

THE SUBSTITUTION OF SiO_4 - AND SO_4 -GROUPS FOR
 PO_4 -GROUPS IN THE APATITE STRUCTURE;
ELLESTADITE, THE END-MEMBER

DUNCAN McCONNELL,
University of Minnesota, Minneapolis, Minnesota.

INTRODUCTION AND ACKNOWLEDGMENTS

During the course of an extensive structural investigation¹ of the isomorphism of the apatite group, it has become necessary to investigate the substitutions of the sort found in wilkeite. Although this mineral is reported to contain approximately 12 per cent of SO_3 , 9 per cent of SiO_2 and only 21 per cent of P_2O_5 , it was correctly assigned to the apatite group by Eakle and Rogers (1) on the basis of its crystallographic, physical and optical properties.

For several reasons it seemed desirable to obtain a new analysis of this most unusual mineral from Crestmore, California. Accordingly some material, supposedly wilkeite, was prepared for analysis by separating it from contaminating minerals (idocrase, calcite, wollastonite, diopside, okenite, etc.) through the use of Thoulet's solution, followed by selection under the binocular microscope. Eight grams of this material was furnished to Dr. Ellestad for analysis, but the results of his determinations are quite different from wilkeite. Indeed, the differences between this mineral and wilkeite are so great as to require a new name. The differences may be summarized as follows:

(1) The new mineral very closely approaches an end-member of the apatite group which has not been previously known to exist.

(2) There seem to be no theoretical objections to the existence of the ultimate end-member.

(3) This material contains only about three per cent of P_2O_5 , whereas wilkeite contains nearly 21 per cent, according to the original description (1).

The name ellestadite is proposed for the end-member of the apatite group which contains SiO_4 - and SO_4 -groups substituting for PO_4 -groups. Ellestadite is selected in honor of Dr. R. B. Ellestad, of the Laboratory for Rock Analysis, University of Minnesota, in recognition of his invaluable assistance to geologists and mineralogists as an analytical chemist who has devoted much thought and effort to the composition of earth materials.

¹ The results of this work will appear later.

Three different lots of material from Crestmore, California, were examined in this study, and certain differences were found, as mentioned below. These will be referred to as follows:

I. Pale rose-colored stringers of ellestadite associated with wollastonite, vesuvianite, diopside, etc., $\omega = 1.655 \pm .002$, $\epsilon = 1.650 \pm .002$. Kindly furnished by Dr. A. Pabst, of the University of California.

II. Individual crystals and small groups of pale rose-colored wilkeite in a matrix of coarse blue calcite and associated with diopside, $\omega = 1.650 \pm .002$, $\epsilon = 1.646 \pm .002$. Obtained from Mr. R. M. Wilke, Palo Alto, California.

III. Lavender-colored stringers of sugary wilkeite in a fine grained matrix of vesuvianite, pale blue calcite, etc., $\omega = 1.640 \pm .002$, $\epsilon = 1.636 \pm .002$. Obtained from Ward's Natural Science Establishment, Rochester, New York.

All of these specimens are uniaxial and negative. The specific gravities and the dimensions of the unit cells show considerable differences, but these properties do not necessarily furnish sufficient data by which to identify these minerals. This is true because of the complications introduced by the variability of the fluorine, chlorine and carbon dioxide. However, it was found that the chlorine content increased with the silica content, whereas the fluorine content decreased, and it is believed that the amount of silica present may be the factor controlling the chlorine content. The problem is further complicated by the presence of the voelckerite molecule $(\text{Ca}, \text{X})_{10}\text{O}_2(\text{PO}_4)_6$.²

The writer is indebted to Dr. J. W. Gruner for his kind interest in the problems pertaining to the isomorphism of the apatite group and for his many valuable suggestions. He is greatly indebted to Dr. A. Pabst, of the University of California, who furnished material for the analysis, and to Mr. A. S. Dadson, of Toronto, who supplied the analyzed specimen of fluor-apatite which was used as a basis of comparison. Dr. R. B. Ellestad has furnished several analyses which have been extremely valuable in contributing to an understanding of the isomorphism of the minerals of this group. Messrs. E. L. Berg and Lynn Gardiner have also kindly assisted in several instances.

STRUCTURAL DATA

Náray-Szabó (2) and Mehmel (3) have shown that the unit cell of fluor-apatite contains: 10 Ca-ions, 6 P-ions, 24 O-ions and 2 F-ions.

² The formula of voelckerite is advisedly written as $(\text{Ca}, \text{X})_{10}\text{O}_2(\text{PO}_4)_6$ rather than $\text{Ca}_{10}\text{O}(\text{PO}_4)_6$ which is the formula previously suggested (11). Under these circumstances X has a valence greater than two and is usually carbon. This is discussed more fully below.

The positions of these ions are indicated in Fig. 1, in accordance with the parameters given by Mehmel (4).³ The P-ions lie at the centers of regular tetrahedra, surrounded by four O-ions. In ellestadite, as shown below, nearly all of these P-positions are occupied by S- and Si-ions and these ions also lie at the centers of tetrahedra. In wilkeite II about one-third of the positions contain phosphorus and the other two-thirds contain S- and Si-ions. These substitutions are possible because the radii of these ions are very similar.

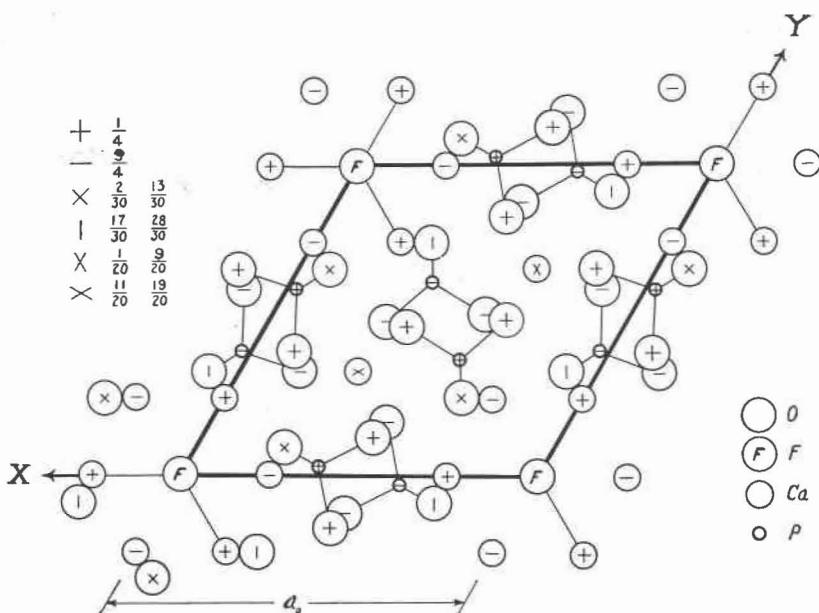


FIG. 1. Projection of the unit cell of fluor-apatite on {0001}. The symbols indicate the distances of the various ions above the base. The F-ions are at $\frac{1}{4}$ and $\frac{3}{4}$ c . The symmetry is $C_{6h}^2-C6_3/m$.

The interplanar distances obtained for ellestadite are compared with those obtained for fluor-apatite, in Table 1. The fluor-apatite is a specimen from Faraday Township, Hastings County, Ontario, which has been analyzed by Dadson (5, anal. II, p. 59). The unit cell dimensions obtained for ellestadite, wilkeite and fluor-apatite are comparable, as follows:

³ Although Fig. 1 is based on the parameters given by Mehmel, it is slightly different from Mehmel's diagram. Why there should be this slight discrepancy is not apparent.

	a_o	c_o	c/a	Vol.	Theor. density	Meas. density	P ₂ O ₅ (wt. %)
Ellestadite, I	9.53Å	6.91Å	.7251	544	3.046	3.068	3.07
Wilkeite, II	9.48	6.91	.7289	538	—	3.120	14.4
Wilkeite, III	9.40	6.89	.7330	527	—	3.157	32.2
Fluor-apatite	9.36	6.88	.7350	522	3.187 ⁴	3.18 ⁵	41.30 ⁶

(All values for a_o and c_o are $\pm 0.01\text{\AA}$.)

The dimensions obtained for fluor-apatite are quite similar to those obtained by Náray-Szabó, namely, $c_o = 9.37$ and $a_o = 6.88$ (both $\pm 0.01\text{\AA}$). If these values were determined on analyzed material, this fact was not recorded. It has been found, however, during the measurement of more than twenty specimens of the apatite group, that the differences in the a -dimension are considerably greater than those of the c -dimension. This is apparent on comparison of ellestadite and wilkeite with fluor-apatite.

The axial ratio obtained by goniometric measurement for wilkeite (1) was .730 and this value is in close agreement with the value obtained by x -ray methods (.7289) for specimen II. The slight differences are to be accounted for in terms of chemical differences in the specimens. Contrary to the supposition by Eakle and Rogers (1) wilkeite is *not* nearly constant in composition, but shows considerable variability in the single occurrence at Crestmore.

For reasons which have been fully discussed by Gruner and McConnell (6) in an investigation of carbonate-apatites, it is necessary to assume that the carbon occupies either the P-positions or positions on the threefold axes on which the Ca-ions are located (Fig. 1) or both of these positions. If the carbon occurs on the three fold axes it substitutes for calcium; otherwise it substitutes for phosphorus, but a discussion of these unusual types of substitution cannot be entered into here, and is only mentioned by way of preparing the reader for the disposition which is made of CO₂ in the analysis given below.

⁴ Value calculated from the molecular weight of the theoretical fluor-apatite (1008.9) rather than the constituents reported by Dadson (5, anal. II, p. 59).

⁵ This value is preferable to the value (3.176) previously reported (5, p. 59), according to a personal communication from Mr. A. S. Dadson.

⁶ This value was actually determined, as compared with 42.27% (for theoretical fluor-apatite), which was used in calculating the theoretical density. This produces a slight discrepancy between the theoretical density and the measured density, because the analysis showed the presence of very small amounts of elements which would tend to decrease the density. Nevertheless, the agreement is excellent, and the use of the constituents actually determined would considerably increase the complexity of the calculations, without furnishing compensating benefits.

TABLE 1. COMPARISON OF POWDER DIAGRAMS OF FLUOR-APATITE AND ELLESTADITE
(Unfiltered Fe Radiation— $r=57.3$ mm.)

No.	Indices	Fluor-apatite		Ellestadite	
		<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
1	002	3.432	2	3.452	3
2	120, 210	3.060	3	3.118	2
3	300 β	2.975	0.5	3.034	0.5
4	202 β	2.884	0.5	2.920	0.5
5	121, 211	2.798	>10	2.845	>10
6	112	2.769	4	2.798	4
7	300	2.702	6	2.750	6
8	202	2.616	3	2.647	3
9	301	2.517	0.5	2.557	0.5
10	130 β	2.477	0.5	2.523	0.5
11	122, 212	2.289	0.5	2.315	0.5
12	130, 310	2.248	2	2.289	3
13	131, 311	} 2.135	1 {	—	—
14	222 β			2.161	1
15	113	2.057	1	2.074	0.5
16	123 β	2.026	0.5	2.046	0.5
17	203	2.001	0.5	—	—
18	231 β	—	—	2.013	0.5
19	222	1.937	4	1.961	6
20	132, 312	1.883	1	1.909	2
21	123, 213	1.838	6	1.857	6
22	231, 321	1.795	3	1.827	3
23	140, 410	1.769	3	1.802	3
24	402	1.745	3	1.771	3
25	004	1.720	3	1.727	3
26	232, 322	1.637	1	1.661	1
27	133, 313	1.605	0.5	—	—
28	240, 420	1.533	0.5	1.560	0.5
29	331	1.521	0.5	1.548	0.5
30	124, 214	1.498	1	1.511	0.5
31	502	1.468	2	1.490	2
32	304	1.452	1	} 1.464	3
33	233, 323	1.445	1		
34	151, 511	1.424	1	1.451	2

PHYSICAL AND OPTICAL DATA

Although the theoretical density of ellestadite (3.046) does not show particularly close agreement with the measured value (3.068), this discrepancy is no greater than .7 of 1%. Using a fused silica pycnometer (capacity 10 cc.) and a four gram sample, the value obtained was 3.067 (4°C.). Small fragments were used and great care was used to liberate air. An independent determination, using a centrifuge and Thoulet's solution, was made by Mr. E. L. Berg and the value obtained was 3.069 (4°C.). Values for specimens II and III were obtained by the latter method and were, respectively, 3.120 and 3.157. This indicates that the value reported by Eakle and Rogers (1) for wilkeite (3.234) is considerably too high. This value cannot be correct for theoretical reasons because all of the constituents of wilkeite (except manganese, of which 0.77% was reported) are lighter than the corresponding constituents of fluor-apatite. Therefore, the theoretical density cannot be greater than that of fluor-apatite (3.18-3.19), and is probably always considerably less—judging from the specimens examined in this study.

It is noteworthy that the refractive indices decrease with an increase in density in this isomorphous series (Fig. 2). This somewhat unusual relationship obtains because the atomic refractivity of chlorine is much greater than that of fluorine, but chlorine increases the size of the unit cell more rapidly than it increases the molecular weight, thus lowering the density.

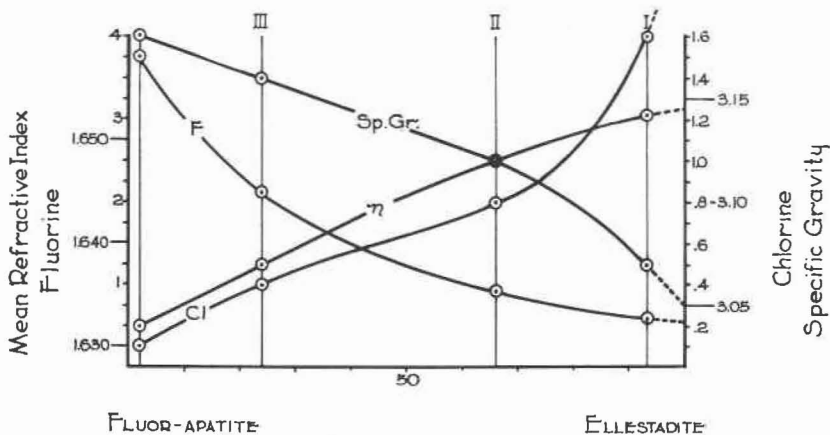


FIG. 2. Comparisons of refringence, specific gravity, chlorine and fluorine for the end-members and two intermediate compounds of the ellestadite-apatite series. The positions of the different members were calculated in terms of the P_2O_5 content, by comparing the amount determined with 42.27% (the theoretical value for fluor-apatite). This approximation is used because the molecular ratio $SO_3:SiO_2$ is not necessarily 1:1, and other complications (oxy-apatite, chlor-apatite, etc.) would make the calculations extremely tedious.

CHEMICAL DATA

An analysis of ellestadite is given in Table 2. The analysis was made on material which was selected as described above. Separate portions were used for P₂O₅ and CaO determinations. The samples were dissolved in HNO₃, and the silica was separated by double evaporation. CaO was determined by the ammonium oxalate-oxalic acid method of Hillebrand and Lundell. P₂O₅ was determined by precipitation as phospho-molybdate, followed by double precipitation as magnesium ammonium phosphate, and ignition to pyrophosphate. A double sodium carbonate fusion, each followed by a water extraction, was used to separate the sulphate from calcium. Silica was removed from this extract by double evaporation from acid solution, and the sulphate was finally precipitated as BaSO₄. A sodium carbonate fusion was also made for the chlorine determination. The leached extract from this was acidified with HNO₃, and the chlorine precipitated as AgCl. Fluorine was determined by Armstrong's modification (7) of the method of Willard and Winter (8). Water and carbon dioxide were determined by the usual methods.

TABLE 2. CHEMICAL ANALYSIS AND NUMBER OF IONS IN ELLESTADITE

	1	2	3	4	5	6	7	8	9
	Wt. %	Mol. ratios	Ionic ratios	Impurities deducted	Ionic ratios	Number of ions in cell	Positive charges	Negative charges	Molecular weight
CaO	55.18	9.841	9.841	.052	9.789	9.920	19.840		397.49
MgO	0.47	.117	.117	.060	.057	.058	.116		1.41
MnO	0.01	—	—		—	—	—		—
CO ₂	0.61	.139	.139		.139	.141	.564		1.69
P ₂ O ₅	3.06	.215	.430		.430	.436	2.180		13.53
SO ₃	20.69	2.584	2.584		2.584	2.619	15.714		83.97
SiO ₂	17.31	2.882	2.882	.093	2.789	2.826	11.304		79.30
Cl	1.64	.462	.462		.462	.468		.468	16.60
F	0.57	.300	.300		.300	.304		.304	5.78
H ₂ O+	{ 0.45	.250	.500		.500	.507		.507	8.62
	{ 0.08*	—							
H ₂ O—	0.10	—							
Fe ₂ O ₃	0.22	.015	.030	.030					
Al ₂ O ₃	0.13	.013	.026	.026					
Less O	100.52				O =	24.721		49.442	395.54
	.61								
	99.91					42.000	49.7	50.7	1003.93

* Removed at 300°C.

In Table 2, column 1 contains the weight per cents of the oxides; column 2 contains the molecular ratios, and column 3 the ionic ratios. Column 5 contains the ratios of the ions after the deduction of the impurities contained in column 4 (see below). Column 6 contains the number of ionic positions relegated to each element; columns 7 and 8 contain the charges of these ions; and column 9 contains the molecular weight.

Although great care was used in selecting the specimen for analysis, it was not possible to obtain material which was entirely uncontaminated. For this reason the deductions shown in column 4 (Table 2) were made because both the original material and the insoluble residue were found to contain idocrase. The insoluble residue, however, was analyzed and found to contain iron oxide, alumina, calcia and silica and these are allotted to idocrase, as is also about half of the magnesia. Calcite was not found in the ellestadite specimen and, because wilkeite and numerous other apatites contain CO_2 , there is no reason for believing that the CO_2 reported is not a constituent of the ellestadite molecule.

The calculation of the charges shows a slight discrepancy, but this is not excessive when it is remembered that several of the factors for the positive ions are as great as five and six.

The various ions of the structure are relegated to the four different sorts of ionic positions of fluor-apatite as follows:

$$\begin{aligned} 10 \text{ Ca} &= 9.92 \text{ Ca} + 0.06 \text{ Mg} + 0.02 \text{ C} \\ 6 \text{ P} &= 0.44 \text{ P} + 2.62 \text{ S} + 2.82 \text{ Si} + 0.12 \text{ C} \\ 2 \text{ F} &= 0.30 \text{ F} + 0.47 \text{ Cl} + 0.51 \text{ OH} + 0.72 \text{ O} \\ 24 \text{ O} &= 24 \text{ O}_\omega \end{aligned}$$

— = ionic positions of fluor-apatite.

The ratio of the carbon in Ca-positions to carbon in P-positions is 0.02:0.12 which, peculiarly enough, is similar to the distribution found in the case of francolite (0.113:0.652) where there was, however, 3.36% of CO_2 instead of only 0.61% (6). Not only do both of the wilkeite specimens examined contain CO_2 , but both of them contain halogens, as follows:

	D ⁷	$n_{\omega+e/2}$	P ₂ O ₆ ⁷	SiO ₂ ⁷	Cl ⁷	F ⁷	CO ₂ ⁷
Ellestadite, I	3.07	1.652	3.1	17.3	1.6	0.6	0.6
Wilkeite, II	3.12	1.648	14.4	11.2	0.8	0.9	*
Wilkeite, III	3.16	1.638	32.2	2.9	0.4	2.1	*
Fluor-apatite	3.18	1.632	41.3	—	0.1	3.7	0.5

* Present, but not determined.

⁷ These values have been reduced by one significant figure for simplicity. This has no bearing on the more exact values given elsewhere.

Because the methods used to determine the halogens are extremely reliable, there can be little doubt regarding the existence of the voelckerite molecule. Even if it were to be assumed that CO_3 -groups can enter the structure in the F-positions, there would still be a deficiency which would require the assumption of the voelckerite molecule. Because CO_2 cannot enter the structure in this manner as has been shown (6) and because Bredig, Franck and Fuldner (9) have obtained synthetic preparations containing 60–70% of this molecule, there can be no further doubt concerning its existence. These authors, however, found that pure oxy-apatite (voelckerite) cannot exist and this is probably to be explained on the basis of the hypothesis, advanced here, that the composition is not $\text{Ca}_{10}\text{O}(\text{PO}_4)_6$, but $(\text{Ca}, \text{X})_{10}\text{O}_2(\text{PO}_4)_6$. The additional negative charges which arise through the introduction of an additional O-ion may be compensated by carbon substituting for calcium on the threefold axes, in which case the balanced formula becomes $(\text{Ca}_9\text{C})\text{O}_2(\text{PO}_4)_6$. For structural reasons the formula $\text{Ca}_{10}\text{O}(\text{PO}_4)_6$ seems highly improbable.

A sulfate-apatite was reported by Brauns (10) from the Laacher See district. He states, however, that it was not possible to ascertain the true relationship of the SiO_2 to the other constituents.⁸ Recalculation of Brauns' analysis suggests that part of the insoluble matter, of which there was 4.80%, was silica which replaced phosphorus in the structure. If this be true Brauns was dealing with wilkeite from a second locality, but this supposition requires further confirmation.

SUMMARY AND CONCLUSIONS

The apatite group is composed of a number of isomorphous series. The series apatite-wilkeite-ellestadite has been investigated in terms of both end-members and two intermediate members. Ellestadite has not been previously recognized, and a substance very close to this end-member was found to have the following properties:

Chemical composition: a calcium sulfate-silicate, containing halogens and minor amounts of CO_2 and P_2O_5 .

Structure: space group C_{6h}^2 , with $a_o = 9.53 \pm 0.01 \text{ \AA}$, $c_o = 6.91 \pm 0.01 \text{ \AA}$ and $c/a = .7251$.

Optical properties: uniaxial, negative, $\epsilon = 1.650 \pm .002$, $\omega = 1.655 \pm .002$.

Physical properties: sp. gr. 3.068 (4°C.), cleavage and other properties essentially similar to apatite.

Locality: Crestmore, Riverside County, California.

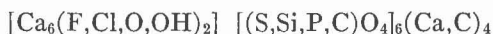
⁸ "Aus dem Umstand, dass bei der Auflösung dieses Apatits eine zarte Haut von Kieselsäure in dem Umriss des aufgelösten Kristalls zurückbleibt, könnte man weiter schliessen, dass auch Kieselsäure als eine der Nebensäuren auftritt; diese Frage kann aber aus Mangel an Material nicht entschieden werden." (10, p. 89.)

Although ellestadite and wilkeite contain halogens and carbon dioxide, it is necessary to assume that they also contain the oxy-apatite molecule. A slightly modified formula for this molecule is suggested for structural reasons, and this is $(\text{Ca}, \text{X})_{10}\text{O}_2(\text{PO}_4)_6$.

The almost complete replacement of phosphorus, one of the chief constituents of apatite, by sulfur and silicon without appreciably altering the structure is most interesting and has rather broad implications.

Carbon dioxide was found to play a dual rôle in its manner of entering the apatite structure, as has been previously found in the case of francolite. This and other features contribute to the great complexity of the isomorphism of the apatite group.

The structural formula of ellestadite and (with slight modification) of wilkeite is:



This formula indicates that two-fifths of the Ca-ions are located on threefold axes and can be replaced by carbon. Three-fifths of the Ca-ions are tied to F-, Cl- and O-ions or OH-groups, and cannot be replaced by carbon. All of the Ca-ions are tied to O-ions which are arranged in tetrahedral configurations with S-, Si-, P- or C-ions at their centers.

REFERENCES

1. Eakle, A. S., and Rogers, A. F., Wilkeite, a new mineral of the apatite group, and okenite, its alteration product, from Southern California: *Am. Jour. Sci.*, [4], vol. 37, pp. 262-267, 1914.
2. Náráy-Szabó, St., The structure of apatite $(\text{CaF})\text{Ca}_4(\text{PO}_4)_3$: *Zeits. Krist.*, vol. 75, pp. 387-398, 1930.
3. Mehmel, Martin, Über die Struktur des Apatits I: *Zeits. Krist.* vol. 75, pp. 323-331, 1930.
4. Mehmel, Martin, Beziehungen zwischen Kristallstruktur und Formel des Apatits: *Zeits. physik. Chem.*, [B], vol. 15, pp. 223-241, 1931.
5. Dadson, A. S., A study of some Canadian apatites: *Univ. Toronto Studies. Geol. Ser., Contributions to Canadian Mineral.*, no. 35, pp. 51-59, 1933.
6. Gruner, J. W., and McConnell, Duncan, The problem of the carbonate-apatites. The structure of francolite: *Zeits. Krist.*, vol. 96 (in press).
7. Armstrong, W. D., Modification of the Willard-Winter method for fluorine determination: *Jour. Amer. Chem. Soc.*, vol. 55, pp. 1741-1742, 1933.
8. Willard, H. H., and Winter, O. B., Volumetric method for determination of fluorine: *Ind. and Eng. Chem., Anal. Edition*, vol. 5, pp. 7-10, 1933.
9. Bredig, M. A., Franck, H. H., and Fuldner, H., Beiträge zur Kenntnis der Kalk-Phosphosäure-Verbindungen II: *Zeits. Elektrochem.*, vol. 39, pp. 959-969, 1933.
10. Brauns, R., Über den Apatit aus dem Laacher Seegebiet. Sulfatapatit und Carbonatapatit: *Neues Jb. Min., Geol., Pal., Beil. B.*, vol. 41, pp. 60-92, 1917.
11. Rogers, A. F., Dahllite (podolite) from Tonopah, Nevada, voelckerite, a new basic calcium phosphate; remarks on the chemical composition of apatite and phosphate rock: *Am. Jour. Sci.*, [4], vol. 33, pp. 475-482, 1912.