MONOCLINIC CHLORAPATITE FROM ONTARIO

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ABSTRACT

Chlorapatite, a new occurrence at Bob's Lake, southeastern Ontario, is monoclinic with space group $P2_1/a$ and unit cell dimensions $a = 19.210$ Å $(=2c)$, $b = 6.785$ Å, $c = 9.605$ Å, $\beta = 120°$. It is optically biaxial, negative, with $\alpha = 1.665$, $\gamma \sim \beta = 1.667$, $2V \simeq 10°$. $D_m = 3.181$, $D_x = 3.172$. The chemical formula based on 25 cationic charges is $Ca_{4.95}(PO_4)_{3.02}Cl_{0.91}OH_{0.05}F_{0.04}$. The transitional (hexagonal to monoclinic) composition probably lies between 0.82 and 0.91 atom of chlorine per formula.

INTRODUCTION

Chlorapatite, in contrast to fluorapatite and hydroxyapatite, is a relatively rare mineral. It has been reported only from Norway and Japan and has been found as microgranules in meteorites, (Palache, Berman & Frondel 1944). An apatite from one of the small skarn deposits on the northern end of Bob's Lake, Oso Township, Frontenac County, southeastern Ontario has been identified as chlorapatite with a chlorine content higher than any yet reported. In addition, the Canadian chlorapatite was found to be monoclinic with a space group $P2_1/a$ in agreement with the findings on synthetic chlorapatite, (Young & Elliott 1966).

Geological setting

The area of the chlorapatite occurrence (Fig. 1) is part of the Grenville tectonic province and consists mainly of granites, granitic gneisses and gneissic granodiorites with some (usually smaller) anorthositic gabbros. Interfingering with the granitic rocks are irregular bands of amphibolite and marble. Most of the skarn deposits in the area are of the phlogopite-fluorapatite type occasionally with considerable quantities of scapolite (Spence 1920).

MINERALOGY

Description and association

The chlorapatite at Bob's Lake occurs in calc-silicate marbles as a thin vein 6–8 inches wide and traceable for 15 feet. The apatite is associated with actinolite, diopside and lesser amounts of calcite, quartz and talc. The vein minerals with the exception of the chlorapatite also occur in the

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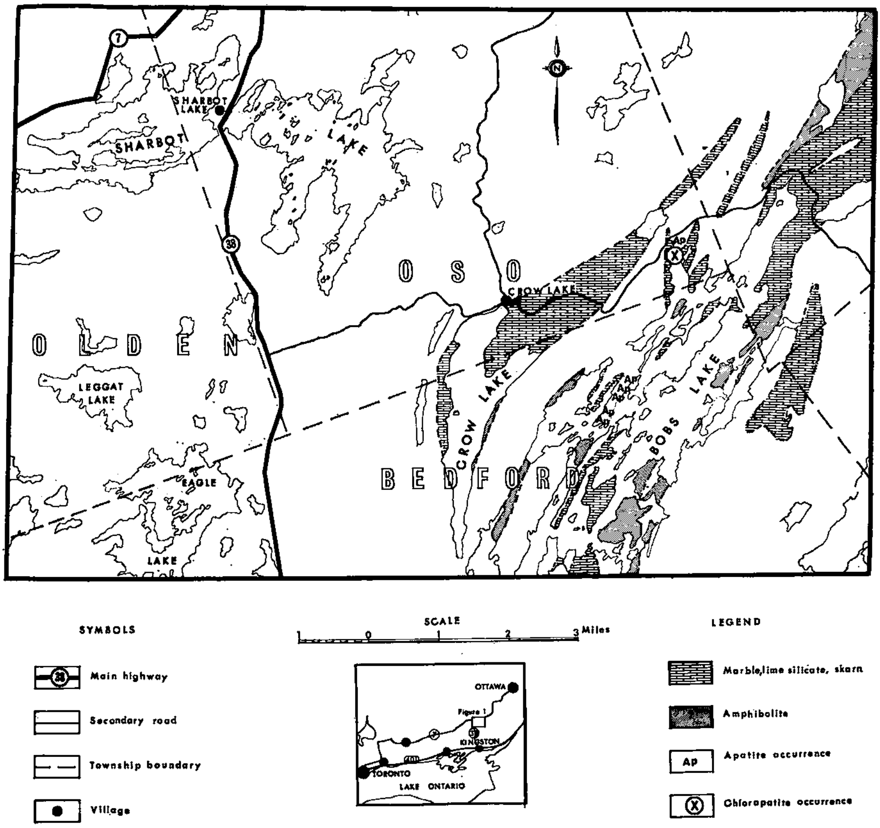

FIG. 1. Map showing the locality of the monoclinic chlorapatite occurrence and the geology of its surroundings. After Hewitt (1964). Redrafted by J. G. MacDonald.

surrounding marble. Mica and scapolite are noticeably absent. Talc coats much of the actinolite and occurs as inclusions in the calcite and apatite. In some cases the calcite has weathered to a rhombohedral framework of talc.

In general the chlorapatite crystals are pinkish-white and have a chalky lustre due to the included talc, some crystals observed have a thin chalky coating and transparent cores. Completely transparent, pale yellow crystals have also been found but these are not very common.

Chemical analysis and structural formula

Several transparent crystals were crushed and cleaned using conventional methods. The purified sample was dissolved in dilute HCl and the solution diluted to volume. Calcium was determined by titrating with

Zn–EDTA in a NH_4OH/NH_4Cl buffer (pH 10) using Eriochrome black T indicator (Cimerman, Alon & Mashall 1958) and phosphorus was determined spectrophotometrically as molybdivanadophosphoric acid by measuring the percent transmittance at 470 nm (Kitson & Mellon 1944). Chlorine was determined by dissolving a separate portion of the sample in dilute HNO_3 and almost neutralizing to bromphenol blue indicator and titrating with mercuric nitrate using diphenyl carbizone indicator (Roberts 1936). Fluorine and water were determined on separate portions of the sample by F. J. R. Muysson.

The chemical analysis of the Canadian chlorapatite and a compilation of other analyses from the literature are shown in Table 1. As the accuracy of the anion determinations is generally lower than the accuracy of the cation determinations the structural formulae of the apatites listed were calculated by a computer on the basis of 25 cationic charges (Foster, 1960). Although substantial cation substitution is possible in apatites it is assumed that cations other than Ca, Mn and P reported in published analyses were most likely due to inclusions and consequently these were not used in the calculation. The results are given in Table 2.

X-ray data

Single crystal photographs were taken using Weissenberg and precession cameras with filtered Cu$K\alpha$ and filtered Mo$K\alpha$ radiations respectively. These photographs revealed a superlattice which had the effect of doubling one of the hexagonal *a*-axes (Fig. 2). Extinctions occur in zero $0k0$ where k is odd and also in $h0l$ where h is odd. The space group thus is $P2_1/a$.

Cell dimensions (Table 2) were obtained by least squares refinement of powder diffraction data from photographs taken with Cu$K\alpha$ radiation and a 114.6 mm diameter camera. The measured 2θ values were corrected for film-shrinkage. The *d*-spacings and relative intensities of the Norwegian, Canadian and synthetic chlorapatites, the latter from ASTM card 12–263, are listed in Table 3.

Optical properties and density

Refractive indices were measured using sodium illumination and standard refractive index liquids. The Canadian chlorapatite was found to be biaxial negative with a $2V$ of approximately 10°. This is in agreement with the reported biaxial character of synthetic chlorapatites, (Prener 1967; Young 1967). As γ was very close to β the former was not determined.

The density was measured by means of a Berman balance, using five separate grains. The refractive indices, observed and calculated densities are given in Table 2.

TABLE 1. COMPILATION OF CHEMICAL ANALYSES OF CHLORAPATITES

(The abbreviations used in the Table have the following meaning: LOI—loss on ignition; Tr—trace; N.D.—not detected)

	Norway						Japan			Canada
	S-1	N-1	N-2	N-3	N-4	N-5	J-1	J-2	J-3	C-1
CaO	53.84	52.97	53.81	53.53	55.63	51.5	54.01	52.40	53.85	53.4
MnO	—	—	—	—	—	N.D.	Tr	1.52	0.41	N.D.
P_2O_5	40.89	40.50	40.50	40.30	41.64	41.2	40.15	40.98	41.78	41.2
Cl_2	6.81	4.31	6.24	6.02	1.40	5.6	4.16	3.74	1.42	6.2
F_2	—	0.17	0.00	0.00	0.00	0.20	1.32	1.15	0.44	0.13
H_2O^+	—	0.48	0.25	0.03	0.57	0.08	—	0.06	0.10	0.09
*LOI	—	—	—	—	—	—	0.63	—	—	—
*SiO_2	—	1.16	0.12	0.18	0.35	—	0.14	—	—	—
*Al_2O_3	—	—	—	—	—	—	0.52	—	—	—
*Fe_2O_3	—	0.18	0.04	0.11	0.06	Tr	0.36	—	0.61	Tr
*FeO	—	—	—	—	—	—	—	0.21	—	—
*MgO	—	0.29	—	—	—	—	0.20	0.54	0.54	—
*K_2O	—	0.10	—	—	—	—	0.15	0.0	0.0	—
*Na_2O	—	0.22	0.19	0.18	0.03	—	0.37	0.0	0.0	—
*CO_2	—	—	0.08	0.09	0.08	N.D.	—	—	—	N.D.
Total	101.54	100.38	100.86	100.35	99.68	99.56	102.01	100.60	99.15	101.02
O = F, Cl	1.54	0.98	1.37	1.32	0.30	1.35	1.49	1.33	0.35	1.45
Corr. Total	100.00	99.40	99.49	99.03	99.38	97.23	100.52	99.27	98.80	99.57

*Not used in structural formula calculation.

S-1 $Ca_5(PO_4)_3Cl$ ASTM 12-263
N-1 Hendricks *et al.*, 1932
N-2, N-3, N-4 Morton, 1964
N-5 Analyst A.W.H., H_2O, F.J.R. Muysson
J-1 Seto, 1932
J-2 Inner part of chlorapatite crystal, Harada, 1938
J-3 Outer part of chlorapatite crystal, Harada, 1938
C-1 Analyst A.W.H., H_2O, F.J.R. Muysson

TABLE 2. COMPILATION OF CHEMICAL FORMULAE AND PHYSICAL PROPERTIES OF CHLORAPATITES
(e.s.d.'s of cell dimensions and density are given in parenthesis)

	Norway						Japan			Canada
	S-1	N-1	N-2	N-3	N-4	N-5*	J-1	J-2	J-3	C-1*†
Chemical formulae										
Ca^{+2}	5.00	4.98	5.03	5.03	5.04	4.84	5.06	4.87	4.92	4.95
Mn^{+2}	—	—	—	—	—	N.D.	—	0.11	0.03	N.D.
P^{+5}	3.00	3.01	2.99	2.99	2.98	3.06	2.97	3.01	3.02	3.02
F^{-1}	—	0.05	0.00	0.00	0.00	0.06	0.37	0.32	0.12	0.04
OH^{-1}	—	0.28	0.14	0.02	0.31	0.05	—	0.03	0.06	0.05
Cl^{-1}	1.00	0.64	0.92	0.89	0.20	0.83	0.62	0.55	0.21	0.91
O^{-2}	12.00	12.02	11.97	12.04	12.24	12.03	11.83	12.05	12.31	12.00
F + OH + Cl	1.00	0.97	1.06	0.91	0.51	0.94	0.99	0.90	0.39	1.00
Cell dimensions (hexagonal)										
a	9.634	9.52 (3)				9.606 (2)				9.606 (4)
c	6.778	6.85 (3)				6.782 (2)				6.785 (3)
Density										
D_m	—	3.25				3.173 (8)	3.176			3.181 (5)
D_x	3.174	3.20				3.142				3.172
Refractive indices										
ω	1.667					1.665	1.657	1.658	1.640	1.667 (β)
ϵ	1.664					1.662	1.651	1.653	1.635	1.665 (α)

*This study.
†a (mono) = $2a$ (hex)
b (mono) = c (hex)
c (mono) = a (hex)
$\gamma \sim \beta$

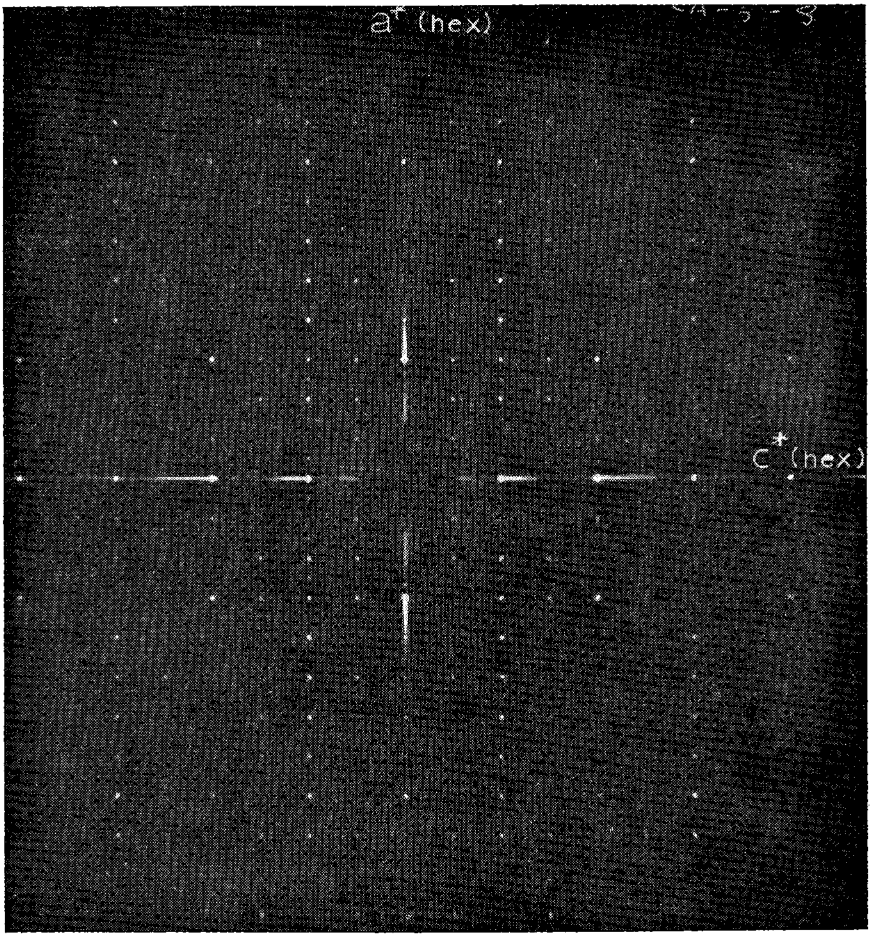

FIG. 2. Precession photograph (Zr filtered Mo $K\alpha$ radiation) of the Canadian chlorapatite showing the superlattice reflections along the hexagonal a^*-axis, which was subsequently chosen as the monoclinic a^*-axis.

DISCUSSION

Apatites N-4 and J-3 are low chlorine apatites associated with chlorapatites from Norway and Japan respectively. Their mode of occurrence would suggest that they are most likely to be alteration products of the higher chlorine apatites. This idea is further supported by the low sum of Cl + F + OH peculiar to these apatites which may also be evidence that vacancies may exist in this structural site.

The chlorine content per formula of the fresh chlorapatites thus varies

TABLE 3. CHLORAPATITE POWDER DIFFRACTION DATA

	Norwegian Chlorapatite			Canadian Chlorapatite		Synthetic Chlorapatite (ASTM 12-263)	
*hkl**	*d*	I/I_0	*hkl*[1]	*d*	I/I_0	*d*	I/I_0
100	8.34	10	200	8.34	5	8.32	10
101	5.23	10	210	5.28	5	—	—
110	—	—	201	—	—	4.87	4
201	3.54	5	410	3.54	5	3.55	6
002	3.39	30	020	3.39	40	3.39	14
210	3.14	5	401	3.15	15	3.15	10
211	2.850	100	411	2.853	100	2.861	60
300 112	2.773	100	600 221	2.770	100	2.779	100
202	2.626	15	420	2.628	5	2.630	6
130	2.306	55	203	2.306	40	—	—
311	2.182	10	611	2.181	15	2.190	4
302	—	—	620	—	—	2.145	4
113	2.044	15	231	2.046	5	2.044	4
222	1.958	55	422	1.960	50	1.963	18
312 320	1.908	30	621 602	1.910	25	1.909	10
213 321	1.834	55	431 612	1.838	50	1.836	20
410	1.814	20	801	1.814	25	—	—
402	1.770	10	820	1.772	10	1.774	4
004	1.695	10	040	1.695	10	1.692	8
322	1.661	5	622	1.663	15	1.663	4
313	1.614	5	631	1.616	5	1.616	4
412	1.594	3	821	—	—		
421	1.530	5	812	1.530	5		
214	1.494	20	441	1.494	10		
511	1.458	20	10.1.1	1.460	15		
034	1.446	15	043				

*Indices referred to hexagonal cell. The hexagonal to monoclinic transformation matrix is 200/001/010.

[1] Indices referred to monoclinic cell.

from 0.55 atom for the Japanese material to 0.91 atom for the Canadian apatite. The fluorine content is highest in the Japanese chlorapatite while the hydroxyl content is highest in the Norwegian chlorapatite.

Prener (1967) concluded from an optical examination of synthetic fluor-chlorapatite that the hexagonal form becomes the stable one above a certain atomic ratio of F/(F + Cl) somewhere between 0.16 and 0.36. The atomic ratio of (F + OH)/(F + OH + Cl) for the Canadian chlorapatite is 0.09 and for the Norwegian chlorapatite is 0.12, however, the sum of F + OH + Cl for the Norwegian chlorapatite is only 0.94 atom which, if not due to experimental error, may be due to vacancies in the halide site in the structure. If these vacancies are real then the sum of F + OH + vacancies becomes 0.18 indicating that Prener's lower figure of 0.16 is probably very close to the transitional composition. The data indicate a transition from hexagonal to the monoclinic structure between 0.82 and 0.91 atom of chlorine per formula of apatite.

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