MINERALOGICAL NOTES

MANGANESE- AND STRONTIUM-BEARING FLUORAPATITE FROM THE PEERLESS PEGMATITE, SOUTH DAKOTA[1]

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INTRODUCTION

Naturally occurring apatite crystals with one or two unusual chemical components are of great value in elucidating the relations between physical properties and chemical properties. The usual chemical components are, of course, Ca, O, P, F, and sometimes Cl and OH. This apatite from the Peerless pegmatite contains only two unusual components, 1.82 per cent MnO and 0.97 per cent SrO.

Relatively high magnetic susceptibility, refractive indices, and pale-pink color are attributed to Mn, whereas relatively high specific gravity results from both Mn and Sr in this fluorapatite. It is suggested that oxygen replaces F to a small degree because the formula calculated from the chemical composition shows too much positive valence and because the calculated density is closer to the measured density when enough oxygen is added to balance the valence.

LOCATION AND GEOLOGIC SETTING

The Peerless pegmatite, which has been a major source of beryl and scrap mica, is in the Precambrian core of the southern Black Hills half a mile south of Keystone, Pennington County, South Dakota. It is one of a group of productive zoned pegmatites comprising the Keystone district, which is located near the northeastern margin of a large area of Precambrian granitic rocks surrounding Harney Peak. The Precambrian metamorphic rocks intruded by the Peerless pegmatite are quartz-mica schist, quartz-mica-staurolite schist and quartz-mica-chlorite schist.

The Peerless is a large complex pegmatite consisting of seven zones, two replacement units, and two types of fracture fillings. These internal lithologic and structural units and their mineral deposits are described by Sheridan *et al.* (1957). The pegmatite is tadpole-shaped and is about 580 feet long at the surface; its cross-section anticlinal.

Fluorapatite occurs as the major mineral in drusy fracture fillings, $\frac{1}{4}-\frac{1}{2}$ inch thick, that occur along both the northwestward-trending fault just southwest of the large unmined pinnacle and the main westward-trending fault northwest of this pinnacle (Sheridan *et al.*, 1957). These thin fracture fillings, called "tourmaline-quartz pegmatite" by Sheridan

et al. (1957, p. 17), were not studied in as great detail as were the main lithologic units of the pegmatite which contain economically important deposits of beryl, mica, feldspar and amblygonite. John W. Adams (oral comm., 1959) examined some samples from these fracture fillings and concluded that the major mineral is probably apatite rather than tourmaline. More recent detailed laboratory studies by Young have verified Adams' conclusion. The rather unusual crystal habit and pale-pink color of the mineral, together with an erroneous hardness test (probably caused by the interspersed quartz crystals), led to the original mistake in identifying it as tourmaline. As noted by Sheridan *et al.* (1957), these fracture fillings are not necessarily directly related in origin to the main mass of the Peerless pegmatite, because they occur on slickensided surfaces of faults that cut all the zones, replacement units, and core, and because their drusy structure is undisturbed.

PHYSICAL PROPERTIES

The colorless to very pale-pink fluorapatite[1] has a rather unusual crystal development. The crystals look like small bundles of wheat due to tiny corrugations in the prism faces (Fig. 1). Generally the length of the crystals, which may attain a quarter of an inch, is two to three times the thickness. Basal pinacoids are well developed, whereas pyramidal faces are very small and scarce. (A thin limonite scale covers some of the fluorapatite crystals. This scale was removed by several cycles of boiling with ammonium tartrate solution and metallic Al before chemical and physical analyses of the fluorapatite.) No fluorescence of this apatite was noted in either short- or long-wave ultraviolet light.

A minor amount of quartz, in crystals of approximately the same size as the apatite crystals, occurs with the apatite. Sparse muscovite crystals occur in some samples.

Optical data. The spindle stage of Wilcox (1959), with the following innovations, was used for refractive index determinations. A metal slot was affixed to the stage so that it could receive a thermometer graduated in tenths of a degree Centigrade. From 5 to 8 grains of apatite were placed on the glass window between the supporting blocks, and cover glass and index liquid were added in the usual manner. After observations were taken on each of the grains, tips of blotting paper were used to remove the liquid without disturbing the grains. Another liquid was then added and further observations were made on the same grains. To minimize contamination from the previous index liquid, the cell was rinsed several

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[1] Vasileva (1958) noted three color types of manganapatite: pale pink; blue, dark blue and blue green; and violet.

times with each new liquid. Determination of ω could be made in this manner on every grain, but determination of ϵ could be made on only a few grains lying on prism faces.

Observations of ω were taken on 20 grains. ω ranges from 1.6361 to 1.6373, but the value given in Table 1 represents the great majority of the apatite. ϵ was observed on 5 grains. Some of the apatite is anomalously biaxial with 2V as much as 20°. The unusual corrugations on the prism
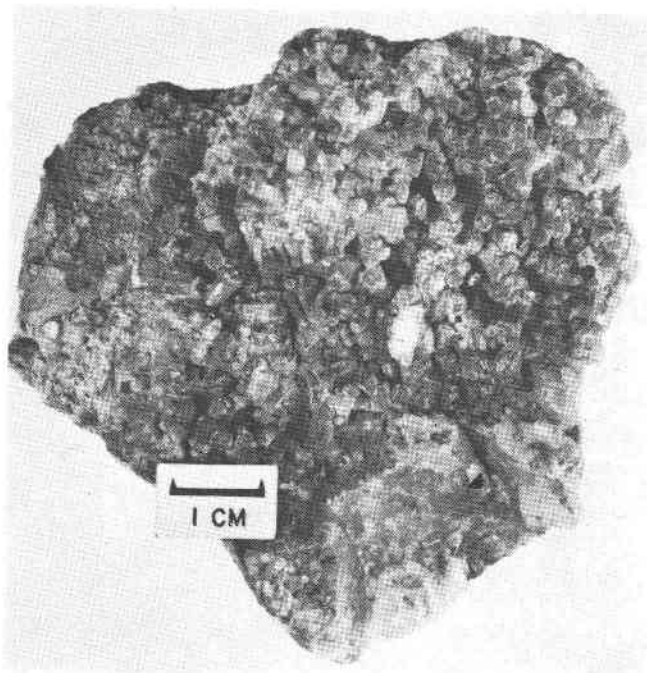

FIG. 1. Manganese- and strontium-bearing fluorapatite from the Peerless pegmatite, South Dakota.

faces represent aggregates of crystals growing together and thus interfering with each other's growth. The resultant strain may have caused much of the biaxial character noted.

X-ray data. X-ray diffractometry was done at a chart speed of $\frac{1}{4}°$ 2θ per minute using halite as an internal standard. These basic observational data were subjected to least-squares refinement to determine the cell parameters, which are given in Table 1. Table 2 gives the indexed interplanar spacings.

Magnetic susceptibility. Magnetic susceptibility was measured on a calibrated Frantz Isodynamic separator following McAndrew (1957). The method is precise enough to show differences in apatites.

This fluorapatite is unusual in that it possesses a relatively high magnetic susceptibility (Table 1), which is no doubt attributable to its manganese content (Vernon, 1961). Three other fluorapatites and a chlora-

TABLE 1. PHYSICAL PROPERTIES OF MANGANESE- AND STRONTIUM-BEARING
FLUORAPATITE FROM THE PEERLESS PEGMATITE, SOUTH DAKOTA

Optical	ω 1.6367 ± 0.0005 (sodium light) ϵ 1.6343 ± 0.0008 Birefringence 0.0024, Uniaxial (−) (some grains anomalously biaxial (−), 2V ranging to 20°)	
Unit cell	a 9.3759 ± 0.0008 Å c 6.880 ± 0.001 Å c/a 0.7338 Volume = 523.79 ± 0.09 Å³	
Magnetic susceptibility	2.7 ± 0.2 emu/g	
Density	Measured	3.228 ± 0.006
	Calculated	3.207[1] 3.214[2]

[1] Calculated on the basis of 25.87 (O, F, Cl, OH) in the unit cell.

[2] Calculated on the basis of 25.87 (O, F, Cl, OH) plus 0.13 oxygen (per unit cell) to balance formula valency.

patite were also measured and their magnetic susceptibilities were found to be considerably less, the greatest being 0.47 ± 0.03 emu/g.

Density. Grains of the fluorapatite were suspended in a mixture of methylene iodide and N,N-Dimethylformamide (Meyrowitz *et al.*, 1960). The density of the liquid was then determined using a constant temperature bath and a pycnometer whose volume was precisely known. The range of measured density is from 3.222 to 3.234, but the average of 3.228 ± 0.006 shown in Table 1 would include almost all of the apatite.

Density was calculated using the equation $D = 1/N(nM/V)$, where N equals Avogadro's number, n = number of molecules in the unit cell, M = molecular weight, and V = volume of unit cell = $a^2c \sin 60° \times 10^{-24}$.

TABLE 2. X-RAY POWDER DATA FOR MANGANESE- AND STRONTIUM-BEARING
FLUORAPATITE FROM THE PEERLESS PEGMATITE, SOUTH DAKOTA[1]

I	d (meas.)	d (calc.)[2]	kkl	I	d (meas.)	d (calc.)[2]	kkl
5	8.11	8.12	100	11	1.7984	1.7981	321
2	5.25	5.25	101	9	1.7723	1.7719	410
		4.688	110			1.7497	303
5	4.062	4.060	200	7	1.7486	1.7483	402
4	3.873	3.874	111	21	1.7202	1.7200	004
		3.497	201			1.7159	411
58	3.444	3.440	002			1.6827	104
11	3.169	3.168	102			1.6393	223
18	3.071	3.069	210	5	1.6380	1.6381	322
100	2.805	2.803	211			1.6240	500
46	2.775	2.773	112			1.6148	114
41	2.708	2.707	300	2	1.6065	1.6068	313
15	2.625	2.625	202			1.5838	204
2	2.520	2.519	301			1.5805	501
		2.344	220			1.5752	412
3	2.289	2.290	212			1.5627	330
25	2.253	2.252	310	3	1.5343	1.5345	420
3	2.219	2.219	221			1.5238	331
		2.207	103			1.5200	403
4	2.140	2.140	311			⎰1.5005	214
		2.127	302	4	1.4990	⎱	
3	2.060	2.060	113			1.4977	421
		2.030	400	5	1.4681	1.4686	502
		1.9968	203			1.4584	510
		1.9470	401	4	1.4513	1.4517	304
16	1.9371	1.9371	222	6	1.4461	1.4459	323
7	1.8841	1.8842	312	6	1.4262	1.4267	511
2	1.8628	1.8628	320	5	1.4103		332
25	1.8367	1.8371	213				

[1] CuKα radiation, Ni filter (λ = 1.5418 Å) for d ≥ 2.252. CuKα1 radiation, Ni filter (λ = 1.5405 Å) for d ≤ 2.219.

[2] d-spacings were calculated by Daniel E. Appleman using a computer-based least-squares refinement method.

CHEMICAL AND SPECTROGRAPHIC PROPERTIES

Chemical and spectrographic properties of the fluorapatite are given in Table 3. This fluorapatite is rather unique in that Mn and Sr are the only two unusual components of any quantitative significance. All other unusual components are less than 0.1 per cent. Reference to only three other fluorapatites containing over 1.0 per cent each of MnO and SrO were found in the literature. They are:

MnO, weight per cent	*SrO*, weight per cent	*Reference*
7.59	1.37	Mn apatite III, Finland, Volborth (1954).
2.13	1.60	Apatite B-40 from Dzhid, USSR, Vasileva (1958).
1.02	1.88	Eastern Kounrad, USSR, Chukrov (1960).

Of further interest is the fact that the Peerless pegmatite is beryl-bearing, which raises the question of how much Be the apatite structure will tolerate. Volborth (1954) has reported as much as 0.3 per cent Be in manganapatite. For four-fold coordination Be^{2+} has the ionic size 0.33 Å, which is exactly the same as that of P^{5+}, but the charge difference of 3 no doubt restricts substitution of Be for P. As mentioned above, there may be no genetic connection between the apatite-bearing fracture fillings and

TABLE 3. CHEMICAL AND SPECTROGRAPHIC ANALYSES OF FLUORAPATITE
FROM THE PEERLESS PEGMATITE, SOUTH DAKOTA

	Weight percent	Weight percent recalc. to 100%[1]	Ratios	Metal equivalent	Oxygen equivalent	Atoms per unit cell[2]
CaO	53.13	53.35	0.9513	0.9513	0.9513	9.65
MnO	1.82	1.83	.0258	.0258	.0258	.26
SrO	0.97	0.97	.0094	.0094	.0094	.10
P_2O_5	41.68	41.85	.2948	.5897	1.4742	5.98
F	3.25	3.26	.1716	—	.0858	1.74
Cl[3]	0.02	0.02	.0006	—	.0003	.01
H_2O+	0.04	0.04	.0022	.0044	.0022	.05
CO_2	0.04	0.04	.0009	.0009	.0018	.01
SO_3	0.01	0.01	.0001	.0001	.0004	.00
Al_2O_3	0.08	0				
Fe_2O_3	0.05	0				
FeO	0	0				
MgO	0.01	0				
Na_2O	0	0				
K_2O	0	0				
Acid insol. res.[4]	0.05	0				
Sub-total	101.15	101.38				
Less O	1.37	1.38				
Total	99.78	100.00				

[1] Acid insol. residue, Al_2O_3, Fe_2O_3, and MgO have been discounted as impurities.

[2] Calculated on the basis of 25.87 (O, F, Cl, OH) in the unit cell.

[3] <1 ppm Br and <50 ppm I reported by Pauline J. Dunton from x-ray spectrographic analysis.

[4] <0.005 percent soluble silica reported by Wayne Mountjoy.

Formula: $Ca_{9.65} Mn_{0.26} Sr_{0.10} (PO_4)_{5.98} (CO_3)_{0.01} F_{1.74} Cl_{0.01} (OH)_{0.05} O_{0.13}$

Oxygen has been added to balance valence.

MW = 1014.0

Analyst: Elaine L. Munson

TABLE 3—(*Continued*)

Spectrographic analysis

	Weight percent[5]	
Si	0.015	Also looked for but not detected:
Al	0.001	Ag, As, Au, B, Bi, Cd, Ce[6], Co, Ga, Ge, Hf, Hg, In, La, Li, Mo, Nb, Ni,
Fe	.03	Pb, Pd, Pt, Re, Sb, Sc, Sn, Ta, Te, Th, Tl, U, W, Y, Yb, Zn, Zr.
Mg	.001	[5] Results are reported in percent to the nearest number in the series 1,
Ca	M	0.7, 0.5, 0.3, 0.2, 0.15, and 0.1, etc.; which represent approximate mid-
Na	.05	points of group data on a geometric scale. The assigned group for semi-
K	0	quantitative results will include the quantitative value about 30% of the
Ti	0	time.
P	M	M = major constituent—greater than 10%.
Mn	2.0	0 = looked for but not detected.
Ba	.001	[6] Using the visual detection limit for the rare earths the sum of the rare
Be	.002	earths plus Y that could be present and still remain undetected would be
Cr	0.0003	0.013%.
Cu	.0001	
Sr	1.0	
V	.002	

Analyst: Nancy M. Conklin.

the main mass of the beryl-bearing pegmatite. Only 0.002 per cent Be was found in this fluorapatite (Table 3).

DISCUSSION OF CRYSTAL CHEMISTRY

Relation of ω index of refraction to chemical composition. The ω index of refraction of this fluorapatite is calculated, by use of the factors (except for slight changes) arrived at by Young (1964), as follows:

Oxide or element	*Weight per cent*	*Factor*
Cl	0.02	×0.0054 = 0.00011
MnO	1.82	×0.00142 = 0.00258
SrO	0.97	×0.00013 = 0.00013
H_2O+	0.04	×0.00912 = 0.00036
		0.00318
	ω of pure fluorapatite	1.6325
	Calculated ω	= 1.6357

As the measured omega is 1.6367 ± 0.0005, the calculated ω is 0.0010 too low. This is a fairly accurate check, but as MnO is by far the most influential oxide on the omega index of refraction in this fluorapatite, the factor for MnO is suspected of being too low. If this is true, we can subtract the negligible effects of Cl, SrO, and H_2O+ (0.0006) from the measured ω index of refraction and impute the remainder of the effect to MnO. When this is done, 1 per cent of MnO raises omega by 0.00198, or approximately 0.002.

Relation of c/a to birefringence. Hausen (1929) showed an interesting inverse relation between c/a (determined by crystal measurement) and birefringence in apatite. In part, Hausen's data are:

A patite from	c/a	$\omega - \epsilon$
Laacher See	0.7330	0.0033
Göschenen	.7340	.0027
St. Gotthard	.7342	.0025
Schöllenen	.7344	.0024
Auburn, Me.	.7348	.0019
Peerless pegmatite	.7338	.0024

The rule of Gladstone and Dale. The rule of Gladstone and Dale, $(n-1)/d = K$, does not apply very well for this fluorapatite. Using the specific refractive energy values presented by Larsen and Berman (1934), K, the total specific refractive energy for the mineral, calculates to 0.20338. Thus $dK+1$ equals 1.6565, and the mean index of the mineral $\frac{2\omega+\epsilon}{3}$ is 1.6359. Hence the calculated $dK+1$ is 0.0206 higher than the mean index. This is in the same general range as the +0.016 cited for fluorapatite by Jaffe (1956). Our interpretation of this rather large discrepancy is that the specific refractive energy values for either CaO or P_2O_5, or both, are too high.

Oxygen replacement for fluorine. Slightly different formulas result from different bases of calculation, but all of them yield the same valence imbalance of +0.26. As electrostatic neutrality must be maintained in a mineral, the addition of 0.13 atom/unit cell of oxygen (0.20 weight per cent of oxygen) in the halogen sites would satisfy neutrality. This is the best way the authors know of solving the valence imbalance. The formula calculated on the basis of 25.87 (O, F, Cl, OH) in the unit cell is believed to be the best according to the argument presented by Young and Munson (1966).[1] Calculated densities follow:

Basis on which formula is calculated	Calculated density	Plus oxygen to balance valence
(1) 25.87 (O, F, Cl, OH) in the unit cell.	3.207	3.214
(2) 26 (O, F, Cl, OH) in the unit cell.	3.223	3.230
(3) P+S=6.	3.219	3.225

The measured density is 3.228 ± 0.006. Calculated densities of (2) and (3) fit the measured density better than (1), but when it is remembered

[1] Although the authors prefer the view presented, it must be admitted that the valence imbalance of +0.26 might be caused by error in chemical analysis. Many more careful and comprehensive analyses of very pure apatites will be needed before this question can be settled.

that the sum of the chemical analysis (Table 3) does not quite total 100 per cent, implying that certain components are probably too low, all of the calculated densities therefore represent a minimum value. If we allow for slight increases in these calculated densities (perhaps as much as 0.01), the calculated density of (1) would fit very well, whereas those of (2) and (3) would be too high.

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STABILITY AND PROPERTIES OF THE SYNTHETIC PYROXENE CaAl₂SiO₆[1]

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Clark, *et al.*, (1962) report the synthesis of a clinopyroxene having the composition $CaAl_2SiO_6$, which they refer to as "lime Tschermak's mole-

[1] Published under the auspices of the committee on Experimental Geology and Geophysics and the Dept. of Geological Sciences, Harvard University.