The crystal chemistry of the apatites

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Summary. The compositions of more than eighty synthetic members of the apatite group with the general formula $A_{10}(XO_4)_6Z_2$ have been used as a basis for classifying the apatites into three groups. The ratios of the mean sizes of the 'A' ions to those of the 'X' ions for all these compositions lie between the limits of 1·89 and 4·43. A discontinuity occurs between ratios of 2·50 and 2·60 and probably another between 3·25 and 3·35, and these discontinuities provide a structural basis for the division into the three groups. The groups are named after well-known mineral species occurring in each group, i.e. the vanadinite–svabites with an $A:X$ ratio less than 2·5, the apatite–mimetites between 2·60 and 3·25, and the pyromorphites with $A:X$ greater than 3·25.

THE naturally occurring apatites form a numerous and diverse group of minerals, while in addition a large number of synthetic compounds with the apatite type structure are known. Syntheses of various members of the group have been successful under a great variety of conditions such as chemical precipitation at ambient temperatures, hydrothermally, and by solid state reactions or from the melt at high temperatures (1000° C or more), and more than half the naturally occurring elements are known to be accommodated in the apatite lattice to a significant extent.

Several species, particularly the type mineral fluorapatite, $Ca_{10}(PO_4)_6F_2$, its hydroxy analogue hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$, and the lead apatite, pyromorphite, $Pb_{10}(PO_4)_6Cl_2$, have been the subject of detailed studies, but despite this work no wholly satisfactory systematic classification has so far been proposed. Indeed, probably the best classification, and certainly one with the most satisfactory paragenetic basis, has been the division into the 'apatites' containing little or no lead, and the 'lead apatites' or 'pyromorphites'. These latter have the general formula $Pb_{10}(XO_4)_6Z_2$, where X is usually P, but may be V or As, and Z usually Cl, but may be F or Br in synthetic pyromorphites. Some synthetic lead apatites have been prepared that contain iodine,

but other apatites containing iodine are unknown. Published data for lattice parameters of apatites show that a ranges from 9·12 to 10·48 Å and c from 6·71 to 7·98 Å for the compounds $Ca_5Cd_5(PO_4)_6F_2$ and $Ba_{10}(VO_4)_6(OH)_2$ respectively. Trömel and Eitel (1957) have, however, described a synthetic calcium yttrium abukumalite with an exceptionally small c parameter of 6·58 Å. The separation of the lead apatites (i.e. the pyromorphites) from the rest of the group corresponds to a division at about a 9·75 Å, c 6·92 Å, i.e. the lattice parameters of svabite, $Ca_{10}(AsO_4)_6F_2$.

Recent studies (Cockbain and Smith, 1967) have shown that a number of alkaline-earth–rare-earth silicates and germanates also have the apatite structure, and these have cell sizes that span this division between the 'apatites' and the 'pyromorphites'. Some, particularly the barium lanthanum apatites, have lattice parameters comparable with members of the pyromorphite group. Thus $Ba_2La_8(SiO_4)_6O_2$ has a 9·76 Å c 7·30 Å and $Pb_{10}(PO_4)_6F_2$ a 9·76 Å c 7·29 Å while $Ba_3La_7(GeO_4)_6O_{1·5}$ has a 9·99 Å, c 7·39 Å, and $Pb_{10}(AsO_4)_6F_2$ has a 10·07 Å, c 7·42 Å. During these synthetic studies, however, it became apparent that prediction of the composition of compounds with apatite-type structures could not be made solely on the basis of satisfying valency considerations, since the occurrence of the apatite type structure appears also to be determined by the ratio of the mean size of the 'A' ions (i.e. the Ca ions in fluorapatite) to the mean size of the 'X' ions in the XO_4 group. In simple structures, a dependence of structure type on factors such as the ratio of ionic radii is well known, as is the occurrence of morphotropy (i.e. the progressive change in crystal structure brought about by systematic chemical substitution), and it is hardly surprising that such a fundamental rule also applies to much more complex structures.

Size ratios for thirty-six elements in the 'A' and 'X' positions and for thirty-one elements in combination with the pairs of ions $Si^{4+}+S^{6+}$ and $Cr^{3+}+2Cr^{6+}$ are given in table I. Most of the ions listed have known radii for eight-fold coordination, but for those that do not normally exhibit eight-fold coordination an effective radius has been calculated, together with the values of the effective $A:X$ ratio. Thus when these ions are in the apatite lattice, their contribution to the over-all $A:X$ ratio may be calculated. Wyckoff (1965) lists some sixty apatite compositions, and these compositions and their $A:X$ ratios together with those for compositions listed by Cockbain and Smith (1967) are given in table II. Carbonate apatites have however been excluded, and the reasons for

this will be discussed later. Data for table II include some compounds deficient in the '*A*' site, e.g. $La_8(SiO_4)_6$ and for these the normal $A:X$ ratio has been multiplied by 0·8.

TABLE I. Ratio of size of 'A' ion to 'X' ion in $(XO)_4$ group

Size of 'A' ions in [8] (Å)	*'X' ion*						
	P^{5+} (0·33 Å)	$Si^{4+}+S^{6+}$ (0·34 Å)	Si^{4+} (0·40 Å)	As^{5+} (0·44 Å)	Ge^{4+} (0·5C Å)	$Cr^{3+}+2Cr^{6+}$ (0·53 Å)	V^{5+} (0·56 Å)
*Mg^{2+} 0·69	2·09	2·03	1·72	1·57	1·38	1·30	1·23
*Ni^{2+} 0·72	2·18	2·12	1·80	1·64	1·44	1·36	1·29
*Sc^{3+} 0·84	2·54	2·47	2·10	1·91	1·68	1·58	1·50
*Lu^{3+} 0·88	2·67	2·59	2·20	2·00	1·76	1·66	1·57
*Yb^{3+} 0·89	2·70	2·62	2·23	2·02	1·78	1·68	1·59
*Tm^{3+} 0·90	2·73	2·65	2·25	2·04	1·80	1·70	1·61
*Er^{3+} 0·92	2·79	2·71	2·30	2·09	1·84	1·74	1·64
Ho^{3+} 0·94	2·85	2·76	2·35	2·14	1·88	1·77	1·68
Yb^{2+} 0·94	2·85	2·76	2·35	2·14	1·88	1·77	1·68
Dy^{3+} 0·95	2·88	2·79	2·37	2·16	1·90	1·79	1·70
Pr^{4+} 0·95	2·88	2·79	2·37	2·16	1·90	1·79	1·70
*Y^{3+} 0·95	2·88	2·79	2·37	2·16	1·90	1·79	1·70
Tb^{3+} 0·96	2·91	2·82	2·40	2·18	1·92	1·81	1·71
Ce^{4+} 0·97	2·94	2·85	2·42	2·20	1·94	1·83	1·73
Tl^{3+} 0·99	3·00	2·91	2·47	2·25	1·98	1·87	1·77
Bi^{3+} 1·00	3·03	2·94	2·50	2·27	2·00	1·98	1·79
Cd^{2+} 1·01	3·06	2·97	2·52	2·29	2·02	1·90	1·80
Gd^{3+} 1·01	3·06	2·97	2·52	2·29	2·02	1·90	1·80
Na^{1+} 1·01	3·06	2·97	2·52	2·29	2·02	1·90	1·80
U^{4+} 1·01	3·06	2·97	2·52	2·29	2·02	1·90	1·80
Eu^{3+} 1·02	3·09	3·00	2·55	2·32	2·04	1·92	1·82
Ca^{2+} 1·03	3·12	3·03	2·57	2·34	2·06	1·94	1·83
Sm^{3+} 1·04	3·15	3·06	2·60	2·36	2·08	1·96	1·86
Th^{4+} 1·06	3·21	3·12	2·65	2·41	2·12	2·00	1·89
Nd^{3+} 1·08	3·27	3·18	2·70	2·45	2·16	2·04	1·93
Pr^{3+} 1·10	3·33	3·23	2·75	2·50	2·20	2·07	1·96
Ce^{3+} 1·11	3·36	3·26	2·77	2·52	2·22	2·09	1·98
Eu^{2+} 1·12	3·39	3·29	2·80	2·54	2·24	2·11	2·00
Sr^{2+} 1·16	3·51	3·41	2·90	2·64	2·32	2·19	2·07
U^{3+} 1·16	3·51	3·41	2·90	2·64	2·32	2·19	2·07
La^{3+} 1·18	3·57	3·47	2·95	2·68	2·36	2·23	2·11
Th^{3+} 1·19	3·61	3·50	2·97	2·70	2·38	2·24	2·12
Pb^{2+} 1·24	3·76	3·65	3·10	2·82	2·48	2·34	2·21
*K^{1+} 1·39	4·21	4·09	3·47	3·16	2·78	2·62	2·48
*Ba^{2+} 1·40	4·24	4·12	3·50	3·18	2·80	2·64	2·50
*Rb^{1+} 1·54	4·67	4·53	3·85	3·50	3·08	2·91	2·75
*Tl^{1+} 1·54	4·67	4·53	3·85	3·50	3·08	2·91	2·75
*Cs^{1+} 1·74	5·27	5·12	4·35	3·95	3·48	3·28	3·11

* Size adjusted for eight-fold coordination.

The $A:X$ ratio of all these compositions lies between the limits of 1·89 (for $La_8(GeO_4)_6$) and 4·43 (for $Pb_{10}(SiO_4)_2(BO_3)_4$). No single phase hexagonal apatite has as yet been prepared with an $A:X$ ratio of $2{\cdot}57 \pm 0{\cdot}05$, and as will be discussed later, this discontinuity affords a natural division between Group I and Group II apatites. Only two apatite compositions have been recorded which have $A:X$ ratios between 3·23 and 3·49 and these two compositions are $Pb_{10}(GeO_4)_2(PO_4)_4$ with $A:X$ of ratio of 3·33 and $Pb_{10}(SiO_4)(GeO_4)(PO_4)_4$ with a ratio of 3·44.

TABLE II. A classification of synthetic and natural apatites; the natural species are in bold-face type.

Group I apatites The vanadinite–svabites		Group II apatites The apatite-mimetites		Group III apatites The pyromorphites	
Composition	$A:X$ ratio	Composition	$A:X$ ratio	Composition	$A:X$ ratio
$La_6(GeO_4)_6$	1·89	$Ca_6Nd_4(SiO_4)_6$	2·62	$Pb_{10}(GeO_4)_2(PO_4)_4$	3·33
$Ca_{10}(CrO_4)_6(OH)_2$	1·94	$Ca_4Nd_4(SiO_4)_6(OH)_2$	2·65	$Pb_{10}(SiO_4)(GeO_4)(PO_4)_4$	3·44
$Pb_8Na_2(VO_4)_6$	2·13	$Ca_8Ce_2La_2(SiO_4)_6$	2·68	$Pb_{10}(PO_4)_4(SiO_4)_2$	3·49
$Ca_4Ce_6(GeO_4)_6.Cl_2$	2·16	$Ca_6Ce_2(GeO_4)_2(PO_4)_4$	2·68	$Pb_8Na_2(SO_4)_2(PO_4)_2(SiO_4)_2$	3·50
$Ca_6La_4(GeO_4)_6$	2·18	$Pb_8Na_2(AsO_4)_6$	2·71	$Sr_{10}(PO_4)_6.(OH,F)_2$	3·51
$Ca_4La_3Ce_3(GeO_4)_6(OH)_2$	2·20	$Pb_{10}(GeO_4)_2(AsO_4)_4$	2·71	$Ca_4Na_6(SO_4)_6.F_2$	3·52
$Pb_{10}(VO_4)_6.(F,Cl,Br,I)_2$	**2·21**	$Ca_{10}La_3Ce_5(SiO_4)_{12}(OH)_2$	2·71	$Pb_9Na(PO_4)_5(SiO_4)$	3·59
$Pb_8Tl_2(VO_4)_6$	2·22 (2·13–2·32)	$Ca_6La_4(SiO_4)_6$	2·72	$Pb_8Na_2(PO_4)_6$	3·62
$Ca_4La_6(GeO_4)_6.(OH)_2$	2·24	$Ca_4La_3Ce_3(SiO_4)_6.(OH)_2$	2·74	$Pb_8KNa(PO_4)_6$	3·73
$Pb_8K_2(VO_4)_6$	2·26	$Ca_6La_3(SiO_4)_6.OH$	2·76	**$Pb_{10}(PO_4)_6(F,Cl,Br,OH)_2$**	**3·76**
$Sr_4Dd_6(SiO_4)_6(OH)_2$*	2·26	$Ca_4La_6(SiO_4)_6(OH)_2$	2·80	$Pb_8Tl_2(PO_4)_6$	3·80 (3·66–3·94)
$Pb_{10}(GeO_4)_2(VO_4)_4$	2·30	$Ca_4La_6(SiO_4)_6F_2$	2·80	$Pb_8K_2(PO_4)_6$	3·85
$Sr_4La_6(GeO_4)_6(OH)_2$	2·34	$Pb_8KNa(AsO_4)_6$	2·80	$Pb_8Rb_2(PO_4)_6$	3·94
$Ca_{10}(AsO_4)_6.(F,Cl)_2$	**2·34**	**$Pb_{10}(AsO_4)_6.(F,Cl,Br,I)_2$**	**2·82**	$Pb_8Cs_2(PO_4)_6$	4·06
$Ca_4Ce_6(GeO_4)_4(SiO_4)_2.Cl_2$	2·34	$Pb_8Tl_2(AsO_4)_6$	2·82 (2·70–2·95)	$Ba_{10}(PO_4)_6(F, OH)_2$	4·24
$La_6(SiO_4)_6$	2·36	$Tl_2La_8(SiO_4)_6(OH)_2$	2·85	$Pb_{10}(SiO_4)_2(BO_3)_4$	4·43
$Ca_4Ce_4(GeO_4)_4(PO_4)_2.Cl_2$	2·41	$Ba_{10}(MnO_4)_6.(OH)_2$	2·86		
Ca_4Y_6†$(SiO_4)_6.(OH)_2$	2·45	$Ba_{10}(CrO_4)_6.(OH)_2$	2·86		
$Ba_2La_8(GeO_4)_6.O_2$	2·45	$Pb_8K_2(AsO_4)_6$	2·89		
$Ba_3La_7(GeO_4)_6.O_{1·5}$	2·49	$Pb_{10}(SiO_4)_3(AsO_4)_4$	2·91		
$Ca_4Ce_6(GeO_4)_2(SiO_4)_4.Cl_2$	2·49	$Sr_4La_6(SiO_4)_6(OH)_2$	2·93		
$Ba_{10}(VO_4)_6.(OH)_2$	2·50	$Pb_8Rb_2(AsO_4)_6$	2·96		
$Pb_{10}(SiO_4)_2(VO_4)_4$	2·51	$Pb_{10}(SiO_4)_3(VO_4)_2(PO_4)_2$	3·02		
$Sr_{10}(MnO_4)_6.(OH)_2$ (?)	2·52	$Ca_9Mg(PO_4)_6.Cl_2$	3·02		
		$Ca_9Ni(PO_4)_6.O$	3·03		
		$Ca_{10}(SiO_4)_3(SO_4)_3(OH)_2$	**3·03**		
		$Pb_{10}(SiO_4)(GeO_4)(PO_4)_2(AsO_4)_2$	3·05		
		$Ca_6Cd_5(PO_4)_6.F_2$	3·09		
		$Ba_3La_7(SiO_4)_6.(OH)_2$	3·11		
		$Ca_9Cd(PO_4)_6.F_2$	3·11		
		$Ca_{10}(PO_4)_6.(F,Cl,Br,OH)_2$	**3·12**		
		$Pb_9Bi_2(SiO_4)_6(PO_4)_2$	3·16		
		$Ca_9Sr(PO_4)_6.O$	3·16		
		$Ca_9Pb(PO_4)_6.(O, Cl_2)$	3·18		
		$Ca_9Ba(PO_4)_6.(O, Cl_2)$	3·23		

* Dd_2O_3 = Didymium oxide. † Y_2O_3 = Mixed rare earth containing 56% Y_2O_3, 4% Gd_2O_3, 13% Dy_2O_3 and the remainder other rare earths.

Although therefore the evidence for a discontinuity is not as good as that between Groups I and II, it is suggested that one probably exists at $3{\cdot}28 \pm 0{\cdot}05$ and thus forms a division between Group II and Group III apatites. This value for $A:X$ in any case provides a convenient division, since Group II apatites display a considerable range of composition, while Group III apatites are predominantly lead apatites. From the occurrence of well-known mineral apatites in each group it is suggested that these three groups are known as the vanadinite–svabite ($A:X$ less that 2·5), apatite–mimetite ($A:X$ between 2·60 and 3·25), and pyromorphite groups ($A:X$ more than 3·25) respectively.

Although $A:X$ ratios for carbonate apatites may be calculated, they have been excluded from table II largely on the grounds that there is some doubt about the structural role of the CO_3^{2-} group in apatites. However, assuming that carbon proxies for phosphorus, a carbonate apatite such as $Ca_9Ba(CO_4)(PO_4)_5(OH)_2$ has an $A:X$ ratio of 3·6, and therefore belongs to Group III, i.e. the pyromorphites. A further reason for excluding them lies in an attempt to base table II on end-members produced by high-temperature processes and which are either stoichiometric or which contain a stable cation-deficient configuration such as $La_8(SiO_4)_6$.

Apatites produced by synthetic processes at low temperatures display a number of peculiarities, including non-stoichiometry, and these make an assessment of stable ionic configurations difficult. For example, bone apatites are piezoelectric, although true apatites with the space group $P6_3/m$ are not. Montel (1958) has shown that the composition of fluorapatite is dependent on preparation process and Posner *et al.* (1960) have shown that cation stoichiometry varies and affects the nature of the bonding in the hydroxylapatite lattice. From this point of view, the status of the solid-solution series among the lead apatites and particularly between pyromorphite, mimetite, and vanadinite is of considerable interest. Baker (1966) has claimed that complete solid-solution series exist between the end-members prepared by wet chemical methods, while Adler (1964) has suggested that intergrowths (where present) may be distinguished from solid solution series by infra-red spectra. Baker (1966) appears to have assumed that his precipitated lead apatites are stoichiometric.

Data compiled in table II suggests that the vanadinites should be separated from the mimetites and pyromorphites, i.e. that the solid-solution series is discontinuous in the range of $A:X$ ratios between 2·50 and 2·60, although this discontinuity may only be found in samples

prepared or annealed at high temperatures. The comparative purity of vanadinites may be a geochemical accident but on the other hand it may have a structural significance. Annealing and other experiments on a composition comprising 0·41 of $Pb_{10}(VO_4)_6Z_2$ and 0·59 of $Pb_{10}(AsO_4)_6Z_2$ with an $A:X$ ratio of 2·57 would be of interest in establishing the existence or otherwise of continuous solid-solution series among these two members, and could clarify the status of the mineral endlichite, which is notable for a V:As ratio of 1:1.

The possible existence of a discontinuity in solid-solution series in the apatites, or the non-existence of stable hexagonal apatites with $A:X$ ratios in the range 2·50 to 2·60 suggested on the basis of data compiled in table II, receives some experimental support from recent synthetic work on alkaline-earth apatites. For example, in the series $Ca_4Y_6(SiO_4)_6(OH)_2$–$Ca_4La_6(SiO_4)_6(OH)_2$, both the end-members exist and have $A:X$ ratios of 2·45 and 2·80 and c parameters of 6·78 and 7·13 Å respectively. A composition $Ca_4Y_{3\cdot9}La_{2\cdot1}(SiO_4)_6(OH)_2$ has been made up from rare-earth oxides containing at least 99 % Y_2O_3 and La_2O_3, and this composition has the bulk $A:X$ ratio of 2·57. It does not form a simple single-phase apatite: the X-ray diffraction pattern is complex and probably contains two coexisting apatites but may contain only one highly distorted apatite phase. Assuming two are present, c parameters of 6·82 and 6·96 Å have been obtained for the two phases.

If Vegard's Law holds for variation of c with composition, then interpolation shows that these two apatites have the compositions $Ca_4Y_{5\cdot3}La_{0\cdot7}(SiO_4)_6(OH)_2$ and $Ca_4Y_{2\cdot9}La_{3\cdot1}(SiO_4)_6(OH)_2$ and $A:X$ ratios 2·49 and 2·63 respectively. These are in excellent agreement with values predicted for two apatite phases coexisting on either side of the proposed discontinuity. It is tempting to associate this postulated gap between $A:X$ ratios of 2·50 to 2·60 with the existence of the calcium silicate structure with an $A:X$ ratio of 2·57, within this range, and a composition $Ca_6Tl_4(SiO_4)_6$ not containing any rare earths but with an $A:X$ ratio of 2·53 appears only to contain a phase closely resembling pseudowollastonite (α-$CaSiO_3$) when fired at high temperatures (1300° C) in air.

The largest $A:X$ ratio known for an apatite is 4·43 for the compound $Pb_{10}(SiO_4)_2(BO_3)_4$, originally described by Geller and Bunting (1939), and classed as an apatite by Moore and Eitel (1957). It seems likely that the limit for the apatites of Group III is in the range 4·1 to 4·5.

A europium silicate Eu_2SiO_4 has been described and in the course of attempting to synthesize this material, an apatite-type europium silicate

was prepared. It is a yellow or greenish yellow compound prepared by heating the mixed oxides in hydrogen. The composition is probably $Eu_4^{2+}Eu_6^{3+}(SiO_4)_6(OH)_2$, and if this composition is correct, the compound has an $A:X$ ratio of 2·65. Although little systematic work has been done on synthesizing rare-earth apatites from the smaller rare-earth ions, it is interesting that while yttrium forms silicate apatites quite readily, e.g. $Ca_4Y_6(SiO_4)_6(OH)_2$ with an $A:X$ ratio of 2·37, and the compounds $Ca_{10}(CrO_4)_6(OH)_2$ and $Pb_8Na_2(VO_4)_6$ with ratios of 1·94 and 2·13 respectively, are known as apatites, the corresponding scandium compound $Ca_4Sc_6(SiO_4)_6(OH)_2$ does not appear to exist. Synthetic mixtures of this composition in fact contain a scandium garnet $Ca_3Sc_2(SiO_4)_3$, thortveitite $Sc_2Si_2O_7$, and Sc_2O_3, despite the favourable $A:X$ ratio for Sc:Si of 2·10. There is therefore either a critical size for the trivalent ion, either close to that of Y^{3+} at $\sim$ 0·95 Å or between 0·95 Å and 0·84 Å, the adjusted radius for scandium, or alternatively the scandium ion is unable to be in eight-fold coordination at all. The probable existence of the scandium garnet was predicted by Strens (1965).

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