SILICATE APATITES AND OXYAPATITES

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ABSTRACT

Various synthetic compounds of the silicate-apatite group are isomorphous with the minerals abukumalite, beckelite, britholite and lessingite. Three different types were synthesized hydrothermally at 2 kilobars: $(Ca, Sr, Ba, Pb, Mn$ and $Cd)_4^{2+}(Ln, Y)_6^{3+}Si_6O_{24}(OH)_2$, $(Na, Li)_2^{+}(Ln, Y)_8^{3+}Si_6O_{24}(OH)_2$ and $Na_2^{+}Ca_x^{2+}(Ln, Y)_{8-x}^{3+}Si_{6-x}P_xO_{24}(OH)_2$, $x = 0$ to 6.

Complete solid solution exists between hydroxylapatite $Ca_{10}P_6O_{24}(OH)_2$ and $Ca_4Y_6Si_6O_{24}(OH)_2$ (abukumalite). Unit-cell dimensions of all compounds and indexed X-ray powder data of the typical end compounds are tabulated.

Anhydrous silicate oxyapatites, with the probable formulas $M_2^{2+}(Ln, Y)_8^{3+}Si_6O_{26}$ and $M^{+}(Ln, Y)_9^{3+}Si_6O_{26}$ and more generally $(M^{+}, M^{2+}, Ln^{3+}, Y^{3+}$ and $Th^{4+})_{10}(Si, P$ and $B)_6O_{26}$, were prepared at temperatures from 950 to 1260°C in air. The following solid solution systems of oxyapatite were established: $Ca_2Y_8Si_6O_{26} \rightleftarrows Ca_8Y_2P_6O_{26}$, $Ca_2La_8Si_6O_{26} \rightleftarrows Ca_3La_2$-$P_6O_{26}$, $Pb_8^{4+}Pb_5^{2+}Y_2Si_6O_{26} \rightleftarrows Pb_2^{2+}Y_8Si_6O_{26}$, $Mg_2Y_8Si_6O_{26} \rightleftarrows Y_{10}Si_4B_2O_{26}$, and $Ca_2Y_8Si_6O_{26} \rightleftarrows Y_{10}Si_4B_2O_{26}$.

Infrared spectroscopic analysis, water determination by two different methods, and differential thermal analysis of selected compounds demonstrated the presence of OH in silicate-apatite and its absence in oxyapatite.

$NaLa_8Si_9O_{26}$ was obtained as transparent needles up to 0.05 mm by slow cooling in a flux (Na_2WO_4) from 1150 to 750°C. Euhedral transparent crystals of $Na_2Ln_8Si_6O_{24}F_2$ up to 8 mm were grown by the combination of slow cooling and evaporation of the flux (NaF) at temperatures from 1350 to 900°C. New fluorescent yttrium and gadolinium analogues of oxyapatites activated by europium and terbium were prepared.

INTRODUCTION

The isostructural relation of the minerals lessingite (Zilbermintz, 1929), britholite and beckelite (Morozewicz, 1905 and Winther, 1901), as well as abukumalite (Hata, 1938) to apatite, calcium phosphate $Ca_{10}(PO_4)_6$ $(OH)_2$, hexagonal $P6_3/m$ with the general formula $(Na, Ca, Th, Ln[1])_{10}$ $(Si, P)_6O_{24}(OH)_2$, was first pointed out by Machatschki (1939) and was confirmed by later studies (Hägele and Machatschki, 1939; Gay, 1957; Omori and Hasegawa, 1953; Nechaeva and Borneman-Starynkevich, 1956; Sakurai and Kato, 1962; Kupriyanova and Sidorenko, 1963). Tritomite (Neumann, Sverdrup and Saebo, 1957) and spencite (Frondel, 1961) are metamict minerals, which were probably fluoro-boro-silicate apatites. They recrystallize as oxyapatite with the formula $(Ln, Th, Ca)_{10}$-$(Si, B)_6O_{24}O_2$ when heated (Jaffe and Molinski, 1962).

The synthesis and crystal growth of analogous end members of the above rare-earth silicate apatites have been an attractive field for research. Trömel and Eitel (1957) reported the growth of abukumalite

[1] Ln—Lanthanides.

$Ca_4Y_6Si_6O_{24}(OH)_2$, and La and Nd-britholite $(Na, Ca, La, Nd)_{10}Si_6O_{24}$-$(OH)_2$ by solid-state reaction or flame fusion in air at high temperature. They speculated that hydroxyl ions were introduced from atmospheric moisture. Ce-britholite (Ceftosil) $(Ca, Ln)_{10}Si_6O_{24}F_2$ was found in blast-furnace slags (Rudneva, Nikitin and Belov, 1962) and a similar compound was synthesized by Lenov (1963). Keler, Godina and Sav-chenko (1961); Lenov (1962); and Miller and Rase (1964) synthesized in air rare-earth orthosilicates having the apatite structure, with empirical formula $Ln_4Si_3O_{12}$ (Ln = La, Nd, Ce, Sm and Gd). At the time of prepara-tion of this manuscript, Cockbain and Smith (1967) published the re-sults of the syntheses of alkaline-earth rare-earth silicate and germanate apatites by solid-state reaction at atmospheric pressure. They claimed that hydroxyl compounds were synthesized simply by passing steam through the reaction chamber at high temperature. They proposed a classification of naturally occurring minerals based on their results from rather limited experiments. They also showed random distribution of La^{3+} and Ca^{2+} over the $4f$ and $6h$ sites, and reported apatites with halogen sites vacant, partly occupied or fully occupied, depending on cation ratio.

None of the above studies for hydroxylapatite shows proof of the presence of OH ions in synthetic apatites. Unlike phosphate-apatite, silicate-apatite loses water at temperatures below 1100°C. In my view to be presented here hydrated end members can only be synthesized hy-drothermally.

Oxyapatite,[1] in which $2a$ sites are partly or completely vacant, has been the subject of controversy since voelckerite $Ca_{10}(PO_4)_6O$ was de-scribed (Rogers, 1912). It is certain that the difficulty of high tempera-ture (1400°C) water analysis is responsible for earlier misleading reports. Korber and Trömel (1932) discredited the existence of oxygen-deficient oxyapatite $Ca_{10}(PO_4)_6O$ previously reported (Trömel, 1932); however, they synthesized oxyapatite $Ca_8La_2P_6O_{26}$ with 26 oxygen sites fully oc-cupied. Nevertheless, the concept of oxygen-deficient oxyapatite per-sisted. Wondratschek (1963) described series of oxypyromorphite Pb_{10} $(PO_4)_6O$, Dietzel and Paetsch (1956) synthesized a single crystal of lead oxysilico phosphate apatite $Pb_{10}Si_2P_4O_{24}$ in which all the halogen sites were said to be vacant. Recently Young and Munson (1966) reported a partly dehydrated oxygen-deficient apatite from Colorado (OH, O, F plus Cl = 25.68 compared with 26). None of the above studies, however, gave sufficient evidence to establish the presence of vacant halogen sites

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[1] In this paper, compounds of the type $Ca_{10}P_6O_{24}(OH)_2$ will be referred to as hydroxyl-apatite, those of the type $Ca_{10}P_6O_{24}O_2$ as oxyapatites, and those of types $Ca_{10}P_6O_{24}O$ as oxygen-deficient oxyapatites.

(McConnell, 1965). After Kuzmin and Belov (1965) discarded the empirical formula for rare-earth orthosilicate apatite $Ln_4Si_3O_{12}$ and introduced the cation defect formula $Ln_{4.66}Si_3O_{13}$, Cockbain and Smith (1967) again brought up the same concept of halogen-site vacancy.

My investigation was undertaken to establish isomorphous relations between rare-earth silicate and phosphate apatites, and to give additional information for the characterization of these complex rare-earth silicates by the determination of the conditions and the complete compositional range of formation. It was later extended to include the oxyapatite problem in an attempt to contribute to its clear definition, especially as regards the deficiency of sites and total charge balance. Moreover, new fluorescent light emitters activated by rare-earth elements were sought among these compounds. An investigation of single-crystal growth was undertaken with sodium tungstate and sodium fluoride flux fusion in order to supply good quality single crystals for further studies of the detailed structure of apatite and for possible applications in materials science.

SYNTHESIS

Reagents used for the preparation of starting gels included oxides of lanthanum, neodymium, samarium, gadolinium, dysprosium, yttrium, erbium, holmium and lutetium; thorium nitrate, manganese chloride, strontium chloride, calcium nitrate, lead nitrate, magnesium nitrate, barium chloride, barium hydroxide, cadmium sulfate, lithium carbonate, ammonium dihydrogen phosphate, boric acid, sodium silicate and potassium silicate.

Starting gels for lead rare-earth silicates were precipitated at pH 9 with ammonia from 300 ml of 0.5 millimolar solution of apatite. The resulting precipitates were washed in a centrifuge with 300 ml of distilled water. The gels for calcium analogues were prepared by precipitation with an ammonium carbonate solution stabilized in ammonia at pH 9. Gels for strontium, manganese and magnesium analogues were prepared by mixing Mg-$(OH)_2$, $MnCO_3$ or $SrCO_3$ (all powdered) into a suspension of rare earth silicate at the time of precipitation by ammonia at pH 9. Use of NaOH solution was avoided because analogues containing divalent ions readily form solid solutions with sodium analogues of the silicate apatite. The gels of the sodium, barium and lithium analogues were prepared in a porcelain evaporating dish of 100 ml capacity, by mixing exact amounts of concentrated solutions of sodium silicate, lithium carbonate or barium hydroxide with the precipitated rare-earth silicate gels. Phosphate- and borate-bearing gels were also prepared in the same way as described above, mixing solutions of boric acid, phosphoric acid or sodium phosphate into the precipitated silicate gels.

All the gels were air-dried at 110°C, except the manganese and barium analogues. These were dried in an evacuated oven at 120°C in order to avoid oxidation or absorption of carbon dioxide, respectively.

Dry syntheses were carried out by heating gels in a box furnace at temperatures ranging from 800 to 1250°C for 3–20 hours. A porcelain boat containing approximately 100 mg of dried gels was placed in a preheated furnace. Manganese analogues were synthesized at 1250°C in order to avoid the formation of manganese oxides of higher valencies, which might be produced at temperatures below 1100°C.

TABLE 1. UNIT-CELL DIMENSIONS OF THE SILICATE APATITES (HYDROXYL)
Synthesized Hydrothermally at 650°C and 2 kbars (450°C for Pb analogues)

Formula	a (Å)	c (Å)	V (Å³)	Formula	a (Å)	c (Å)	V (Å³)
$Mn_4La_6 Si_6O_{24}(OH)_2$	9.66	7.05	569	$Sr_4Gd_6Si_6O_{24}(OH)_2$	9.53	7.00	550
$Mn_4Nd_6 Si_6O_{24}(OH)_2$	9.50	6.90	539	$Sr_4Dy_6Si_6O_{24}(OH)_2$	9.43	6.92	532
				$Sr_4Y_6Si_6O_{24}(OH)_2$	9.52	6.91	543
$Mn_4Sm_6Si_6O_{24}(OH)_2$	9.43	6.82	525	$Sr_4Ho_6Si_6O_{24}(OH)_2$	9.42	6.91	531
$Mn_4Gd_6Si_6O_{24}(OH)_2$	9.38	6.78	521	$Sr_4Er_6Si_6O_{24}(OH)_2$	9.42	6.83	525
$Mn_4Dy_6Si_6O_{24}(OH)_2$	9.33	6.68	503	$Sr_4Lu_6Si_6O_{24}(OH)_2$	9.50	6.79	532
$Mn_4Y_6Si_6O_{24}(OH)_2$	9.31	6.65	499	$Pb_4La_6Si_6O_{24}(OH)_2$	9.80	7.26	604
$Mn_4Er_6Si_6O_{24}(OH)_2$	9.28	6.63	494	$Pb_4Ce_6Si_6O_{24}(OH)_2$	9.77	7.19	594
				$Pb_4Nd_6Si_6O_{24}(OH)_2$	9.76	7.13	588
$Ca_4La_6Si_6O_{24}(OH)_2$	9.66	7.12	575	$Pb_4Sm_6Si_6O_{24}(OH)_2$	9.74	7.05	579
$Ca_4Ce_6Si_6O_{24}(OH)_2$	9.61	7.09	567	$Pb_4Gd_6Si_6O_{24}(OH)_2$	9.72	6.99	572
$Ca_4Nd_6Si_6O_{24}(OH)_2$	9.56	7.00	554	$Pb_4Dy_6Si_6O_{24}(OH)_2$	9.70	6.90	562
$Ca_4Sm_6Si_6O_{24}(OH)_2$	9.50	6.94	542	$Pb_4Y_6Si_6O_{24}(OH)_2$	9.68	6.86	567
$Ca_4Gd_6Si_6O_{24}(OH)_2$	9.43	6.89	531	$Pb_4Er_6Si_6O_{24}(OH)_2$	9.68	6.84	551
$Ca_4Dy_6Si_6O_{24}(OH)_2$	9.40	6.83	523	$Pb_4Lu_6Si_6O_{24}(OH)_2$	9.64	6.75	543
$Ca_4Y_6Si_6O_{24}(OH)_2$	9.40	6.81	519				
$Ca_4Er_6Si_6O_{24}(OH)_2$	9.38	6.78	517	$Ba_4Nd_6Si_6O_{24}(OH)_2$	9.76	7.18	593
$Ca_4Lu_6Si_6O_{24}(OH)_2$	9.35	6.74	510	$Ba_4Sm_6Si_6O_{24}(OH)_2$	9.73	7.10	582
$Sr_4La_6Si_6O_{24}(OH)_2$	9.71	7.23	591	$Ba_4Gd_6Si_6O_{24}(OH)_2$	9.72	7.03	575
$Sr_4Ce_6Si_6O_{24}(OH)_2$	9.67	7.14	578	$Ba_4Dy_6Si_6O_{24}(OH)_2$	9.66	6.95	561
$Sr_4Nd_6Si_6O_{24}(OH)_2$	9.62	7.10	569	$Na_2Y_8Si_6O_{24}(OH)_2$	9.34	6.78	512
$Sr_4Sm_6Si_6O_{24}(OH)_2$	9.60	7.05	563	$Na_2La_8Si_6O_{24}(OH)_2$	9.74	7.17	589

Hydrothermal syntheses were done in cold-seal steel bombs of 25 ml capacity at temperatures from 500°C to 750°C under two kilobars pressure. Approximately 50 mg of dried gels were placed in a silver liner made of 0.03 mm of silver foil (10 mm long and 3 mm I.D.). The bombs were filled with the exact amounts of distilled water to give the desired water pressure. After the reaction, the bombs were always quenched by compressed air and the products were washed out from the liner and air dried.

All the products of the syntheses were examined by the X-ray diffraction powder method using filtered CuKα radiation and an internal silicon standard. Powder diffraction patterns of apatites were indexed according to the established apatite hexagonal cell of space group $P6_3/m$. Unit-cell dimensions were calculated from the following reflections (appropriately weighted): 002, 102, 210, 211, 112, 300, 310, 113, 410 and 004, and are given in Tables 1, 2 and 3. X-ray powder data of four typical compounds are compared with those of the natural minerals in Table 4.

FLUX GROWTH OF SINGLE CRYSTALS

Single crystal growth of oxyapatite for crystal structure work and for chemical analysis was attempted by flux fusion. An extended search showed that sodium tungstate was an effective flux. The optimum composition for growth was found to be La$_2$O$_3$, 2.0 g; SiO$_2$, 0.6 g; and Na$_2$WO$_4\cdot$2H$_2$O, 40 g. Cooling from 1150°C to 750°C was carried out at the rate of 1°C/hr. The melt was then quenched from 750°C to room temperature and the remaining flux dissolved by boiling in hot dilute NaOH solution. Unreacted amorphous material was

TABLE 2. UNIT-CELL DIMENSIONS OF THE SILICATE APATITES (OXY)
Synthesized at 1200°C in Air. (900°C for Lead Analogues and 1050°C for Mg
Analogues and Alkali Analogues)

Formula	a (Å)	c (Å)	V (Å³)	Formula	a (Å)	c (Å)	V (Å³)
$Ba_2La_8Si_6O_{26}$	9.77	7.32	605	$Pb_2Gd_8Si_6O_{26}$	9.54	6.95	548
$Ba_2Nd_8Si_6O_{26}$	9.66	7.16	579	$Pb_2Dy_8Si_6O_{26}$	9.47	6.87	534
$Ba_2Sm_8Si_6O_{26}$	9.62	7.06	566	$Pb_2Y_8Si_6O_{26}$	9.42	6.80	522
$Sr_2La_8Si_6O_{26}$	9.69	7.22	586				
$Sr_2Nd_8Si_6O_{26}$	9.57	7.09	562	$Mn_2La_8Si_6O_{26}$	9.63	7.08	568
$Sr_2Sm_8Si_6O_{26}$	9.51	7.02	550	$Mn_2Nd_8Si_6O_{26}$	9.47	6.91	537
$Sr_2Gd_8Si_6O_{26}$	9.47	6.97	541	$Mn_2Sm_8Si_6O_{26}$	9.42	6.85	526
$Sr_2Dy_8Si_6O_{26}$	9.42	6.90	530	$Mn_2Gd_8Si_6O_{26}$	9.34	6.79	518
$Sr_2Y_8Si_6O_{26}$	9.38	6.86	523	$Mn_2Dy_8Si_6O_{26}$	9.33	6.71	506
$Sr_2Er_8Si_6O_{26}$	9.36	6.81	517	$Mn_2Y_8Si_6O_{26}$	9.32	6.69	503
$Ca_2La_8Si_6O_{26}$	9.63	7.12	571	$Mn_2Er_8Si_6O_{26}$	9.30	6.65	498
$Ca_2Nd_8Si_6O_{26}$	9.52	7.00	549	$Mg_2La_8Si_6O_{26}$	9.59	7.05	561
$Ca_2Sm_8Si_6O_{26}$	9.44	6.93	535	$Mg_2Nd_8Si_6O_{26}$	9.45	6.86	530
$Ca_2Gd_8Si_6O_{26}$	9.39	6.87	525	$Mg_2Sm_8Si_6O_{26}$	9.38	6.80	518
$Ca_2Dy_8Si_6O_{26}$	9.37	6.81	518	$Mg_2Gd_8Si_6O_{26}$	9.33	6.75	509
$Ca_2Y_8Si_6O_{26}$	9.34	6.77	511	$Mg_2Dy_8Si_6O_{26}$	9.31	6.69	504
$Ca_2Er_8Si_6O_{26}$	9.33	6.75	509	$Mg_2Y_8Si_6O_{26}$	9.31	6.64	498
$Ca_2Lu_8Si_6O_{26}$	9.28	6.68	498	$Mg_2Er_8Si_6O_{26}$	9.28	6.58	491
$Cd_2La_8Si_6O_{26}$	9.64	7.09	571	$NaLa_9Si_6O_{26}$	9.69	7.18	583
$Pb_2La_8Si_6O_{26}$	9.71	7.20	588	$NaY_9Si_6O_{26}$	9.33	6.75	509
$Pb_2Nd_8Si_6O_{26}$	9.65	7.12	574	$LiY_9Si_6O_{26}$	9.34	6.72	508
$Pb_2Sm_8Si_6O_{26}$	9.58	7.06	561	$(Na,Th,La)_{10}Si_6O_{26}$	9.66	7.13	576

separated by selective flotation. A mass of very fine transparent crystals (0.05 mm) were obtained. Approximately 1.0 g (95%pure) was used for the chemical analyses.

Larger crystals of $Na_2La_8Si_6O_{24}F_2$ were grown as euhedral transparent crystals up to 8 mm in size with well developed faces using sodium fuoride flux by the combination of slow cooling (2°C/hr) and flux evaporation at temperatures from 1350°C to 950°C. The optimum composition for growth was found to be SiO_2, 0.45 g; La_2O_3, 2.0 g; and NaF, 10 g. Short prismatic crystals with {100} {101} and {001} are common. Also thick tabular crystals with {111} {101} {100} and relatively large {001} were formed.

The crystals of Nd (purple), Pr (blue), Sm (yellow) and Gd (colorless) analogues were also grown successfully. For non-alkaline species such as $Ca_2Y_8Si_6O_{26}$, potassium tungstate or fluoride were promising as flux.

Melting points of the compounds were not determined because most of the compounds melt incongruently and at temperatures higher than 1400°C.

LUMINESCENCE

Most of the compounds show a faint fluorescence in a variety of colors under ultraviolet excitation. Intense visible luminescense was observed in the yttrium and gadolinium analogues when activated by 5–10 percent of europium or terbium. The following compounds synthesized in

TABLE 3. UNIT-CELL DIMENSIONS OF THE PHOSPHATE- AND BORATE-BEARING
SILICATE APATITES AND HIGHLY OXIDIZED LEAD
YTTRIUM SILICATE APATITES

Formula	a_0(Å)	c_0(Å)	V (Å^3)	P,T
$Ca_8Y_2Si_2P_4O_{24}(OH)_2$	9.41	6.87	527	500°C 2 kb
$Ca_6Y_4Si_4P_2O_{24}(OH)_2$	9.39	6.83	522	550°C 2 kb
$Ca_2Na_2La_6Si_4P_2O_{24}(OH)_2$	9.62	7.11	570	550°C 2 kb
$Ca_4Na_2La_4Si_2P_4O_{24}(OH)_2$	9.51	7.00	548	550°C 2 kb
$Pb_2{}^{4+}Pb_8{}^{2+}P_4Si_2O_{26}$	9.78	7.33	607	900°C 1 bar
$Ca_8Y_2P_6O_{26}$	9.37	6.84	520	1200°C 1 bar
$Ca_6Y_4Si_2P_4O_{26}$	9.36	6.84	519	1200°C 1 bar
$Ca_4Y_6Si_4P_2O_{26}$	9.35	6.82	516	1200°C 1 bar
$Ca_8La_2P_6O_{26}$	9.48	6.95	541	1200°C 1 bar
$Ca_6La_4Si_2P_4O_{26}$	9.57	7.02	557	1200°C 1 bar
$Ca_4La_6Si_4P_2O_{26}$	9.62	7.07	566	1200°C 1 bar
$MgY_9Si_5BO_{26}$	9.18	6.73	491	1150°C 1 bar
$Y_{10}Si_4B_2O_{26}$	9.15	6.75	489	1150°C 1 bar
$Pb_3{}^{4+}Pb_5{}^{2+}Y_2Si_6O_{26}$	9.77	6.94	573	900°C 1 bar
$Pb_2{}^{4+}Pb_4{}^{2+}Y_4Si_6O_{26}$	9.72	6.87	562	900°C 1 bar
$Pb^{4+}Pb_3{}^{2+}Y_6Si_6O_{26}$	9.59	6.81	542	900°C 1 bar
$CaY_9Si_5BO_{26}$	9.28	6.78	506	1150°C 1 bar

air at 1280°C fluoresce: $Ca_2(Gd, Eu)_8Si_6O_{26}$, $Sr_2(Y, Eu)_8Si_6O_{26}$, and $Na(Y, Eu)_9Si_6O_{26}$ (scarlet red) and $Ca_2(Gd, Tb)_8Si_6O_{26}$ (bright yellow).

Visible emission spectra of the above compounds under mercury 3130 Å excitation are as follows.[1] Three europium activated analogues of oxyapatite gave almost identical spectra regardless of their matrix elements. The strongest line was observed in the vicinity of 6190 Å, and five medium lines were detected at approximately 7050, 6500, 6260, 5980 and 5850 Å. The terbium activated analogue gave a completely different visible spectrum; strong doublet lines were detected at 5475 Å and 5525 Å, and four medium lines were observed at 6300, 5880, 4950 and 4890 Å.

ANALYSIS FOR HYDROXYL IONS

The presence of OH in $Ca_4Dy_6Si_6O_{24}(OH)_2$ synthesized at 650°C, and 2 kilobars, was ascertained by infrared spectroscopy by Dr. Wilkins of Harvard University. Its spectrum showed clear evidence of the vibration at 3540 cm^{-1} while the anhydrous compound synthesized in air at 1050°C, presumably $Ca_2Dy_8Si_6O_{26}$, did not show this absorption. A later study of $Pb_4Nd_6Si_6O_{24}(OH)_2$ and $Pb_4{}^{2+}Pb_2{}^{4+}Nd_4Si_6O_{26}$ by the same method gave similar results.

[1] Determination of the emission spectra was performed by Dr. L. Grabner at the National Bureau of Standards.

TABLE 4. X-RAY POWDER DATA OF SYNTHETIC AND NATURAL LESSINGITE AND ABUKUMALITE, Na₂La₈Si₆O₂₄(OH)₂ AND Na₂Y₈Si₆O₂₄(OH)₂; INDEXED ON THE BASIS OF HEXAGONAL CELL

Formula, conditions or locality	Lessingite, Kyshtym, Ural		Ca₄La₆Si₆O₂₄(OH)₂ 650°C, 2 kbars			Abukumalite, Suishoyama, Japan		Ca₄Y₆Si₆O₂₄(OH)₂ 650°C 2 kbars			Na₂La₈Si₆O₂₄(OH)₂ 650°C, 2 kbars, 24 hours		Na₂Y₈Si₆O₂₄(OH)₂ 650°C, 2 kbars 24 hours	
a, Å	9.67		9.66			9.43		9.40			9.74		9.34	
c, Å	7.08		7.12			6.81		6.81			7.17		6.78	
hkl	d	I	d obs.	I	d calc.	d obs.	I	d obs.	I	d calc.	d obs.	I	d obs.	I
110	4.83	vw	—	—	—	4.77	5	4.71	5	4.70	—	—	4.64	5
200	4.19	vw	4.19	30	4.18	4.08	25	4.07	55	4.07	4.21	20	4.051	30
111	3.99	w	4.00	30	4.00	3.88	20	3.88	25	3.87	4.03	20	3.844	10
002	3.58	w	3.56	20	3.56	3.394	30	3.411	40	3.41	3.58	5	3.391	10
	3.54	w	—	—	—	—	—	—	—	—	—	—	—	—
102	3.34	w	3.276	30	3.277	3.125	50	3.144	35	3.142	3.297	30	3.127	20
	3.26	mw	—	—	—	—	—	—	—	—	—	—	—	—
210	3.16	mw	3.164	35	3.161	3.087	50	3.074	40	3.076	3.184	35	3.060	50
211	2.89	s	2.891	100	2.889	2.813	100	2.805	100	2.802	2.906	100	2.784	100
112	2.86	m	2.861	50	2.864	2.753	90	2.769	90	2.758	2.886	80	2.738	45
300	2.79	m	2.788	40	2.794	2.727	80	2.710	85	2.717	2.810	40	2.696	70
	—		—	—	—	2.264	5	—	—	—	—	—	—	—
310	2.32	vw	2.319	10	2.319	2.256	5	2.256	15	2.259	2.336	5	2.244	10
302	2.25	vvw	2.195	10	2.198	—	—	2.120	3	2.123	2.212	3	2.112	3
113	2.12	vw	2.127	20	2.131	2.036	20	2.046	10	2.045	2.145	10	2.034	5
400	2.05	vvw	2.088	5	2.091	—	—	2.034	8	2.035	2.106	10	2.021	8
	2.019	vvw	—	—	—	—	—	—	—	—	—	—	—	—
222	1.995	w	1.999	20	1.998	1.936	25	1.932	35	1.929	2.013	45	1.924	20
312	1.941	vw	1.945	15	1.944	1.885	30	1.883	20	1.882	1.958	10	1.870	10
320	—		1.924	5	1.918	1.871	5	1.867	10	1.867	1.937	10	1.857	5
213	1.890	w	1.899	30	1.898	1.823	20	1.826	35	1.827	1.909	50	1.816	20
321	1.855	vw	1.855	20	1.855	1.808	15	1.798	20	1.800	1.865	20	1.791	20
410	1.827	w	1.826	15	1.825	1.784	10	1.776	15	1.775	1.836	20	1.766	20
402	1.802	w	1.804	20	1.803	1.750	20	1.746	25	1.747	1.816	30	1.736	20
004	1.769	vw	1.783	10	1.781	1.695	10	1.705	15	1.703	1.794	10	1.694	8

TABLE 5. RESULTS OF H_2O ANALYSES

Formula	H_2O analyzed temperature range			Theoretical H_2O
	100–180°C	230–650°C	1050°C	
a. $Sr_4Er_6Si_6O_{24}(OH)_2$	—	—	0.7%	0.9%
b. $Ca_4Lu_6Si_6O_{24}(OH)_2$	—	—	0.8%	1.0%
c. $Sr_4Y_6Si_6O_{24}(OH)_2$	—	—	1.1%	1.1%
d. $Ba_4Gd_6Si_6O_{24}(OH)_2$	—	—	1.2%	0.87%
e. $Mn_4Sm_6Si_6O_{24}(OH)_2$	—	—	0.7%	1.0%
f. $Pb_4Nd_6Si_6O_{24}(OH)_2$	0.23%	0.65%	—	0.8%
g. $Pb_2^{4+}Pb_4^{2+}Nd_4Si_6O_{26}$	0.03%	0.04%	—	0.0%

Analyses a, b, c, d, and e were done by Mr. Ralph Paulson at the National Bureau of Standards using a carbon-hydrogen analyzer at 1050°C. Analyses g and f were carried out by Mr. W. Sabine at Harvard University, a micro-coulometric technique.

Results of the analyses for H_2O are given in Table 5. All the hydroxyl-apatites heated at 1100°C gave X-ray powder patterns indistinguishable from those of the oxyapatite $M_2^{2+}Ln_8^{3+}Si_6O_{26}$. In the cases of lead or manganese analogues, formation of oxyapatite could be accompanied by oxidation of the cations to compensate for the loss of hydrogen; in other cases where oxidation was not possible, valency compensation for the loss of hydrogen was achieved by changes of cation proportion from the original hydroxylapatites.

Differential thermal analyses[1] were also made on $Pb_4Nd_6Si_6O_{24}(OH)_2$ and $Pb_2^{4+}Pb_4^{2+}Nd_4Si_6O_{26}$. The former showed an endothermic peak at 350°C while the latter did not show any sign of dehydration. X-ray diffraction powder pattern taken of the former sample after the experiment showed the formation of oxyapatite indicating that the endothermic peak was due to the dehydration of hydroxylapatite.

RESULTS AND DISCUSSION

Compositional range, nomenclature and solid solubility. A large variety of silicate and phosphate compounds having the apatite structure, including some containing borate, were prepared (Tables 1, 2, and 3). Divalent ions from Mg^{2+}(0.66 Å) to Ba^{2+}(1.34 Å) can replace Ca^{2+}. Monovalent ions such as Li^+ and Na^+ can also replace Ca^{2+}, but K^+ can replace Ca^{2+} only partially. Valency compensation is achieved by introduction of rare earth, lanthanum, yttrium or thorium ions.

[1] Differential thermal analysis was performed by Mr. E. M. Levin at the National Bureau of Standards.

Over sixty chemically different compounds which gave single phase apatitic X-ray patterns have been synthesized. The unit-cell dimensions, together with the conditions of the syntheses, are given in Tables 1, 2, and 3. Unit-cell dimensions a and c of hydroxyl analogues are plotted in terms of ionic radii of divalent cations and rare-earth ions in Figures 1 and 2 respectively. The natural minerals can be located in their approximate positions in these diagrams according to the chemical compositions and their unit-cell dimensions. Of the three natural minerals lessingite is the closest to the end composition $Ca_4La_6Si_6O_{24}(OH)_2$. Britholite and beckelite resemble lessingite but contain small proportions of the isomorphous compounds $Na(Ln,Y)_9Si_6O_{24}(OH)_2$ and $Ca_{10}(PO_4)_6(OH)_2$. Abukumalite is close to the end composition $Ca_4Y_6Si_6O_{24}(OH)_2$.

Complete solid solubility exists between hydroxylapatite $Ca_{10}(PO_4)_6$-$(OH)_2$, and $Ca_4Y_6Si_6O_{24}(OH)_2$ (abukumalite), under hydrothermal conditions (Fig. 5). Solid solution is incomplete between $Ca_{10}(PO_4)_6(OH)_2$ and $Ca_4La_6Si_6O_{24}(OH)_2$ (lessingite) under the conditions I used, owing to large differences in their unit-cell dimensions. A complete series between $Sr_{10}(PO_4)_6(OH)_2$ and $Sr_4La_6Si_6O_{24}(OH)_2$ is probable because of the similar sizes of Sr and La.

The following solid solutions of oxyapatite based on 26 oxygens per cell also have been investigated: $Ca_2Y_8Si_6O_{26} \rightleftarrows Ca_8Y_2P_6O_{26}$, $Ca_2La_8Si_6O_{26} \rightleftarrows Ca_8La_2P_6O_{26}$, $Ca_2Y_8Si_6O_{26} \rightleftarrows Y_{10}Si_4B_2O_{26}$ and $Mg_2Y_8Si_6O_{26} \rightleftarrows Y_{10}Si_4B_2O_{26}$.
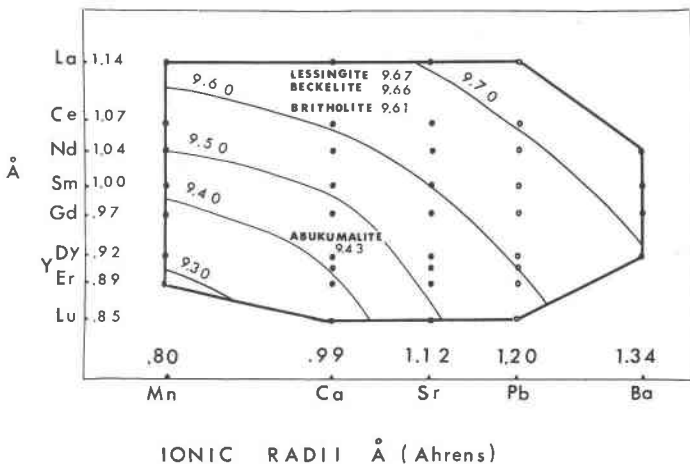

FIG. 1. Chemical stability region of hydroxy-silicate-apatites: $M_4^{2+}(Ln)_6^{3+}Si_6O_{24}(OH)_2$ in terms of ionic radii (Ahrens, 1952) of the divalent cations and lanthanides. Unit-cell dimensions a are given as contours. Natural minerals are plotted according to the approximate chemical compositions. Pb analogues given in open circles do not fit the contours.
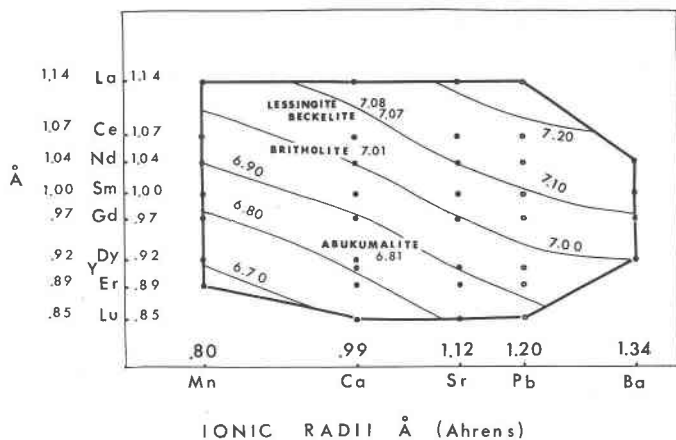
FIG. 2. Chemical stability region of hydroxy-silicate-apatites: $M_4^{2+}(Ln)_6^{3+}Si_6O_{24}(OH)_2$ in terms of ionic radii (Ahrens 1952) of the divalent cations and lanthanides. Unit-cell dimensions c are given as contours. Natural minerals are plotted according to the approximate chemical compositions. Pb analogues given in open circles do not fit the contours.

The unit-cell dimensions have been plotted versus chemical compositions and are given in Figures 6, 7, and 8.

Oxyapatite and hydroxylapatite. Unit-cell dimensions a and c of oxyapatite are given in Table 2 and unit-cell volumes are plotted in Figure 3 in terms of ionic radii of divalent ions and rare-earth ions. The chemical
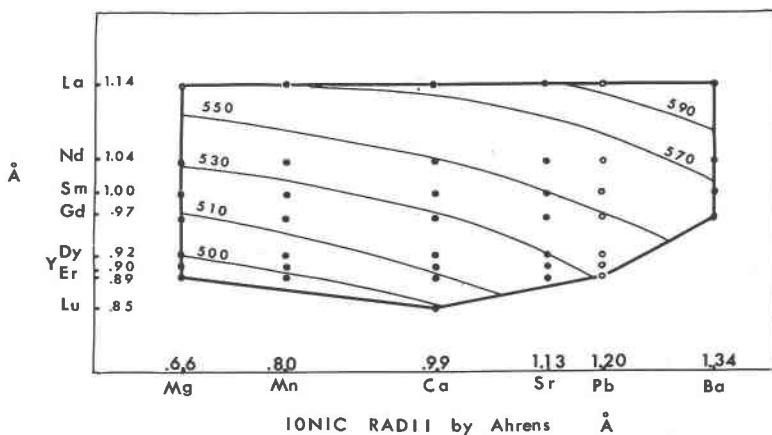

FIG. 3. Chemical stability region of oxy-silicate-apatites: $M_2^{2+}(Ln)_8^{3+}Si_6O_{26}$ in terms of ionic radii (Ahrens 1952) of the divalent cations and lanthanides. Unit-cell volumes are given as contours. Pb analogues in open circles did not fit contours.
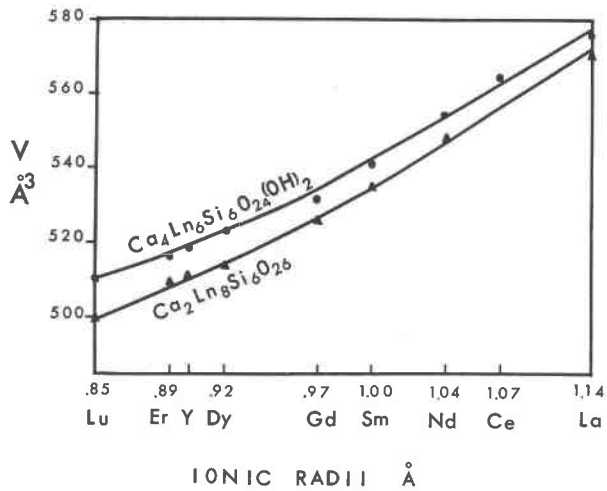
Fig. 4. Unit-cell volumes of Ca analogues of hydroxylapatites $Ca_4Ln_6Si_6O_{24}(OH)_2$ and oxyapatites $Ca_2Ln_8Si_6O_{26}$ versus ionic radii (Ahrens 1952) of lanthanides.
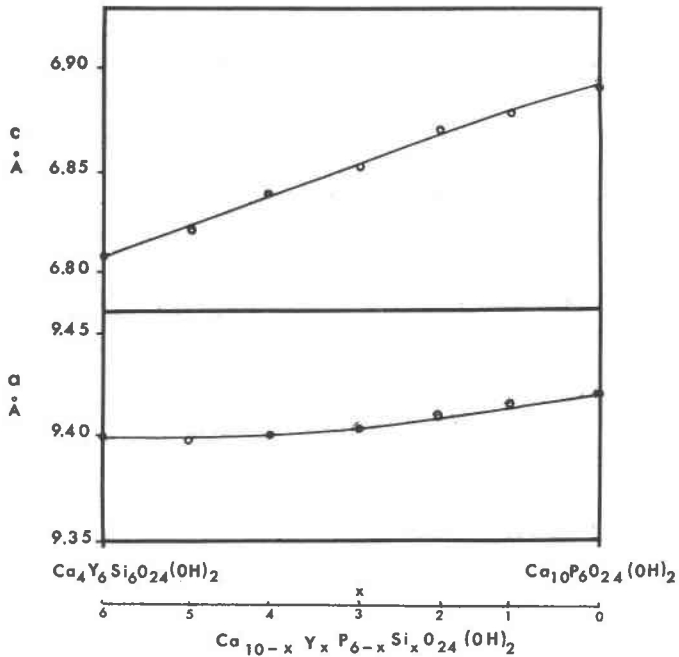
Fig. 5. Unit-cell dimensions of solid solution series of apatite $Ca_{10}P_6O_{24}(OH)_2$—$Ca_4Y_6Si_6O_{24}(OH)_2$ abukumalite.
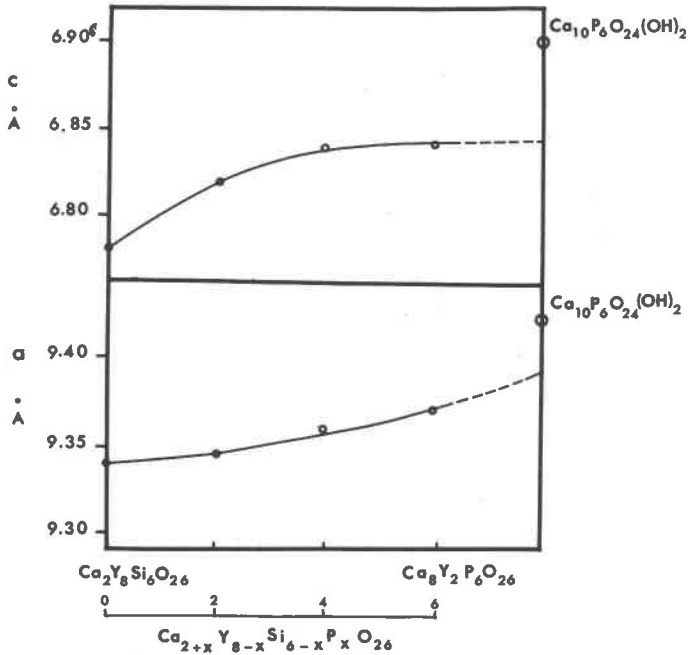
FIG. 6. Unit-cell dimensions of solid solution series of $Ca_2Y_8Si_6O_{26}$—$Ca_8Y_2P_6O_{26}$.

stability region of oxyapatite is considerably greater than that of hydroxylapatites (Figs. 1 and 2).

Unit-cell volumes of Ca analogues of hydroxylapatites and oxyapatites are also plotted against ionic radii of rare earths in Figure 4, showing that the series of hydroxylapatites and oxyapatites are different. Distinction between the hydroxyl and oxyapatites was also clearly indicated by the chemical analysis (Table 5) and infrared spectroscopy discussed in previous sections. Cockbain and Smith (1967) did not observe these differences in their synthetic compounds, which probably are anhydrous.

The compounds synthesized by Trömel and Eitel (1957) are also probably oxyapatite because the present study has demonstrated that it is unnecessary to postulate retention of water in the silicate compounds synthesized in air either by solid-state reaction or by flame fusion at high temperatures. These authors state that the role of water is uncertain because of the difficulty in analyzing for small amounts of water. X-ray data obtained by Trömel and Eitel are not identical with those obtained from the present study or those given by Cockbain and Smith (1967). Some differences are greater than can be accounted for on the basis of errors in measurement.
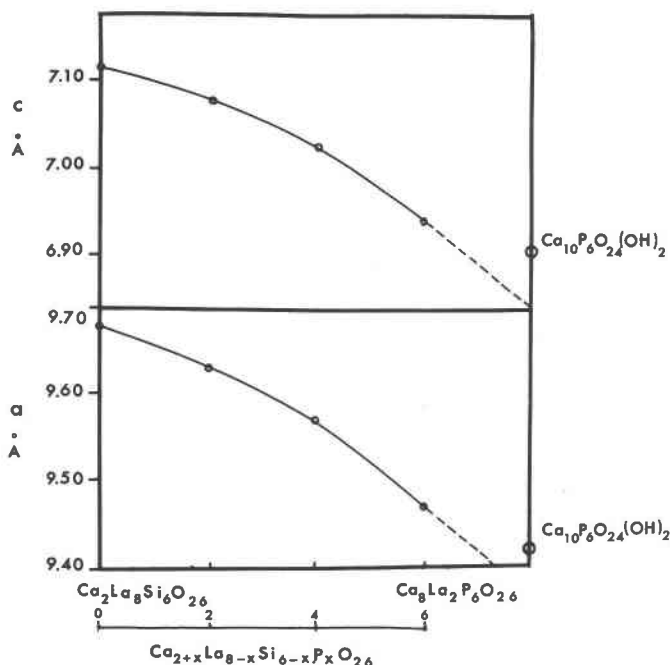
FIG. 7. Unit-cell dimensions of solid solution series of $Ca_2La_8Si_6O_{26}$—$Ca_8La_2P_6O_{26}$.

Chemical analysis of sodium lanthanum silicate oxyapatite, grown by the tungstate flux method, gave La_2O_3 78 percent, SiO_2 21 percent and Na_2O 1.6 percent (analysis by Rains and Ito). The formula derived from this analysis $Na_{0.94}La_{8.65}Si_{6.4}O_{26}$ is close to $NaLa_9Si_6O_{26}$, suggesting a completely oxygen filled structure. In each synthesis of the same cation combination, the resulting oxyapatites, except lead analogues, gave exactly the same unit-cell dimensions, even though the cation ratio in the starting mixtures varied. For instance, mixtures with empirical compositions $Ca_2Y_8Si_6O_{24}(O)_2$ and $Ca_4Y_6Si_6O_{24}(O)$ after heating at 1250°C, gave identical unit-cell dimensions and X-ray diffraction intensities. The same findings were reported by Cockbain and Smith (1967) with Ca-La analogues. Their runs containing Ca and La with the ratio of 4:6, 5:5 and 6:4 gave nearly identical unit cells. I can not agree with their explanation: "the lattice parameters of $Ca_4La_6(SiO_4)_6OH$ and $Ca_6La_4(SiO_4)_6$ are virtually identical, since the substitution of La^{3+} for part of the Ca^{2+} has expanded the lattice sufficiently for $(OH)^-$ or F^- or a vacancy to be accommodated without strain." We have clearly demonstrated (Fig. 4) the differences between hydroxyl- and oxy-compounds. The above observations suggest that there is only one oxyapatite (Table 1 and 2, Fig.
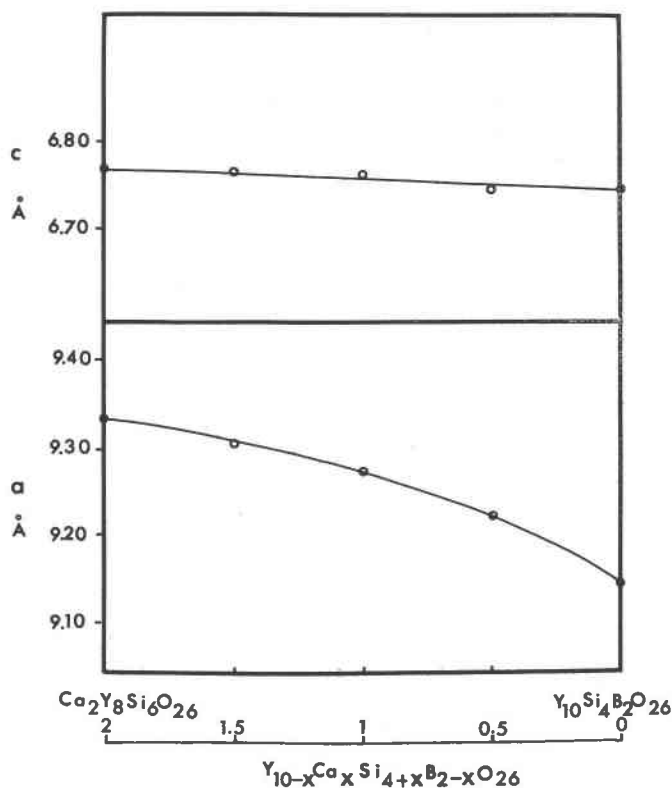
FIG. 8. Unit-cell dimensions of solid solution series of $Ca_2Y_8Si_6O_{26}$—$Y_{10}Si_4B_2O_{26}$.

4) for each combination of cations, in which the loss of hydroxyl ion is compensated by cation replacement, and that stabilized oxyapatite contains 26 oxygens in each unit cell, as originally postulated by Korber and Trömel (1932) and McConnell (1938).

It has lately been known that the simple rare-earth silicate, $Ln_4Si_3O_{12}$ (Ln=La, Pr, Nd, Ce, and Sm) (Keler, Godina and Savchenko, 1961; Leonov, 1962; Miller and Rase, 1964), has the apatite structure. Kuzmin and Belov (1965) reported that this apatite is cation-deficient oxyapatite and suggested the formula $La_{9.32}Si_6O_{26}$. This interpretation fits well with the results of the present experiments because unit cell dimensions of the above compound $a=9.72$; $c=7.18$ are significantly larger than those of $NaLa_9Si_6O_{26}$ $a=9.69$; $c=7.17$. It seems highly unlikely that the unit cell of $La_8Si_6O_{24}$ is larger than that of $NaLa_9Si_6O_{26}$. The finding of cation-defect apatite opens the wide possibilities of cation deficiency in silicate apatites generally. Further investigation is indicated.
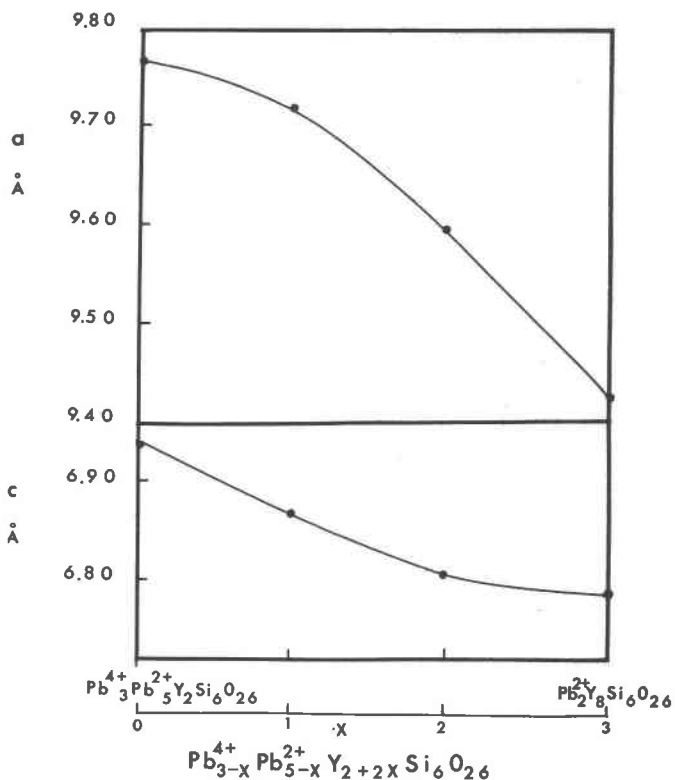
FIG. 9. Unit-cell dimensions of solid solution series $Pb_5^{2+}Pb_3^{4+}Y_2Si_6O_{26}$—$Pb_2^{2+}Y_8Si_6O_{26}$.

Pure calcium phosphate oxyapatite $Ca_{10}P_6O_{25}$ on my interpretation should not exist because the 26 oxygen sites must be filled for the apatite structure. Indeed infrared examination showed a strong OH absorption persisting in a synthetic apatite heated in air at 1100°C for 48 hours. If oxygen deficient Ca oxyapatite exists, it was not found as an end member of the solid solution series extended from the oxyapatites $Ca_2Ln_8Si_6O_{26}$ to $Ca_8Ln_2P_6O_{26}$ (Fig. 6 and 7). However, should oxygen-deficient Ca oxyapatite be stabilized by some mechanism, the extrapolated values of the unit-cell dimensions as given in Figure 6 and 7 lead to predicted values of cell dimensions of oxygen deficient Ca-oxyapatite of $a = 9.38 \pm 0.01$ Å, $c = 6.85 \pm 0.01$ Å.

Unit-cell dimensions of lead analogues of oxyapatite synthesized in air vary depending on the rare earth to lead ratio and on the temperatures of the synthesis. Deficiency of oxygen was at first suspected, but that hypothesis was later discarded. The experimental data fit the exis-

tence of a continuous series from $Pb_2^{2+}Y_8Si_6O_{26}$ to $Pb_5^{2+}Pb_3^{4+}Y_2Si_6O_{26}$ (Fig. 9). Valency compensation is achieved in part by oxidation of divalent lead ions to higher valency. It has been found that the highly oxidized compound is converted to the less oxidized compounds at elevated temperatures due to evaporation or formation of a lead silicate accompanied by partial reduction of lead to the divalent state. The compound Pb_2^{2+}-$Y_8Si_6O_{26}$, containing only divalent lead is stable up to 1150°C and decomposes to yttrium silicate and vapor at 1200°C. Compounds containing more lead, including oxidized lead, shrink in volume on heating at temperatures over 1000°C, but melt before enough sublimation has taken place to reach the stabilized end composition of $Pb_2^{2+}(Ln,Y)_8Si_6O_{26}$.

Presence of higher valency lead was tested qualitatively by dissolving finely ground samples in 3N acetic acid solution containing potassium iodide. Iodine liberated by the reduction of Pb^{4+} gave intense orange-yellow coloration to the solutions.

Oxypyromorphite described by Wondratschek (1963) as $Pb_{10}P_6O_{25}$ and lead oxysilicophosphate-apatite by Dietzel and Paetsch (1956) of supposed formula $Pb_{10}Si_2P_4O_{24}$, were also resynthesized and identified as the oxidized compound containing higher valency lead ions. The formulas may be rewritten as $Pb_8^{2+}Pb_2^{4+}Si_2P_4O_{26}$ and $Pb_9^{2+}Pb^{4+}P_6O_{26}$, respectively.

The writer suspects that manganvoelckerite, a divalent manganese bearing oxyapatite (Wickman, 1954; Mason, 1941), also may not be an oxygen deficient apatite. Its dark reddish brown color and its relative instability indicate the presence of higher valency manganese ions.

From the above results, the writer proposes the following general formula, $(M^+M^{2+}M^{3+}M^{4+})_{10}(Si^{4+}P^{5+}B^{3+})_6O_{26}$ for well stabilized oxyapatite in which both cation and anion sites are filled. The interpretation of compounds studied in this paper does not require the assumption either of oxygen deficiency or cation deficiency, and these substances can all be explained by overall charge balance. Nevertheless, the possibility that oxygen-deficient oxyapatite might exist has not been excluded, particularly under extremely unusual conditions or compositions. Cation deficiency can also not be ruled out, in fact, cation deficiency is more likely to be found than oxygen deficiency.

Steenstrupine. Chemical composition of steenstrupine (Strunz, 1942; Machatschki, 1943) a complex alkali, alkaline-earth silicophosphate indicates this mineral should be found within an isomorphous series from $Ca_{10}(PO_4)_6(OH)_2 \rightleftharpoons Ca_4Ln_6Si_6O_{24}(OH)_2 \rightleftharpoons Na_2Ln_8Si_6O_{24}(OH)_2$. No distinctive phase was found at the steenstrupine composition. Only a mixture of the silicate apatite and monazite phases were observed under diverse

conditions tried by the writer. Published X-ray powder data by Sabina and Traill (1960) of the specimen from Kangerdluarsuk, Greenland, were identified by the writer as a mixture of apatite and monazite. The hydrothermally recrystallized steenstrupine specimen from the same locality preserved at the Mineralogical Museum at Harvard University also gave the X-ray pattern of a mixture of apatite and monazite.

References

Ahrens, L. H. (1952) The use of ionization potentials, I. Ionic radii of the elements. *Geochim. Cosmochim. Acta*, **2**, 155–169.

Cockbain, A. G. and G. V. Smith (1967) Alkaline-earth rare-earth silicate and germanate apatites. *Mineral. Mag.*, **36**, 411–421.

Dietzel, A. and H. Paetsch (1956) Untersuchungen über das System $PbO-SiO_2-P_2O_5$. *Glastech. Ber.*, **29**, 350–355.

Frondel, C. (1961) Two yttrium minerals: spencite and rowlandite. *Can. Mineral.*, **6**, 576–581.

Gay, P. (1957) An X-ray investigation of some rare-earth silicates: cerite, lessingite, britholite, beckelite and stilwellite. *Mineral. Mag.*, **31**, 455–468.

Hata, S. (1938) Abukumalite, a new mineral from pegmatites of Iisaka, Fukushima prefecture. *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, **34**, 1018–1023.

Hägele, G. and F. Machatschki (1939) Der Britholith ist ein Cereden-Silikatpatit! *Zentralbl. Mineral.*, **A**, 165–167.

Jaffe, H. W. and V. J. Molinski (1962) Spencite, the yttrium analogue of tritomite from Sussex county, New Jersey, *Amer. Mineral.*, **47**, 9–25.

Keler, E. K., N. A. Godina and E. P. Savchenko (1961) Reaction in the solid phase of silica with oxides of rare-earth elements (La_2O_3, Nd_2O_3, Gd_2O_3). *Izv. Akad. Nauk SSSR, Ser. Chem.* **10**, 1728–1735.

Korber, F. and G. Trömel (1932) Untersuchungen über Kalk–Phosphosaure und Kalk-Phosphosaure-Kieselsaure-Verbindungen. *Z. Elektrochem.*, **38**, 578–582.

Kupriyanova, I. I. and G. A. Sidorenko (1963) Minerals of the britholite group. *Dokl. Akad. Nauk, SSSR*, **148**, 912–915.

Kuzmin, E. A. and N. V. Belov (1965) Crystalline structure of the simplest silicates of La and Sm. *Dokl. Akad. Nauk. SSSR, Ser. Math. Phys.* **165**, 88–90.

Leonov, A. I. (1962) The valence of cerium in synthetic and natural cerium aluminates and silicates, Pt. 2, cerium silicates. *Izv. Akad. Nauk SSSR, Ser. Chem.* **12**, 2084–2089.

MACHATSCHKI, F. (1939) Sind Abukumalite und Britholith Glieder der Apatitereihe? *Zentralbl. Mineral.*, **1939A,** 161–164.

—— (1943) Steenstrupine ist kein Silikat von Formeltypus Apatit. *Naturwissenchaften,* **31,** 438–439.

MASON, B. (1941) Mangualdite is manganvoelckerite. *Geol. Foren. Forh.*, **63**(4), 383–386.

McCONNELL, D. (1938) A structural investigation of the isomorphism of the apatite group. *Amer. Mineral.*, **23,** 1–19.

—— (1965) Crystal chemistry of hydroxyapatite, its relation to bone mineral. *Arch. Oral. Biol.*, **10,** 431–436.

MILLER, R. O. AND D. E. RASE (1964) Phase equilibrium in the system Nd_2O_3-SiO_2. *J. Amer. Ceram. Soc.*, **47,** 653–654.

MOROZEWICZ, J. (1905) Über Beckelith, ein Cer-Lanthano-Didymo. Silikat von Calcium. *Tschermaks Mineral. Petrogr. Mitt.*, 74, 120–134.

NECHAEVA, E. A. AND I. D. BRONEMAN-STARYNKEVICH (1956) Britholite in Skarn rocks of Western Transbaikalia. *Zap. Mineral. Obshch.*, **85,** 509–514.

NEUMAN, H., T. SVERDRUP AND P. C. SAEBO (1957) X-ray powder patterns for mineral identification. III. Silicates. *Norske Vidensk. Akad. Oslo, I., Mat.-Naturv. Kl.* p. 6, 17, plates 19 and 30.

OMORI, K. AND S. HASEGAWA (1953) Yttrialite and abukumalite from pegmatite of Suishoyama, Iisaka village, Fukushima, Japan. *J. Jap. Ass. Mineral Petrology Econ. Geol.*, **37,** 21–29.

ROGERS, A. F. (1912) Dahllite (pedolite) from Tonopah, Nevada, voelckerite a new basic calcium phosphate. *Amer. J. Sci.*, **33,** 475–482.

RUDNEVA, A. V., R. NIKITIN AND N. V. BELOV (1962) Ceftosil, a cerium britholite. *Dokl. Akad. Nauk SSSR*, **146,** 1182–1183.

SABINA, A. P. AND R. J. TRAILL (1960) Catalogue of X-ray diffraction patterns and specimen mounts on file at the Geological Survey of Canada. *Geol. Surv. Can. Pap.* **60–4,** 98.

SAKURAI, K., AND A. KATO (1962) Abukumalite from Shinden, Gifu, Japan. *J. Mineral. Soc. Jap.*, **5,** 328–334.

STRUNZ, H. (1942) Steenstrupine, ein Silikat von Formeltypus Apatit. *Naturwissenschaften* **30,** 65.

TRÖMEL, G. (1932) Untersuchungen über die Bildung eines Halogen-freien Apatits aus basischen Calciumphosphaten. *Z. Physik, Chem.*, **158,** 422–432.

TRÖMEL, G. AND W. EITEL (1957) Die Synthese von Silikatapatiten der Britholith-Abukumalit Gruppe. *Z. Kristallogr.*, **109,** 231–239.

WICKMAN, F. E. (1954) Minerals of the Varuträsk pegmatite, XXXVIII, Manganvoelckerite. *Geol. Fören. Stockholm Förh*, **76,** 495–500.

WINTHER, C. (1901) Britholith, ein neues Mineral. *Z. Kristallogr. Mineral.*, **34,** 685–687.

WONDRATSCHEK, H. (1953) Untersuchungen zur Kristallchemie der Blei-Apatite (Pyromorphite). *Neues Jahrb. Mineral. Abhandl.*, **99,** 113–160.

YOUNG, E. J. AND E. L. MUNSON (1966) Fluor-chloro-oxy apatite and sphene from Crystal Lode pegmatite near Eagle, Colorado, *Amer. Mineral.*, **51,** 1476–1493.

ZILBERMINTZ, V. A. (1929) Sur le gisement de cérite, de bastanesite et d'un minéral nouveau la lessingite, dans le district minéral, Kuchtym. *Dokl. Akad. Nauk. SSSR, A,* **3,** 55–60.