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Chromium Analogs of Apatite and Spodiosite[1a]

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New chromium analogs of apatite, $Ca_5(CrO_4)_3F$, $Ca_5(CrO_4)_3Cl$, $Sr_5(CrO_4)_3Cl$, $Ba_5(CrO_4)_3F$, and $Ba_5(CrO_4)_3Cl$, were formed. Isomorphism between chromium and phosphorus apatites was established by formation of solid solutions. Unsuccessful attempts were made to substitute Ga(III) and Mo(VI) in the chromium apatites. It was concluded that chromium is probably present in apatites in the pentavalent state. Two new phases B and C were produced by the reaction of $Ca_3(CrO_4)_2$ with water at room temperature. The X-ray data of phase B showed resemblance to that of the mineral ettringite. Three other phases were obtained in the syntheses of chloroapatites. Phase D, Ca_2CrO_4Cl, was found to be isomorphous with chlorospodiosite, Ca_2PO_4Cl. Phase E was identified as the analog Sr_2CrO_4Cl and the green crystals of phase F had the composition of $BaCrO_4$.

Introduction

Syntheses of chromium analogs of apatite, $Ca_5(CrO_4)_3OH$, $Sr_5(CrO_4)_3OH$, and $Ba_5(CrO_4)_3OH$, have been described in the literature.[2–6] In general, these compounds have been formed by ignition of mixtures of alkaline earth carbonates, hydroxides, or oxides with Cr_2O_3 in the presence of water vapor. An intermediate compound, $Ca_3(CrO_4)_2$, is formed by carrying out the ignition in a dry atmosphere. This compound, synthesized by many workers, is isomorphous with $Ca_3(PO_4)_2$, but often it has been identified as $9CaO \cdot 4CrO_3 \cdot Cr_2O_3$.[7–9] Glasser, *et al.*,[10] prepared $Ca_3(CrO_4)_2$ and suggested that the Cr had a valence of five. These authors also showed that the X-ray diffraction patterns of $Ca_3(CrO_4)_2$ and β-$Ca_3(PO_4)_2$ are similar. Klemm and Scholder[2,3,5,11] reported the formation of $Ba_3(CrO_4)_2$ and $Sr_3(CrO_4)_2$ and stated that these compounds appear to be similar to the analogous phosphates, *e.g.*, $Ba_3(PO_4)_2$. Magnetic susceptibility measurements gave a value of 1.73 B.M. for $Ba_3(CrO_4)_2$, which is also the theoretical value for the Cr^{+5} ion. Klemm[12] estimated the ionic radius of Cr^{+5} to be 0.46 Å.

The existence of $Ca_5(CrO_4)_3OH$, which is isomorphous to hydroxyapatite, $Ca_5(PO_4)_3OH$, was reported by Scholder.[5] The formation, X-ray data, and unit cell dimensions of $Ca_5(CrO_4)_3OH$ were reported by Johnson,[6] who assumed that the Cr was present in tri- and hexavalent states with a mean valence of five. Minguzzi[13] substituted about 3% Cr into chloroapatite, $Ca_5(PO_4)_3Cl$, in a ratio of Cr^{+6}/Cr^{+3} equal to 2:1 and assumed that $3P^{+5}$ had been replaced by $2Cr^{+6} + Cr^{+3}$. Formation of $Ba_5(CrO_4)_3OH$ and $Sr_5(CrO_4)_3OH$ was reported by Klemm and Scholder[2,3,5,11]; the unit cell dimensions of $Ba_5(CrO_4)_3OH$ were determined by Klemm.[12] According to Scholder, *et al.*,[4] the magnetochemical analysis supported by X-ray diffraction data indicates that the Cr appears in the pentavalent state in compounds such as $Ba_3(CrO_4)_2$, $Ba_5(CrO_4)_3OH$, and the Ca and Sr analogs.

The aim of this research was to synthesize various chromium apatites including the halogen apatites, to form solid solutions of phosphorus and chromium apatites in order to prove their isomorphism, and to obtain more evidence about the valence state of chromium in these compounds.

The synthesis of $Ca_5(CrO_4)_3Cl$, in which excess $CaCl_2$ was used as a flux, produced a new compound, Ca_2CrO_4Cl. Further investigations revealed that this compound is isomorphous with a synthetic compound, Ca_2PO_4Cl,[14] which is related to the mineral spodiosite,[15] Ca_2PO_4F. The unit cell dimensions of the chlorospodiosite, Ca_2PO_4Cl, were reported by Mackay[16] and Walter-Levy, *et al.*[17]

Experimental

Ignitions were made in a tube furnace using platinum crucibles and A.R. or C.P. grade chemicals. X-Ray powder diffractometer traces were run on Norelco X-ray equipment using Ni-filtered Cu radiation with λ 1.54050.

(1) **Formation of Chromium(V) Apatites.** (a) **Orthochromate: $Ca_3(CrO_4)_2$.**—The compound $Ca_3(CrO_4)_2$[10] was prepared by igniting $CaCO_3$ and Cr_2O_3 mixtures in a molar ratio of CaO/Cr_2O_3 of 3:1 at 980°. Also, mixtures containing 1 mole of CaO in excess of $3Ca_3(CrO_4)_2$ were prepared by a similar procedure. The calcium orthochromate(V) was prepared as an intermediate for later use in the apatite synthesis.

(b) **Apatites: $Ca_5(CrO_4)_3X$ (X = F, OH, Cl). $Ca_5(CrO_4)_3F$.**—Attempts were made to prepare a fluoroapatite of the formula $Ca_5(CrO_4)_3F$ by heating a mixture of $CaCO_3$, CrO_3, and CaF_2 in a molar ratio of 9:3:1 in air at 900°, followed by ignition at 950° in a N_2 atmosphere. The X-ray powder pattern of the product somewhat resembled that of the apatite $Ca_5(CrO_4)_3OH$.[6] The *d*-spacings of the product are listed in Table I. Similar mixtures containing a large excess of CaF_2 as a flux produced the same

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(1) (a) Based on the M.S. thesis submitted by K. L. Jaunarajs in June 1963. (b) Johns-Manville Research Center, Manville, N. J.

(2) W. Klemm, *Angew. Chem.*, **63**, 396 (1951).

(3) R. Scholder, *ibid.*, **65**, 240 (1953).

(4) R. Scholder and E. Suchy, *Z. anorg. allgem. Chem.*, **308**, 295 (1961).

(5) R. Scholder, *Angew. Chem.*, **70**, 583 (1958).

(6) W. Johnson, *Mineral. Mag.*, **32**, 408 (1960).

(7) W. F. Ford and W. J. Rees, *Trans. Brit. Ceram. Soc.*, **47**, 207 (1948).

(8) W. F. Ford and W. J. Rees, *ibid.*, **48**, 291 (1949).

(9) W. F. Ford and J. White, *ibid.*, **48**, 417 (1949).

(10) F. P. Glasser and E. F. Osborn, *J. Am. Ceram. Soc.*, **41**, 358 (1958).

(11) R. Scholder and W. Klemm, *Angew. Chem.*, **66**, 461 (1954).

(12) W. Klemm, *ibid.*, **66**, 468 (1954).

(13) C. Minguzzi, *Periodico Min.*, **12**, 343 (1941).

(14) F. K. Cameron and W. J. McCaughey, *J. Phys. Chem.*, **15**, 463 (1911).

(15) H. V. Tiberg, *Geol. For. Forh.*, **1**, 84 (1872).

(16) A. L. Mackay, *Mineral. Mag.*, **30**, 166 (1953).

(17) L. Walter-Levy, P. M. de Wolff, and J. P. Vincent, *Compt. rend.*, **240**, 308 (1955).

TABLE I

X-RAY DIFFRACTION DATA FOR CALCIUM APATITES

$Ca_5(CrO_4)_3F$				$Ca_5(CrO_4)_3Cl$[a]		
d, Å. (obsd.)	I/I_0	d, Å. (Calcd.)	hkl	d, Å.	I/I_0	hkl
4.187	vw	4.180	200	8.66	vwb	100
3.966	m	3.965	111	5.30	vwb	101
3.601	vvwb	3.590	201	4.019	vw	111
3.497	s	3.500	002	3.660	vw	201
3.218	vwb	3.224	102	3.386	m	002
3.162	w	3.159	210	3.288	vw	210
2.873	vvs	2.878	211	2.957	vs	211
2.820	mb	2.835	112	2.896	vvs	300
2.784	vs	2.784	300	2.803	m	112
2.673	mb	2.680	202	2.673	s	202
2.319	wb	2.316	310	2.409	vw	310
2.197	wb	2.200	311	2.360	vw	221
2.000	wb	1.987	222	2.274	w	311
1.979	wb			2.017	w	222
				1.996	vvw	320
1.886	wb	1.877	213			
1.865	wb			1.963	vw	312
1.843	wb	1.845	321	1.916	vvwb	321
1.823	wb	1.822	410	1.897	w	410
1.751	w	1.751	004	1.861	w	213
				1.829	vw	402
1.691	vwb	1.680	322			
1.674	vw			1.776	vvwb	303
				1.720	wb	322
				1.694	w	004
				1.660	vvw	104
				1.652	w	313
				1.599	vw	421
				1.548	vwd	502
				1.522	vwb	511

[a] Hexagonal; $a = 10.03$ Å., $c = 6.78$ Å.

apatite phase, plus unreacted fluoride, after ignitions up to 1140°.

$Ca_5(CrO_4)_3OH$.—The apatite $Ca_5(CrO_4)_3OH$[6] was formed by igniting various starting materials, such as $3Ca_3(CrO_4)_2 + Ca(OH)_2$, $3Ca_3(CrO_4)_2 + CaO$, or directly from $CaCO_3$ and Cr_2O_3 in a molar ratio of CaO/Cr_2O_3 equal to 10:3 in the presence of water vapor. A solid solution of $Ca_5(CrO_4)_x(PO_4)_{3-x}OH$ was prepared by the following procedure: The apatite $Ca_5(PO_4)_3OH$,[18] formed by heating commercial $Ca_3(PO_4)_2$ with $CaCO_3$ at 900° in the presence of water vapor, and a sample of $Ca_5(CrO_4)_3OH$ were mixed in a weight ratio of 1:1 and ignited in a N_2 atmosphere containing water vapor at 835–910°.

Phases A, B, and C.—Several experiments were carried out using hydrothermal techniques to synthesize the apatite $Ca_5(CrO_4)_3OH$. Samples of previously prepared mixtures of $3Ca_3(CrO_4)_2 + CaO$ were subjected to hydrothermal treatment at saturated steam pressures in a temperature range of 200 to 300° for a duration of 2–5 days. For all samples $CaCrO_4$ and $Ca(OH)_2$ were the main end products as identified by X-ray diffraction. A sample of $Ca_5(CrO_4)_3OH$, when allowed to react hydrothermally at 170 and 200°, produced mainly $CaCrO_4$ and $Ca(OH)_2$, plus a small amount of an unknown, phase A, with its three strongest reflections at 10.27, 5.15, and 2.901 Å. A yellow-green product was formed by heating $Ca_3(CrO_4)_2$ or mixtures of $3Ca_3(CrO_4)_2 + CaO$ in water suspensions at 70 and 95° in air. No conclusive evidence about the phases present could be obtained by X-ray diffraction, owing to poorly crystallized material.

Room-temperature reactions of similar suspensions in closed glass jars for a duration of 2 weeks produced a yellow-green fine-grained material, phase B, and a few visible yellow crystals, phase C, growing on top of the phase B material, plus some $Ca(OH)_2$. The X-ray powder data of phase B somewhat resembled the data reported for synthetic ettringite,[19] $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$, as shown in Table II. The reflections observed for the unknown phase C are also listed in Table II. Microscopic examination of phase C gave the following: biaxial (−), $2V \sim 90°$, $n_\alpha \sim 1.74$, and $n\gamma > 1.75$. The system is probably monoclinic or triclinic.

TABLE II

X-RAY DIFFRACTION DATA FOR PHASES B AND C AND ETTRINGITE

Phase B		Ettringite[19]		Phase C	
d, Å.	I/I_0	d, Å.	I/I_0	d, Å.	I/I_0
9.81	vvs	9.73	100	5.676	s
8.93	m	8.86	13	5.151	m
7.31	w	...	...	4.073	m
5.67	vvs	5.61	80	4.019	s
5.04	m	4.98	25	3.645	m
...	...	4.86	7	3.437	vw
4.766	s	4.69	35	3.129	vs
...	...	4.41	3	3.000	s
4.073	m	4.02	11	2.835	vw
3.914	vs	3.88	50	2.583	vvs
...	...	3.67	7	2.506	w
3.645	m	3.60	15	2.431	m
3.504	s	3.48	30	2.390	w
...	...	3.27	5	2.331	w
3.276	s	3.240	20	2.291	vw
3.056	w	3.016	7	2.263	vvs
...	...	2.806	7	2.215	w
2.803	s	2.773	40	2.184	vw
...	...	2.714	7	2.159	w
2.720	m	2.697	13	2.039	vvw
2.688	vw	2.680	7	2.000	wb
...	...	2.616	20	1.975	w
2.590	s	2.564	45	1.836	wb
2.513	w	...	...	1.819	wd
2.440	m	2.401	11	1.812	m
2.378	w	...	...	1.779	w
2.252	w	2.230	21	1.714	wb
2.236	s	2.209	45	1.688	vwb
2.179	m	2.154	25	1.649	vw
2.144	w	...	...		

$Ca_5(CrO_4)_3Cl$ and Phase D.—The chloroapatite $Ca_5(CrO_4)_3Cl$ was prepared by igniting a mixture containing $Ca_3(CrO_4)_2$ and $CaCl_2$ in a molar ratio of 3:1, at 900–950° in a N_2 atmosphere. It was also prepared directly from a mixture consisting of stoichiometric amounts of $CaCO_3$, Cr_2O_3, and $CaCl_2$ according to the apatite formula. The ignition of this mixture was carried out at first in air and finally in a N_2 atmosphere. A similar test showed that the N_2 atmosphere is not essential to apatite formation as long as the samples are cooled rapidly to room temperature, but its use was continued in this work to ensure higher purity of the products.

By X-ray diffraction the chloroapatite $Ca_5(CrO_4)_3Cl$ is similar to the apatite $Ca_5(CrO_4)_3OH$, except for a shift of 2θ toward lower angles. The *d*-spacings of $Ca_5(CrO_4)_3Cl$ are given in Table I.

A series of solid solutions, of the form $Ca_5(CrO_4)_x(PO_4)_{3-x}Cl$, was prepared at 860–920°, containing 5, 10, 20, and 80 wt. % of the chromium apatite. The apatite $Ca_5(PO_4)_3Cl$[20] used in these preparations was formed by igniting a mixture of $CaHPO_4$, $CaCO_3$, and $CaCl_2$ in a molar ratio of 6:3:1 at 860–930°. A new phase, D, obtained in the $Ca_5(CrO_4)_3Cl$ syntheses using excess $CaCl_2$, will be discussed later.

(c) **Apatites: $Sr_5(CrO_4)_3X$ (X = OH, Cl). $Sr_5(CrO_4)_3OH$.**—The apatite $Sr_5(CrO_4)_3OH$ was prepared by igniting a mixture of $Sr(OH)_2 \cdot 8H_2O$ and Cr_2O_3 in a molar ratio of 10:3. At first the mixture was heated in air at 845° for 5 hr. Then the sample

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(18) ASTM X-Ray Powder Data File, Card 9-432; ASTM Special Technical Publication 48-K (1961).

(19) ASTM X-Ray Powder Data File, Card 9-414; ASTM Special Technical Publication 48-K (1961).

(20) E. B. Jaffe, Geological Survey Circular 135, U. S. Department of the Interior (1951).

TABLE III

X-RAY DIFFRACTION DATA FOR STRONTIUM APATITES

$Sr_5(CrO_4)_3OH$[a]			$Sr_5(CrO_4)_3Cl$[b]		
d, Å.	I/I_0	*hkl*	*d*, Å.	I/I_0	*hkl*
4.329	m	200	4.381	m	200
3.698	s	002	3.660	m	002
3.398	m	102	3.386	wb	102
3.264	s	210	3.312	s	210
2.986	vs	211	3.020	vs	211
2.966	vvs	112	2.966	vvs	112
2.880	vs	300	2.915	vs	300
2.812	w	202	2.812	wb	202
2.396	w	310	2.720	vwb	301
2.366	vw	221	2.527	vvw	220
2.279	vw	311	2.460	vvw	212
2.210	vw	113	2.432	m	310
2.164	vw	400	2.396	vw	221
2.144	vw	203	2.308	w	311
2.070	s	222	2.285	vwb	302
2.013	m	312	2.194	wd	400, 113
1.967	s	213	2.079	s	222
1.916	s	321	2.026	m	312
1.886	s	410	2.013	m	320
1.868	s	402	1.963	s	213
1.850	m	004	1.940	s	321
1.751	vw	322	1.913	s	410
1.717	vw	313	1.879	s	402
1.685	vw	501	1.830	s	004
1.635	w	420	1.789	vvwb	104
1.609	w	214	1.760	vwb	322, 223
1.569	m	502	1.723	vw	313
1.557	m	304	1.694	vw	412
1.548	w	510	1.657	vw	420
1.520	w	511	1.643	vw	331
			1.617	vw	421
			1.604	vw	214
			1.579	wb	502
			1.552	s	304
			1.538	mb	511

[a] Hexagonal; $a = 9.98$ Å., $c = 7.40$ Å. [b] Hexagonal; $a = 10.12$ Å., $c = 7.32$ Å.

was reground and refired at 860–920° for 5 hr. more in a N_2 atmosphere containing water vapor. The *d*-spacings of the apatite $Sr_5(CrO_4)_3OH$ are given in Table III.

$Sr_5(CrO_4)_3Cl$ and Phase E.—A mixture containing $Sr(OH)_2 \cdot 8H_2O$, Cr_2O_3, and $SrCl_2 \cdot 6H_2O$ in a molar ratio of 9:3:1 produced chloroapatite, $Sr_5(CrO_4)_3Cl$, by the use of heating conditions identical with those above. A similar mixture, which contained 3 moles of $SrCl_2$ in excess of the apatite formula, formed chloroapatite and a new phase E after ignition for 22 hr. at 860–918°. The new phase, E, will be identified in the latter part of this work. The X-ray data of $Sr_5(CrO_4)_3Cl$ are presented in Table III.

(d) **Apatites: $Ba_5(CrO_4)_3X$ (X = OH, F, Cl). $Ba_5(CrO_4)_3OH$ and $Ba_3(CrO_4)_2$.**—Calculated amounts of $Ba(OH)_2$ and Cr_2O_3 in a molar ratio of 10:3 produced $Ba_3(CrO_4)_2$[3,11] after heating at 800° in air followed by ignition at 890° in a N_2 atmosphere containing water vapor. The X-ray powder pattern of the product $Ba_3(CrO_4)_2$ was similar to that of $Ba_3(PO_4)_2$.[21] A few extra lines were observed to be present. The *d*-spacings of $Ba_3(CrO_4)_2$ are listed in Table IV.

A mixture of $Ba_3(CrO_4)_2$ and $Ba_5(CrO_4)_3OH$ resulted from heating a sample containing 1 mole of $Ba(OH)_2$ in excess of the stoichiometric quantity for apatite at 820° in air, followed by ignition at 980° in a N_2 atmosphere containing water vapor. The *d*-spacings of $Ba_5(CrO_4)_3OH$ are listed in Table IV.

$Ba_5(CrO_4)_3F$, $Ba_5(CrO_4)_3Cl$, and Phase F.—A fluoroapatite, of the form $Ba_5(CrO_4)_3F$, was prepared using a mixture of $Ba(OH)_2$, Cr_2O_3, and BaF_2 in a molar ratio of 9:3:1 and heating conditions identical with those for the hydroxyapatite. The X-ray analysis indicated the presence of another phase, F, which will be discussed later. The X-ray diffraction data for $Ba_5(CrO_4)_3F$ are given in Table IV.

A sample, containing $Ba(OH)_2$, Cr_2O_3, and $BaCl_2 \cdot 2H_2O$ in a molar ratio of 9:3:1, produced fine-grained $Ba_5(CrO_4)_3Cl$ together with small amounts of phase F when identical heating conditions were used as for the hydroxyapatite. Hexagonal crystals of the chloroapatite, in the range of about 50–300 μ, were prepared by the following procedure: A mixture, consisting of $Ba(OH)_2$, Cr_2O_3, and $BaCl_2 \cdot 2H_2O$ in a molar ratio of 9:3:4, was heated at 820° in air for 4 hr. The sample was removed from the furnace, ground in a mortar, and refired at 890° for 4 hr. more in a N_2 atmosphere. The X-ray pattern of the product showed the presence of $Ba_5(CrO_4)_3Cl$ and phase F in about equal amounts. Five additional moles of $BaCl_2$ was added to this sample and the ignition continued at 900° for 3 hr. followed by 16 hr. at 860°. The product was washed with distilled water to remove the excess chloride. By microscopic observation the chloroapatite appeared as black hexagonal crystals, whereas phase F consisted of bright green irregular grains. The X-ray powder data of $Ba_5(CrO_4)_3Cl$, obtained from crystals which were picked out from the mixture, using a microscope, are given in Table IV.

(e) **Unit Cell Dimensions of Chromium(V) Apatites.**—The lattice constants of the apatites prepared in this work were calculated using the formula for hexagonal unit cells.[22] The unit cell dimension *a* was calculated from Miller indices *hk*0: 210, 300, 310, or 410. The dimension *c* was obtained from the indices 004. It proved impossible to fit a hexagonal apatite-like unit cell to the pattern of the compound $Ca_5(CrO_4)_3F$. The close resemblance of the X-ray diffraction data of this compound to that of $Ca_5(CrO_4)_3OH$ suggests that the fluoride analog is pseudohexagonal, with a distorted apatite structure. A comparison of observed *d*-spacings with those calculated for a hexagonal unit cell with $a = 9.64$ and $c = 7.00$ Å. is shown in Table I.

The calculated unit cell dimensions of the apatites are presented in Table V, which also contains the lattice constants reported by other workers for identical or isomorphous compounds.

(f) **Attempted Substitution of Ga(III) and Mo(VI) in Chromium Apatite.**—Attempts were made to substitute Ga(III) for Cr(III) in the chromium apatite, assuming that the Cr exists in the apatite as a mixture of Cr(III) and Cr(VI). Several ignitions were made in order to prepare a compound of the composition $9CaO \cdot 4CrO_3 \cdot Ga_2O_3 \cdot Ca(OH)_2$, or the chloro and fluoro analogs. The starting materials were the same as those used in the preparations of the apatites $Ca_5(CrO_4)_3X$, except that some Cr_2O_3 was replaced by Ga_2O_3 or $Ga(OH)_3$ in amounts determined by the ratio Cr/Ga 2:1.

Low-temperature reactions (up to 790°) produced CaO, $CaCrO_4$, and unreacted Ga_2O_3. Samples which were ignited at higher temperatures produced mixtures of various phases such as CaO, $3CaO \cdot Ga_2O_3$,[23] $CaO \cdot Ga_2O_3$,[23] and small amounts of $Ca_5(CrO_4)_3OH$ or the halogen analogs. The color of the products appeared to be dark green, resulting from the apatites $Ca_5(CrO_4)_3X$. This green color persisted even when rapid air flow was provided through the tube furnace. Several trials were also made to substitute Mo(VI) for Cr(VI) in the apatites, with $CaMoO_4$ used as a source of Mo in amounts such that Cr/Mo = 0.5, according to the formula $9CaO \cdot 4MoO_3 \cdot Cr_2O_3 \cdot Ca(X)_2$. In all cases the ignition products consisted of unreacted compounds and $CaCrO_4$, $Ca_3(CrO_4)_2$, or $Ca_5(CrO_4)_3X$. Also, the synthesis of an apatite with the chemical composition of $9CaO \cdot 4MoO_3 \cdot Ga_2O_3 \cdot Ca(OH)_2$ was not successful.

(2) **Formation of Spodiosite Analogs.**—The unknown phases D, E, and F, as mentioned before, were obtained in the prepara-

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(21) ASTM X-Ray Powder Data File, Card 4-0582; ASTM Special Technical Publication 48-K (1961).

(22) C. W. Bunn, "Chemical Crystallography," Clarendon Press, Oxford, 1946, pp. 134–136.

(23) J. Jeevaratnam and F. P. Glasser, *J. Am. Ceram. Soc.*, **44**, 563 (1961).

TABLE IV

X-RAY DIFFRACTION DATA FOR BARIUM ORTHOCHROMATE(V) AND APATITES

$Ba_3(CrO_4)_2$		$Ba_5(CrO_4)_3OH$[a]			$Ba_5(CrO_4)_3F$[b]			$Ba_5(CrO_4)_3Cl$[c]		
d, Å.	I/I_0	*d*, Å.	I/I_0	*hkl*	*d*, Å.	I/I_0	*hkl*	*d*, Å.	I/I_0	*hkl*
4.818	w	4.458	m	200	4.444	wb	200	5.242	vwb	110
3.630	w	3.880	m	002	3.889	wb	002	4.548	mb	200
3.224	vvs	3.559	m	102	3.559	m	102	4.350	wb	111
2.851	vs	3.380	m	210	3.373	s	210	3.864	m	002
2.460	vvw	3.103	vs	211, 112	3.103	vs	211, 112	3.566	m	102
2.409	vw	2.986	s	300	2.981	s	300	3.431	w	210
2.366	w	2.864	w	ni	2.878	m	ni	3.118	vvsd	112, 211
2.241	wd	2.319	vvw	113	2.483	vw	310	3.025	vs	300
2.140	s	2.222	vw	400	2.354	vw	311	2.891	m	ni
1.955	m	2.154	md	222	2.319	vw	113	2.520	m	310
1.865	vvw	2.097	w	312	2.154	sd	222	2.390	wb	302
1.823	w	2.060	m	213	2.092	m	312	2.319	wb	113
1.767	vvw	1.988	w	321	2.061	m	213	2.172	s	222
1.714	m	1.943	md	004, 410	1.984	w	321	2.111	m	312
1.652	m	1.691	vw	420	1.951	m	410	2.063	s	213
1.614	w	1.630	vvw	502	1.943	m	004	2.013	m	321
1.454	vwb	1.579	vvw	511	1.748	vvw	501	1.984	m	410
1.430	wb				1.703	vwb	420	1.959	m	402, 303
1.407	mb				1.630	vwb	502	1.934	vw	004
								1.763	vwb	322
								1.705	vwb	331
								1.685	vwb	214
								1.643	vwb	502
								1.633	s	304
								1.630	s	510
								1.594	m	511

[a] Hexagonal; $a = 10.34$ Å., $c = 7.77$ Å. [b] Hexagonal; $a = 10.33$ Å., $c = 7.77$ Å. [c] Hexagonal; $a = 10.50$ Å., $c = 7.73$ Å.

TABLE V

UNIT CELL DIMENSIONS OF APATITES

	a, Å.	*c*, Å.
$Ca_5(PO_4)_3OH$[18]	9.418	6.884
$Ca_5(CrO_4)_3OH$	9.66	7.01
$Ca_5(CrO_4)_3OH$[6]	9.67	7.01
$Ca_5(CrO_4)_x(PO_4)_{3-x}OH$	9.54	6.93
$Ca_5(CrO_4)_3Cl$	10.03	6.78
$Sr_5(PO_4)_3OH$[a]	9.74	7.20
$Sr_5(CrO_4)_3OH$	9.98	7.40
$Sr_5(CrO_4)_3Cl$	10.12	7.32
$Ba_5(PO_4)_3OH$[a]	10.19	7.70
$Ba_5(CrO_4)_3OH$	10.34	7.77
$Ba_5(CrO_4)_3OH$[12]	10.46	7.85
$Ba_5(CrO_4)_3F$	10.33	7.77
$Ba_5(CrO_4)_3Cl$	10.50	7.73

[a] R. Klement, *Z. anorg. allgem. Chem.*, **242**, 215 (1939).

tion of apatites of the form $M_5(CrO_4)_3Cl$ (M = Ca, Sr, Ba) using excess alkaline earth chlorides as a flux. These phases are described separately in this section since further investigation revealed that phases D and E are isomorphous with chlorospodiosite.

(a) **The System $Ca_3(PO_4)_2$–$CaCl_2$.**—Several ignitions were performed using $Ca_3(PO_4)_2$ and various amounts of $CaCl_2$ in excess of the stoichiometric quantity required for chloroapatite, $Ca_5(PO_4)_3Cl$, formation. The product (sample 126), formed by ignition at 920° and subsequent removal of the excess $CaCl_2$ by washing with water, was identified as chlorospodiosite, Ca_2PO_4Cl.[16,17] The unit cell dimensions of this compound were calculated for the orthorhombic system.[22] The following comparison was obtained with the values reported in the literature.

	Mackey[16]	Walter-Levy[17]	Sample 126
a, Å.	6.17	6.20	6.17
b, Å.	6.89	6.99	6.97
c, Å.	10.74	10.82	10.78

(b) **Phase D: Ca_2CrO_4Cl.**—The X-ray powder pattern of phase D, obtained in the synthesis of $Ca_5(CrO_4)_3Cl$ using excess $CaCl_2$, showed definite similarity to the pattern of chlorospodiosite discussed above. Therefore, further attempts were made to prepare larger and purer samples of this material.

A pure sample of phase D was prepared by igniting a mixture containing 3.015 g. of $Ca_3(CrO_4)_2$ and 1.305 g. of $CaCl_2$ in a tube furnace at 800° for 66 hr. The sample was removed from the furnace at 782°, cooled rapidly to room temperature, and purified by washing with distilled water to remove excess $CaCl_2$. The product consisted of a fine-grained material, which appeared to be dark blue-purple as compared to the green color of the apatites. The X-ray data of phase D are presented in Table VI.

Anal. Calcd. for Ca_2CrO_4Cl: Ca, 34.6; Cr^{+6}, 14.93; Cr^{+3}, 7.47; Cl, 15.3. Found: Ca, 34.7; Cr^{+6}, 14.7; Cr^{+3}, 7.9; Cl, 15.1.

A solid solution of the form $Ca_2(CrO_4)_x(PO_4)_{1-x}Cl$ was produced by heating Ca_2PO_4Cl, Ca_2CrO_4Cl, and $CaCl_2$ in a molar ratio of 1.1:1:1.7 at 790–840°. The sample was purified as in the previous case. The unit cell dimensions for the product $Ca_2(CrO_4)_x(PO_4)_{1-x}Cl$ were: $a = 6.20$, $b = 7.03$, $c = 10.84$ Å. The color of this sample was blue-purple as compared to the light lavender color of a similar preparation containing only 5% of phase D by weight.

(c) **Phase E: Sr_2CrO_4Cl.**—Eight moles of excess $SrCl_2$ was added to the previously prepared sample containing phase E and $Sr_5(CrO_4)_3Cl$. The mixture produced a pure sample of phase E after heating for 15 hr. at 800° in a N_2 atmosphere. The sample was purified as in the case of phase D. The X-ray diffraction pattern of phase E appeared to be similar to that of Ca_2CrO_4Cl. Thus the formula Sr_2CrO_4Cl may be postulated for phase E. The X-ray data of this compound are given in Table VI.

(d) **Phase F.**—This phase was previously observed in the synthesis of $Ba_5(CrO_4)_3F$ and $Ba_5(CrO_4)_3Cl$. Further experiments were performed to determine whether this phase was isomorphous to phases D and E. Several preparations were made using $Ba(OH)_2$, Cr_2O_3, and $BaCl_2 \cdot 2H_2O$ mixtures in a molar ratio of 3:1:3. The ignitions, in a N_2 atmosphere, lasted from 24 to 74 hr. at 765–935°. In all cases, the product consisted of phase F and unreacted $BaCl_2$; no $Ba_5(CrO_4)_3Cl$ was detected.

TABLE VI

X-RAY DIFFRACTION DATA FOR PHASES D, E, AND F

Phase D, Ca_2CrO_4Cl[a]			Phase E, Sr_2CrO_4Cl,[b]			Phase F	
d, Å.	I/I_0	hkl	d, Å.	I/I_0	hkl	d, Å.	I/I_0
6.232	wb	100	6.411	vvw	100	4.350	wb
5.500	m	002	5.694	w	002	3.931	s
4.691	wb	110	4.525	m	012	3.872	m
4.329	m	012	4.480	s	111	3.645	m
4.308	m	111	4.287	vvw	102	3.504	m
3.552	vs	020	3.720	s	020	3.386	vs
3.124	w	200	3.238	m	200	3.151	m
2.981	vsd	022, 121	3.108	vsd	121, 022	2.966	vw
2.860	m	210	2.976	m	210	2.887	s
2.748	vsd	004, 211	2.873	s	211	2.838	vw
2.697	md	122, 202	2.845	s	004	2.803	w
2.540	s	212	2.820	sd	202, 122	2.744	s
2.348	md	220, 123	2.635	vs	212	2.620	wb
2.291	w	221	2.466	w	123	2.496	w
2.255	w	213	2.453	m	220	2.236	s
2.218	w	130	2.396	vvwb	221	2.231	sd
2.172	w	024	2.342	vw	213	2.189	vw
2.052	m	124	2.319	w	130	2.171	vvs
1.982	m	214, 223	2.268	w	024	2.144	m
1.947	w	302	2.138	w	124	2.130	s
1.890	w	133	2.065	m	115	1.957	wb
1.786	mb	224, 232	2.056	md	223, 214	1.897	vs
1.779	md	040	2.026	w	302	1.792	s
1.763	w	106	1.975	vvw	133	1.697	w
1.711	wb	140	1.940	vwb	231	1.652	wd
1.657	w	304	1.865	vs	040	1.627	vvw
1.627	wb	026	1.843	vvw	321	1.609	vw
1.620	w	314	1.796	wb	140	1.564	m
1.562	wb	400, 135	1.773	vw	322	1.559	m
1.558	wb	234	1.751	vvw	233	1.536	vvw
1.543	wb	240, 401	1.691	vwb	026	1.458	vwd
1.504	wb	402, 332	1.671	vvw	043	1.442	vw
			1.625	w	135	1.438	vw
			1.621	wb	400, 234	1.381	vw
			1.599	vw	401	1.377	vw

[a] Orthorhombic: $a = 6.25$ Å., $b = 7.12$ Å., $c = 10.99$ Å.
[b] Orthorhombic: $a = 6.48$ Å., $b = 7.46$ Å., $c = 11.38$ Å.

The samples were purified as in the case of phase D. The irregular crystals were transparent and of a dark to bright green color, which changed into light green upon grinding. The crystals were biaxial (+), with a refractive index of about 1.96. The X-ray data of phase F are shown in Table VI.

Anal. Calcd. for $BaCrO_4$: Ba, 54.25; Cr, 20.50. Found: Ba, 54.0; Cr, 20.3 (or as Cr^{+6}, 19.2).

Conclusions

The apatites $Ca_5(CrO_4)_3OH$, $Sr_5(CrO_4)_3OH$, and $Ba_5(CrO_4)_3OH$, syntheses of which have been reported in the literature by Klemm,[2] Scholder,[3–5] and Johnson,[6] were also prepared in this research work. In addition, several new apatites, isomorphous with those above, in the form of $Ca_5(CrO_4)_3F$, $Ca_5(CrO_4)_3Cl$, $Sr_5(CrO_4)_3Cl$, $Ba_5(CrO_4)_3F$, and $Ba_5(CrO_4)_3Cl$, were prepared.

The compound $Ca_5(CrO_4)_3F$ could not be indexed on the basis of a hexagonal unit cell, although the X-ray powder pattern of this compound resembled that of $Ca_5(CrO_4)_3OH$. Most of the observed *d*-spacings fit the hexagonal unit cell except the one having indices 222, 213, and 322 which apparently are split as shown in Table I. It appears that the F^- ion, which is slightly smaller than the OH^- ion, caused formation of a pseudohexagonal structure.

The formation of solid solutions, $Ca_5(CrO_4)_x(PO_4)_{3-x}OH$ and $Ca_5(CrO_4)_x(PO_4)_{3-x}Cl$, clearly indicates the isomorphism between the phosphorus and chromium apatites.

Several unsuccessful attempts were made to prepare apatites in which the Cr(VI) and Cr(III), whose existence had been postulated in the apatite $Ca_5(CrO_4)_3OH$,[6] were replaced by Mo(VI) and Ga(III). Theoretically at least, based on the above postulate, such replacement should be feasible. Thus the existence of two oxidation states of Cr in the compound $Ca_5(CrO_4)_3OH$ was not confirmed. The replacement of 2Cr(VI) + Cr(III) for three P(V) atoms in the apatite $Ca_5(PO_4)_3OH$ would be expected to cause a lattice distortion, since two ions of a smaller and a larger size than P(V) would have been substituted in the lattice. Tetrahedral coordination of Cr(III) has not been reported in the literature. Furthermore, it has been estimated that the site-preference energy of Cr^{3+} for octahedral over tetrahedral coordination is of the order of 45 kcal./mole, owing to the fact that one of the electrons must enter an excited t_{2g} level in the tetrahedral case, in order to obey Hund's rule.[24,25] Acceptance of the coexistence of Cr(VI) and Cr(III) in compounds such as $Ca_3(CrO_4)_2$ and $Ca_5(CrO_4)_3OH$ may have resulted from the chemical analysis of acid solutions in which these compounds were dissolved and in which the disproportionation of Cr(V) into Cr(VI) and Cr(III) was probably not considered.

The apatite $Ca_5(CrO_4)_3OH$ could not be prepared by hydrothermal methods at 170–300° using saturated steam pressures. Furthermore, it was established that $Ca_5(CrO_4)_3OH$ is not stable under such conditions at least to 200°.

Room temperature reactions of $Ca_3(CrO_4)_2$ with water produced two new phases, B and C. The X-ray diffraction pattern of phase B showed similarity to the pattern of the mineral ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$,[19] and the isomorphous compounds: $3CaO \cdot Al_2O_3 \cdot 3Ca(OH)_2 \cdot 30H_2O$,[26] $3CaO \cdot Al_2O_3 \cdot 3CaCrO_4 \cdot 30H_2O$,[26] and $3CaO \cdot (Al,Fe)_2O_3 \cdot 3(CaSO_4,Ca(OH)_2) \cdot 30\text{–}32H_2O$.[27]

Thus one of the following compositions could be postulated for phase B: $3CaO \cdot Cr_2O_3 \cdot 3Ca(OH)_2 \cdot xH_2O$ or $3CaO \cdot Cr_2O_3 \cdot 3CaCrO_4 \cdot xH_2O$, but further work in this system, such as chemical and structural analysis as well as the formation of solid solutions, is required to prove this hypothesis.

Phase D, Ca_2CrO_4Cl, was found to be isomorphous with chlorospodiosite, Ca_2PO_4Cl, by comparing the X-ray diffraction data, the chemical composition, and the formation of solid solutions with Ca_2PO_4Cl. Use of the same arguments as in case of the chromium(V) apatites appears to substantiate the existence of Cr(V) in Ca_2CrO_4Cl. Work has been started on the crystal structure of these phases, as well as attempts to verify

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the presence of Cr(V) by magnetic and spectroscopic measurements.

Phase E was identified by comparison of its X-ray powder pattern with those of phase D as the isomorphous compound Sr_2CrO_4Cl. The unknown phase F had the chemical composition of $BaCrO_4$, but X-ray diffraction data and the green color of this phase indicated that this compound is not the familiar pale yellow $BaCrO_4$. The observed color change and shifts of X-ray reflections may suggest the presence of impurities in the crystal lattice or represent a polymorphic transition of $BaCrO_4$.

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Linear Correlation of the Phosphorus–Hydrogen Spin Coupling Constant with Proton Chemical Shifts in a Series of Polycyclic Phosphorus Compounds[1]

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Stable phosphonium salts are reported of the type [R(I)]X and [R(II)]X where I and II are the polycyclic phosphites 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane and 2,8,9-trioxa-1-phosphaadamantane, respectively, wherein R is $(C_6H_5)_3C$ or CH_3CH_2 and X is a perchlorate or tetrafluoroborate anion. Conductivity and n.m.r. spectral studies confirm their salt-like formulation and the caged structure of the phosphonium cation. A linear correlation is observed for the increase in the POCH coupling constant for the protons on the carbon β to the phosphorus atom with the downfield chemical shifts of protons on C_β, C_γ (axial), and C_δ in a series of derivatives of I and II including the salts. The results are discussed in terms of the decrease in s character of the phosphorus σ-bond to the fourth coordinate position on the phosphorus atom and the consequent increase in s character of the P–O links. Some new Arbuzov reactions of I and II are also reported.

Introduction

Although the reactions of trialkyl phosphites with a carbonium ion and a nucleophilic anion involve the Arbuzov reaction, similar reactions with nonnucleophilic anions have been limited to the salts formed from the reaction of trialkyl phosphites and $[(CH_3CH_2)_3O]BF_4$ or $[(C_6H_5)_3C]BF_4$.[2,3] Recently the Arbuzov reactions involving nucleophilic halides and the phosphites II[4,5] and the 4-ethyl analog of I[6] (shown in Figure 1) were described, and evidence was presented for the conformations of the products.

In this paper we report the preparation of stable phosphonium salts of I and II by the reaction of these ligands with triphenylmethyl perchlorate, triphenylmethyl tetrafluoroborate, or triethyloxonium tetrafluoroborate. Arbuzov products similar to those previously discussed[3-5] are also reported for the reactions of I and II with benzyl *p*-toluenesulfonate as well as triphenylmethyl chloride.

The proton chemical shifts and POCH coupling constants of I and II and their adducts formed with a series of Lewis acids were reported recently from our laboratories.[7] In the extension of this study to the H^1 and P^{31} resonances of these ligands in their transition metal complex ions,[8,9] it became of interest to measure the proton chemical shifts in phosphonium salts of I and II wherein phosphorus is tetracovalent as in the metal coordination compounds. In this way the effect of a positive charge on the proton chemical shifts of the base moiety could be ascertained in the absence of influences stemming from the more complex geometries and multiple bonding possibilities of the metal complexes formed with these polycyclic ligands.[9-12]

Experimental[13]

Solvents.—All solvents were reagent grade. Acetonitrile was refluxed over phosphorus pentoxide 3 hr. and distilled at atmospheric pressure. Acetone and methanol were dried over Linde 4-A Molecular Sieve. Pyridine was dried by refluxing over barium oxide for 2 days followed by distillation at atmospheric pressure. The constant-boiling fraction was stored over Linde 4-A Molecular Sieve.

Measurements.—Conductivities were measured on 0.001 *M* solutions at 25° with an Industrial Instruments Inc. Model RC-16B2 conductivity bridge at 1000 c.p.s. Proton n.m.r. spectra were obtained on approximately 10 to 30% by weight solutions at 14,100 gauss on a Varian HR-60 n.m.r. spectrometer. Infrared spectra in the sodium chloride region were obtained in Nujol and hexachlorobutadiene mulls on a Perkin-Elmer Model 21 spectrometer. Melting points were taken in open capillary tubes and are uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory. Silver tetrafluoroborate was obtained from Alfa Inorganics, Inc.

Salts of Trialkyl Phosphites.—The tetrafluoroborate salts of

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