

A contribution to the crystal chemistry of ellestadite and the silicate sulfate apatites¹

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Abstract

A series of calcium silicate sulfate apatites from Crestmore, California, which contain the coupled substitution $\text{Si}^{\text{IV}}\text{S}^{\text{VI}}$ for 2P^{V} , has been investigated using electron microprobe, powder diffraction, and single-crystal diffraction methods. Chemical analysis of eighteen specimens of different phosphorus contents proves that the Si:S ratio is essentially 1:1 and yields the idealized general formula $\text{Ca}_{10}(\text{SiO}_4)_{3-x}(\text{SO}_4)_{3-x}(\text{PO}_4)_{2x}(\text{OH},\text{F},\text{Cl})_2$, where $x = 0$ to 3. The members of this series for which $x = 0$ and $3/2$ have been labelled "ellestadite" and "wilkeite", respectively, by previous workers. "Ellestadite" is actually a solid solution involving the end-members $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{Z}_2$, where $\text{Z} = \text{OH}$ (hydroxyllelestadite), F (fluorellestadite), or Cl (chlorellestadite). The term ellestadite is redefined to make it a group name for all compositions having $\Sigma(\text{Si},\text{S}) > \text{P}$. Wilkeite is not a valid mineral species, since it is only one of many solid solutions involving the six end-members fluorapatite, hydroxyapatite, chlorapatite, fluorellestadite, hydroxyllelestadite, and chlorellestadite.

Although natural hydroxyllelestadite is monoclinic, precession photographs of type "ellestadite" and "wilkeite" show hexagonal symmetry and no evidence of Si-S ordering as suggested by the Si:S ratio of 1:1. The silicate sulfate apatites from Crestmore show a strong linear relationship between their P and F contents, such that these two variables simultaneously go to zero. Linear relationships also exist between their unit cell parameters and their P, F, and (Si+S) contents. These correlations imply a convergence of the Crestmore apatite series towards a hypothetical member of composition $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH},\text{Cl})_2$ and cell constants $a = 9.543$ and $c = 6.917\text{\AA}$.

Introduction

Crystal structures of the apatite type, general formula $\text{A}_{10}(\text{XO}_4)_6\text{Z}_2$, are notable for their ability to accommodate a great variety of atoms in their A, X, and Z sites by means of simple or coupled ionic substitutions (Dihm and Klement, 1942; Schwarz, 1967a, b, c; Cockbain, 1968; Ito, 1968; Kreidler and Hummel, 1970; McConnell, 1973). An example of the latter mechanism is the substitution $\text{Si}^{\text{IV}}\text{S}^{\text{VI}} \rightleftharpoons 2\text{P}^{\text{V}}$, which occurs in the minerals wilkeite and

ellestadite, conventionally formulated as $\text{Ca}_5(\text{SiO}_4, \text{SO}_4, \text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$ and $\text{Ca}_5(\text{SiO}_4, \text{SO}_4)_3(\text{OH}, \text{F}, \text{Cl})$, respectively. Since these phases are of some industrial (Pliego-Cuervo and Glasser, 1978; Trivino Vazquez, 1979) as well as crystal chemical and mineralogical interest and since very little modern analytical data exists for either the natural minerals or their synthetic analogues, we have undertaken a re-examination of ellestadite and wilkeite using type and cotype materials from Crestmore, California. In this report we present new analytical chemical, powder diffraction, and single-crystal diffraction data, which bear upon the crystal chemistry of the silicate sulfate apatites and the interpretations made of it by previous

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Historical review

The replacement of a substantial portion (~50%) of the PO_4 by $(\text{SiO}_4, \text{SO}_4)$ in a new mineral of the apatite group was reported by Eakle and Rogers (1914) in their description of wilkeite from Crestmore. This was the first example of a coupled atomic substitution in an apatite structure to be recognized as such. Additional data on wilkeite were given by Rogers (1929), McConnell (1937, 1938), and Taylor (1953), who showed the supposed mineral crestmoreite to be a submicroscopic intergrowth of wilkeite and the calcium silicate hydrate, tobermorite. More recently, wilkeite has been reported from Timna', Israel (Würzberger, 1970), Takiue, Japan (Harada *et al.*, 1971), and the Adirondack Mountains of New York (J. W. Valley, personal communication). Apatites containing a few percent SiO_2 and SO_3 occur at other localities, *e.g.*, the Rhineland (Brauns, 1916) and the Ural and Aldan regions of the Soviet Union (Vasileva, 1958), but these are better termed silicatian sulfatian apatites rather than wilkeite. In fact, as we shall later show, the name wilkeite is itself superfluous and should be discarded.

Ellestadite was also first described from Crestmore by McConnell (1937), who distinguished it from wilkeite chiefly on the basis of chemical composition. Whereas type wilkeite had 20.85% P_2O_5 , McConnell found a specimen with only 3.06% P_2O_5 and called it ellestadite. No difference in paragenesis or space group symmetry was evident for ellestadite and the mineral is visually indistinguishable from wilkeite. The crystal chemistry of ellestadite, wilkeite, and intermediate compositions was further explored by McConnell (1938). Dihn and Klement (1942) synthesized the pure compounds $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{F}_2$ and $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH})_2$, which we shall call fluorellestadite and hydroxyllellestadite, respectively, along with a number of other exotic apatite isotypes containing PO_4 , SiO_4 , and SO_4 in various proportions, some of which deviated from the ideal $\text{A}_{10}(\text{XO}_4)_6\text{Z}_2$ stoichiometry. Pliego-Cuervo and Glasser (1978) synthesized a third ellestadite-like phase, $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{Cl}_2$, which we shall call chlorellestadite. Further developments along these lines appear in papers by Schwarz (1967a, b, c), Ito (1968), and Kridler and Hummel (1970).

The term "hydroxyllellestadite" was introduced by Harada *et al.* (1971) to denote an impure form of $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH})_2$, which occurs at Doshinkubo in the Chichibu mining district of Japan. The new mineral was found to be crystallographically and chemically similar to ellestadite, except for the fact that $\text{OH} > (\text{F} + \text{Cl})$, and the space group was assigned as $P6_3/m$ on the basis of precession photographs. More recently, however, Sudarsanan (1980) has reported natural hydroxyllellestadite to be monoclinic-pseudohexagonal with space group $P2_1/m$ and $a = 9.476(2)$, $b = 9.508(2)$, $c = 6.919(1)\text{\AA}$, and $\gamma = 119.53(2)^\circ$. The monoclinic cell is not of the same type as that found in monoclinic phosphate apatites, since the latter is a supercell having $b = 2a$ and $\gamma = 120.0^\circ$ (Young, 1975). Whether all hydroxyllellestadites are monoclinic remains an open question. Sudarsanan's results were obtained from one crystal and it is possible that, like hydroxyapatite, some crystals are monoclinic and others hexagonal.

Trivino Vazquez (1979) reported ellestadite as a constituent of the incrustations formed in cement heat-exchange cyclones. He further stated that the thermal decomposition of ellestadite in the presence of potassium yields a "K ellestadite" of probable formula $\text{Ca}_{10}\text{KSi}_3\text{S}_2\text{O}_{22}\text{F}$. The existence of this compound remains unproven as of this writing.

Experimental

Chemical analysis of eighteen silicate sulfate apatites including type ellestadite and cotype wilkeite are presented in Table 1. All analyses were performed on an ARL-SEM-Q electron microprobe using an operating voltage of 15 kV, a beam current of 0.15 μA , and the following standards: hornblende for Si; fluorapatite for P, Ca, and F; scapolite for Cl; and celestine for S. The data were corrected using Bence-Albee factors. The low summations in Table 1 are due mostly to the fact that CO_2 and H_2O were not determined. Published values for these two components are 2.10% CO_2 and a trace of H_2O in wilkeite (Eakle and Rogers, 1914) and 0.61% CO_2 and 0.63% H_2O in ellestadite (McConnell, 1937). Although McConnell reported minor quantities of MgO, MnO, Al_2O_3 , and Fe_2O_3 (<0.5% each with the Fe and Al attributed to admixed vesuvianite) in ellestadite, our specimens show traces of Mn as the only other detectable element of atomic number greater than nine.

Single-crystal fragments of type ellestadite (NMNH #103072) and cotype wilkeite (NMNH #95685) were examined by the precession method.

Table 1. Electron microprobe analyses of silicate sulfate apatites from Crestmore, California

NMNH #	SiO ₂	CaO	SO ₃	P ₂ O ₅	F	Cl	O=F,Cl	Total
B17219	3.8	55.5	4.2	33.1	2.6	0.5	1.2	98.5
R5256	4.1	55.5	5.1	33.0	2.8	0.5	1.3	99.7
95685	9.4	55.2	11.7	18.2	1.6	0.8	0.8	96.1
94033-3	9.6	55.9	12.7	18.1	1.3	0.8	0.7	97.7
94463	10.1	55.8	13.9	16.4	1.3	0.7	0.7	97.5
94033-2	10.8	55.5	14.0	15.6	1.2	0.7	0.7	97.1
93417	10.8	54.7	14.3	15.0	1.3	0.7	0.6	96.2
94416	11.4	55.2	14.5	14.2	1.1	0.8	0.6	96.6
C4050	11.1	55.1	14.9	13.8	1.2	0.7	0.7	96.1
R18742	11.5	55.0	14.7	13.4	1.1	0.8	0.6	95.9
94033-1	12.9	55.2	17.3	9.9	0.8	0.8	0.5	96.4
C4105	12.8	54.7	16.6	9.8	0.9	0.8	0.5	95.1
87287	14.1	55.8	17.7	8.8	0.7	1.0	0.6	97.5
R9217-1	15.5	55.7	20.4	4.7	0.4	0.4	0.3	96.8
R9213	16.0	55.4	21.0	4.3	0.4	0.5	0.3	97.3
R9217-3	16.2	55.3	19.9	3.8	0.3	0.5	0.2	95.8
R9215	16.2	56.3	20.9	3.8	0.4	0.5	0.3	97.8
103072	16.8	55.7	21.2	3.2	0.3	1.7	0.5	98.4
Theory†	17.41	54.12	23.18			6.84	1.55	100.0
Theory††	17.98	55.90	23.94		3.78		1.60	100.0
Theory†††	18.05	56.12	24.04					100.0*

*---Includes 1.79 percent H₂O.

†---For end-member chloroellestadite.

††---For end-member fluorellestadite.

†††---For end-member hydroxylellestadite.

NMNH 94463 is type wilkeite; NMNH 95685 is cotype wilkeite.

Accuracy of data: ±4 percent of the amount present for S.

±3 percent of the amount present for other elements.

Zero and upper level photographs of both minerals show no deviation from the expected *6/m* Friedel symmetry, indicating space group *P6₃* or *P6₃/m* when the extinctions are taken into account, and no evidence of monoclinic superstructure reflections. The Debye-Scherrer powder data in Table 2 were obtained with a 114.6 mm diameter camera and an

Table 2. Powder X-ray diffraction data for type ellestadite and wilkeite

I	Ellestadite			Wilkeite			I	Ellestadite			Wilkeite		
	d _{obs}	d _{cal}	hkl	d _{obs}	d _{cal}	hkl		d _{obs}	d _{cal}	hkl	d _{obs}	d _{cal}	hkl
2	8.28	8.25	8.26	8.21	100		4	1.855	1.854	1.847	1.849	213	
<1	5.30	5.30	5.27	5.28	101		1	1.826	1.826	1.818	1.817	321	
<<1	4.74	4.76	4.76	4.74	110		1	1.801	1.801	1.792	1.792	410	
1	4.14	4.13	4.14	4.11	200		1	1.772	1.772	1.764	1.764	402	
<1	3.927	3.923	3.920	3.908	111		2	1.727	1.728	1.726	1.726	004	
5	3.458	3.457	3.456	3.453	002		<1	1.660	1.661	1.653	1.653	322	
1	3.180	3.188	3.181	3.183	102				1.657	1.651	1.651	223	
2	3.116	3.119	3.105	3.103	210		<<1	1.625	1.625	1.618	1.622	114	
10	2.843	2.843	2.833	2.831	211				1.624	1.619	1.619	313	
4	2.800	2.798	2.786	2.791	112		<<1b	1.554	1.560	1.550	1.552	420	
									1.548	1.540	1.540	331	
7	2.751	2.751	2.736	2.737	300		<<1b	1.514	1.521	1.512	1.514	421	
3	2.651	2.650	2.648	2.642	202				1.512	1.509	1.509	214	
<<1	2.558	2.556	2.546	2.544	301		<1	1.488	1.490	1.485	1.483	502	
<1	2.309	2.316	2.301	2.308	212		1	1.462	1.464	1.461	1.460	304	
3	2.286	2.289	2.275	2.277	310				1.463	1.458	1.458	323	
<1	2.173	2.173	2.163	2.163	311		<1	1.448	1.449	1.443	1.442	511	
<1	2.075	2.075	2.069	2.070	113				1.422	1.415	1.415	422	
<<1	2.010	2.012	2.007	2.008	203		<<1	1.420	1.419	1.418	1.414	413	
4	1.964	1.962	1.956	1.954	222								
2	1.908	1.908	1.900	1.901	312								

Samples used: NMNH #103072 (ellestadite) and NMNH #95685 (wilkeite)

114.6 mm Debye-Scherrer camera, Si internal standard, CuKα radiation, visually estimated intensities, b = broad line

NBS silicon ($a = 5.43088\text{\AA}$) internal standard. The *d*-values represent a considerable improvement over those previously published for ellestadite and wilkeite. In addition, unit cell parameters for five of the chemically analyzed specimens (but not for the same crystals which had been analyzed) were calculated from the powder data using a silicon internal standard. These were refined by the method of least-squares assuming hexagonal symmetry. The results appear in Table 3.

Results and discussion

Chemical composition

The chemical formula assigned to ellestadite in most reference books is $\text{Ca}_5(\text{SiO}_4, \text{SO}_4)_3(\text{OH}, \text{F}, \text{Cl})$ or some variant thereof. All of them are derived from the only published analysis of this mineral by Ellestad in McConnell (1937). A new computation of the unit cell contents using our refined cell parameters and Ellestad's analysis recalculated to 100% after deducting Ca, Mg, Fe, and Al due to vesuvianite yields $[\text{Ca}_{10.01}\text{Mg}_{0.06}\Sigma_{10.07}[(\text{SiO}_4)_{2.85}(\text{SO}_4)_{2.64}(\text{PO}_4)_{0.44}(\text{CO}_3)_{0.14}]\Sigma_{6.07}[(\text{OH})_{0.51}\text{F}_{0.31}\text{Cl}_{0.47}]\Sigma_{1.29}]$. Our partial chemical analysis of type ellestadite (Table 1) is consistent with this result. In the above formula all of the carbon has been allotted to the phosphorus site, McConnell's allotment of some to the calcium site as C^{4+} being chemically unrealistic. Carbonate ion may also be situated in the Z (halide) site according to Young (1975), but this would not alleviate the apparent deficit of 0.7 atom in $\Sigma(\text{OH}, \text{F}, \text{Cl})$. The source of the deficit may be an error in the determination of H₂O, or the presence of O²⁻ ions in the Z site as proposed by McConnell (1937), or the existence of atomic vacancies at this site. In fact, a substantial fraction (up to 50%) of the hydroxyl sites may be vacant in biogenic apatites and synthetic hydroxyapatites (Young, 1975).

Table 3. Unit cell parameters of several silicate sulfate apatites from Crestmore, California

Sample	Wt.% P	a (Å)	c (Å)	V (Å ³)	c/a
B17219	14.4	9.414(2)	6.896(2)	529.2(2)	0.7327
95685	7.9	9.480(2)	6.905(2)	537.5(3)	0.7284
93417	6.4	9.491(2)	6.906(1)	538.8(2)	0.7276
94033-1	4.3	9.498(2)	6.913(2)	540.0(2)	0.7278
103072	1.4	9.530(2)	6.914(2)	543.8(2)	0.7255

Estimated standard deviations in parentheses refer to last digit. NBS silicon internal standard.

A most important feature of the ellestadite formula is the Si:S ratio, which is 28:26 or nearly 1:1. Reference to Figure 1 shows the same to be true of all analyses in Table 1, except perhaps for the silician sulfatian apatite B17219. If this specimen is excluded, the average deviation from 1:1 stoichiometry is only 4% and in no case does it exceed 9%. Ignoring the minor CO₂ content and possible Z site vacancies, the correct structural formula for natural ellestadite is therefore Ca₁₀(SiO₄)₃(SO₄)₃(OH,F,Cl)₂, which is in accord with the tetrahedral anion ratio in the synthetic phases of Dihn and Klement (1942). Extending this to the whole solid solution series in Table 1, the general formula is Ca₁₀(SiO₄)_{3-x}(SO₄)_{3-x}(PO₄)_{2x}(OH,F,Cl)₂, where x varies from 0 (ellestadite) to 3 (apatite). The constancy of the Si:S ratio at 1:1 is, of course, a consequence of the necessity to maintain overall electrostatic neutrality in the crystal structure, *i.e.*, the average valence of SiO₄⁴⁻ and SO₄²⁻ is the same as the valence of PO₄³⁻. Moreover, the mean bond lengths Si-O = 1.62 Å in silicates (Liebau, 1972) and S-O = 1.47 Å in sulfates (Wuensch, 1972) average to 1.54 Å, which is equal to the mean P-O bond distance in monophosphates (Liebau, 1970).

The presence of SiO₄ and SO₄ groups in consistently equal numbers suggests the possibility of silicon-sulfur ordering in the ellestadite structure if not in its more phosphate-rich congeners. If the space group is really *P*6₃ or *P*6₃/*m* as indicated by the precession photographs, no such ordering can occur since all tetrahedrally coordinated atoms must be situated in the same 6-fold equipoint, 6*c* in *P*6₃ or 6*h* in *P*6₃/*m*, to be consistent with the apatite structure. However, in the structure of monoclinic hydroxyellestadite (Sudarsanan, 1980), the tetrahedrally coordinated atoms (X) are divided among three 2-fold equipoints and from the variation in X-O distances there does appear to be some degree of silicon-sulfur ordering. Whether the same phenomenon obtains in ellestadite, wilkeite, any of the intermediate compositions, or even in all hydroxyellestadites cannot be determined from the data presently available.

Elemental correlations

McConnell (1937) found an unexpected correlation between the elements in the X and Z sites in the silicate sulfate apatites from Crestmore. Specifically, as the phosphorus content decreased toward the ellestadite composition, the fluorine and chlorine

contents decreased and increased, respectively. The converse would, of course, be true for the variation of fluorine and chlorine with Σ(Si,S). Reference to Table 1 shows that there is, in fact, no correlation between phosphorus and chlorine contents. Indeed, the latter element remains nearly constant for all specimens analyzed except for #103072, which is type ellestadite. The mean chlorine content, excluding #103072, is 0.7 wt.% with a range of ±0.3 wt.%.

There is, however, a strong positive correlation between fluorine and phosphorus as shown in Fig. 2. A linear regression of wt.% F on wt.% P yields the relationship

$$\text{wt.}\% \text{ F} = 0.03 + 0.18 \text{ wt.}\% \text{ P} \quad r = 0.994, \\ (0.04) \quad (0.02)$$

where *r* is the correlation coefficient and the numbers in parentheses are the standard errors of the regression coefficients. The two variables go to zero simultaneously, the apparent residual of 0.03% F being statistically insignificant. It is tempting to speculate that the regression line in Fig. 2 might become somewhat nonlinear in the region above 10% P curving upwards to terminate at the composition point for fluorapatite, which is the theoretical limit for fluorine content. In any case, Figure 2 shows that the composition of the Crestmore silicate sulfate apatite series converges toward a fluo-

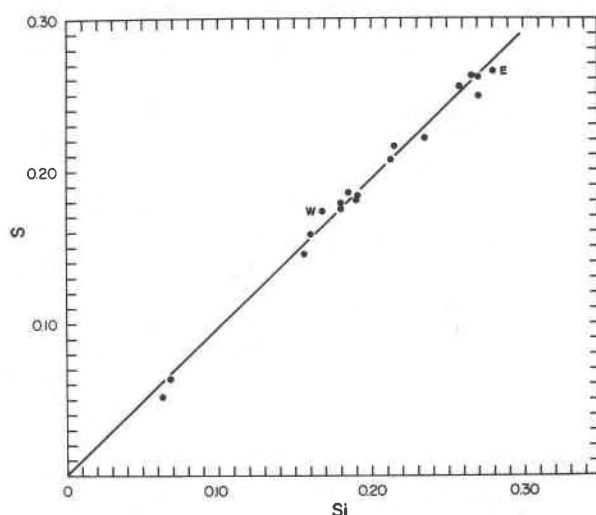


Fig. 1. Variation of the atomic proportions of silicon with those of sulfur. The slope of the regression line is 0.970 (correlation coefficient *r* = 0.995) indicating that Si:S is essentially 1:1. W and E are composition points of type wilkeite and type ellestadite, respectively.

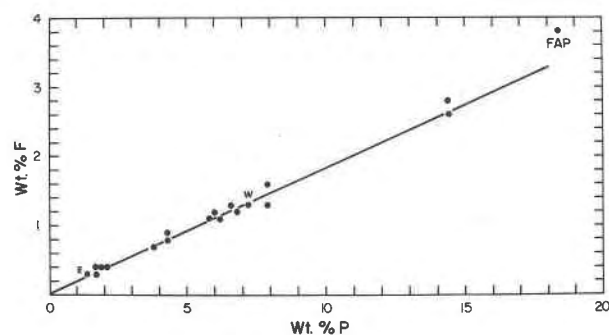


Fig. 2. Variation of wt.% fluorine with wt.% phosphorus. W, E, and FAP are the composition points of type wilkeite, type ellestadite, and pure fluorapatite, respectively.

rine- and phosphorus-free entity, $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH},\text{Cl})_2$.

Cell parameter variations

Comparison of the data in Tables 1 and 3 shows some systematic relationships between the unit cell parameters and chemical composition. Both a and c increase linearly as wt.% P decreases (Figs. 3 and 4), although the latter parameter does so at a much slower rate. Vegard's Law is therefore obeyed by this solid solution series. Here a and c have been plotted against wt.% P for convenience; plots against wt.% (Si+S) and wt.% F are also linear. The regression equations are

$$\begin{aligned} a &= 9.543 - 0.0087 \text{ wt.\% P} & r &= -0.990 \\ & \quad (0.006) \quad (0.0007) \\ c &= 6.917 - 0.0014 \text{ wt.\% P} & r &= -0.985 \\ & \quad (0.001) \quad (0.0001) \end{aligned}$$

which at 0% P predict parameters $a = 9.543$ and $c = 6.917 \text{ \AA}$ for the hypothetical series member $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH},\text{Cl})_2$ mentioned earlier. Un-

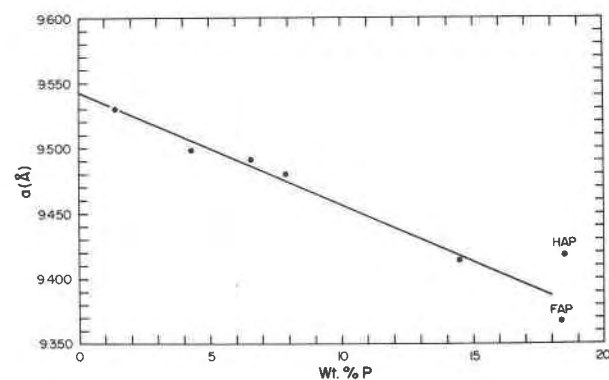


Fig. 3. Variation of the cell parameter a with wt.% phosphorus. FAP and HAP represent pure fluorapatite and hydroxyapatite, respectively.

fortunately, these values cannot be compared to those of pure hydroxyllelestadite and chlorellestadite, since cell parameters for the latter compound are unavailable.

The cell constants of the apatite group are known to be affected by substitutions in the A (cation), X (tetrahedral), and Z (halide) sites. According to McConnell (1973), an increasing chlorine content increases a but decreases c , while increasing hydroxyl increases both parameters. LeGeros (1965) found that increasing the amount of carbonate ion in the X site shortens a by about 0.01 \AA for each 1.66 wt.% CO_3 but lengthens c only slightly. Among the apatite isotypes listed in Table 1, chlorine remains approximately constant and will therefore contribute negligibly to the observed systematic changes in a and c . The only available values for CO_2 (0.61% in type ellestadite and 2.10% in type wilkeite) correspond to decreases of 0.005 and 0.017 \AA in a relative to the same compositions without carbonate. Since two CO_2 determinations are not enough to establish any systematic changes, if any exist, in the carbonate content of the Crestmore silicate sulfate apatites, the effect of CO_3 ion on their cell dimensions cannot be evaluated at this time.

As noted previously, the Si:S ratio is essentially constant at 1:1 and the mean of the effective radii of SiO_4 and SO_4 is equal to the effective radius of PO_4 . Thus changes in the (Si,S):P ratio should not affect the size of the unit cell. Moreover, substitutions for calcium in the A site are negligible in the specimens analyzed. This leaves only the increasing degree of OH for F substitution in the Z site and a possible, but unproven, systematic decrease in carbonate content as the principal causes of the increase in a and c as the ellestadite composition is approached.

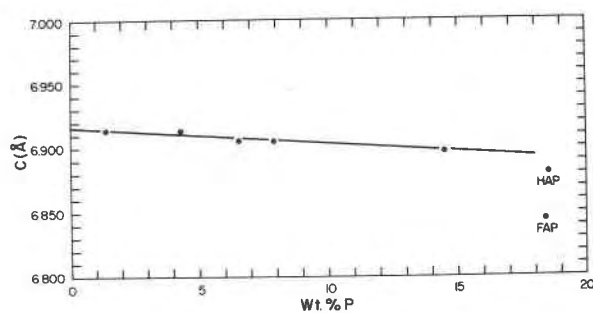


Fig. 4. Variation of the cell parameter c with wt.% phosphorus. FAP and HAP represent pure fluorapatite and hydroxyapatite, respectively.

Nomenclature revisions

From the foregoing discussion it is apparent that ellestadite and wilkeite are members of several solid solution series involving (Si,S,P,C) and (OH,F,Cl,O?). Neglecting the two minor components, the carbonate and oxide ions (the presence of the latter is problematical), the solid solution relationships among the calcium silicate sulfate apatites are best displayed on a trigonal prismatic composition diagram. The upper triangular face consists of the three pure end-members $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{Z}_2$, where Z = OH (hydroxyllelestadite), F (fluorellestadite), or Cl (chlourellestadite), while the lower triangular face consists of the end-members $\text{Ca}_{10}(\text{PO}_4)_6\text{Z}_2$, where Z = OH (hydroxyapatite), F (fluorapatite), or Cl (chlorapatite).

Since the atomic ratios in type ellestadite are Si:S:P = 28:26:4 and OH:F:Cl = 5:3:5, the composition of this mineral falls just below the approximate center of the ellestadite face of the composition prism. The tetrahedral atom ratio in type wilkeite is Si:S:P = 16:15:30 (F and Cl were not determined by Eakle), which places this material somewhere in the median plane of the prism. Note that the composition of wilkeite does not approach that of any of the end-members defined above. Wilkeite is, in fact, merely one of numerous compositions intermediate between the ellestadite and apatite faces. There is therefore no chemical justification for regarding this compound as a distinct mineral species. Moreover, the single-crystal and powder diffraction data indicate that there is nothing in the known crystallography of wilkeite to set it apart from other intermediate compositions in the series. Its cell parameters follow the same trends illustrated in Figures 3 and 4 as those of other compositions.

There is one additional difficulty with attempting to maintain the validity of wilkeite as a distinct species. Whereas in the case of ellestadite the type material is well-defined, there exists no exact type specimen of wilkeite. The one designated as the type in Table 1 (NMNH #94463) is only one specimen from the type lot. Documentation of the type status of #94463 is inadequate and the correspondence between our chemical analysis of this specimen and the analysis in Eakle and Rogers (1914) is poor. The composition of NMNH #95685 is in better agreement with Eakle's analysis, but the connection between this specimen and his is very tenuous.

In view of the foregoing arguments, it may be asked whether the term "ellestadite" should not

also be discarded in favor of fluorellestadite, hydroxyllelestadite, and chlourellestadite. We believe that "ellestadite" still has utility as a group name for all of the apatite isotypes of composition $(\text{Ca} \dots)_5[(\text{Si},\text{S},\text{P},\text{C})\text{O}_4]_3(\text{OH},\text{F},\text{Cl})$ when that composition does not approximate any of the pure end-members named above. The only restriction is that $\Sigma(\text{Si},\text{S})$ must exceed P in atomic percent. Specimens having $\Sigma(\text{Si},\text{S}) \leq \text{P}$ are best termed silicatian sulfatian apatites.

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