

FLUOR-CHLOR-OXY-APATITE AND SPHENE FROM
CRYSTAL LODGE PEGMATITE NEAR
EAGLE, COLORADO¹

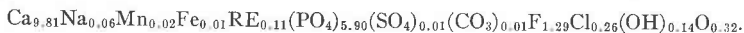
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ABSTRACT

The Crystal Lode pegmatite, located in Devils Canyon near Eagle, Eagle County, Colorado, is a perthite-quartz pegmatite in granodiorite. Major constituents in the pegmatite's vugs are crystals, as much as 1 inch long, of pale-greenish-yellow apatite and dark-brown sphene. Some of the apatite is encased irregularly in a whitish-cream altered apatite which contains much less rare earths than the greenish-yellow apatite. The fluor-chlor-oxy-apatite has the following physical properties: density 3.205 ± 0.002 g/cm³; ω 1.6432, ϵ 1.6392 both ± 0.0005 ; a 9.413 ± 0.003 , c 6.882 ± 0.005 Å; magnetic susceptibility $0.24 \pm 0.04 \times 10^{-6}$ emu/g; exhibits fluorescence and absorption spectra.

Chemical analysis has shown the greenish-yellow apatite to be deficient in halogens. Moreover, water content as determined by three different methods, has been found insufficient to make up the anion deficiency. The three methods are the Penfield, the infrared, and a method in which the sample is heated to 1400° C. and the evolved water is converted to hydrogen. The apatite contains less than 0.005 per cent silicate (SiO₄)⁻⁴ and less than 10 ppm of Br and I.

The results of several different methods of calculating a formula for this mineral all agree in showing an excess positive charge of 0.65. With the concomitant deficiency of anions, the most reasonable way for the charges to be neutralized is to add 0.32 oxygen per unit cell (0.50 weight per cent) to the formula. The formula considered to be the best fit has been calculated on the basis of 25.68 atoms of (O, F, Cl, OH) in the unit cell. The calculated density is 3.174, but when enough oxygen has been added to the molecular weight to balance valence, the calculated density rises to 3.190. These values fit the measured density of 3.205 better than calculated densities based on other methods of calculating a formula. The suggested formula is



INTRODUCTION

Apatite is without doubt one of the more important minerals to study exhaustively inasmuch as its compositional differences reflect the chemical environment of the wide variety of rock types in which apatite is an accessory mineral. Because of the great variety of ions which may enter the lattice of apatite, practical difficulties arise in its chemical analysis and many analyses reported in the literature are either justifiably suspect or incomplete. In contrast to the shortcomings of chemical analysis, refractive indices and density of apatite are within the range of precise determination, unlike the high refractive indices and densities of many other accessory minerals.

The possible substitution of oxygen for the halogens in apatite was

¹ Publication authorized by the Director, U. S. Geological Survey.

first recognized by Voelcker (1883), and Rogers (1912) proposed the name voelckerite (oxy-apatite) for $\text{Ca}_{10}(\text{PO}_4)_6\text{O}$ or those apatites which contain more oxygen than halogens in the halogen positions. Later synthesis studies by Bredig *et al.* (1932) indicated an oxy-apatite phase when tricalcium phosphate is heated with excess lime, but subsequent experimentation (Trömel, 1932) revealed that in the presence of atmospheric moisture the system is not anhydrous and the presumed oxy-apatite phase was actually hydroxylapatite. However, the oxy-apatite molecule may have limited solid solution in natural apatite.

Wickman (1954) described a manganvoelckerite from the Varuträsk pegmatite, Sweden, which shows a deficiency of halogens and hydroxyl and a consequent positive valence imbalance. The valence would be satisfied by the addition of 0.58 oxygen/unit cell. Wickman makes the hypothesis that the oxygen ions will occupy one-half of the chlorine positions, an alternation of occupied and empty sites, which still affords electrostatic compensation. In this scheme, the distances between oxygen and calcium II ions will be greater than the distances between fluorine and calcium II ions in normal fluorapatite. This may explain why voelckerite is more sensitive to weathering than fluorapatite. Wickman (1954) illustrated the greater weatherability of the manganvoelckerite compared to normal manganapatite.

Mason (1941) also described a manganvoelckerite (originally called mangualdite) from Portugal, which mineral requires the addition of 0.52 oxygen unit/cell to balance its valence.

As theoretical oxy-apatite has never been verified, the finding that apatite from the Crystal Lode pegmatite is deficient in halogen and water content thus warrants our intensive study of its composition and physical properties for its bearing on establishing the existence and nature of oxy-apatite substitution.

CRYSTAL LODGE PEGMATITE—SETTING AND PETROGRAPHY

Apatite crystals, unusually well suited for study, occur in the Crystal Lode pegmatite, which is in the south half of sec. 11, T. 6 S., R. 83 W., in Devils Canyon, a part of the Salt Creek drainage, Eagle County, Colorado. The pegmatite is about 12 miles southeast of Eagle and lies at an elevation of about 10,000 feet.

As exposed, the main pegmatite dike is 8 feet wide, striking N. 65° E. and dipping 53° NW., but interfingering veins of pegmatite and grayish-green fine-grained granodiorite or quartz monzonite broaden the pegmatite zone to 25 feet. The granodiorite veinlets are as much as 8 inches wide and are generally very friable owing to decomposition.

Mineralogically the pegmatite consists of dominant perthite, minor

quartz, traces of altered biotite and chlorite, pale-greenish-yellow apatite, dark-brown sphene, and specularite. Vuggy cavities are lined with well-formed crystals of pinkish perthitic orthoclase as much as 5×5 cm, clear quartz crystals and dark-brown sphene crystals as much as 4×2 cm, and pale-greenish-yellow (Y-GY 8/4) apatite crystals (Fig. 1) almost as large. The sphene crystals tend to be tabular and they are locally concentrated between the wallrock and the pegmatite (Fig. 2). Only partially formed faces are present on most of the apatite, and prismatic forms dominate.

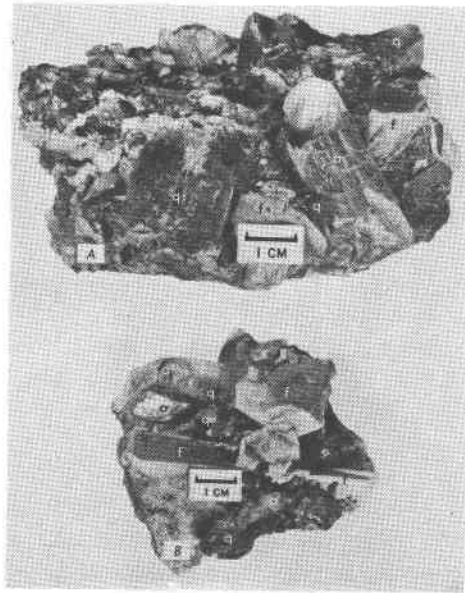


FIG. 1. Fluor-chlor-oxy-apatite from Crystal Lode pegmatite near Eagle, Colorado. f, feldspar; q, quartz; a, apatite. A. Note whitish-cream zone at upper end of apatite crystal. B. Another hand specimen of the pegmatite. Photographed by Ernest P. Krier.

Some of the apatite crystals are encased irregularly in a whitish-cream zone (Fig. 1A) which attains several millimeters in thickness. This deuteric zone of altered apatite differs slightly in refractive indices, density and composition from the unaltered crystal (Table 3).¹

Host rock for the pegmatite is an intrusive stock, about 10 square miles in area, of felsic rock ranging from quartz diorite to granite (Gabelman, 1950).

At the pegmatite the host rock is a fine- to medium-grained, somewhat

¹ Aslanyan and Ivchinova (1962) described an apatite from pegmatite occurring in monzonitic rock which seems to be very similar chemically, physically, and in geologic environment to the fluor-chlor-oxy-apatite of this paper. Like the fluor-chlor-oxy-apatite, it is greenish yellow and is encased in a white enamellike crust on the prism faces.

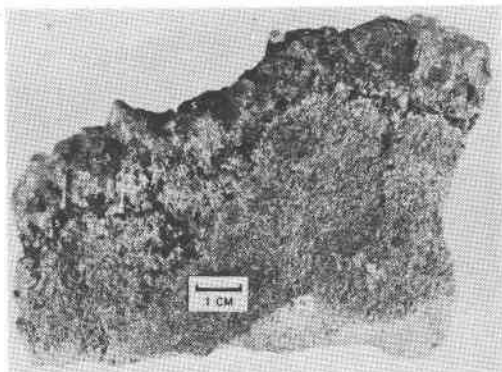


FIG. 2. Local concentration of sphenite crystals between wall rock and pegmatite. Pegmatite—upper edge, wall rock—lower half, sphenite—dark crystals (s). Photographed by Ernest P. Krier.

porphyritic, grayish rock containing abundant biotite phenocrysts as large as several millimeters. Orthoclase is untwinned and nonperthitic. The plagioclase is zoned; some grains contain cores of older plagioclase not in optical continuity with its overgrowth. Most of the plagioclase is oligoclase, but interior zones are as mafic as labradorite and rarely bytownite. Average composition of the plagioclase is andesine. Biotite is pleochroic from pale yellow to dark brown, and is deuterically altered to pale-green chlorite. Muscovite also shows alteration to chlorite. Ilmenite and apatite are dispersed evenly, whereas sphenite tends to be concentrated locally. An unidentified colorless mineral, whose optical properties are suggestive of a pyroxene, was noted also as a sparse constituent of the rock.

Modal analysis of the rock from about 100 point counts indicates it to be granodiorite, or quartz monzonite according to the Johannsen classification.

The mode is as follows:

	<i>Volume per cent</i>
Plagioclase (average An ₃₅)	42.5
Orthoclase	24.4
Quartz	19.8
Chlorite	6.6
Muscovite	1.4
Biotite	0.9
Sphenite	2.0
Ilmenite	1.8
Apatite	0.4
Zircon	0.2
	100.0

TABLE 1. PHYSICAL PROPERTIES OF APATITE AND SPHENE

	Density (measured) g/cm ³	Refractive indices	Optic angle	Lattice constants				Magnetic susceptibility emu/g	Fluorescence at 20° C. Short wave ultraviolet 254 m μ
				a, Å	c, Å	c/a	Volume Å ³		
Pale greenish-yellow fluor-chlor-oxo-apatite from pegmatite	3.205 ± 0.002	$\omega = 1.6432 \pm 0.0005$ $\epsilon = 1.6392$ $\omega - \epsilon = 0.0040$	Uniaxial (-)	9.413 ± 0.003 (9.417) ¹	6.882 ± 0.005 (6.883)	0.7311 (0.7309)	528.1	0.24 ± 0.04 × 10 ⁻⁶	607 ± 4 m μ pale pinkish orange, moderately strong intensity
Altered whitish-cream apatite from pegmatite	3.186 ± 0.002	Variable $\omega = 1.638$ to 1.640 $\epsilon = 1.635$ to 1.636 $\omega - \epsilon = 0.003$ to 0.004	Uniaxial (-)	9.402 ± 0.002 (9.387)	6.886 ± 0.002 (6.887)	0.7324 (0.7337)	527.1	< 0.22 × 10 ⁻⁶	606 ± 4 m μ pale pinkish orange, weak intensity
Colorless apatite from granodioritic host rock	—	$\omega = 1.6391 \pm 0.0005$ $\epsilon = 1.6353$ $\omega - \epsilon = 0.0038$	Uniaxial (-)	9.409 ± 0.001 (9.410)	6.876 ± 0.001 (6.874)	0.7308 (0.7305)	527.2	—	—
Dark-brown sphene from pegmatite	3.613 ± 0.005	$\alpha = 1.913 \pm 0.005$ $\beta = 1.925$ $\gamma = 2.18$ (calc.) $\gamma - \alpha = 0.27$	(+)27° ± 2° ²					6.4 ± 1.2 × 10 ⁻⁶	None
Yellow sphene from granodioritic host rock	3.601 ± 0.005	$\alpha = 1.902 \pm 0.005$ $\beta = 1.913$ $\gamma = 2.19$ (calc.) $\gamma - \alpha = 0.29$	(+)25° ± 2° ²					6.6 ± 1.1 × 10 ⁻⁶	None

¹ Lattice constants in parentheses were calculated by hand from d-spacings for the (402) and (502) planes.

² Measured using Mallard's constant.

ANALYTICAL DATA

Physical properties of the fluor-chlor-oxy-apatite and sphene. The densities, refractive indices, optical properties, lattice constants, magnetic susceptibilities and fluorescence properties of the apatite and sphene are listed in Table 1, the interplanar spacings of three apatites are given in Table 2; and the thermal curves of the fluor-chlor-oxy-apatite are shown on Fig. 3.

a. *Density.* Density of the apatite was measured using a combined suspension pycnometer method. First, the volume of a standard 10-ml pycnometer was established as 9.973 ± 0.001 ml by a series of five measurements, at 26° C., using a National Bureau of Standards liquid, methylcyclohexane (density = 0.76414 g/ml at 26° C.). Apatite grains were then suspended in a mixture of methylene iodide and acetone and the temperature of suspension noted to within 0.1° C. The liquid mixture was poured into the pycnometer, and pycnometer and liquid were brought to equilibrium several degrees above room temperature in a constant temperature bath. After being taken out of the bath the pycnometer and liquid were weighed and the density of the liquid mixture was calculated. Using the density-temperature relation of methylene iodide, the density of the liquid during suspension was determined. The results are within 0.002 g/cm³.

Density of the sphenes was measured using a combined suspension-Westphal balance method with Clerici solution as suspensoid. These values are within 0.005 g/cm³.

b. *Refractive indices.* Refractive indices were determined using the immersion method with the spindle stage of Wilcox (1959) modified by a metal holder for a thermometer showing 0.1° C gradations and placed as close to the mount as possible. Temperature variation of several degrees each side of room temperature was accomplished with the aid of ice or the heat from a lamp. Several tests of the method using the omega value of quartz as a standard and sodium light showed that the accuracy at best was within 0.0003 .

Values for the apatite refractive indices are estimated to be within 0.0005 . Owing to the corrosive high index oils used for the determination of the refractive indices of sphene such accuracy could not be obtained for this mineral and values are estimated to be within only 0.005 .

c. *Lattice constants and interplanar spacings.* As a preliminary step the three apatites were analyzed in an x-ray diffractometer, using halite as an internal standard, from $52^\circ 2\theta$ (Cu $K\alpha$) at a chart speed of $\frac{1}{4}^\circ 2\theta$ per minute. In this region at the $\frac{1}{4}^\circ 2\theta$ per minute chart speed peaks were

TABLE 2. X-RAY POWDER DATA FOR THREE APATITES¹

hkl	Pale-greenish-yellow fluor-chlor-oxy-apatite from Crystal lode pegmatite			Altered whitish-cream apatite from Crystal Lode pegmatite			Colorless apatite from granodioritic host rock		
	I	d(meas.) Å	d(calc.) ² Å	I	d(meas.) Å	d(calc.) Å	I	d(meas.) Å	d(calc.) Å
100	13	8.11	8.15	19	8.16	8.14	8	8.17	8.15
101	6	5.24	5.26	9	5.27	5.26	5	5.26	5.26
110		4.707	4.707		4.701	4.701		4.704	4.704
200	12	4.075	4.076	11	4.071	4.071		4.079	4.074
111	11	3.883	3.885	10	3.882	3.882	6	3.885	3.883
201			3.507			3.504			3.505
002	42	3.432	3.441	58	3.444	3.443	32	3.440	3.438
102	14	3.166	3.170	16	3.171	3.171	11	3.174	3.168
210	19	3.083	3.081	19	3.077	3.077	16	3.079	3.080
211	100	2.814	2.812	100	2.815	2.810	100	2.815	2.811
112	56	2.775	2.778	46	2.777	2.778	35	2.776	2.776
300	60	2.715	2.717	69	2.713	2.714	46	2.715	2.716
202	22	2.629	2.629	28	2.628	2.629	20	2.628	2.628
301	9	2.528	2.528	6	2.527	2.525	3	2.527	2.526
220			2.353			2.350			2.352
212	4	2.294	2.296	7	2.296	2.294	4	2.294	2.294
310	20	2.264	2.261	21	2.257	2.258	15	2.260	2.260
221			2.227			2.224			2.226
103			2.208			2.209			2.206
311	5	2.149	2.148	3	2.143	2.146	5	2.148	2.147
302			2.133			2.131			2.131
113	2	2.062	2.062	5	2.062	2.062	6	2.061	2.060
400			2.038			2.036			2.037
203	1	2.003	1.999			1.999			1.998
401			1.954			1.952			1.953
222	20	1.944	1.943	18	1.939	1.941	18	1.938	1.941
312	8	1.890	1.890	8	1.886	1.888	8	1.888	1.888
320			1.870			1.868			1.869
213	24	1.840	1.840	30	1.839	1.840	19	1.838	1.839
321	11	1.806	1.805	11	1.801	1.803	10	1.804	1.804
410	10	1.781	1.779	8	1.775	1.777	8	1.778	1.778
402	7	1.754	1.754	7	1.750	1.752	7	1.753	1.753
303			1.753			1.753			1.752
411			1.722	16	1.721	1.720			1.721
004	10	1.719	1.721			1.721	9	1.718	1.719
104			1.684			1.684			1.682
322	5	1.644	1.643	6	1.640	1.642	3	1.642	1.642
223			1.643			1.642			1.642
500			1.630			1.628			1.630
114			1.616			1.616			1.615
313	3	1.611	1.610			1.610	2	1.609	1.609
501			1.587			1.585			1.586
204			1.585			1.585			1.584

¹ Cu K α radiation, Ni filter ($\lambda = 1.5418$ Å) for $d \geq 2.25$.Cu K α radiation, Ni filter ($\lambda = 1.5405$ Å) for $d \leq 2.15$.² d-spacings were calculated by Howard T. Evans, Jr. and Daniel E. Appleman using a computer-based least squares refinement method.

TABLE 2—(Continued)

hkl	Pale-greenish-yellow fluor-chlor-oxy-apatite from Crystal lode pegmatite			Altered whitish-cream apatite from Crystal Lode pegmatite			Colorless apatite from granodioritic host rock		
	I	d(meas.) Å	d(calc.) ² Å	I	d(meas.) Å	d(calc.) Å	I	d(meas.) Å	d(calc.) Å
412			1.580			1.579			1.579
330			1.569			1.567			1.568
420	4	1.542	1.541			1.539	3	1.541	1.540
331			1.530			1.529			1.529
403			1.524			1.523			1.523
421			1.503			1.502			1.503
214	6	1.500	1.502			1.502	3	1.501	1.501
502	7	1.474	1.473	6	1.470	1.472	5	1.473	1.473
510	3	1.461	1.464			1.462			1.463
304			1.454	6	1.452	1.454	5	1.453	1.453
323	8	1.450	1.450			1.449	6	1.449	1.449
511	5	1.433	1.432			1.430	3	1.431	1.431
332			1.428			1.426			1.427
413						1.405			1.405
422						1.405			1.405

clearly separated into α_1 and α_2 components. The positions of the reflections from the two planes 402 and 502 were ascertained and the unit cell constants a and c were calculated from the hexagonal formula

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{3a^2} (h^2 + hk + k^2) + \frac{\lambda^2}{4c^2} l^2.$$

Final unit cell constants were obtained by Howard T. Evans, Sr. and Daniel E. Appleman using most of the d-spacing data in conjunction with an electronic computer program.

d. *Magnetic susceptibility.* Magnetic susceptibilities of the apatites and sphenes were measured on a calibrated Frantz Isodynamic separator after the method developed by McAndrew (1957). It might be noted that the dual vibration system (separate vibration for trough and feeder) developed by Faul and Davis (1959) for the Frantz separator is a distinct improvement over the original vibratory system for this type of measurement.

An innovation was made in the recovery of the grains from the magnetic and nonmagnetic ports involving the use of small tared aluminum foil pans weighing 0.1 g, which make possible the measurement of very small samples consisting of 100 grains or less (150–325 mesh).

The accuracy of the measurements obtained by use of the Frantz separator was verified by Frank E. Senftle using a quartz helix magnetic susceptibility balance (Senftle and others, 1958) on the same samples.

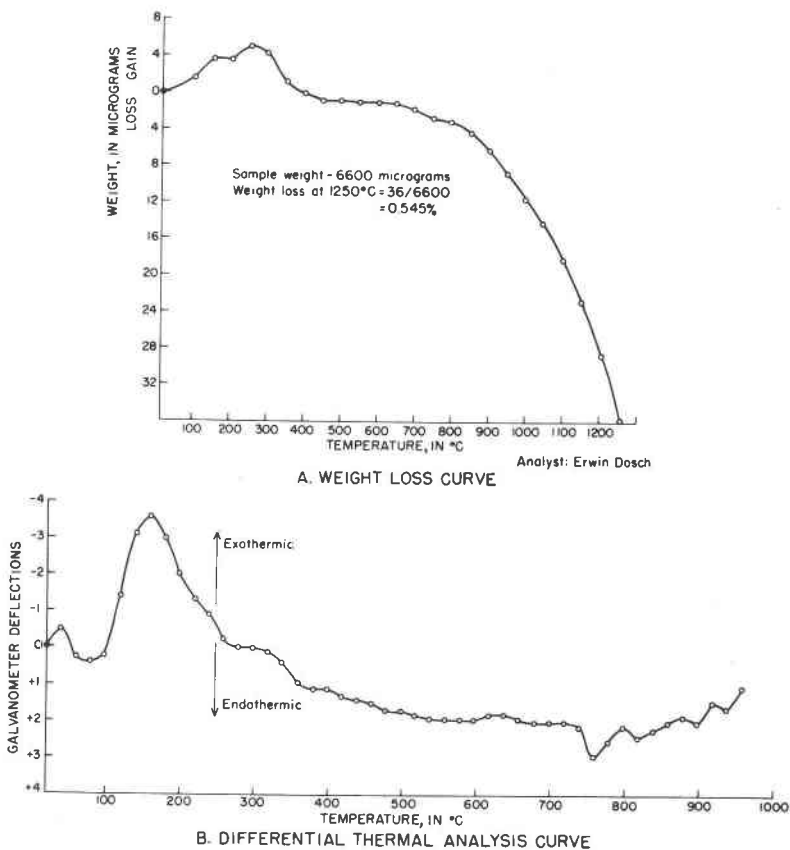


FIG. 3. Thermal curves for fluor-chlor-oxy-apatite.

	Magnetic susceptibility Frantz separator (Electromagnetic units/g)	Magnetic susceptibility Quartz helix balance
Fluor-chlor-oxy-apatite	$0.24 \pm 0.04 \times 10^{-6}$ emu/g	0.268×10^{-6} emu/g
Sphene from pegmatite	$6.4 \pm 1.2 \times 10^{-6}$ emu/g	5.85×10^{-6} emu/g

e. *Fluorescence*. With a calibrated colorimeter the color of the fluorescence of the fresh pale-greenish-yellow fluor-chlor-oxy-apatite from the pegmatite and its whitish-cream alteration phase was measured (Table 1). No difference in color of fluorescence was noted between the two, but the former fluoresced more strongly. Only short-wave ultraviolet radiation ($254 \text{ m}\mu$) caused the apatite to fluoresce. Long-wave ultraviolet radiation ($366 \text{ m}\mu$) had very little or no effect. Heating to 55°C ., as suggested by Taborszky (1962), intensified the fluorescence color slightly.

f. *Absorption spectra.* A crystal of the pale-greenish-yellow fluor-chlor-oxy-apatite from the pegmatite was ground slightly on two parallel prism faces to a thickness of 9 mm. A calibrated absorption spectroscopy was then used to measure the absorption spectra of the ordinary and extraordinary rays. These two spectra are significantly different as the following tabulation shows.

ω			ϵ	
512 $m\mu$	} very weak band	green	519	very weak
514			521	very weak
564	moderately strong		562	moderately strong
			568	moderately strong
573	} moderately strong broad band	yellow	573	weak
579			581	very weak

The absorption bands are due to neodymium and praseodymium (Adams, 1965). Much smaller crystals and fragments do not show absorption bands.

Thermogravimetry and DTA. A preliminary thermal gravimetric study of 0.4858 g of the fluor-chlor-oxy-apatite was made on a Chevenard instrument, but no weight change was detected during the heating to 982° C. After the complete run, however, a weighing of the heated sample showed that it had lost 1.0 mg or 0.21 per cent of its weight, which is only a crude approximation. Apparently the heating had little effect on the apatite; ω measured 1.6425 ± 0.0005 , which is only 0.0007 less than that of the unheated apatite. Driving off about 0.2 per cent water from the apatite lattice could account for the slight decrease in refractive index.

Through the courtesy of Irwin Dosch, Chief Engineer of Technical Equipment Co. of Denver, 6.60 mg of the fluor-chlor-oxy-apatite were run on a Deltatherm thermal gravimetric analyzer to 1250° C. Figure 3A shows the weight loss data. Although 0.545 per cent weight loss is indicated, one cannot interpret this loss as being entirely due to water. Small amounts of SO₃ and CO₂ may have evolved, and probably there has been some sublimation of P₂O₅ in the finely powdered mineral, especially at the higher temperature. P₂O₅ sublimes at 250° C. Noteworthy is the fact that at the end of the run the weight loss was still accelerating. The implication here is that thermal gravimetric analyses of apatite are worthless unless one can recover and analyze the evolved gases.

The portable differential thermal analysis instrument of Eberbach was used to study the thermal behavior of the fluor-chlor-oxy-apatite. A high sensitivity run was made and is shown in Figure 3B. About all that can be said with certainty is that there is a small endothermic peak at 75° C., a

strong sharp exothermic peak at 150°–170° C. and a small sharp endothermic peak at 760° C. All the other peaks are ill defined and weak.

Taborszky (1962), who did not mention the strong exothermic peak at 150°–170° C., observed the following peaks:

1. A strong endothermic peak between 50° and 250° C. (attributed to adsorptive water).
2. A broad exothermic peak at 660°–680° C.
3. A broad exothermic peak at 880–900° C.
4. An endothermic peak at 730°–750° C.
5. An endothermic peak at 810°–830° C. (May go down to 780° C. in apatite from felsic rocks.)
6. An endothermic peak at 940°–950° C.

Chemical and spectrographic properties of the fluor-chlor-oxy-apatite. Chemical and spectrographic analyses of the fluor-chlor-oxy-apatite and spectrographic analyses of the altered apatite, sphene from the pegmatite, and sphene from the country rock are given in Table 3.

A total of approximately 15 g of the fluor-chlor-oxy-apatite was distributed among the various analysts. The constituents, types of analysis, number of determinations, and reproducibility¹ of the major oxides are as follows:

Constituent	Type of analysis	Number of determinations	Reproducibility in weight per cent
CaO	Chemical	2	±0.1
P ₂ O ₅	Chemical	2	±0.1
F	Chemical	3	±0.05
Cl	Chemical	2	±0.05
Fe ₂ O ₃	Chemical	1	
FeO	Chemical	1	
MnO	Chemical	1	
Na ₂ O	Chemical	1	
K ₂ O	Chemical	1	
Sr	Semiquanti. spectrographic	2	
Rare earth oxides (all rare earths considered to be in the 3+ state)	Quanti. spectrographic	1	±0.27
	Semiquanti. spectrographic	2	
	Chemical	2	
SO ₃	Chemical	1	
CO ₂	Microchemical	1	
H ₂ O	Chemical	3	
	Infrared	3	
	Special	1	
Acid insoluble	Chemical	2	
Sol. silica	Chemical	1	
Br	X-ray fluorescence	2	
I	X-ray fluorescence	2	

¹ The satisfactory summation of 99.92 weight per cent for the mineral is an indication that the precision and accuracy of the analysis is satisfactory.

As an accurate determination of water content in the fluor-chlor-oxy-apatite was essential to the interpretation of its formula, a special method of water determination by Irving Friedman and R. L. Smith (1959) was employed. In brief, the method is as follows:

- (1) 5 grams of sample are dried in a vacuum at 110° C.
- (2) The sample is then heated to about 1400–1450° C. in a vacuum; the water is condensed at liquid nitrogen temperature and finally converted to H₂ by reaction with hot uranium metal.
- (3) The hydrogen is measured volumetrically. This method is probably the best available, and as the result from its use is virtually the same as that from use of the Penfield method, the accuracy of the Penfield method for apatite analysis, when carefully applied, is upheld.

CRYSTAL CHEMISTRY

Relation of omega index of refraction to chemical composition. The ω index of refraction of the fluor-chlor-oxy-apatite, by use of the factors arrived at by Young (1964), may be calculated as follows:

Oxide or element	Weight percent	Factor
Cl	0.91	× 0.0054 = 0.00491
H ₂ O ¹	0.12	× 0.0091 ₂ = 0.00109
MnO ²	0.11	× 0.0019 ₈ = 0.00022
FeO	0.04	× 0.0040 = 0.00016
SO ₃	0.11	× 0.0003 = 0.00003
SrO ¹	0.04	× 0.00013 = 0.00001
Rare earth oxides	1.79	× 0.0018 ₄ = 0.00318
		0.00960
	ω of pure fluorapatite	1.6325
		Calculated $\omega = 1.6421$

¹ Slight change in factor from that originally published by Young (1964).

² This factor is from Young *et al.* (1965).

As the measured ω of this fluor-chlor-oxy-apatite is $1.6432 \pm .0005$, the calculated ω is only 0.0011 too low, a not unreasonable check.

Relation of axial ratio, c/a, to birefringence. Hausen (1929) showed an interesting inverse relation between the axial ratio, c/a (determined by crystal measurement), and birefringence in apatite. Data from the fluor-chlor-oxy-apatite and from the apatite in the granodioritic host rock fit his data reasonably well, as shown in the following:

Apatite from	c/a	$\omega - \epsilon$	Source
Rossa, Val Devero.....	0.7297	0.0054	Hausen (1929).
Granodioritic host rock, Crystal Lode pegmatite, Eagle, Colo.	0.7308 ¹	0.0038	This paper.
Pegmatite, Crystal Lode, Eagle, Colo.....	0.7311 ¹	0.0040	This paper.
Rothenkopf, Zillertal.....	0.7313	0.0043	Hausen (1929).
Katzenbuckel, Odenwald.....	0.7315	0.0048	Hausen (1929).
Malmberget mine, Gellivare, Sweden.....	0.7320	0.0038	Hausen (1929).

¹ c/a determined by x -ray.

The rule of Gladstone and Dale. The rule of Gladstone and Dale, $(n-1)/d = K$, where n is the mean index of refraction, d is the density and K is the total specific refractive energy of a mineral, does not apply very well for this fluor-chlor-oxy-apatite. By use of the specific refractive energy values presented by Larsen and Berman (1934) and the newer ones for the rare earth oxides by Jaffe (1956), K is calculated to be 0.20571. Thus $dK+1$ equals 1.6593, and the mean index of the mineral $\frac{2\omega+\epsilon}{3}$ is 1.6419. Hence the calculated $dK+1$ is 0.0174 higher than the mean index. This is in the same general range as the +0.016 cited for fluorapatite by Jaffe (1956) and the +0.0206 cited for a manganese- and strontium-bearing apatite by Young *et al.* (1965).

Such discrepant values are probably to be expected in view of the variable specific refractive energy values for CaO and P_2O_5 . A test of the specific refractive energy value k , for CaO , was made on two well-documented wollastonites and one diopside with the following result: $k_{\text{CaO}} = 0.229, 0.221$ and 0.217 , respectively (Deer *et al.*, 1963, Vol. 2, p. 170, Nos. 3 and 2, p. 54, No. 37). For P_2O_5 , values of $k = 0.177, 0.175$, and 0.175 were found for the fluor-chlor-oxy-apatite, the manganese- and strontium-bearing apatite, and an apatite listed by Deer *et al.*, (1963, Vol. 5, p. 325, No. 3), respectively. Values for $k_{\text{P}_2\text{O}_5}$, however, were found to be 0.184 for synthetic hannayite and 0.187 for schertilite (Frazier *et al.*, 1963).

Oxygen replacement for fluorine. The theory of oxygen replacement for fluorine in apatite would have great support if it were possible to show that addition of oxygen to the formula in an amount necessary to balance valence would bring the calculated density closer to the measured density. The chief obstacle to this approach is the fact that the calculated density is dependent on the formula of the apatite, and the formula is dependent on the method of calculation used to obtain the formula. All the results using the different methods of calculation, however, agree in one important respect: the positive, or cationic, charges are 0.65 greater

than the negative or anionic charges.¹ Particularly in this fluor-chlor-oxy-apatite study every effort has been made to check the presence of any possible anion such as Br^- , I^- , AsO_4^{3-} or VO_4^{3-} (Table 3) which, if overlooked, would explain the positive imbalance. As the imbalance is no longer a possibility but a certainty, the only solution to the problem apparent to the authors is the substitution of oxygen for some of the halogen positions, as suggested by many authors, for electrostatic neutrality is a prerequisite for any mineral. The partial substitution of oxygen for the halogens affects the calculation of the formula in the following way. Normally apatite is considered to have 26 (O, F, Cl, OH) in its unit cell, that is 24 oxygens plus 2F or 2Cl or 2(OH) or some combination which totals 2. In theoretical oxy-apatite, however, there are only 24 oxygens plus 1 oxygen (25 oxygens), because oxygen is divalent. Consequently, an apatite which has part of its halogens replaced by oxygen will contain more than 25 but less than 26 oxygens in its unit cell. Specifically it will contain 26 oxygens minus the number of oxygens required for electrical neutrality in its unit cell. The formula calculated on that basis, shown in Table 3, is the one believed by the authors to be the best available (Young, 1965).

Tests of the basis of formula calculation by measured and calculated densities. Formulas have also been calculated on the basis of $\text{P} + \text{S} = 6$ atoms and on the basis of 26 (O, F, Cl, OH) in the unit cell, in one case discounting Al_2O_3 and Fe_2O_3 as impurities and in the other considering them as occurring in the crystal lattice (Fe^{3+} substituting for Ca^{2+} and Al^{3+} substituting for P^{5+} to give the anion $(\text{AlO}_4)^{5-}$). Calculated densities based on these several formulas, including densities after addition of sufficient oxygen to balance valence, are as follows:

Formula calculated on basis of	Calculated density	Calculated density after addition of sufficient oxygen to balance valence
1. 25.68 (O, F, Cl, OH) in the unit cell and discounting Fe_2O_3 and Al_2O_3 as impurities.	3.174	3.190
2. 25.68 (O, F, Cl, OH) in the unit cell and including Fe^{3+} and $(\text{AlO}_4)^{5-}$ in the lattice.	3.174	3.190
3. 26 (O, F, Cl, OH) in the unit cell and discounting Fe_2O_3 and Al_2O_3 as impurities.	3.214	3.230

¹ Although error in analytical data might cause a valence imbalance, it would have to be a whopper, as calculations show that if CaO was reported 0.1% too high and P_2O_5 0.1% too low the valence imbalance would still be +0.57. It might also be mentioned here, that there is little likelihood of any of the rare earths being in the 2+ state. Some of the Ce could be in the 4+ state, but this event would make the cationic charges greater than that calculated.

4. 26 (O, F, Cl, OH) in the unit cell and including Fe^{3+} and $(\text{AlO}_4)^{5-}$ in the lattice. 3.214 3.231
5. $\text{P}+\text{S}=6$ in the unit cell and discounting Fe_2O_3 and A_2O_3 as impurities. 3.221 3.237
6. $\text{P}+\text{S}=6$ in the unit cell and including Fe^{3+} and $(\text{AlO}_4)^{5-}$ in the lattice. 3.225 3.242

TABLE 3. CHEMICAL AND SPECTROGRAPHIC ANALYSES OF FLUOR-CHLOR-OXY-APATITE AND SPECTROGRAPHIC ANALYSES OF ALTERED APATITE AND TWO SPHENES

Chemical analysis of fluor-chlor-oxy-apatite						
	Weight per cent	Weight per cent recalculated to 100% ¹	Ratios	Metal equivalent	Oxygen equivalent	Atoms per unit cell ²
CaO	53.89	54.22	0.9669	0.9669	0.9669	9.81
P ₂ O ₅	41.00	41.25	0.2906	0.5812	1.4530	5.90
Al ₂ O ₃	0.04	—	—	—	—	—
Fe ₂ O ₃	0.10	—	—	—	—	—
FeO	0.04	0.04	0.0006	0.0006	0.0006	0.01
MnO	0.11	0.11	0.0016	0.0016	0.0016	0.02
Na ₂ O	0.17	0.17	0.0027	0.0055	0.0027	0.06
K ₂ O	0.01	0.01	0.0001	0.0002	0.0001	0.00
SrO	0.04	0.04	0.0004	0.0004	0.0004	0.00
RE ox.	1.79	1.80	0.0055	0.0110	0.0165	0.11
SO ₃	0.11	0.11	0.0014	0.0014	0.0041	0.01
CO ₂	0.03	0.03	0.0007	0.0007	0.0014	0.01
H ₂ O ⁺³	0.12	0.12	0.0067	0.0133	0.0067	0.14
H ₂ O ⁻	0.00	0.00	—	—	—	—
F	2.40	2.41	0.1269	—	0.0634	1.29
Cl	0.91	0.92	0.0260	—	0.0130	0.26
Acid insol.	0.38	—	—	—	—	—
Total	101.14	101.23				
Less O	1.22	1.23				
Total	99.92	100.00				

¹ Acid insol. residue, Al₂O₃, and Fe₂O₃, have been discounted as impurities.

² Calculated on the basis of 25.68 (O,F,Cl,OH) in the unit cell.

³ H₂O⁺ determined by Penfield method.

Formula: $\text{Ca}_{9.81} \text{Na}_{0.06} \text{Mn}_{0.02} \text{Fe}_{0.01} \text{R.E.}_{0.11} (\text{PO}_4)_{5.90} (\text{SO}_4)_{0.01} (\text{CO}_2)_{0.01}$
 $\text{F}_{1.29} \text{Cl}_{0.26} (\text{OH})_{0.14} \text{O}_{0.32}$ MW = 1014.8

Oxygen has been added to balance valence.

Analyst: Elaine L. Munson

Analytical notes:

- Al₂O₃, Na₂O and K₂O were determined by Leonard Shapiro.
- MnO and SO₃ were determined by Blanche Ingram.
- CO₂ was determined by Jesse J. Warr, Jr.
- Rare earths and Sr were determined by spectrographic analysis by Nancy Conklin.
- Soluble silica is less than 0.005 per cent according to Wayne Mountjoy.
- Br and I are less than 0.001 per cent according to x-ray fluorescence analysis by Harry J. Rose, Jr.
- H₂O⁺ = 0.115 ± 0.005 per cent as determined by Irving Friedman. Method described in text.
 H₂O⁺ = 0.08 ± 0.03 per cent as determined by James H. Turner using infrared analysis.
 H₂O⁺ < 0.07 per cent as determined by John Chandler using infrared analysis.

Spectrographic analysis in weight per cent⁴

	Fluor-chlor-oxy-apatite	Altered apatite	Sphene in pegmatite	Sphene in country rock
Si	0.3	0.3	—	—
Al	.07	.07	1.5	1.5
Fe	.1	.03	2.	2.
Mg	.07	.007	.07	.05
Ca	M	M	M	M
Na	.15	.05	0	0
Ti	0	.003	M	M
P	M	M	0	0
Mn	.1	.02	.15	.1
Ba	.0005	.0005	0	.015
Cu	<.001	.0003	0	0
Nb	0	0	.15	.1
Sc	0	.0007	0	0
Sr	.03	.03	0	0
Zr	0	0	.07	.1
La	.34 ⁵	.03	.5	.5
Ce	.69 ⁵	.07	1.5	1.5
Pr	.15	—	.15	.15
Nd	.23 ⁵	.03	.7	.7
Sm	.03	0	.7	.15
Y	.046 ⁵	.03	.7	.3
Gd	.015	.007	.15	.07
Dy	.015	.007	.15	.07
Ho	.003	0	.03	0
Er	0	.007	0	0
Yb	0.0045 ⁵	0.002	0.1	0.07
Lu	0	0	.015	0

Analyst: Nancy M. Conklin

Also looked for but not detected: Ag, As, Au, B, Be, Bi, Cd, Co, Cr, Eu, Ga, Ge, Hf, Hg, In, Li, Mo, Ni, Pb, Pd, Pt, Re, Sb, Sn, Ta, Tb, Te, Th, Tl, Tm, U, V, W, Zn.

⁴ Results are reported in per cent to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15 and 0.1, etc.; which represent approximate midpoints of group data on a geometric scale. The assigned group for six-step spectrographic results will include the quantitative value about 30 per cent of the time.

M major constituent—greater than 10 per cent.

0 looked for but not detected.

— not looked for.

⁵ Quantitative analysis. Precision is ± 15 per cent.

As the measured density is 3.205, it is seen that the formula calculated on the basis of 25.68 (O, F, Cl, OH) in the unit cell provides the most reasonable calculated density. Inclusion or exclusion of Fe^{3+} and $(\text{AlO}_4)^{5-}$ from the lattice has only negligible effect on the calculated density. Formulas calculated on the other bases provide calculated densities which are too high.

In summary, partial substitution of oxygen for fluorine in this apatite is well borne out by the present study. In other words, the postulate of 26 (O, F, Cl, OH) in this apatite, which presupposes no oxygen substitu-

tion for fluorine, is inadequate, as the calculated density based on it is too high. The postulate of 25.68 (O, F, Cl, OH) in the unit cell, which presupposes the substitution of 0.32 oxygen in the unit cell for fluorine, yields a satisfactory calculated density and is therefore preferred.

Rare earths in the apatite and sphene. Sphene from the pegmatite contains more total rare earths and relatively more of the yttrium group elements than does the sphene from the host rock. The cerium group elements include La, Ce, Pr, Nd, Sm and Eu. The yttrium group elements include Y, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

	<i>Sphene from pegmatite</i>	<i>Sphene from host rock</i>
Total rare earths, elemental (weight per cent)	4.70	3.51
Ce/Y earths	3.10	5.88

Although there are no chemical data for the apatite from the host rock, its lower refractive indices suggest that it contains less rare earths than the fluor-chlor-oxy-apatite from the pegmatite. The altered whitish-cream apatite from the pegmatite contains decidedly less rare earths than the fluor-chlor-oxy-apatite, but it is relatively enriched in the yttrium group elements.

	<i>Fluor-chlor-oxy-apatite</i>	<i>Altered apatite</i>
Total rare earths, elemental (weight per cent)	1.52	0.18
Ce earths/Y earths	17.25	2.45

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