753	1.71
D	–	3.08	–	3.52	3.30	3.27	3.35	3.488	–	–	–

* Derived from the value of 12.14 Kx units.

1. Plazolite, Crestmore (Pabst, 1942); 2. Hibschite, Bug River (Nalivkina, 1960); 3. Plazolite, Crestmore (Basso et al., 1983; microprobe data), all Fe has been calculated as Fe_2O_3 and H_2O as difference to 100%; 4. "Green jade", Bushveld complex, Transvaal (Hall, 1925); 5. Hydrogrossular, Ayrshire (Bloxam, 1964); 6. South African "jade", pink variety, Bushveld complex (Tilley, 1957); 7. Hydrogrossular, Dun Mt. New Zealand (Hutton, 1943); 8. South African "jade", Bushveld complex (Frankel, 1959); 9. Hibschite, Nikortzminda , USSR (Belyankin and Petrov, 1941b). 10. Hydrogrossular, King Island, Tasmania (Scott, 1951); 11. Hydrogrossular, Hatrurim formation, Israel (Gross, 1977).

    The samples are listed in order of increasing total Fe content. The analyses of the "jade" samples are not very reliable due to the possibility of grossular-hydrogrossular admixture as pointed out by Zabinski (1966).

TABLE I. — *Chemical compositions and physical properties of hydrogrossular group minerals.*
Composition chimique et propriétés physiques des minéraux du groupe de l'hydrogrossulaire.

quarry in Pietramassa near Montalto di Castro (Viterbo, Italy). The quarry exploits a 4-5 m thick effusive rock formation reported on the 1:100.000 Geological Map of Italy (no. 136) as "tefrite di Castellacio dei Vulsci θ_1", and classified as phonolite (Passaglia & Galli, 1977). The top of the lava flow has a high concentration of metamorphosed inclusions of variable dimensions (from a few mm to a few cm), and of fractures and cavities where hydrothermal minerals occur. The inclusions, consisting of fragments of argillaceous marls of Pliocene age, through which the effusion took place, become rarer towards the bottom of the formation until they completely disappear. They are generally characterized by the presence of garnet, wollastonite, gehlenite and tobermorite. The fractures and cavities, of very variable dimensions, are filled or lined with several associations of minerals.
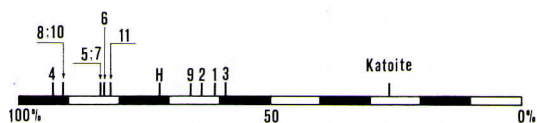
Passaglia & Galli (1977) described the find-

FIG. 1. — *Linear plot of Gr% in minerals of the hydrogrossular group* : numbers refer to table I ; H : calculated Gr% value for the holotype hibschite from Marienberg (see text).

Diagramme linéaire du pourcentage de Gr dans les minéraux du groupe de l'hydrogrossulaire : la numérotation est celle du tableau I ; H : valeur en Gr% de l'hibschite holotype de Marienberg (voir texte).

ing, in one of these cavities, of the new hydrated silicate vertumnite associated with tobermorite and ettringite. Recently Passaglia & Turconi (1982) gave a detailed account of all the minerals so far identified in the samples collected, on various field trips to the Campomorto quarry, by members of the "Gruppo Mineralogico Lombardo". Besides the above mentioned ones, they reported the following minerals : hydrocalumite, opal, portlandite, quartz, haematite, gypsum, calcite, afwillite, apophyllite, cordierite, jennite, straetlingite, chabazite, gismondine, phillipsite, and katoite. The last one was provisionally reported as hydrogrossular.

In the holotype sample, a large fragment of phonolite with a wide cavity, katoite occurs as rounded microcrystals 0.1-0.3 mm in diameter, tightly associated to form a thin crust, generally milky white, rarely transparent. At high magnification the rare coarser crystals show a regular octahedral morphology. Generally the katoite coating rests directly on the rock, less frequently it grows on a thin layer of milky white tobermorite and in a few cases it was found surrounding extremely thin opaque black unidentified fibers thereby forming tightly associated columnar aggregates (Figure 2). Scanning electron microscope observation of these aggregates reveals the octahedral morphology of the crystals (Figure 3). Figures 3b) and 3c) show the growth pattern of the crystals and the octahedral morphology of an isolated crystal of katoite respectively. In the same sample, on top of the katoite layer, one may observe prismatic transparent crystals of afwillite rarely isolated, more frequently associated in the form of subspherical aggregates, and large transparent lamellar crystals of hydrocalumite with irregular hexagonal
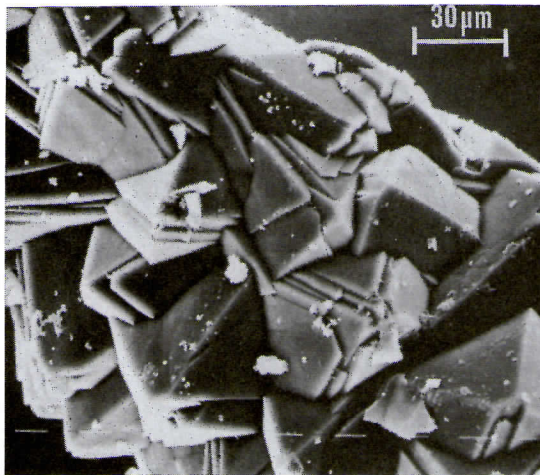

FIG. 2. — *Optical micrograph of columnar aggregate of katoite crystals* (photo B. Turconi).

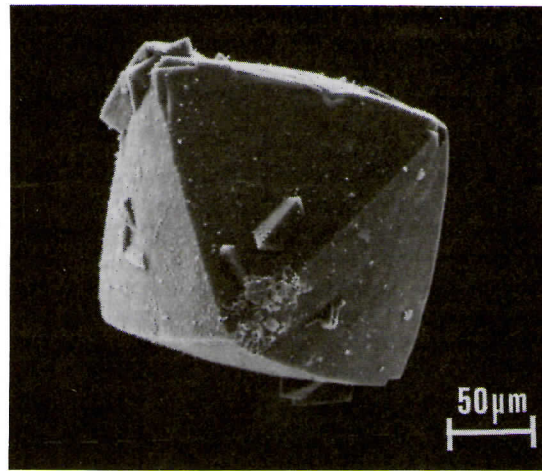*Microphotographie d'aggrégats en colonnes de cristaux de katoite* (photo B. Turconi).

outlines and a pearly luster. Katoite was also found in the cavities of two more hand specimens where it occurs as a thin opalescent layer on top of tobermorite.
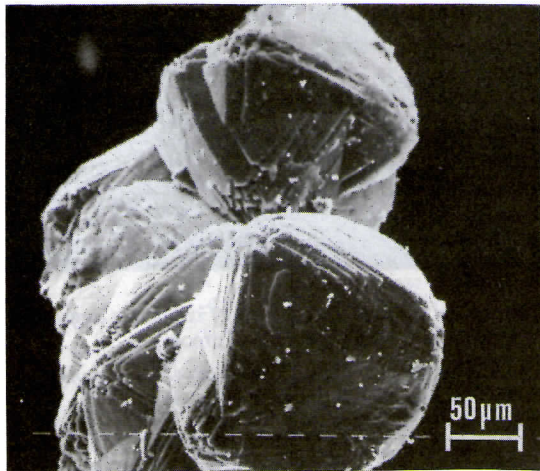
Chemistry

Electron microprobe analyses of katoite were carried out in the wavelength dispersive mode on an ARL-SEMQ instrument operated at 15 kV, 20 nA probe current with on-line data reduction by the ZAF correction method (MAGIC IV ; Colby, 1968) using natural garnet (Si, Al), clinopyroxene (Ca, Mg) and barite (S) as standards. Qualitative spectral scans excluded the presence of appreciable amounts of Fe, Cr, Ti, Mn, Sr, Ba, K, and Na. The chemical composition (Table II), was obtained by averaging eight point-analyses on a transparent crystal with per-

a)

c)

b)

Fig. 3. — *Scanning electron micrographs of katoite ;*
a) columnar aggregate of figure 2 revealing the oc-
tahedral morphology of the crystals ; *b)* growth pat-
tern of octahedral crystals ; *c)* perfect morphology
of isolated crystal.

Microphotographies au M.E.B. de la katoïte ;
a) aggrégats en colonnes de la figure 2 révélant la
morphologie octaédrique des cristaux ; *b)* figures de
croissance dans les cristaux octaédriques ; *c)* mor-
phologie parfaite d'un cristal isolé.

Chemical composition		Atomic ratios	
SiO_2	10.58	Si	0.69
Al_2O_3	24.01	Al	1.85
CaO	42.27	Ca	2.96
MgO	0.07	Mg	0.01
SO_3	2.27	S	0.11
H_2O	20.80	H	9.07
		O	12.00
Tot.	100.00		

Unit formula:

$Ca_{2.96}(Al_{1.85}Mg_{.01})_{\Sigma=1.86}(Si_{.69}S_{.11})_{\Sigma=.80}O_{2.93}(OH)_{9.07}$

$\underline{a}(Å) = 12.358(2)$; Volume$(Å^3) = 1887(1)$; Space group Ia3d

Gr% = 26.67 ; Z = 8 ; n = 1.632 ; $D_{calc.} = 2.76$

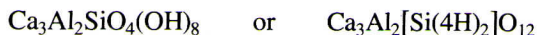TABLE II. — *Chemical, crystallographic and physical*
data of katoite.

Données chimiques, physiques et cristallographi-
ques de la katoïte.

fect octahedral morphology which had been
used for X-ray data collection in the crystal
structure determination (Sacerdoti & Passaglia,
1984). Several microprobe analyses carried out
on various other crystals, both transparent and
opalescent yielded chemical compositions within
the experimental uncertainty (2-3 % relative)
when compared with the analysis reported in
table II.

The total H_2O content, obtained by TG analy-
sis as total weight loss at 750 °C (20.8 %), was
used to normalize the microprobe data to 100 %
due to the undeterminate loss of water caused by
electron bombardment in the vacuum of the ins-
trument ; the total correction thus applied was
less than 1 %. A small slow reaction occurring
between 750 °C and 900 °C in the TG experi-
ment can be ascribed to the volatilization of S in

the form of SO_3. The corresponding weight per-
cent loss is in good agreement with the amount
of S determined in the microprobe analysis ;
only the latter, being more reliable, is reported
in table II.

The empirical formula (on the basis of 12
oxygens) obtained from the chemical composi-
tion is :

$$Ca_{2.96}(Al_{1.85}Mg_{0.01})_{\Sigma=1.86}$$
$$(Si_{0.69}S_{0.11})_{\Sigma=0.80}O_{2.93}(OH)_{9.07}$$
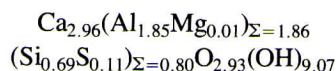
which nearly corresponds to the idealized formulae :

$$Ca_3Al_2SiO_4(OH)_8 \quad \text{or} \quad Ca_3Al_2[Si(4H)_2]O_{12}$$

The second formula emphasizes the fact that in the structure of katoite only one third (or even less) of the tetrahedra are centered by Si ; 4H are present in the other two thirds of the tetrahedral cavities.

The appreciable amount of S replacing Si in the tetrahedra has so far not been reported for hydrogrossulars although it can easily be accounted for on the basis of crystallochemical considerations and, in the case of katoite, also as a result of its genetic environment as shown by the presence of sulphate minerals (ettringite and gypsum) among the hydrothermal phases identified at the same locality.

Thermal analysis

The TG curve of katoite was obtained on 1.49 mg of powdered pure material (obtained by hand picking only clear crystals under the microscope) using a Du Pont thermal analyzer operating in air with a heating rate of 10 °C/min. The curve (Figure 4) shows a slow gradual loss from 50 °C to 270 °C approximately corresponding to 7 % in weight. Starting at 270 °C a faster reaction brings the total loss at 580 °C to 20.80 % ; from 580 to 750 °C no appreciable weight loss occurs. From 750 °C to the final temperature of the experiment (900 °C) there is a further slow weight loss which can be ascribed to the volatilization of S in the form of SO_3, in agreement with the amount of S from the microprobe analysis.

TG curves of typical compounds of the hydrogrossular group have been reported in the literature only for hibschite from Nikortzminda and for synthetic $Ca_3Al_2(OH)_{12}$ (Zabinski, 1966). Both curves are reported in figure 4 together with the curve obtained for katoite. Hibschite shows a slow and slight loss ($\sim$ 2.5 %) up to 600 °C followed by two fairly fast reactions in the temperature intervals of 600-750 °C (2.5 % of loss) and 750-900 °C (2 % of loss) respectively. The synthetic compound has a first loss ($\sim$ 4 %) before 250 °C followed by a very fast ma-
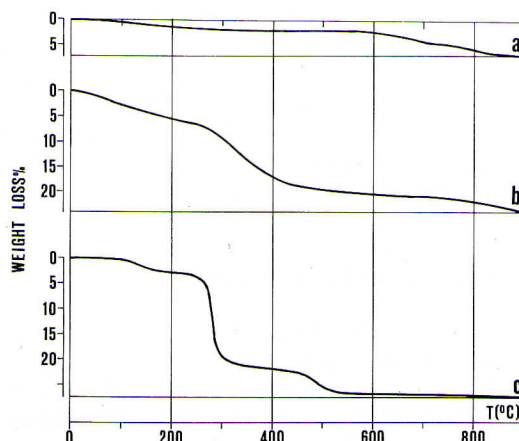

FIG. 4. — *TG curve of katoite (b) compared with those of hibschite from Nikortzminda (a) and the synthetic compound $Ca_3Al_2(OH)_{12}$ (c) (the last two after Zabinski, 1966).*

Courbe ATG de la katoïte (b) par comparaison avec celle de l'hibschite de Nikortzminda (a) et du composé synthétique $Ca_3Al_2(OH)_{12}$ (c) (les deux dernières d'après Zabinski, 1966).

jor loss ($\sim$ 17 %) between 250 °C and 310 °C and by another fast although much smaller loss between 450 °C and 550 °C. By comparing the three curves in figure 4, one may note that all three compounds have a first slow loss which persists up to 650 °C in hibschite and up to 250 °C in katoite and the synthetic compound followed by a faster and larger loss due to OH release. In hibschite and the synthetic compound this release of OH groups occurs in two consecutive steps whereas in katoite it occurs in only one step although over a larger temperature interval which in fact is comparable with that comprising the two above mentioned steps.

Yoder (1950) found a dependence of the amount of energy required to drive out the OH groups on the percentage of silicon present in the compounds. As "amount of energy" he assumed the temperature corresponding to that of the first major endothermic peak in the DTA curve which nearly corresponds to the final temperature of the first major weight loss in the TG curve. In the light of this assumption, the "amount of energy" pertaining to katoite (26.7 Gr%) corresponds to a temperature of about 500 °C which, when compared with that of

350 °C for the synthetic compound (0 Gr%) and that of about 720 °C for hibschite (66 Gr%), is in good agreement with its silicon content. Therefore the thermal behaviour of katoite confirms Yoder's (1950) hypothesis that the greater the percentage of silicon present, the more tightly the hydroxyl groups are held.

X-Ray data and physical properties

Single crystal X-ray diffraction (Ni-filtered CuKα) measurements (Sacerdoti & Passaglia, 1984) on the octahedral crystal used for both microprobe analysis and structure determination, gave $a = 12.379$ Å and space group $Ia3d$. The X-ray powder pattern of katoite (Table III) was obtained with Ni-filtered CuKα$_1$ radiation ($\lambda = 1.54051$ Å) and $Pb(NO_3)_2$ as an internal standard on a Philips diffractometer ; least squares refinement of the lines indexed on the basis of space group $Ia3d$ yielded $a = 12.358(2)$ Å. In table III the X-ray powder diffraction data of katoite are compared with those reported for grossular (JCPDS card no. 26-293), hibschite from Marienberg (Pabst, 1942 ; JCPDS card no. 4-723), plazolite from Crestmore (Pabst, 1937 ; JCPDS card no. 3-801) and the synthetic compound $Ca_3Al_2(OH)_{12}$ (JCPDS card no. 24-217). The katoite pattern is very similar to that of the synthetic compound $Ca_3Al_2(OH)_{12}$ as regards both the number and spacings of the diffraction planes d_{hkl}. Furthermore, by comparing the patterns in table III one may observe that a decrease of Gr% (or conversely an increase of OH content), corresponds to an almost uniform increase of the d_{hkl} spacings (which in turn corresponds to a cell edge increase from 11.850 to 12.573 Å) and to the progressive appearance of the 211, 321 and 220 diffraction lines, in that order. This last effect confirms the gradual decrease of the intensities of low angle reflections with increasing Si content in the series as already pointed out by Pabst (1937, 1942) for plazolite and hibschite from Marienberg and by Roy & Roy (1960) and Flint et al. (1941) for the synthetic terms.

The presence of the 220 line in the X-ray powder pattern of hibschite from Nikortzminda (66 Gr%) as reported by Zabinski (1966) would seem to contradict the data reported in table III. However, the intensity of the 220 reflections becomes stronger with increasing Fe content (Zur

Sample	Grossular		Hibschite		Plazolite		Katoite		Synthetic	
Gr%	100		.72*		60.67		26.67		0	
a(Å)	11.850		12.02**		12.16**		12.358		12.5727	
h k l	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
2 1 1	—		4.89	5	4.96	40	5.046	37	5.13	90
2 2 0	—		—		—		4.369	21	4.442	40
3 2 1	—		—		3.25	40	3.303	32	3.358	55
4 0 0	2.959	25	3.00	80	3.03	80	3.089	50	3.142	45
4 2 0	2.647	100	2.68	100	2.71	100	2.763	100	2.810	80
3 3 2	2.524	11	2.57	20	2.60	20	2.636	12	2.680	6
4 2 2	2.417	20	2.46	50	2.48	60	2.518	21	2.566	15
5 1 0 / 4 3 1	2.321	18	2.36	40	2.38	60	2.424	22	2.465	30
5 2 1	2.162	17	2.19	50	2.21	80	2.257	58	2.295	100
4 4 0	2.093	4	2.12	5	2.14	20	2.187	5	2.222	4
6 1 1 / 5 3 2	1.921	25	1.95	60	1.97	80	2.004	58	2.039	95
6 2 0	1.872	2	1.89	5	1.92	20	1.956	5	1.989	8
6 3 1	—		—		—		—		1.8536	1
4 4 4	1.710	17	1.73	50	1.76	50	1.7833	10	1.8148	10
5 4 3	—		—		—		—		1.7785	2
6 4 0	1.643	25	1.66	60	1.68	80	1.7134	29	1.7437	40
7 2 1	1.612	2	—		—		1.6814	11	1.7111	20
6 4 2	1.581	50	1.61	80	1.62	100	1.6507	37	1.6800	50
7 3 2 / 6 5 1	1.504	2	—		—		1.569B	2	1.5964	11
8 0 0	1.481	10	1.50	50	1.52	50	1.5457	10	1.5715	13
7 4 1	1.458	2	—		—		—		1.5478	1
8 2 0	—		—		—		—		1.5249	1
6 5 3	1.417	1	—		—		—		1.5030	2
6 6 0	—		—		—		—		1.4818	3
8 3 1	—		—		—		—		1.4616	1
7 5 2	—		—		—		—		1.4243	1
8 4 0	1.324	10	1.35	50	1.36	60	1.3823	8	1.4058	12

* Calculated value, see text.

** Derived from the original Kx units.

Grossular from Georgetown, JCPDS card 26-293; hibschite from Marienberg, JCPDS card 4-723; plazolite from Crestmore, JCPDS card 3-801; Synthetic $Ca_3Al_2(OH)_{12}$, JCPDS card 24-217.

TABLE III. — *X-ray powder patterns of members of the $Ca_3Al_2(SiO_4)_3$-$Ca_3Al_2(OH)_{12}$ solid solution series.*

Diagrammes de poudre des termes de la solution solide $Ca_3Al_2(SiO_4)_3$-$Ca_3Al_2(OH)_{12}$.

Strassen, 1958), it is present in hydrougrandite (Tsao Yung-Lung, 1964), and therefore its presence in hibschite from Nikortzminda is probably due to the appreciable Fe content (3.7 wt.% Fe_2O_3) of this sample.

On account of its d_{hkl} spacings (hence its cell edge) and the absence of the 220 and 321 reflections, hibschite from Marienberg is appreciably less hydrated than plazolite.

Under the polarizing microscope katoite crystals are colourless and free from inclusions. A very weak and diffuse birefringence may be observed with crossed polars as already observed

by Yoder (1950) in synthetic crystals and by Pabst (1942) and Hutton (1943) in natural ones. The refractive index, determined by the Becke line method, is $n = 1.632(1)$.

Due to the extremely small dimensions of the crystals no experimental determination of the specific gravity could be obtained ; the calculated value is 2.76.

The compatibility among the refractive index, density, and chemical data based on the Gladstone-Dale relationship and expressed by the value of $1-(K_p/K_c)$ using Mandarino's (1976) K coefficients, yielded a value of 0.024 which, according to Mandarino (1979), represents an excellent degree of compatibility.

Infrared absorption analysis

The infrared absorption spectrum of katoite, obtained with a Perkin Elmer model 700 spectrophotometer with the KBr pellet method, is reported in figure 5 for the frequency intervals between 550 and 1250 cm^{-1} and between 3100 and 3900 cm^{-1}. The IR spectrum is best interpreted by comparison with those reported, in the same figure, for anhydrous grossular (a), hibschite (b), and synthetic $Ca_3Al_2(OH)_{12}$ (c) (Zabinski, 1966). Cohen-Addad *et al.* (1967) report an analogous IR spectrum for the synthetic $Ca_3Al_2(OH)_{12}$.

In the range between 550 and 1250 cm^{-1} the strong bands at 840, 860 and 915 cm^{-1} of the anhydrous grossular corresponding to the Si-O stretching modes (Zabinski, 1966 ; Farmer, 1974), become weaker and more diffuse with decreasing Si content going from hibschite to katoite, to synthetic $Ca_3Al_2(OH)_{12}$. The decrease in Gr% is responsible for two more changes in this spectral region ; the appearance of a new weak band at approximately 1100 cm^{-1} and the gradual reduction of the band at 618 cm^{-1} which is strong and sharp in grossular, weak and shifted towards lower wave numbers in hibschite and absent in both katoite and the synthetic compound. This last effect therefore seems to be particularly sensitive to the $(OH)_4 \rightleftharpoons (SiO_4)$ substitution as already noted by Zabinski (1966).

In the region between 3100 and 3900 cm^{-1} which includes the OH stretching modes (Zabinski, 1966 ; Cohen-Addad *et al.*, 1967), the
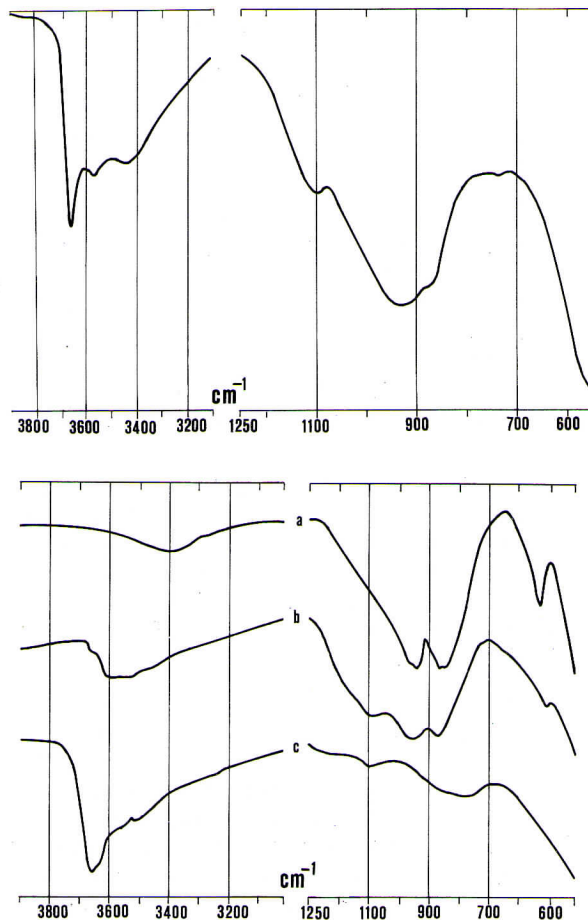

FIG. 5. — *Infrared absorption spectra of katoite (top) and other members of the $Ca_3Al_2(SiO_4)_3$-$Ca_3Al_2(OH)_{12}$ solid solution series (bottom) ; a) anhydrous grossular ; b) hibschite from Nikortzminda ; c) synthetic $Ca_3Al_2(OH)_{12}$ (the last three after Zabinski, 1966).*

Spectres infrarouges de la katoïte (haut) et d'autres termes de la série $Ca_3Al_2(SiO_4)_3$-$Ca_3Al_2(OH)_{12}$ (bas) ; a) grossulaire ; b) hibschite de Nikortzminda ; c) $Ca_3Al_2(OH)_{12}$ synthétique (les trois dernières d'après Zabinski, 1966).

anhydrous grossular shows a weak and very broad band with a maximum at about 3400 cm^{-1} whereas hibschite shows two diffuse bands at 3660-3670 and 3620-3630 cm^{-1}. Katoite, much like the synthetic compound, shows a complex band with a sharp and strong maximum at about 3650 cm^{-1}.

Kobayashi and Shoji (1983), in their IR study

of six samples of the grossular-hydrogrossular series hydrothermally synthesized, also observed the strong dependence of the absorption bands occurring at approximately 620 cm^{-1} and in the region between 3620 and 3670 cm^{-1} on the degree of $(OH)_4 \rightleftharpoons (SiO_4)$ substitution.

The infrared spectrum of katoite has therefore intermediate features between those of grossular and synthetic $Ca_3Al_2(OH)_{12}$ in the (Si-O) stretching region, and it is almost identical to that of the synthetic compound in the OH stretching region.

DISCUSSION AND NOMENCLATURE

Among the natural terms (hibschite, plazolite, hydrogrossulars, etc., see table I) of the $Ca_3Al_2(SiO_4)_3$ (grossular) - $Ca_3Al_2(OH)_{12}$ (synthetic phase) solid solution series, katoite with the schematic formula $Ca_3Al_2(SiO_4)(OH)_8$ represents the first natural occurrence of a term with a Gr content less than 50 % (Figure 1).

The existence of a complete isomorphous series between the two end-members with $SiO_4 \rightleftharpoons$ $(OH)_4$ (or $Si \rightleftharpoons 4H$) substitutions, had already been inferred from laboratory experiments (Flint et al., 1941). On the other hand Shoji (1974), from similar synthesis experiments in the series, pointed out the existence of a miscibility gap between 33.3 and 13.3 Gr%. The finding of katoite (26.6 Gr%) clearly contradicts, at least in nature, this latter hypothesis and confirms the existence of a complete solid solution. Furthermore, the statements of Yoder (1950) and Zabinski (1966) who considered plazolite $Ca_3Al_2(SiO_4)_2(OH)_4$ the most hydrated term to be found in nature, must now be revised and natural occurrences of terms even more hydrated than katoite may be expected.

The crystallographic and physical properties of katoite are in very good agreement with its chemical composition and confirm the strong dependence of these parameters on the degree of $(OH)_4 \rightleftharpoons (SiO_4)$ substitution in the isomorphous series. A clear indication of this can be obtained by the two diagrams of figures 6 and 7 where the Gr percentages are plotted against the unit cell edge and refractive index respectively. On account of the increase of both unit cell and refractive index with the substitution of Al by Fe^{3+} (Flint et al., 1941), the samples of table I with a

total Fe content (as Fe_2O_3) greater than 5 wt.% were not reported in these diagrams. The same criterion applies to the synthetic terms reported by Flint et al. (1941).

In figure 6 (Gr% vs a) two points are reported for plazolite according to the data quoted by Pabst (1942) and Basso et al. (1983). Most points occur in the vicinity of the line joining the two end-members, the larger deviations corresponding to hydrogrossular from Ayrshire (Bloxam, 1964) and hibschite from Bug River (Nalivkina, 1960). The deviations of the "jade" samples can, at least in part, be attributed to the poor quality of their chemical data (see Introduction).
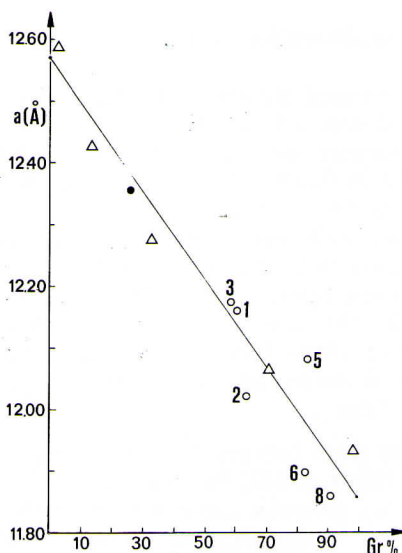

FIG. 6. — Gr% vs unit cell edge for members of the $Ca_3Al_2(SiO_4)_3$-$Ca_3Al_2(OH)_{12}$ solid solution series. Filled circle : katoite ; open circles : natural members (numbers refer to table I) ; triangles : synthetic members (Flint et al., 1941). The straight line joins the value given by Skinner (1956) for grossular with that reported on JCPDS card 24-217 for synthetic $Ca_3Al_2(OH)_{12}$.

Variation de la maille élémentaire en fonction de Gr% pour les termes de la solution solide $Ca_3Al_2(SiO_4)_3$-$Ca_3Al_2(OH)_{12}$. Cercle noir : katoïte ; cercles vides : termes naturels (numérotation du tableau I) ; triangles : termes synthétiques (d'après Flint et al., 1941). La ligne réunit la valeur donnée par Skinner (1956) pour le grossulaire à celle de la fiche JCPDS N. 24-217 pour $Ca_3Al_2(OH)_{12}$ synthétique.

In figure 7 (Gr% vs n) all the experimental points plot in the vicinity of the straight line joining the two end-members, the refractive indices of which were calculated by McConnell (1964). This confirms the close dependence of the refractive index on the Si content.
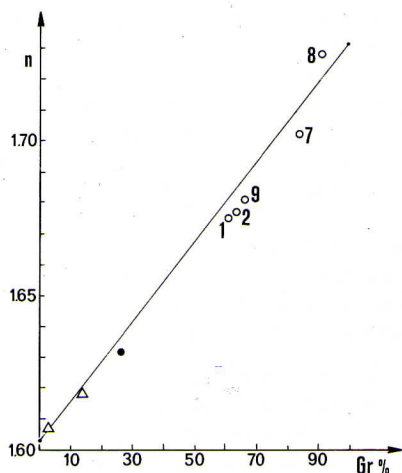

FIG. 7. — *Gr% vs refractive index for members of the* $Ca_3Al_2(SiO_4)_3$-$Ca_3Al_2(OH)_{12}$ *solid solution series.* Filled circle : katoite ; open circles : natural members (numbers refer to table I) ; triangles : synthetic members (Flint *et al.*, 1941). The straight line joins the points corresponding to the theoretical values of the two end-members as calculated by McConnell (1964).

Variation de l'indice de réfraction en fonction de Gr% pour les termes de la solution solide $Ca_3Al_2(SiO_4)_3$-$Ca_3Al_2(OH)_{12}$. Mêmes symboles que sur la figure 6. La droite réunit les points correspondant aux valeurs théoriques des deux extrêmes, selon McConnell (1964).

A progressive decrease of density with the Si content has also been reported in the literature (Yoder, 1950 ; Zabinski, 1966) however this correlation was not considered here because of the lack of experimental values for the most representative samples of the series (hibschite, plazolite, katoite).

The close dependence of both cell edge and refractive index on the Gr% (or conversely the OH content), can be expected to provide a fairly accurate method for estimating the Gr% of the holotype hibschite from Marienberg for which only very approximate chemical data are available (Cornu, 1906). By plotting its cell edge

(12.02 Å) and refractive index (1.69) as obtained by Pabst (1942) on the straight lines of the diagrams of figures 6 and 7, one obtains Gr percentages of 76 and 68 respectively from which one may conclude that a fairly accurate value for this sample is 72 Gr%.

Katoite is hence the first natural occurrence with more than half its tetrahedral cavities occupied by 4H instead of Si (Si < 1.5 per formula unit).

Distinguishing features of katoite, when compared with other terms of the natural series are : the presence of the 220 powder diffraction at about $d = 4.37$ Å ; the complete dehydration (and destruction of the crystal structure) at about 600 °C as shown by the TG curve in figure 4 ; the lack of the absorption band at approximately 600 cm^{-1} and the simultaneous presence of a strong and narrow band at about 3650 cm^{-1} in the infrared spectrum (Figure 5).

As in an isomorphous mineral series the discriminant value of 50 % of one or the other of the two components must be utilized to distinguish between the two fields of existence, which in turn, must be identified with different names, the approval of the new mineral and mineral name led us to propose a new nomenclature for the whole series.

The name *grossular* must obviously be retained for the anhydrous end member (100 Gr%).

For members of the series with more than 50 Gr% (*i.e.* $50 \leqslant$ Gr% < 100) the name *hibschite* has priority over all other names later introduced (plazolite, grossularoid, hydrogarnet, garnetoid, and hydrogrossular ; see Introduction) and although its chemical characterization is still somewhat unsatisfactory, the original description is certainly adequate for a sure identification of the mineral.

The name *katoite* should be adopted to represent all members with Gr% less than 50, including the $Ca_3Al_2(OH)_{12}$ end-member (*i.e.* $0 \leqslant$ Gr% < 50).

The name *hydrogrossular*, being reminiscent of the crystal chemical properties of the whole group of minerals and owing to its widespread usage, is the most appropriate as a group name covering both hibschite and katoite and is to be used for members of the series with appreciable

OH content but with an indetermined $SiO_4/(OH)_4$ ratio.

This new nomenclature has been approved by the appropriate Commission of the International Mineralogical Association.

The distinctive crystal physical properties of the katoite members with respect to those of the hibschite members are :
1. refractive index lower than 1.67 ;
2. unit cell edge larger than 12.21 Å ;
3. presence of the 220 line in the X-ray powder pattern.

The above reported discriminant values for the cell parameter and refractive index are derived from the diagrams of figures 6 and 7 respectively and must be regarded as merely indicative ; more reliable values will have to be derived from experimental data on other members of the series as they become available.

GENESIS

According to Zabinski (1966), most natural "hydrogarnets" were recorded in the following geological environments : a) in calc-silicate rocks formed as a result of metamorphism of marls or marly limestones at the contact with magmatic intrusions ; and b) as hydrothermal alteration products of basic igneous rocks. Hydrogarnet crystals from the first type of environment are characterized by their small size, euhedral shape, and higher OH content. On account of both its genetic environment and crystal features (small, 0.1-0.3 mm, euhedral octahedral crystals, high OH content) katoite clearly belongs to this type of occurrence.

Laboratory investigations on natural and synthetic "hydrogarnets" (Flint et al., 1941 ; Yoder, 1950 ; Roy & Roy, 1957 ; Pistorius & Kennedy, 1960) indicated a high water pressure and a moderate temperature as the essential factors favouring the crystallization of hydrogrossulars from a hydrothermal solution rich in SiO_2, Al_2O_3 and H_2O where the ratio of SiO_2 to Al_2O_3 and CaO is smaller than that found in grossular. Yoder's (1950) work also showed that, above 1 kbar, the (OH) content is virtually unaffected by water pressure whereas it increases (and hence the Si content decreases) in response to a decreasing temperature of crystallization. The

same conditions were verified by Shoji (1974). For members with approximately the same composition as plazolite, Yoder (1950) and Roy & Roy (1957) evaluated a crystallization temperature of 300-400 °C ; therefore the crystallization temperature of katoite must be approximately 300 °C. This relatively low temperature associated with a relatively high water pressure is clearly responsible for the low Si content of katoite. The hydrothermal solution from which katoite crystallized was certainly rich in Si as revealed by the paragenetic sequence of crystallization which consists of : tobermorite (hydrated calcium silicate), katoite, and afwillite (hydrated calcium silicate). The Si content of the solution was most probably exhausted with the crystallization of afwillite as testified by the successive and final growth of hydrocalumite (a hydrated calcium aluminate).

The strong dependence of the OH content on the temperature could also explain the existence of crystals with different $SiO_2/(OH)_4$ ratios in the same sample. The slight differences observed in analyzing different crystals of katoite could therefore be real and not solely due to experimental bias.

ACKNOWLEDGEMENTS

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