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Pentavalent Ion Substitutions in the Apatite Structure Part A. Crystal Chemistry*

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The substitution of pentavalent arsenic, vanadium, chromium, manganese and antimony for phosphorus in apatites has been investigated. Arsenic, vanadium, and chromium completely replaced phosphorus in the calcium, strontium and barium fluor- and chlorapatites. X-Ray diffraction data showed that the calcium fluorvanadate, -arsenate, and -chromate structures were distorted relative to the normal hexagonal apatite. Manganese completely replaced phosphorus in only the barium apatites while chromium and manganese could not be incorporated into lead apatites. Excluding these exceptions, continuous solid solutions were formed between the phosphate and/or vanadate and the chromate or manganate analogues for given divalent and halide ions. The substitution of large amounts of antimony (> 20 mole %) for phosphorus was unsuccessful.

Introduction

To date, no complete survey has been made regarding the pentavalent ions capable of replacing phosphorus in the apatite structure. In the present work, partial and complete replacements of pentavalent arsenic, vanadium, chromium, manganese and antimony for phosphorus in calcium, strontium, barium and lead fluor- and chlorapatites have been investigated.

Literature

Pentavalent arsenic and vanadium are well-known substitutes for phosphorus in apatite. Oddly, little information is available for alkaline earth fluorvanadate and fluorarsenate apatites whereas most of the chlor- and bromapatite analogues of the alkaline earths and lead have been reported as noted in Table I.

Compounds containing pentavalent chromium were first reported by Weinland and Fridrich (*1*) and Riesenfeld et al. (*2*). Although Tjabbes (*3*) and Klemm and Werth (*4*) used magnetochemical methods to show the existence of Cr^{5+} in compounds such as K_3CrO_8, the Cr^{5+} species was often challenged since it seemed more logical to think in terms of a $Cr^{3+}:2Cr^{6+}$ charge coupled substitution. Scholder (*5*) pointed out that Cr^{5+} could not be detected by most standard chemical analyses since in an acidic media, Cr^{5+} disproportionated into Cr^{3+} and Cr^{6+}.

Recently, much information has dispelled all doubts about the existence of Cr^{5+}. Scholder and Klemm (*6*) reported a magnetic moment of 1.71 Bohr magnetons for calcium orthochromate, $Ca_3(CrO_4)_2$, compared to the 1.73 theoretical value for Cr^{5+}. Scholder and Suchy (*7*) noted the isostructural nature between alkaline earth orthophosphates and orthochromates. Scholder and Schwarz (*8*) observed that similar X-ray patterns were obtained from Li_3VO_4 and Li_3CrO_4 while Schwarz (*9*) reported a series of rare-earth chromates of the type $RECrO_4$. Finally, as noted in Table I, lattice parameters for apatites containing pentavalent chromium have been reported by Wilhelmi and Jonsson (*10*) and Banks and Jaunarajs (*11*).

Until recently, pentavalent manganese was also

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TABLE I

REPORTED APATITES ($R_{10}(XO_4)_6Z_2$) AND LATTICE PARAMETERS (Å) CONTAINING DIFFERENT PENTAVALENT IONS[a,b]

	P		As		V		Cr	
	a	*c*	*a*	*c*	*a*	*c*	*a*	*c*
Ca–F	9.370	6.883 (*2*)	*U*		9.67	*D* 7.01 (*4*)	9.64	7.00 (*5*)
Ca–Cl	9.629	6.776 (*2*)	*Δ* (*1*)		10.16	*D* 6.79 (*4*)	10.03	6.78 (*5*)
Ca–Br	9.714	6.758 (*2*)	*Δ* (*1*)		*Δ* (*1*)		*U*	
Sr–F	9.719	7.276 (*2*)	*U*		*U*		9.96	*D* 7.44 (*5*)
Sr–Cl	9.874	7.184 (*2*)	10.12	7.50 (*1*)	*Δ* (*1*)		10.12	7.32 (*5*)
							10.15	7.33 (*6*)
Sr–Br	10.00	7.59 (*1*)	*Δ* (*1*)		*Δ* (*1*)		*U*	
	9.959	7.184 (*2*)						
Ba–F	10.220	7.665 (*2*)	*U*		*U*		10.33	7.77 (*5*)
Ba–Cl	10.25	7.65 (*1*)	10.44	7.59 (*1*)	*Δ* (*1*)		10.50	7.73 (*5*)
	10.275	7.647 (*2*)					10.511	7.764 (*6*)
Ba–Br	10.28	7.72 (*1*)	10.46	7.62 (*1*)	*O* (*1*)		*U*	
	10.34	7.648 (*2*)						
Pb–F	9.76	7.29 (*3*)	10.07	7.42 (*3*)	10.10	7.34 (*3*)	*U*	
Pb–Cl	9.97	7.32 (*3*)	10.25	7.46 (*3*)	10.32	7.33 (*3*)	*U*	
Pb–Br	10.07	7.37 (*3*)	10.31	7.47 (*3*)	10.39	7.36 (*3*)	*U*	

[a] References: (*1*) Klement and Harth (*20*); (*2*) Niaki (*21*); (*3*) Wondratschek (*22*); (*4*) Aia and Lublin (*23*); (*5*) Banks and Jaunarajs (*11*); (*6*) Wilhelmi and Jonsson (*10*).

[b] Key to Symbols: *O*, apatite formation not observed; *Δ* apatite formation observed—no lattice parameters reported; *D*, distorted apatite; *U*, no information available.

considered as a charge coupled substitution, for example, $Mn^{4+}:Mn^{6+}$ in the compound $3Na_2O \cdot MnO_3 \cdot MnO_3$ reported by Auger (*12*). Lux (*13*) is credited with the preparation and recognition of the first compound containing Mn^{5+}, $Na_3MnO_4 \cdot 10H_2O$, presumably a hydrate of Auger's compound. Lux showed why Mn^{5+} was difficult to detect in solution since it was only stable in strong alkali solutions and disproportionated with changes in pH and temperature. He also observed that solid solutions were formed between sodium manganate and the phosphate, arsenate or vanadate analogues.

Klemm (*14*) reported a molecular susceptibility corresponding to Mn^{5+} in both sodium manganate and barium orthomanganate, $Ba_3(MnO_4)_2$. Strontium and barium hydroxymanganate apatite were reported by Scholder and Klemm (*6*). Traces of Mn^{5+} in calcium apatites have been reported by Johnson (*15*), Parodi and Segelken (*16*) and Kingsley (*17*), all of whom illustrated the similarity of the absorption spectra of the apatites with that of the MnO_4^{3-} ion in aqueous solution.

Experimental Procedure

The solid state synthesis and subsequent X-ray examination of the reaction products have been described earlier by the present authors (*18*). Reagent grade pentoxides were used as sources of arsenic, antimony and vanadium while the sesquioxide and carbonate were used to supply the chromium and manganese respectively. Most of the apatites

TABLE II

SUMMARY OF THE STRUCTURE TYPES OF THE HALOAPATITE COMPOSITIONS BASED ON X-RAY DIFFRACTION PATTERNS[a]

	Tetrahedral Site Ions				
Divalent and Halide Ions	*P*	*As*	*Cr*	*Mn*	*V*
Ca,F	*N*	*D*	*D*	*O*	*D*
Ca,Cl	*N*	*N*	*N*	*O*	*N*
Sr,F	*N*	*N*	*N*	*O*	*N*
Sr,Cl	*N*	*N*	*N*	*O*	*N*
Ba,F	*N*	*N*	*N*	*N*	*N*
Ba,Cl	*N*	*N*	*N*	*N*	*N*
Pb,F	*N*	*N*	*O*	*O*	*N*
Pb,Cl	*N*	*N*	*O*	*O*	*N*

[a] *N* and *D* represent normal and distorted apatite structures while *O* represents compositions which did not form apatite.

containing pentavalent chromium were prepared in dried nitrogen while apatites containing pentavalent manganese were fired in dried oxygen.

Results and Discussion

Arsenic and Vanadium

The substitution of phosphorus by arsenic or vanadium and subsequent X-ray analysis indicated that continuous solid solutions are formed in the fluor- and chlorapatites of strontium, barium, or lead. The *d*-spacing shifts showed that for given divalent and halide ions, the lattice expanded from phosphate to arsenate to vanadate apatites as would be expected on the basis of ionic size. The fluorarsenate and fluorvanadate apatites of calcium were unique since they were distorted while the analogous chlorapatites yielded normal X-ray diffraction patterns (see Table II). The distortion was detected by the splitting of some of the diffraction peaks. The splitting was more pronounced in the fluorvanadate than the fluorarsenate. Up to 80 mole % of the phosphorus was replaced by vanadium (1000°C) without any peak splitting although some broadening occurred. The above results infer that the upper limit of the ionic size which can completely fill the tetrahedral site of calcium fluorapatite and still maintain the structure is slightly less than the radius of pentavalent arsenic, given as 0.46 Å by Ahrens (*19*).

The radius of pentavalent vanadium listed by Ahrens (*19*) as 0.59 Å is probably much smaller in

TABLE III

X-RAY POWDER DATA FOR STRONTIUM, BARIUM, AND LEAD FLUORVANADATE APATITES

$Sr_{10}(VO_4)_6F_2$			$Ba_{10}(VO_4)_6F_2$			$Pb_{10}(VO_4)_6F_2$		
d (Å)	I	hkl	d (Å)	I	hkl	d (Å)	I	hkl
4.330	20	200	4.504	12	200	5.048	7	110
3.715	25	002	4.334	7	111	4.374	26	200
3.415	23	102	3.922	11	002	4.164	25	111
3.277	32	210	3.598	26	102	3.759	4	201
2.933	100	211, 112	3.410	26	210	3.680	11	002
2.889	61	300	3.131	100	211, 112	3.394	44	102
2.820	16	202	3.009	35	300	3.308	53	210
2.404	15	310	2.960	6	202	3.019	100	211
2.288	6	311	2.500	8	310	2.976	80	112
2.221	5	113	2.338	7	113	2.919	49	300
2.168	4	400	2.261	7	400	2.816	6	202
2.077	38	222	2.169	30	222	2.393	9	221
2.020	17	312	2.109	19	312	2.288	11	302
1.975	44	213	2.074	31	320	2.189	8	400
1.920	26	321	2.001	20	321	2.083	43	222
1.890	25	410	1.967	26	410, 004	2.026	22	312
1.871	25	402	1.959	33	402	2.008	11	320
1.858	23	004	1.831	5	322	1.970	42	213
1.753	8	322	1.759	5	412	1.937	23	321
1.638	8	420	1.704	11	420	1.909	36	410
1.627	9	331	1.700	14	214	1.881	42	402, 303
1.616	10	214	1.696	10	331	1.840	18	004
1.570	19	502	1.667	4	421	1.761	6	223
1.562	16	304	1.643	17	304	1.729	4	313
1.551	12	323	1.639	15	502	1.698	6	204
1.522	16	511	1.622	13	510, 322	1.696	8	412
1.387	5	520	1.587	15	511, 323	1.654	11	420
1.384	5	333	1.457	3	431	1.642	15	331
1.3535	11	215	1.446	7	520	1.608	17	214
1.3299	5	432	1.426	10	324	1.580	18	502
1.3252	14	414	1.422	9	521	1.556	18	323
1.3222	11	610	1.404	4	602	1.537	11	511
1.3180	8	513	1.390	14	414	1.533	19	332
1.3001	13	611	1.376	7	610	1.410	4	404
			1.356	12	611, 522	1.401	4	520
						1.389	6	333
						1.377	8	521
						1.357	11	602
						1.335	9	610
						1.325	18	513
						1.316	5	305
						1.313	10	611

TABLE III continued

$Sr_{10}(VO_4)_6F_2$		$Ba_{10}(VO_4)_6F_2$		$Pb_{10}(VO_4)_6F_2$	
d (Å)	hkl	d (Å)	hkl	d (Å)	hkl
Remainder of reflections weak.		Remainder of reflections weak.		Remainder of reflections weak.	
1.2509	440	1.3023	440	1.2636	440
1.2352	433	1.2903	433	1.2304	424
1.2284	424	1.2874	424	1.2170	106
1.2257	106	1.2657	523	1.2142	620
1.2118	523	1.2501	514	1.1977	621
1.2021	116	1.2248	702	1.1953	116
1.1902	206	1.1953	710	1.1845	702
1.1745	702	1.1693	226	1.1729	613
1.1478	710	1.1639	524	1.1596	710
1.1097	540	1.1602	316	1.1087	541
1.1011	316	1.1433	712	1.1060	712
1.0973	541	1.1272	614	1.1038	630
1.0750	406	1.1086	542	1.0910	631
1.0475	632	1.0921	632	1.0887	623
1.0399	802	1.0848	444	1.0808	614
1.0375	444	1.0207	812	1.0723	542
0.9699	714	0.9699	526	1.0701	720
0.9017	911	0.9552	822	1.0567	632
		0.9185	706	1.0490	802
		0.9022	10, 00	1.0420	444
		0.8898	913	1.0152	811
		0.8786	10, 02	1.0135	624
		0.8662	546	1.0110	550
		0.8584	636	1.0053	640
		0.8546	806	0.9873	812
		0.8523	840	0.9850	730
		0.8448	744	0.9816	714
		0.8345	930	0.9808	723
		0.8143	10, 13	0.9765	731
				0.9248	822
				0.9143	733
				0.9110	911
				0.8816	742
				0.8761	10, 00
				0.8601	913
				0.8276	840
				0.8259	10, 11
				0.8220	841
				0.8215	662
				0.8108	10, 12
				0.8089	338
				0.8074	842

apatite. The literature values for the radius of this ion in tetrahedral coordination are as low as 0.48 Å reported by Scholder and Klemm (*6*). The X-ray results of the present investigation support the smaller value. For given divalent and halide ions, the vanadate apatites possess only slightly larger *d* spacings than the arsenate, chromate and manganate apatites, all of which have *d* spacings considerably larger than the phosphate apatites.

Since little X-ray data were available for fluorvanadate apatites, accurate *d* spacings and *hkl* values for the strontium, barium and lead fluorvanadate apatites were obtained. These data are presented in Table III while their lattice parameters are included in Table IV. All standard deviations are ±0.002 Å.

Antimony

Attempts to completely replace phosphorus by antimony in the alkaline earth and lead apatites were not successful. Small amounts of antimony were substituted for phosphorus or vanadium in the barium haloapatites. X-Ray examination of the compositions (listed in Table V) showed the solubility limits were less than 10 and 20 mole % antimony in the fluor- and chlorapatites, respectively.

Chromium

Attempts to prepare alkaline-earth apatites in air containing pentavalent chromium were partially successful. The calcium and strontium samples fired

TABLE IV

APATITE LATTICE PARAMETERS (Å)

	a_0	c_0
$Sr_{10}(PO_4)_6F_2$	9.717	7.284
$Pb_{10}(PO_4)_6F_2$	9.777	7.310
$Sr_{10}(VO_4)_6F_2$	10.006	7.430
$Ba_{10}(VO_4)_6F_2$	10.420	7.854
$Pb_{10}(VO_4)_6F_2$	10.113	7.375
$Ba_{10}(MnO_4)_6Cl_2$	10.459	7.762

at 950°C or greater were dark green and contained only apatite by X-ray diffraction. By contrast, the outside portion of the barium sample fired at 1000°C changed from dark green to yellow during cooling. X-Ray diffraction confirmed the presence of $BaCrO_4$ in the yellow portion of the sample, but only apatite was detected in the dark green portion. These results were in agreement with Banks and Jaunarajs (*11*) who likewise found it possible to only prepare the calcium and strontium apatites in air. Subsequent syntheses were accomplished in a nitrogen atmosphere to insure the purity of these apatites.

The partial and complete replacement of phosphorus by pentavalent chromium in the alkaline earth fluor- and chlorapatites yielded X-ray data similar to the vanadium substitutions. The chromium apatites possessed slightly smaller *d* spacings than the vanadate analogues. The calcium fluorchromate apatite was distorted, as noted in Table II, but the peak splitting was less than that observed in the calcium fluorvanadate. The strontium and barium fluorchromate apatites formed continuous solid solutions with their respective fluorphosphate and fluorvanadate analogues as noted in Table V. No lead apatites containing pentavalent chromium could be synthesized in air or nitrogen.

TABLE V

COMPOSITIONS AND FORMATION CONDITIONS OF APATITE SOLID SOLUTIONS CONTAINING DIFFERENT PENTAVALENT IONS

Compositions		Atmosphere	Formation Temperature (°C)/Time (Hours)
$Sr_{10}(PO_4)_{6-x}(VO_4)_xF_2$	x = 1.2,2.4,3.6,4.8, and 6.0	Air	1000/8
$Ba_{10}(PO_4)_{6-x}(VO_4)_xF_2$	"	Air	1000/8
$Pb_{10}(PO_4)_{6-x}(VO_4)_xF_2$	"	Air	800/4
$Sr_{10}(PO_4)_{6-x}(CrO_4)_xF_2$	x = 1.2,2.4,3.6,4.8, and 6.0	Nitrogen	1000/10
$Ba_{10}(PO_4)_{6-x}(CrO_4)_xF_2$	"	Nitrogen	1000/10
$Sr_{10}(VO_4)_{6-x}(CrO_4)_xF_2$	"	Nitrogen	1000/10
$Ba_{10}(VO_4)_{6-x}(CrO_4)_xF_2$	"	Nitrogen	1000/10
$Ba_{10}(PO_4)_{6-x}(MnO_4)_xF_2$	x = 0.6,1.2,2.4,3.6,4.8, and 6.0	Oxygen	1000-1025/10
$Ba_{10}(PO_4)_{6-x}(MnO_4)_xCl_2$	"	Oxygen	1000-1025/10
$Ba_{10}(VO_4)_{6-x}(MnO_4)_xF_2$	"	Oxygen	975-1000/10
$Ba_{10}(VO_4)_{6-x}(MnO_4)_xCl_2$	"	Oxygen	975-1000/10
$Ca_{10}(PO_4)_{6-x}(VO_4)_xF_2$	$x \leq 4.8$	Air	1000/10
$Ca_{10}(PO_4)_{6-x}(CrO_4)_xF_2$	$x \leq 4.8$	Nitrogen	1000/10
$Ba_{10}(PO_4)_{6-x}(SbO_4)_xF_2$	$x \leq 0.6$	Air	1000/10
$Ba_{10}(VO_4)_{6-x}(SbO_4)_xF_2$	$x \leq 0.6$	Air	1000/10
$Ba_{10}(PO_4)_{6-x}(SbO_4)_xCl_2$	$x \leq 1.2$	Air	950/8
$Ba_{10}(VO_4)_{6-x}(SbO_4)_xCl_2$	$x \leq 1.2$	Air	950/8

Manganese

Pentavalent manganese cannot be incorporated to any appreciable extent (less than 5 mole %) in calcium halophosphate apatites. When the attempted substitution of manganese was 20 mole % or more, X-ray examination showed that at least part of the manganese was tetravalent and formed $CaMnO_3$.

Strontium fluorapatite solid solutions fired in oxygen (phosphate-manganate and vanadate-manganate) were seldom pure by X-ray diffraction and were blue-gray to blue-black suggesting the presence of more than one oxidation state of manganese. An opaque phase was detected by optical examination in all samples. The large chlorapatite accepted large amounts of pentavalent manganese and the resulting apatites were blue to dark turquoise in color. Although the pure chlormanganate could not be prepared, up to about 50 mole % pentavalent manganese was incorporated in the strontium chlorphosphate and chlorvanadate apatites.

Pentavalent manganese was partially and completely substituted for phosphorus and vanadium in the barium fluor- and chlorapatites and gave rise to the continuous solid solutions listed in Table V. This infers that a continuous solid solution exists in the manganate–arsenate haloapatites of barium although only a few samples were prepared for obtaining reflectance spectra. As with the above strontium chlorapatites, samples prepared in oxygen were brighter in color and were homogeneous under optical examination.

TABLE VI

X-RAY POWDER DATA FOR $Ba_{10}(MnO_4)_6Cl_2$

d(Å)	I	hkl	d(Å)	I	hkl	d(Å)	hkl
5.23	4	110	1.671	4	421	1.3075	440
4.52	16	200	1.642	13	502	1.2839	424
4.326	10	111	1.632	21	304	1.2653	523
3.873	12	002	1.620	11	323	1.2560	620
3.563	14	102	1.590	15	511	1.2467	514
3.418	23	210	1.450	3	520	1.2440	206
3.128	90	211	1.426	5	521	1.2277	702
3.115	100	112	1.414	12	215	1.1998	710
3.015	49	300	1.406	8	602	1.1602	540
2.941	3	202	1.390	3	432	1.1502	316
2.510	6	310	1.385	14	414	1.1464	712
2.383	4	302	1.377	6	513	1.1293	631
2.317	6	113	1.358	13	522	1.1232	406
2.261	3	400	Remainder of reflections weak			1.0951	632
2.166	30	222				1.0869	802
2.106	10	312				1.0846	444
2.076	3	320				1.0599	810
2.062	24	213				1.0444	633
1.975	13	410				1.0207	227
1.954	19	402				1.0105	731
1.940	11	004				0.8713	660
1.801	4	313					
1.760	78	501, 412					
1.713	5	420					
1.700	6	331					
1.687	11	214					

Barium fluor- and chlorapatites were prepared at 1000°C in which 10 mole % each of pentavalent manganese and antimony were substituted for phosphorus or vanadium. The fluorphosphate and chlorapatites were pure by X-ray diffraction while the fluorvanadate contained traces of impurities. All the samples were a dull gray-green.

The X-ray diffraction pattern of the barium fluormanganate apatite was very similar to that of the barium fluorvanadate given in Table III. Powder data for the barium chlormanganate are given in Table VI.

Summarizing, Table V lists the continuous solid solution series found by simple replacement in the tetrahedral site. All of the compositions were fired from 4 to 10 hr at the selected formation temperature and those prepared in nitrogen or oxygen were cooled in the furnace atmosphere. X-Ray examinations showed reasonable trends, namely, that pentavalent chromium or manganese expanded the halophosphate apatites but contracted the halovanadate apatites.

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