

HYDROXYELLESTADITE, A NEW APATITE FROM
CHICHIBU MINE, SAITAMA PREFECTURE, JAPAN

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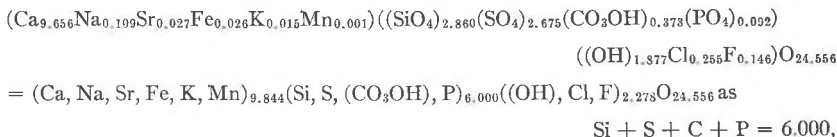
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ABSTRACT

Chemical analysis by K.N. and K.N. gave CaO 54.51, MgO, trace, MnO 0.04, SrO 0.28, Na₂O, 0.34, K₂O 0.07, CO₂ 1.65, P₂O₅ 0.66, SiO₂ 17.30, SO₃ 21.56, Al₂O₃ trace, Fe₂O₃ 0.21, F 0.28, Cl 0.91, H₂O⁺ 2.04, H₂O⁻ 0.72, -O=F₂, Cl₂ 0.32, total 100.25, corresponding to



or ideally Ca₁₀((SiO₄)₃(SO₄)₃)(OH, Cl, F)₂ with OH > Cl, F. This is the OH analogue of ellestadite, which has Cl > OH, F. X-ray powder data as well as precession photographs showed it to be hexagonal, with space group C_{6h}²-P6₃/m, with *a* 9.491 Å, *c* 6.921 Å (both ± 0.001 Å), and *Z* = 1. Synthetic Ca₁₀((SiO₄)₃(SO₄)₃)(OH)₂ has *a* 9.484, *c* 6.927 (Takemoto and Kato, 1968). The strongest lines are 3.462(40)(0002), 2.839(100)(21.1), 2.801(44)(11.2), 2.739(60)(30.1), 2.655(45)(20.2), 1.853(43)(21.3), 1.484(20)(50.2). Optically hydroxyl-ellestadite is uniaxially negative, with *ε* 1.650 and *ω* 1.654 (both ± 0.001). DTA, TGA, and IR data are given.

Mineral data and modes of occurrences of pale rose-pink wilkeite from Takiue as well as of yellowish green OH-Cl-F-apatite from Uzunosawa, both in the Chichibu Mining Area, are also described.

INTRODUCTION

Ellestadite, silicate-sulfate apatite, was first described by McConnell (1937 and 1938) as one of the skarn minerals from Crestmore, Riverside County, California, where the rose-pink or orange ellestadite was associated with diopside, wollastonite, idocrase, monticellite, okenite, and blue calcite. Although there are some related minerals, such as silicate-sulfate bearing Permian phosphorites from the western United States

(Gulbrandsen, 1966; Gulbrandsen *et al.*, 1966), and a sulfate apatite from the Nadezhnoe Mine, Kurung Khonku, USSR (Vasil'eva *et al.*, 1958), Crestmore is the only reported locality for ellestadite. Hydroxyllelestadite and F-ellestadite have been synthesized by Dihn and Klement (1942). Takemoto and Kato (1968) also synthesized hydroxyllelestadite in the system $\text{CaO-SiO}_2\text{-CaSO}_4$ at 235°C , under attendant pressures of water vapor, together with portlandite, hillebrandite, xonotlite, and anhydrite. During the course of mineralogical studies of the Doshinkubo ore deposit of Chichibu mine in 1961, Harada found a purplish mass of unidentified mineral among the pre-ore skarn minerals of zone 3 (Harada, 1962; and Harada *et al.*, 1965) in association with diopside, wollastonite, xanthophyllite, idocrase, and white calcite. Later Mr. Takaharu Imayoshi of the National Science Museum, Tokyo, also found a rose pink mass of unidentified mineral in the pre-ore skarn associated with idocrase and pale-blue calcite from Takiué in the Chichibu mining area. Chemical analyses, infrared absorption spectra, and X-ray powder data confirmed that the Doshinkubo mineral is the OH analogue of ellestadite and that the Takiué mineral is wilkeite. The modes of occurrences of the Chichibu hydroxyllelestadite and the wilkeite are quite similar to those from the type locality (McConnell, 1937). Aluminum-deficient and sulfate-saturated conditions may promote the formation of ellestadite or wilkeite instead of scapolite which contains aluminium as well as sulfate. It should be noted that no scapolite is found in the Chichibu mining area.

Recently, apatites and related substances have attracted the interest of many investigators because of their complex chemical compositions and wide ionic substitutions. Thus, detailed chemical analyses of the hydroxyllelestadite and wilkeite should be of value. This report contains various data, including chemical compositions, for the hydroxyllelestadite, wilkeite, and a yellowish-green OH-Cl-F-apatite found in the skarn at Uzunosawa, in the Chichibu mine, associated with magnetite, chlorite, tremolite, and calcite. Chichibu hydroxyllelestadite is the OH analogue of ellestadite, which has $\text{Cl} > \text{OH}$, F.

PHYSICAL AND OPTICAL PROPERTIES

Chichibu hydroxyllelestadite is translucent pale purplish with vitreous luster. Cleavable aggregates up to 100 kg occur and individual cleavage pieces are up to 2 cm along the *c* axes. All specimens are anhedral. The hardness (Table 1) is slightly less than that of normal apatite. The specific gravity determined by a 2 ml pycnometer at 20°C (Table 1) is in good agreement with the calculated value derived from chemical analysis and unit-cell data. Refractive indices determined by

TABLE 1. CHEMICAL COMPOSITIONS AND PHYSICAL PROPERTIES OF OH-ELLESTADITE, WILKEITE AND A OH-Cl-F-APATITE

	1	2	3	4
CaO	55.18	54.51	52.69	53.58
MgO	0.47	trace	trace	trace
MnO	0.01	0.04	0.05	0.05
SrO	-	0.28	0.86	0.55
Na ₂ O	-	0.34	0.06	0.11
K ₂ O	-	0.07	0.06	0.06
CO ₂	0.61	1.65	2.18	none
P ₂ O ₅	3.06	0.66	15.90	40.62
SiO ₂	17.31	17.30	11.99	0.64
SO ₃	20.69	21.56	13.47	trace
Al ₂ O ₃	0.13	trace	trace	trace
Fe ₂ O ₃	0.22	0.21	0.29	0.26
F	0.57	0.28	0.43	1.08
Cl	1.64	0.91	1.44	2.38
H ₂ O ⁺	0.53	2.04	0.36	0.70
H ₂ O ⁻	0.10	0.72	0.29	0.19
Total	100.52	100.57	100.07	100.22
Less O	0.61	0.32	0.50	0.99
Total	99.91	100.25	99.57	99.23
Hardness (Mohs)		4.5	-	5
S.G.(obs.)	3.068	3.01 ₈	3.07 ₁	3.14 ₂
S.G.(calc.)	3.046	3.080(ca.)	-	3.199(ca.)
ω	1.655(±0.002)	1.654(±0.001)	1.652(±0.001)	1.650(±0.001)
ϵ	1.650(±0.002)	1.650(±0.001)	1.649(±0.001)	1.648(±0.001)
$\omega-\epsilon$	0.005	0.004	0.003	0.002
$\frac{a}{c}$	9.53(±0.01)	9.491(±0.001)	9.510(±0.001)	9.490(±0.001)
$\frac{c}{a}$	6.91(±0.01)	6.921(±0.001)	6.897(±0.001)	6.851(±0.001)
$\frac{c}{a}$	0.7251	0.729	0.725	0.722
$\frac{V}{V}$	544	540	539	533

Note: 1. Original ellestadite from Crestmore, California (McConnell, 1937; Analyst, R. B. Ellestad), 2. OH-ellestadite from Doshinkubo (Present work; Analyst, Kazuso Nakao and Kozo Nagashima), 3. Wilkeite from Takiue (Present work; Analyst, Kazuso Nakao and Kozo Nagashima), 4. OH-Cl-F apatite from Uzunosawa (Present work; Analyst, Kazuso Nakao and Kozo Nagashima).

the immersion method at 20°C in sodium light are shown in Table 1; they agree well with ellestadite from the type locality (McConnell, 1937). The immersion media were checked with an Abbé refractometer using sodium light.

Takiué wilkeite is pale rose-pink and finely granular, forming compact aggregates less than 1 mm, contaminated with calcite. Physical properties of the mineral are listed in Table 1.

OH-Cl-F-apatite is yellowish-green and megascopically translucent, and generally massive up to 3 by 4 cm, sometimes showing prismatic forms 2 cm in maximum length. The prismatic cleavage of the OH-Cl-F-apatite is dominant. Physical properties of the apatite are also listed in Table 1.

Hydroxyllellestadite and wilkeite are rapidly soluble in cold dilute HCl (1N). After careful hand picking and washing with pure water, hydroxyllellestadite, wilkeite, and OH-Cl-F-apatite samples were ground to -60 mesh powder and immersed in tetrabromomethane of specific gravity 2.95 to remove contaminating materials. Purified samples thus obtained were initially tested by X ray as well as microscopically, then ground again to -200 mesh powder and used for the following studies.

X-RAY DATA

X-ray powder diffraction data for hydroxyllellestadite, wilkeite, and OH-Cl-F apatite are given in Table 2. All lines agree well with those of the usual apatite and no d spacing inconsistent with the space group of apatite $C_{6h}^{2}-P6_3/m$ was observed. This space group for the three apatites was confirmed also by precession photographs. Hexagonal lattice dimensions for the hydroxyllellestadite, wilkeite, and OH-Cl-F-apatite were determined by back-reflection photographs using filtered copper radiation (Table 1). Unit-cell data for the hydroxyllellestadite and wilkeite fit well with those given by McConnell (1937 and 1938) for natural ellestadite as well as those given by Takemoto and Kato (1968) for synthetic hydroxyllellestadite (a 9.48₄, c 6.92₇, and c/a 0.730). Data given by Dihn and Klement (1942) for both synthetic F- and hydroxyllellestadites are a 9.54, c 6.99, and c/a 0.732; these are somewhat larger. Unit-cell data for OH-Cl-F-apatite from Uzunowska are intermediate between F- and Cl-apatite end-members described by Walters and Luth (1969). X-ray powder data for hydroxyllellestadite and wilkeite are more detailed than those given by McConnell (1937 and 1938). The increase in c of the hydroxyllellestadite seems to be largely attributable to SiO_4 for PO_4 since F-apatite and OH-apatite are both about 6.88 Å for c . The effect of S seems to be very small for either a or c dimensions (McConnell, 1970; personal communications). The dimensions for hydroxyllellestadite, wilkeite, and OH-Cl-F-apatite fit well with the coefficients recently given by McConnell (1970).

CHEMICAL ANALYSES

Using 5 to 7 g purified samples chemical analyses were made, adopting the following procedures in which classical wet chemical techniques by Hillebrand *et al.* (1953) and the special methods for chemical analysis of apatite proposed by Cruft *et al.* (1965) were chiefly utilized:

TABLE 2. X-RAY DIFFRACTION POWDER FOR OH-ELLESTADITE, WILKEITE
 AND A OH-Cl-F-APATITE FROM THE CHICHIBU MINE¹

hk.l	1 Wilkeite (from Takiue)		2 OH-ellestadite (from Doshinkubo)		3 OH-Cl-F-apatite (from Uzunosawa)	
	d(obs.)	I d(calc.)	d(obs.)	I d(calc.)	d(obs.)	I
10.0	8.238	8 8.230	8.230	8 8.213	8.238	8
10.1	5.310	3 5.285	5.267	5 5.295	5.279	3
11.0	-	-	4.744	3 4.742	-	-
20.0	4.120	7 4.113	4.113	5 4.107	4.116	5
11.1	3.922	6 3.912	3.919	7 3.914	3.904	4
00.2	3.452	40 3.452	3.462	40 3.465	3.452	35
10.2	3.183	5 3.183	3.187	4 3.192	3.160	6
21.0	3.112	18 3.183	3.110	9 3.105	3.108	16
21.1	2.835	95 2.838	2.839	100 2.833	2.827	100
11.2	2.796	38 2.793	2.801	44 2.797	2.775	30
30.0	2.746	100 2.746	2.739	60 2.738	2.730	75
20.2	2.645	25 2.645	2.655	45 2.648	2.632	16
30.1	2.554	3 2.552	2.554	3 2.546	2.544	3
21.2	2.312	2 2.311	2.317	4 2.312	2.298	3
31.0	2.284	40 2.284	2.282	10 2.278	2.281	10
22.1	-	-	2.242	1 2.244	-	-
31.1	2.168	4 2.169	2.165	5 2.164	2.162	3
11.3	2.070	2 2.071	2.075	3 2.076	2.062	1
20.3	2.009	2 2.008	2.013	3 2.013	1.997	4
22.2	1.958	30 1.958	1.960	16 1.957	1.950	32
31.2	1.909	13 1.904	1.905	5 1.903	1.901	7
23.0	-	-	1.886	3 1.884	1.883	9
21.3	1.850	25 1.850	1.853	43 1.853	1.842	50
32.1	1.823	12 1.823	1.822	5 1.819	1.819	9
41.0	1.797	12 1.798	1.792	5 1.792	1.794	10
40.2	1.768	7 1.767	1.767	12 1.766	1.761	5
00.4	1.725	8 1.725	1.730	14 1.732	1.718	7
32.2	1.658	4 1.658	1.656	5 1.655	1.653	3
13.3	1.621	3 1.622	1.621	3 1.622	1.614	5
50.1	1.603	4 1.602	1.600	1 1.598	1.600	1
42.0	1.557	3 1.557	-	-	-	-
32.1	1.545	2 1.545	-	-	1.542	1
42.1	1.518	4 1.519	-	-	1.514	2
21.4	1.510	1 1.509	1.503	5	1.499	3
50.2	1.486	6 1.486	1.484	20	1.481	1
32.4	1.461	8 1.460	1.464	10	1.453	7
51.1	1.446	7 1.447	1.444	2	1.445	3
41.3	1.417	2 1.417	-	-	-	-

¹Data obtained using copper radiation with nickel filter.

Determination of P₂O₅. Apatite and wilkeite: After decomposition of the sample by sintering with sodium carbonate and following treatment with nitric acid to remove silica, phosphate was separated by precipitating with ammonium molybdate. The yellow precipitate was dissolved in ammonia solution, and after double precipitation by the addition of magnesia mixture, phosphate was weighed as Mg₂P₂O₇. *Hydroxyllelestadite:* A small amount of the sample was decomposed by treating with hydrofluoric, nitric, and perchloric acids, and dissolved in water. Phosphate was determined colorimetrically after the addition of sodium sulfite and a solution of ammonium molybdate and hydrazine sulfate.

Determination of SO_3 . Samples were dissolved in dilute hydrochloric acid, and sulfate was precipitated with barium chloride. The precipitate was purified with hydrofluoric and sulfuric acid; the insoluble residue was ignited and weighed as $BaSO_4$.

Determination of SiO_2 . Samples were sintered with sodium carbonate and acidified with hydrochloric acid. Aluminum chloride was added to mask fluoride ion, then the solution was evaporated to dryness. The separated silica was determined gravimetrically.

Determination of F . After sintering the sample with sodium carbonate, fluoride was separated by the steam-distillation from sulfuric acid solution containing silica powder. Fluoride was titrated with a standard thorium nitrate solution.

Determination of Cl . Samples were dissolved in dilute nitric acid, filtrated, and chloride was precipitated as silver chloride. The precipitate was dissolved in ammonium chloride-hydroxide solution, and potassium dicyanickelate was added to the solution. The librated nickel was titrated with a standard EDTA solution.

Determination of Al_2O_3 , CaO , and MgO . *Apatite:* The sample was fused with sodium carbonate after addition of a small amount of silica. It was acidified and evaporated to remove silica and fluoride. In order to precipitate the phosphate ion, zirconyl chloride was added to the acidic solution. After filtering, aluminium, iron, and remaining phosphate and zirconium were precipitated with ammonium hydroxide. Aluminium in the precipitate was determined as phosphate after the separation of iron and zirconium. To the filtrate from the ammonium hydroxide precipitation ammonium persulfate was added to precipitate manganese dioxide. Calcium was double precipitated with ammonium oxalate, ignited, and weighed as CaO . From the oxalate filtrate, magnesium was precipitated with ammonium phosphate, ignited, and weighed as $Mg_2P_2O_7$. Calcium was recovered from the ignited precipitate. *Hydroxyllellstadite and wilkeite:* Same as above. However, because of its low concentration, phosphate was separated by precipitating with excessive ferric ion from a slightly ammonical solution.

Determination of SrO , Na_2O , and K_2O . These metals were determined by flame photometry. Apatite was dissolved in dilute hydrochloric acid, whereas hydroxyllellstadite and wilkeite were decomposed by hydrofluoric and sulfuric acid treatment. Dilute hydrochloric acid solutions were used for the determination of sodium and potassium. To analyse for strontium, samples were fused with sodium carbonate, leached with water, and the residue was dissolved in dilute hydrochloric acid.

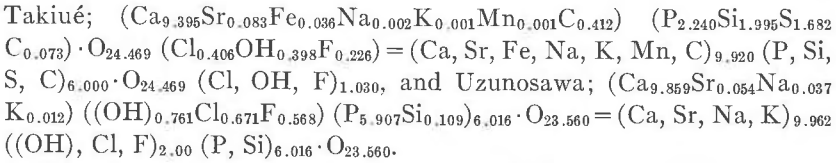
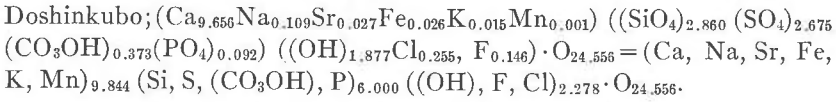
Determination of MnO and Fe_2O_3 . Standard spectrophotometric procedures were applied.

Determination of CO_2 . Carbonate dioxide was determined by evolution from hydrochloric acid and weighed on absorbants. Combustion method was also tried to make sure of the results.

Determination of $H_2O^{(+)}$. The Penfield method specially refined by Cruft *et al.* (1965) was adopted. The sample was decomposed using a flux for silica, lead chromate, and litharge, and the evolved water was collected in a long glass tube.

The results of the chemical analyses are given in Table 1. The structural formulae with $Si+S+C+P=6.000$ for the hydroxyllellstadite and

wilkeite, and OH+Cl+F = 2 for OH-Cl-F-apatite are represented below as:



Those formulae are in good agreement with ideal formulae of apatites. The hydroxyllestadite containing 0.66 percent of P₂O₅ is close to the ideal end composition of hydroxyllestadite. It should be noted that the hydroxyllestadite and the wilkeite contain some carbonate in the tetrahedral site as well as the 3-fold Ca site of these structures (McConnell, 1952, 1959; Walters *et al.*, 1969; and McClelland and Lehr, 1969). This fact is verified by the infrared absorption spectra. The OH-Cl-F-apatite is free from CO₂ as well as calcite. Hydroxyllestadite, wilkeite, and OH-Cl-F-apatite are free from contaminating calcite. Hydroxyllestadite, wilkeite, and OH-Cl-F-apatite contain large amounts of structural OH as was confirmed by DTA as well as infrared absorption spectra.

A most interesting situation results for the hydroxyllestadite: if, instead of taking summation of C, Si, S, and P as 6, one takes all cations to sum to 16. This yields:

<i>Given</i>		<i>Adjusted</i>
9.84	sites for Ca	9.94 plus 0.09 = 10.03 (incl. 1/4 of 0.38)
5.63	Tetrahedral	5.69 plus 0.29 = 5.98 (incl. 3/4 of 0.38)
0.37	Carbonate	0.38
<hr/>		
15.84		16.01 16.01

This calculation is consistent with the theory that one-fourth of the C atoms are displacing Ca on the 3-fold axes in such manner that three fourths of the C is additive to the tetrahedral sites whereas, one-fourth is additive to the Ca sites (McConnell, 1952, 1959, 1960, 1961, 1970, and personal communications). Also quite apparent is the summation of hydroxyls plus halogens to 2.64 versus 2.00 for the theoretical structure. This fits the theory recently advocated by McConnell (1970).

INFRARED ABSORPTION SPECTRA

Infrared absorption spectra for hydroxyllellestadite, wilkeite, and OH-Cl-F-apatite were obtained using a Hitachi EPI grating-type spectrophotometer and KBr disks. All specimens and KBr had been initially kept in a phosphorus pentoxide desiccator to eliminate absorbed water. The results are shown in Figure 1. Hydroxyllellestadite gives bands of absorption at 3600, 1470, 1420, 1140, 920, 845, 640, and 610 cm^{-1} . Wilkeite gives bands at 3500, 1470, 1420, 1140, 1040, 920, 845, 640, 610, 602, and 575 cm^{-1} . OH-Cl-F-apatite gives bands at 3550, 1090, 1040, 960, 602, and 575 cm^{-1} .

According to Gulbrandsen *et al.* (1966), Brophy *et al.* (1968), and Bhatnager (1968), the absorption bands, such as those we find at 1470 and 1420 in hydroxyllellestadite and wilkeite, do not originate from admixture of calcite but from CO_3^{2-} in the apatite structure. However, in our infrared absorption spectra for hydroxyllellestadite and wilkeite the

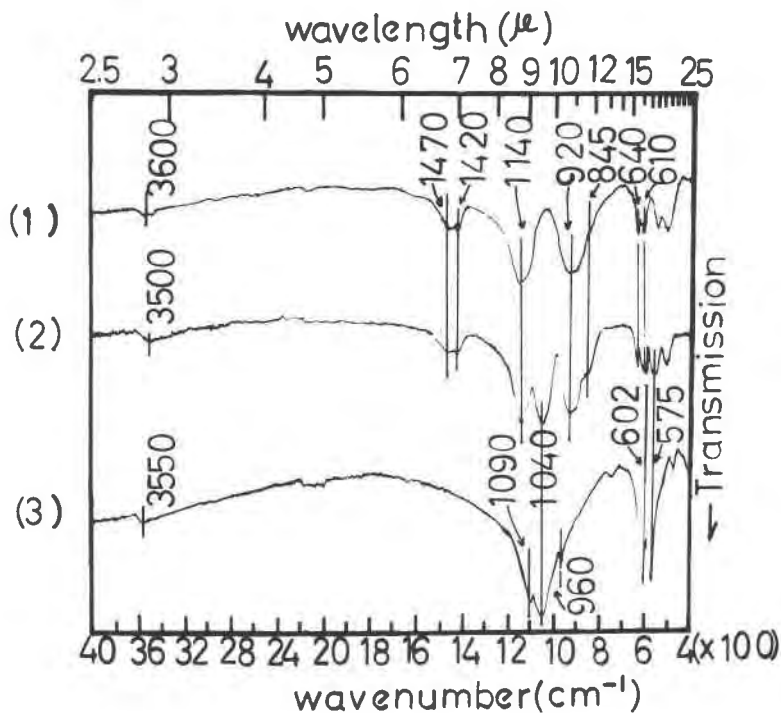


FIG. 1. Infrared absorption spectra of hydroxyllellestadite (1), wilkeite (2), and OH-Cl-F apatite (3).

splitting of the CO_3 band at 1400 cm^{-1} into two bands (1470 and 1420 cm^{-1}) is not as pronounced when compared with the carbonate-phosphate apatite (Gulbrandsen *et al.*, 1966). Hydroxylelestadite, wilkeite, and OH-Cl-F-apatite give bands at 3600 , 3500 , and 3550 cm^{-1} of OH origin. Bands at 1140 , 640 , 610 of hydroxylelestadite and wilkeite correspond to the stretching vibration of SO_4 according to the work on sulfate minerals by Omori (1968). The bands at 920 cm^{-1} and 845 cm^{-1} of hydroxylelestadite and wilkeite may be assigned to stretching vibrations of SiO_4 . The bands at 1090 , 1040 , 960 , 602 , and 575 cm^{-1} for OH-Cl-F-apatite and wilkeite are the stretching of PO_4 which agree well with the data by Alder (1964), Gulbrandsen *et al.* (1966), Bhatnager (1966), and Omori (1969). Thus, infrared absorption spectra for hydroxylelestadite, wilkeite, and normal OH-Cl-F-apatite are quite distinct. Hydroxylelestadite and wilkeite contain structurally bound CO_3 . Wilkeite, OH-Cl-F-apatite, and hydroxylelestadite are free from contamination by carbonate minerals.

DTA AND TGA DATA FOR APATITES AND HEAT TREATMENT OF HYDROXYLELESTADITE

DTA and TGA curves for hydroxylelestadite, wilkeite, and OH-Cl-F-apatite were made by the use of a Shimadzu automatic recorder; heating rate of $10^\circ\text{C}/\text{min.}$, reference junction at 0°C , Pt/Pt-13%Rh thermocouple, in an atmosphere of air. The results are shown in Figure 2. DTA of hydroxylelestadite gives endothermic peaks at 160° , 181° , 800° , and 1180°C and TGA gives a gradual loss of weight about 0.70 percent between 0° to 200°C , and 3.42 percent between 600° to 1300°C , probably due to partial escape of H_2O , SO_3 , and CO_3 . DTA of wilkeite gives endothermic peaks at 142° , 820° , and 1180°C . TGA gives a gradual loss of weight about 4.10 percent from 0° to 1300°C . DTA of OH-Cl-F-apatite is smooth with a weak exothermic peak at 1150°C . TGA of OH-Cl-F-apatite is also smooth and gives gradual loss of weight of about 0.60 percent from 600°C to 1300°C . X-ray powder diffractions of the hydroxylelestadite heated at 1200°C for 1 hour showed several strong anhydrite lines among weak unidentified peaks.

IONIC SUBSTITUTIONS IN SULFATE APATITES AND HYDROXYLELESTADITE

The general formula of ellestadite-wilkeite-apatite series can represent as;



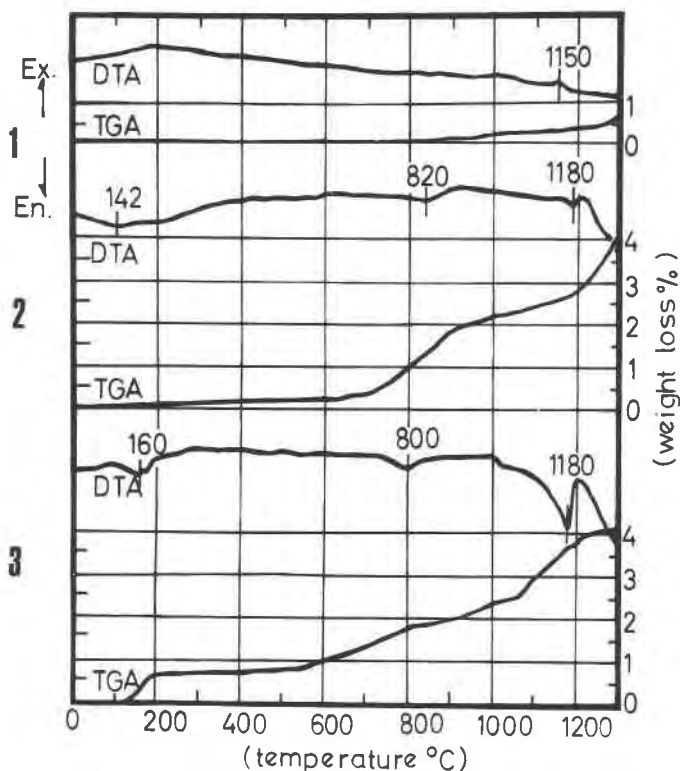


FIG. 2. DTA and TGA curves of OH-Cl-F apatite (1), wilkeite (2) and hydroxyllestadite (3).

In this case, S^{6+} for P^{5+} substitutions are compensated by the substitutions of Si^{4+} for P^{5+} , and complete solid solubility has been suggested (McConnell, 1937, 1938). Any Na^+ for Ca^{2+} substitution, which is found in silicate-free, sulfate-bearing apatite with the ideal formula $Na_3Ca_2S_3O_{12}$ (Cl, F, OH) (Vasil'eva *et al.*, 1958) has compensating S^{6+} for P^{5+} substitution. Such substitution has not been recognized in silicate-bearing ellestadite, wilkeite, and F-Cl-apatite solid-solution series. Thus, the name wilkeite (Eakle and Rogers, 1914) should have limited use in the intermediate minerals between ellestadite and apatite as a varietal name. The Chichibu hydroxyllestadite can be ideally written as $Ca_{10}((SiO_4)_3(SO_4)_3)(OH, Cl, F)_2$ with $OH > Cl, F$. This is the OH analogue of ellestadite in which $Cl > OH, F$. Accordingly, we propose the new mineral name hydroxyllestadite for the Chichibu OH-ellestadite.

This name was approved by the Commission on New Minerals and Mineral Names, IMA, before publication. The type material is preserved at National Science Museum, Ueno, Tokyo, Japan 110.

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Note added in proof. After submitting our paper, the following paper appeared: Cooray, P. G. (1969) A carbonate-bearing fluor-chlor-hydroxyapatite from Matale, Ceylon. *Amer. Mineral.* **55**, 2038-2041. This apatite is similar to the OH-Cl-F apatite from Uzunosawa described in the present report.