UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

ABSTRACTS OF THE LITERATURE

ON

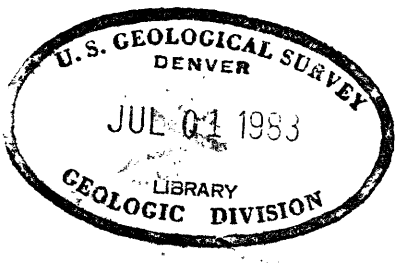
SYNTHESIS OF APATITES AND SOME RELATED PHOSPHATES

PART I

by

Elizabeth B. Jaffe

December 1950



Trace Elements Investigations Report 132, Part I

USGS-TEI Rept. 132, Part I
Consisting of 76 pages
Issued to (see below)

The distribution of this report is as follows:

2 copies	AEC, Washington (J. C. Johnson)
8 copies	AEC, New York (P. L. Merritt)
1 copy	AEC, Washington (J. O. Hosted)
2 copies	AEC, Washington (E. F. Wilson)
1 copy	AEC, Washington (F. W. McQuiston)
1 copy	AEC, Denver (C. C. Towle, Jr.)
1 copy	AEC, Spokane (E. E. Thurlow)
1 copy	AEC, Grand Junction (T. W. Oster)
1 copy	IMC, Mulberry, Fla. (I. M. LeBaron)
1 copy	Dow Chemical Co., Pittsburg, Calif. (G. L. Allen)
1 copy	MIT, Watertown, Mass. (John Dasher)
1 copy	ORNL, Y-12, Oak Ridge (Glenn Clewett)
1 copy	USGS, Washington (Mineral Deposits Branch)
1 copy	USGS, Washington (Fuels Branch)
1 copy	USGS, Washington (Alaska Branch)
22 copies	USGS, Washington (Geochemistry and Petrology Branch)
1 copy	USGS, Washington (V. E. McKelvey)
1 copy	USGS, Plant City, Fla. (J. B. Cathcart)
1 copy	USGS, Grand Junction (R. P. Fischer)
1 copy	USGS, Denver (L. R. Page)
1 copy	USGS, Spokane (A. E. Weissenborn)
3 copies (including master copy)	USGS, Washington (TEPCO)

CONTENTS

ILLUSTRATIONS

TABLES

ABSTRACTS OF THE LITERATURE ON SYNTHESIS OF APATITES AND SOME RELATED PHOSPHATES, PART I

by

Elizabeth B. Jaffe

INTRODUCTION

The apatite group of minerals has been studied from many points of view--from that of the physiologist, biochemist, or soils scientist, as well as from that of the geologist or mineralogist. Although all these people have run into the same problems, they have not always been sufficiently acquainted with each other's work; the present collection of selected abstracts is intended to clear the ground for those who are concerned with the synthesis of apatites and related phosphates. Following tables 1, 2, and 3, which give a brief summary of the syntheses of apatite attempted by previous workers, is a short discussion of the problems encountered in the synthesis of the minerals of the apatite group.

Thanks are due to T. Botinelly (T.B.) and Z. S. Altschuler (Z.S.A.) of the Geological Survey for their aid in compilation of abstracts, and to Earl Ingerson, Michael Fleischer, and Jane Titcomb, also of the Geological Survey, and Z. S. Altschuler, for their careful review of this paper.

In table 1, like varieties of apatite (e.g. chlor- , fluor-, carbonate- ,) are grouped together. Within each group, apatites synthesized

by wet methods precede those synthesized by dry methods, and calcium apatites precede those of other metals. Beyond this, syntheses are listed in chronological order, beginning with the most recent. This relatively simple classification was used because data in the original papers were too often inadequate for a more elaborate one. The method and reagents used for each synthesis are briefly summarized. Data on which identification of apatites is based are given thus: opt = optical identification; chem = partial or complete chemical analysis; X-ray = examination of the solid product by X-ray diffraction methods; pH = measurement of the pH of the liquid phase, either during or after precipitation, or both; spec = qualitative or semiquantitative spectrographic analysis; pption = precipitation by metathesis; hydrol = precipitation by hydrolysis; formulas of the apatites and mineral and element names are given throughout as in the original papers, as, for example, "Di" (didymium), which has been shown to consist of the elements neodymium and praesiodymium. The initials preceding the year at the end of each listing are those of the authors whose papers are summarized. Papers on apatite synthesis which appeared in the 19th and early 20th centuries have not been abstracted; the more important ones are reported in the Data of Geochemistry, whose section on apatite is quoted here on the first page of Abstracts. None of the syntheses reported in the Data of Geochemistry has been included in the table.

Table 1.--Apatites synthesized by previous workers.

Mineral	Method	Reagents	Time and temp in °C	Checked by	Reference
		Hydroxylapatites			
		Wet methods			
		Ca hydroxylapatites			
Hydroxylapatite	pption	H_3PO_4 and $Ca(OH)_2$ sols (dried at 1100°)	100°	X-ray	CW 50
Hydroxylapatite	pption	H_3PO_4 and $Ca(OH)_2$ sols.	100°	X-ray	CW 49
Hydroxylapatite		$Ca_4P_2O_8Cl_2$ and steam	900°,4 hrs	X-ray	K 41
Hydroxylapatite		$Ca_4P_2O_8Cl_2$, 1 N NaOH, in closed tube	100°,10 days	X-ray	K 41
Hydroxylapatite	pption	H_3PO_4 and $Ca(OH)_2$ sols.		chem,X-ray,pH	F 37
Hydroxylapatite	pption	CaO in H_3PO_4, $Ca(OH)_2$ sol.	25°, slowly mixed	chem,X-ray,pH	K 37
Hydroxylapatite	hydrol	$Ca_3(PO_4)_2$ in water		chem	SH 33
Hydroxylapatite?	hydrol	$CaHPO_4$ in warm water	500 hrs	X-ray	SSK 32
Hydroxylapatite?	hydrol	$Ca_4P_2O_9$ in water		X-ray	SSK 32
Hydroxylapatite?	hydrol	$Ca_3(PO_4)_2$, KOH, water, CO_2 atmosphere		chem,X-ray	SSK 32
Hydroxylapatite?	hydrol	β or γ $Ca_3(PO_4)_2$		X-ray	BFF 32
Hydroxylapatite		Na_3PO_4, $Ca(NO_3)_2$, excess of NH_4OH		chem,X-ray	KT 32
Hydroxylapatite	hydrol	$Ca_3(PO_4)_2$ in neutral ammonium citrate sol.		chem,X-ray	HHJJ 31

Table 1.--Continued

Mineral	Method	Reagents	Time and temp in °C	Checked by	Reference
$3Ca_3(PO_4)_2 \cdot Ca(OH)_2$	hydrol	$Ca_3(PO_4)_2$ in water, or 0.5M or 0.05M NaOH		chem	LTW 29
Hydroxylapatite	pption			chem	B 17
		Ca-Pb hydroxylapatites			
$(Ca,Pb)_{10}(PO_4)_6(OH)_2$ from Ca_{10} to Pb_{10}	hydrol	$(Ca,Pb)(NO_3)_2, KH_2PO_4, NaOH$	boiling 15 hrs	chem,X-ray	M 47
		Sr hydroxylapatites			
Sr hydroxylapatite	hydrol	$SrHPO_4$ in N/10 NaOH	40°	chem,X-ray	K 39
Sr hydroxylapatite	hydrol	$SrHPO_4$ in phosphate buffer sol. of pH 11.0	40°	chem,X-ray	K 39
Sr hydroxylapatite	pption	NaOH, Na_3PO_4, $SrCl_2$	boiling	chem,X-ray	K 39
$3Sr_3(PO_4)_2 \cdot Sr(OH)_2$		$Sr_3(PO_4)_2$, $SrCO_3$, steam	7 hrs,1150°	chem,X-ray	K 39
$3Sr_3(PO_4)_2 \cdot Sr(OH)_2$	hydrol	$Sr_3(PO_4)_2$ in water or 0.5M or 0.05M NaOH		chem	LTW 29
		Dry methods			
		Ca hydroxylapatites			
Hydroxylapatite		brushite and CaO	900°	X-ray, opt.	DBM 49
Hydroxylapatite	fusion	$Ca_3(PO_4)_2$, $Ca_4P_2O_9$, humidity of air	1100°	X-ray,chem	KT 32
Hydroxylapatite	fusion	$Ca_4P_2O_9$ in air		X-ray	T 32
Hydroxylapatite	fusion	α $Ca_3(PO_4)_2$, CaO, humidity of air		X-ray	BFF 32
Hydroxylapatite	fusion	$Ca_4P_2O_9$ (made from $Ca_3(PO_4)_2$ and CaO)		X-ray	SSK 32

Table 1.--Continued

Mineral	Method	Reagents	Time and temp in °C	Checked by	Reference
		Oxyapatites			
		Dry methods			
		Ca oxyapatites			
Hydroxyl-oxyapatite	fusion	$Ca_4P_2O_9$, deficiency of water	1400°	X-ray, chem	BFF 33
$3Ca_3P_2O_8 \cdot CaO$		$Ca_3(PO_4)_2$ and CaO	dried at 950°	X-ray	BD 49
Oxyapatite		$3(3CaO \cdot P_2O_5)$ and CaO		X-ray	CW 49
Oxyapatite		$Ca_2P_2O_7$ and CaO	reheated at 600°	X-ray	CW 49
Oxyapatite	ignition	hydroxylapatite or bone	900°	X-ray	HJM 32
Fluor-oxyapatite	fusion	$Ca_4P_2O_9$ and deficiency of water	1400°	X-ray	BFF 33
		Other oxyapatites			
$3Ca_3P_2O_8 \cdot BaO$		$Ca_3(PO_4)_2$ and BaO	dried at 950°	X-ray	BD 49
$3Ca_3P_2O_8 \cdot SrO$		$Ca_3(PO_4)_2$ and SrO	dried at 950°	X-ray	BD 49
$3Ca_3P_2O_8 \cdot NiO$		$Ca_3(PO_4)_2$ and NiO	dried at 950°	X-ray	BD 49
$3Ca_3P_2O_8 \cdot PbO$		$Ca_3(PO_4)_2$ and PbO	dried at 950°	X-ray	BD 49
		Fluorapatites			
		Dry methods			
		Ca fluorapatites			
Fluorapatite		β $Ca_3(PO_4)_2$ and CaF_2	800°	X-ray	CW 50

Table 1.--Continued

Mineral	Method	Reagents	Time and temp in °C	Checked by	Reference
Fluorapatite		chlorapatite and CaF_2	800°	X-ray	CW 50
Fluorapatite		hydroxylapatite and CaF_2	800°	X-ray	CW 50
Fluorapatite		β $Ca_3(PO_4)_2$ and CaF_2	500°	X-ray	CW 49
Fluorapatite		α $Ca_3(PO_4)_2$ and CaF_2	600°	X-ray	CW 49
Fluor-chlorapatite		CaF_2, $CaCl_2$, and $Ca_3(PO_4)_2$		X-ray	CW 49
Fluor-chlorapatite		chlorapatite and CaF_2		X-ray	CW 49
		Chlorapatites			
		Wet methods			
$3Ca_3P_2O_8 \cdot CaCl_2$	pption?	Na_2HPO_4, $CaCl_2$, NaOH, and H_2O		chem	LTW 29
		Dry methods			
		Ca chlorapatites			
Chlorapatite		β $Ca_3(PO_4)_2$ and $CaCl_2$	800°	X-ray	CW 50
Chlorapatite		hydroxylapatite and $CaCl_2$ in nitrogen atmosphere	800°	X-ray	CW 50
Chlorapatite		$Ca_3(PO_4)_2$ and $CaCl_2$		X-ray,opt	DBM 49
Chlorapatite		$Ca_3(PO_4)_2$ and $CaCl_2$ in nitrogen atmosphere		X-ray	CW 49
Chlorapatite	fusion	$Ca_3(PO_4)_2$ and $CaCl_2$	1200°,3 hrs	opt	P 47
Chlorapatite	fusion	$Ca_3(PO_4)_2$ and $CaCl_2$	1100°	chem,opt	M 41
Chlorapatite	fusion	$CaCl_2$ and anhydrous $Ca_3(PO_4)_2$ in stoichiometric proportions	1400°	X-ray	HJM 32

Table 1.--Continued

Mineral	Method	Reagents	Time and temp in °C	Checked by	Reference
Chlorapatite	fusion	$Ca_3(PO_4)_2$, $CaCl_2$		opt,chem	Z 16
		Rare-earth and related chlorapatites			
13.63% Sm chlorapatite	fusion	$SmPO_4$, dry $CaCl_2$, washed with H_2O	1100°	chem	C 25
1% Ce chlorapatite	fusion	$Ca_3(PO_4)_2$, $CePO_4$, $CaCl_2$	1150°	opt,chem	Z 23
1.6% Ce chlorapatite	fusion	$Ca_3(PO_4)_2$, $CePO_4$, and $CaCl_2$	1200°	opt,chem	Z 23
8% Ce chlorapatite	fusion	$Ca_3(PO_4)_2$, $CePO_4$, and $CaCl_2$	1100°	opt,chem	Z 23
13% Ce chlorapatite	fusion	$Ca_3(PO_4)_2$, $CePO_4$, and $CaCl_2$	1100°	opt,chem	Z 23
3% "Di" chlorapatite	fusion	$Ca_3(PO_4)_2$, "Di"PO_4, and $CaCl_2$	1180°	opt,chem	Z 23
6.3% Y chlorapatite	fusion	$Ca_3(PO_4)_2$, YPO_4, $CaCl_2$	1100°	opt,chem	Z 23
Chlorapatite (Na?)	fusion	$Ca_3(PO_4)_2$, excess NaCl		opt,chem	Z 16
		Cr chlorapatites			
0.38% Cr chlorapatite	fusion	$Ca_3(PO_4)_2$, $CaCl_2$ and $CaCrO_4$	1100°	chem,opt	M 41
0.8% Cr chlorapatite	fusion	$Ca_3(PO_4)_2$, $CaCl_2$ and $CaCrO_4$	1100°	chem,opt	M 41
1.47% Cr chlorapatite	fusion	$Ca_3(PO_4)_2$, $CaCl_2$ and $CaCrO_4$	1100°	chem,opt	M 41
3.06% Cr chlorapatite	fusion	$Ca_3(PO_4)_2$, $CaCl_2$ and $CaCrO_4$	1100°	chem,opt, X-ray	M 41
0.06% Cr chlorapatite	fusion	$Ca_3(PO_4)_2$, $CaCl_2$ and $CrPO_4$	1100°	chem,opt	M 41

Table 1.--Continued

Mineral	Method	Reagents	Time and temp in °C	Checked by	Reference
2.74% Cr, 0.39% Na chlorapatite	fusion	$CaCl_2$, $Ca_3(PO_4)_2$, and Na_2CrO_4	1100°	chem,opt	M 41
3.14% Cr, ?% Na chlorapatite	fusion	$CaCl_2$, $Ca_3(PO_4)_2$, and Na_2CrO_4	1100°	chem,opt	M 41
		Fe chlorapatites			
Fe-Cl-apatite	fusion	Ca-Fe-phosphate, $CaCl_2$		opt,chem	P 47
Fe-Cl-apatite	fusion	Fe phosphate, Ca phosphate, $CaCl_2$	2 hours 45 min 90 min 3 hours 6 hours	opt	P 47
		Pb chlorapatites			
$3Ca_3P_2O_8 \cdot PbCl_2$		$Ca_3(PO_4)_2$ and $PbCl_2$	dried at 950°	X-ray	BD 49
Pb-Cl-apatite	fusion	Ca phosphate, $CaCl_2$, Pb phosphate	1100°, 1 hr	chem,opt, spec	P 47
		Other chlorapatites			
Sr apatite	fusion	$Sr_3(PO_4)_2$, $SrCl_2$, $HgCl_2$	1000°	X-ray,chem, opt,spec	C 50
$3Ca_3P_2O_8 \cdot BaCl_2$		$Ca_3(PO_4)_2$ and $BaCl_2$	dried at 950°	X-ray	BD 49
$3Ca_3P_2O_8 \cdot MgCl_2$		$Ca_3(PO_4)_2$ and $MgCl_2$	dried at 950°	X-ray	BD 49
$3Ca_3P_2O_8 \cdot NiCl_2$		$Ca_3(PO_4)_2$ and $NiCl_2$	dried at 950°	X-ray	BD 49
0.01% Mo chlorapatite	fusion	Ca molybdate, $CaCl_2$, Ca phosphate		spec	P 47

Table 1.--Continued

Mineral	Method	Reagents	Time and temp in °C	Checked by	Reference
		Carbonate-apatites **Dry methods**			
		Ca carbonate apatites			
Carbonate-apatite		α $Ca_3(PO_4)_2$ and $CaCO_3$	900°	X-ray,opt	DBM 49
Carbonate-apatite	fusion?	$CaCO_3$, $Ca(OH)_2$, $NaHCO_3$, and Na_3PO_4		X-ray	BFF 33
Carbonate-apatite		carbonate-apatite produced by BFF reheated in dilute H_2CO_3	700°-800°	X-ray	BFF 33
Carbonate-apatite	fusion	$Ca_3(PO_4)_2$ and $Na_2Ca(CO_3)_2$	1100°	opt,chem	E 24
Carbonate-apatite	fusion	$Ca_3(PO_4)_2$, $CaCO_3$, and $Na_2Ca(CO_3)_2$	1150°	opt,chem	E 24
Carbonate-apatite	fusion	$Ca_3(PO_4)_2$, $CaCO_3$	1190°	opt,chem	E 24
		Ba carbonate apatites			
$3Ca_3P_2O_8 \cdot BaCO_3$		$Ca_3(PO_4)_2$ and $BaCO_3$	dried at 950°	X-ray	BD 49
Ba-carbonate-apatite	fusion	$BaCO_3$, $Ba_3(PO_4)_2$, and Na_2CO_3	1050°	opt,chem	E 24
		Sr carbonate apatites			
$3Ca_3P_2O_8 \cdot SrCO_3$		$Ca_3(PO_4)_2$ and $SrCO_3$	dried at 950°	X-ray	BD 49
Sr-carbonate-apatite	fusion	$SrCO_3$, $Sr_3(PO_4)_2$, and Na_2CO_3	1040°	opt,chem	E 24
		Other carbonate-apatites			
$3Ca_3P_2O_8 \cdot PbCO_3$		$Ca_3(PO_4)_2$ and $PbCO_3$	dried at 950°	X-ray	BD 49
$3Ca_3P_2O_8 \cdot ZnCO_3$		$Ca_3(PO_4)_2$ and $ZnCO_3$	dried at 950°	X-ray	BD 49

Table 1.--Continued

Mineral	Method	Reagents	Time and temp in °C	Checked by	Reference
		Other apatites			
$3Ca_3P_2O_8 \cdot CaF_2$		$Ca_3(PO_4)_2$ and CaP_2	dried at 950°	X-ray	BD 49
Al-apatite	fusion	Al-phosphate, $Ca_3(PO_4)_2$, $CaCl_2$	1100°, 1 hr	chem,opt	P 47
Ellestadite	sintering	Ca silicate, $CaSO_4$ and CaF_2	1100°	X-ray	KD 42
Hydroxyl-ellestadite		ellestadite and steam	1100°	X-ray	KD 42
$Ca_{10}SiP_4SO_{24}F_2$		same as ellestadite	1100°	X-ray	KD 42
$Ca_{10}Si_2P_2S_2O_{24}F_2$		same as ellestadite	1100°	X-ray	KD 42
$Na_6Ca_4S_6O_{24}F_2$	fusion	Na and Ca sulfates and CaF_2	800°	X-ray	KD 42
$Na_2Ca_8P_4S_2O_{24}F_2$		made as above	800°	X-ray	KD 42
$Na_4Ca_6P_2S_4O_{24}F_2$		made as above	800°	X-ray	KD 42
Hydroxy compounds of above		made by treatment with steam of the above compounds synthesized by KD	1100°	X-ray	KD 42
Ellestadite	fusion?			X-ray	KD 41
Hydroxyl-ellestadite		ellestadite and steam	1000°	X-ray	KD 41
$Na_6Ca_4(SO_4)_6F_2$	fusion?			X-ray	KD 41
Aluminate-apatite		$Ca_3(PO_4)_2$, CaO, Al_2O_3		X-ray	BFF 33
Cyanimid-apatite		$Ca_3(PO_4)_2$ and $CaCN_2$		X-ray	BFF 33
Ferri-apatite		$Ca_3(PO_4)_2$, CaO, and Fe_2O_3		X-ray	BFF 33

Table 1.--Continued

Mineral	Method	Reagents	Time and temp in °C	Checked by	Reference
Sulfide-apatite of Ca or Fe	fusion	$Ca_3(PO_4)_2$ and $CaSO_4$ in closed iron bomb	1250°	X-ray	BFF 33
		Disordered apatites (apatites with 9 or 11 metal ions) Dry methods			
$Ca_{10.5}SiP_4O_{24}F_2$	fusion		1100°, 7 hrs	X-ray	KD 42
$Ca_{9.5}P_5SO_{24}F_2$	fusion		1100°, 7 hrs	X-ray	KD 42
$Ca_{10.5}Si_2P_3SO_{24}F_2$	fusion		1100°, 7 hrs	X-ray	KD 42
$Ca_{9.5}SiP_3S_2O_{24}F_2$	fusion		1100°, 7 hrs	X-ray	KD 42
$Na_2Ca_9SiP_4SO_4F_2$	fusion		1250°, 6 hrs	X-ray	KD 42
		Hydrated tri-Me^{++}-phosphates Wet methods			
		Tricalcium phosphates			
$(3CaO \cdot P_2O_5) \cdot nH_2O$	pption	Na_2HPO_4 and $CaCl_2$ in ammoniated medium		X-ray	CW 49
$(3CaO \cdot P_2O_5) \cdot 0.5H_2O$		Above product heated	600°	X-ray	CW 49
Metastable hydrated tricalcium phosphate	pption	H_3PO_4, $Ca(OH)_2$, and water		chem,X-ray,pH	F 37
$Ca_3P_2O_8 \cdot 0.5H_2O$	pption	CaO, H_3PO_4, $Ca(OH)_2$, and water, mixed slowly	25°	chem,X-ray,pH	K 37
$Ca_3(PO_4)_2$	hydrol	brushite in water		chem?	SH 33
$Ca_3(PO_4)_2$	pption	$Ca(NO_3)_2$, $NaHPO_4$, excess of ammonia		chem	SH 33

Table 1.--Continued

Mineral	Method	Reagents	Time and temp in °C	Checked by	Reference
$Ca_3(PO_4)_2$	pption	0.1N $CaHPO_4$, $Ca(OH)_2$ sol.		chem	CB 33
$Ca_3P_2O_8 \cdot nH_2O$	hydrol?	β or γ $Ca_3P_2O_8$		X-ray	BFF 32
Tricalcium phosphate	pption	Na_3PO_4 sol. added slowly to sol. with excess $Ca(NO_3)_2$		X-ray	HJM 31
$Ca_3(PO_4)_2$	hydrol	$CaH_4(PO_4)_2 \cdot H_2O$ and NH_4OH		chem	LTW 29
$Ca_3(PO_4)_2 \cdot H_2O$	pption	$Na_2HPO_4 \cdot 12H_2O$, $CaCl_2$, NH_4OH	65°-70°	chem,X-ray	L 35
$Ca_3P_2O_8$ (probably hydrated)	pption			chem	B 17
		Tristrontium and tribarium phosphates			
$Sr_3(PO_4)_2$		$Sr_2P_2O_7$, $SrCO_3$ in stoichiometric proportions	1000°	chem,X-ray	K 39
$Sr_3(PO_4)_2$	hydrol	$SrH_4(PO_4)_2 \cdot H_2O$ and NH_4OH		chem	LTW 29
$Ba_3(PO_4)_2$	pption	$BaCl_2$, Na_2HPO_4, NaOH, and water		chem	LTW 29

Table 2.--Lattice constants of synthetic apatites

Mineral	a A	c A	c:a	Specific gravity calc.	Specific gravity meas.	Ref.
Hydroxyapatite (Saint-Girons)1/	9.36	6.89	0.7366			BD 49
Hydroxylapatite (Holly Springs)1/	9.43	6.89	0.7311			BD 49
$Ca_{10}(PO_4)_6(OH)_2$	9.40	6.93	0.737			K 39
$Ca_{10}(PO_4)_6(OH)_2$	9.40	6.92				M 47
$Ca_5Pb_5(PO_4)_6(OH)_2$	9.62	7.08				M 47
$Pb_{10}(PO_4)_6(OH)_2$	9.89	7.28				M 47
$Pb_{10}(PO_4)_6(OH)_2$	9.88	7.32	0.741			K 39
$Sr_{10}(PO_4)_6(OH)_2$	9.74	7.20	0.739			K 39
$Ba_{10}(PO_4)_6(OH)_2$	10.19	7.70	0.756			K 39
$3Ca_3P_2O_8 \cdot CaO$	9.474	6.889	0.730			BD 49
$3Ca_3P_2O_8 \cdot PbO$	8.45	6.889	0.729			BD 49
$3Ca_3P_2O_8 \cdot SrO$	9.45	6.89	0.7295			BD 49
$3Ca_3P_2O_8 \cdot BaO$	9.45	6.89	0.7295			BD 49
$3Ca_3P_2O_8 \cdot NiO$	9.434	6.889	0.730			BD 49
$Ca_{10}(PO_4)_6F_2$	9.36	6.88	0.732			K 41
1% Ce chlorapatite					3.165	Z 23
8% Ce chlorapatite					3.3-3.18	Z 23
3%"Di"chlorapatite					3.315-3.170	Z 23
3.06% Cr chlorapatite	9.56	6.73	0.704	3.22	3.21	M 41
$3Ca_3P_2O_8 \cdot BaCl_2$	9.66	6.88	0.7126			BD 49

1/ Natural apatite for purposes of comparison

Table 2.--Continued

Mineral	a A	c A	c:a	Specific gravity calc.	Specific gravity meas.	Ref.
$3Ca_3P_2O_8 \cdot PbCl_2$	9.66	6.88	0.7126			BD 49
$3Ca_3P_2O_8 \cdot MgCl_2$	9.62	6.889	0.7161			BD 49
$3Ca_3P_2O_8 \cdot NiCl_2$	9.61	6.889	0.7169			BD 49
$3Ca_3P_2O_8 \cdot BaCO_3$	9.45	6.91	0.7317			BD 49
$3Ca_3P_2O_8 \cdot PbCO_3$	9.43	6.89	0.7311			BD 49
$3Ca_3P_2O_8 \cdot SrCO_3$	9.45	6.90	0.7306			BD 49
$3Ca_3P_2O_8 \cdot ZnCO_3$	9.470	6.889	0.730			BD 49
Staffelite (Staffel)1/	9.394	6.889	0.7333			BD 49
$3Ca_3P_2O_8 \cdot CaP_2$	9.40	6.889	0.7329			BD 49
$Ca_{10}SiP_4SO_{24}F_2$	9.45	6.96	0.736	3.09	3.13	KD 42
$Ca_{10}SiP_4SO_{24}(OH)_2$	9.44	6.96	0.736	3.08	3.01	KD 42
$Ca_{10}Si_3S_3O_{24}F_2$	9.54	6.99	0.732	3.00	3.06	KD 42
$Ca_{10}Si_3S_3O_{24}(OH)_2$	9.54	6.99	0.732	3.00	3.07	KD 42
$Na_8Ca_4S_8O_{24}F_2$	9.49	6.87	0.724	2.81	2.81	KD 42
$Na_2Ca_8P_4S_6O_{24}F_2$	9.52	6.90	0.725	2.98	2.97	KD 42
$Ca_{10.5}SiP_5O_{24}F_2$	9.35	6.79	0.726	3.19	3.2	KD 42
$Ca_{9.5}P_5SO_{24}F_2$	9.46	6.91	0.731	3.05	3.08	KD 42
$Ca_{10.5}Si_2P_3SO_{24}F_2$	9.40	6.81	0.724	3.23	3.20	KD 42
$Ca_{9.5}SiP_3S_2O_{24}F_2$	9.46	6.91	0.731	3.04	3.10	KD 42
$Na_2Ca_9SiP_4SO_{24}F_2$	9.39	6.89	0.734	3.24	3.10	KD 42

1/ Natural apatite for purposes of comparison

Table 3.--Optical constants of synthetic apatites

Mineral	nO_{Na}	nE_{Na}	$nO_{Na} - nE_{Na}$	Ref.
Chlorapatite			0.005-0.0056	Z 16
Chlorapatite	1.667*			M 41
1% Ce chlorapatite			0.005	Z 23
1.6% Ce chlorapatite			0.001	Z 23
8% Ce chlorapatite	1.6703		0.004	Z 23
13% Ce chlorapatite	1.666-1.673	1.665-1.672		Z 23
6.3% Y chlorapatite	1.669			Z 23
0.38% Cr chlorapatite	1.668*	1.666*		M 41
0.8% Cr chlorapatite	1.676*	1.674*		M 41
1.47% Cr chlorapatite	1.682*	1.680*		M 41
3.06% Cr chlorapatite	1.710*	1.707*		M 41
2.74% Cr, 0.39% Na chlorapatite	1.693	1.690		M 41
3.14% Cr, ?% Na chlorapatite	1.701	1.698		M 41
Fe-Cl-apatite	1.6745-1.6738	1.6711-1.6704		P 47
Pb-Cl-apatite	1.6693			P 47
Mo-Cl-apatite	1.6640	1.6615		P 47
Sr apatite	1.658	1.664		C 50
Ca-carbonate-apatite	1.635	1.626	0.009-0.010	E 24
Ba-carbonate-apatite	1.691	1.683	0.0086	E 24
Sr-carbonate-apatite	1.644	1.638	0.0065	E 24
Al apatite	1.6681	1.6643	0.0038	P 47
α $Ca_3(PO_4)_2$	1.572			DBM 49

* Determined by yellow light

DISCUSSION AND SUGGESTIONS

Each group of scientists concerned with the apatite minerals has its own problem which it has attempted to solve in its own way. The soils scientist is mainly interested in the availability of P_2O_5 to plants; the physiologist, in the prevention of dental caries, or the mechanism of various types of metal poisoning; the geologist, in the mode of formation of phosphorite deposits; the chemist, in equilibrium studies and analytical methods; and the mineralogist, in the crystal chemistry of the entire group. Yet all these workers have run into the same problems.

The problem of carbonate-apatite, under as yet unresolved discussion, is especially interesting to the physiologist, as the mineral matter of bone is known to belong to the apatite group and contains some CO_2. Carbonate-apatite apparently does not precipitate in aqueous systems. Eitel (1924) claims to have crystallized carbonate-apatite from a melt, but he determined CO_2 only qualitatively and on a sample that may have been impure. The structure of carbonate-apatite is not known.

Hydroxylapatite is very difficult to dehydrate, even at high temperatures. As a consequence of this, many workers have mistaken it for oxyapatite. The structure of oxyapatite is not known and is difficult to visualize.

Tricalcium phosphate, whose existence is questioned by some chemists, gives an apatite group X-ray diffraction pattern and is called hydroapatite by some workers. It tends to precipitate as a gel and may absorb enough excess CaO to give the $CaO:P_2O_5$ ratio of apatite on

chemical analysis. Dallemagne, Brasseur, and Melon (see DBM 49) claim that it can be distinguished from hydroxylapatite only by optical methods.

Previous workers in the field of apatite synthesis too often have used only one or two methods to check the product of their synthesis. Unless optical methods are used, one man's apatite may be another man's tricalcium phosphate; unless air is rigidly excluded from the system and water is driven off at a very high temperature, hydroxylapatite will be mistaken for oxyapatite. The product of any synthesis should be checked chemically, as well as by X-ray and mineralogic methods.

In addition to the problems mentioned above, there are many others waiting to be solved by a comprehensive program of apatite synthesis, such as, the effects of other ions on the stability field of hydroxylapatite; the mechanisms of absorption by and hydrolysis of precipitated basic phosphates; the mode of occurrence of rare elements associated with phosphorites.

Elements and radicals that have been substituted synthetically in apatites are: Ba, Pb, Mg, Ni, Sr, Zn, OH, F, Cl, CO_3, O, S, CN, Al, Fe, Si, Sm, Na, SO_4, Cr^{+3}, Cr^{+6}, Ce, "Di", and Y. Elements that have been observed spectrographically in natural phosphorites, though they are not necessarily present in the apatite structure, are: Pb, Cu, Fe, Cr, Ti, Mn, Mg, Si, Na, K, Li, As, Sn, Zn, Cd, Sb, V, Zr, Sr, Mo, Rb, Au, Ga, Pt, Pd, Tl, Ta, Ba, Ce, and other rare earths.

Synthesis of apatite may be useful in solving the problems connected with the apatite group, and may be approached in these various ways:

1. Determination of the conditions of precipitation and stability of phosphorites, not only in the simple system $CaO-P_2O_5-H_2O$, but also in quaternary systems, the fourth component of which would be some element normally present in ground water or sea water, such as F, Cl, Na, Al, to name only a few of the many possibilities.

2. Theoretical and experimental studies of the possible substitutions in the apatite lattice. Many of the possibilities are already known; some are only imperfectly known; and many have not been tried.

3. Study of the effects of alteration on phosphorites, especially with respect to adsorption of ions not normally present in the lattice in large amounts.

4. Synthesis of pure end members of the various isomorphous series as standards for the optical and X-ray identification of natural apatites.

In order to avoid the pitfalls encountered by previous authors the following procedure is tentatively suggested:

1. Synthesis by dry methods of the desired apatites: the products should be checked chemically, optically, by X-ray, differential thermal analysis, electron microscopy, and electron diffraction.

2. Synthesis by wet methods of apatites corresponding to those made by dry methods: crystallization, if necessary, may be speeded by seeding with the corresponding apatite made by dry methods. The product again should be completely checked.

ABSTRACTS

Clarke, Frank Wigglesworth, The data of Geochemistry: Phosphates, Apatite: U. S. Geol. Survey Bull. 770, pp. 357-358, 1924 - quoted directly.

The first synthesis of apatite was effected by A. Daubree,[6] who obtained it in crystals by passing the vapor of phosphorus trichloride over red-hot lime. N. S. Manross[7] fused sodium phosphate either with calcium chloride, calcium fluoride, or both together, and so obtained chlorapatite, fluorapatite, or a mixture of the two, resembling natural apatite, at will. This process, slightly modified, was also adopted by H. Briegleb[8] successfully. G. Forchhammer[9] prepared chlorapatite by fusing calcium phosphate with sodium chloride. When bone ash or marl was used instead of the artificial calcium phosphate, a mixed apatite was formed. Similar results were reported by Deville and Caron,[1] who fused bone ash with ammonium chloride and either calcium chloride or fluoride, and also by A. Ditte,[2] who repeated Forchhammer's experiment. By heating calcium phosphate with calcium chloride and water, under pressure, at 250°, H. Debray[3] prepared chlorapatite. E. Weinschenk[4] also produced it by heating calcium chloride, ammonium phosphate, and ammonium chloride at temperatures of 150° to 180° in a sealed tube. F. K. Cameron and W. J. McCaughey[5] prepared fluorapatite by dissolving calcium fluoride in fused disodium phosphate and lixiviating the cooled melt. Chlorapatite was formed when dicalcium phosphate was added in excess to molten calcium chloride. When precipitated calcium phosphate was used, chlorspodiosite was obtained, $Ca_3(PO_4)_2 \cdot CaCl_2$. R. Nacken,[6] by fusing calcium fluoride or chloride with calcium phosphate, obtained both species of apatite, and also mixed crystals. Apatite has been reported as present in lead-furnace slags by W. M. Hutchins[7] and J. H. L. Vogt.[8] The composition of these slag products, however, seems not to have been verified by analysis.

Footnotes:

6. Compt. Rend., vol. 32, 1851, p. 625.
7. Liebig's Annalen, vol. 82, 1852, p. 353.
8. Idem, vol. 97, 1856, p. 95
9. Idem, vol. 90, 1854, pp. 77, 322.

---

1. Compt. Rend., vol. 47, 1858, p. 985.
2. Idem, vol. 94, 1882, p. 1592.
3. Compt. Rend., vol. 52, 1861, p. 44.
4. Zeitschr. Kryst. Min., vol. 17, 1890, p. 489.
5. Jour. Phys. Chem., vol. 15, 1911, p. 464.
6. Centralbl. Min., Geol. u. Pal., 1912, p. 545. Similar results were obtained by J. R. Mourelo (Chem. Abst., vol. 9, 1915, p. 2749; from Rev. gen. sci., vol. 26, 1915, p. 394).
7. Nature, vol. 36, 1887, p. 460.
8. Mineralbildung in Schmelzmassen, p. 263.

B 17

Bassett, H., The system $CaO-P_2O_5-H_2O$ at 25°: Chem. Soc. London Jour. III, pp. 620-642, 1917.

In the basic part of the system $CaO-P_2O_5-H_2O$, two compounds are precipitated: $Ca_3P_2O_8$ and $3(Ca_3P_2O_8)\cdot Ca(OH)_2$. Bassett calls the apatite phase oxyapatite, although he gives it the formula of hydroxylapatite; in order to make up analytical deficiency, he must assume that water is present, "so firmly held that it could not be driven off even by very strong ignition." Quick mixing of liquid reagents and consequent gel formation led to great difficulty in attaining equilibrium, even after one and a half years. Because Bassett used solid reagents, which are metastable, his equilibrium data do not agree with Kazakov (see K 37). CO_2 is not always successfully excluded from the system: 0.5 to 1.0 percent CO_2 is present in both solid phases. Some of the oxyapatite obtained was pinkish; qualitative tests showed the presence of traces of Cu. Bassett finally suggests that the apatite phase might be hydroxylapatite.

BD 49

Brasseur, Henri A. L., and Dallemagne, Marcel J., La synthèse des apatites: Soc. chim. France Bull., fasc. 3-4, mars-avril pp. 135-137, 1949.

$Ca_3P_2O_8$ and chlorides, fluorides, oxides, carbonates, and sulfates of various metals were mixed (wet) in stoichiometric proportions and the mixture oven-dried at 900-950°C. for several hours; the products were studied by the Bragg-Brentano (?) powder method. The discussion of synthetic apatites includes a listing of c:a ratios calculated from powder patterns (see below). All of the oxyapatites have similar c and

a axes; those of Pb and Ba have slightly larger ones; intensity variations for the same lines are imperceptible. Carbonate-apatites have a larger c:a ratio than oxyapatites. The c axes of chlorapatites and oxyapatites are equal; the a axis is larger in chlorapatites than in oxyapatites. Sulfapatites were not successfully synthesized. In the carbonate-apatite syntheses, the crucible containing the tricalcium phosphate was placed in a closed crucible containing the carbonate. Hendricks, Jefferson and Moosley (sic) are quoted as saying that larger ions substituting for F are placed half way along c between F positions, coordinated with 6 instead of 3 Ca.

Apatite	a in kx	c in kx	c:a
$3Ca_3P_2O_8 \cdot BaCl_2$	9.64	6.87	0.7126
$3Ca_3P_2O_8 \cdot PbCl_2$	9.64	6.87	0.7126
$3Ca_3P_2O_8 \cdot MgCl_2$	9.60	6.875	0.7161
$3Ca_3P_2O_8 \cdot NiCl_2$	9.59	6.875	0.7169
$3Ca_3P_2O_8 \cdot PbO$	8.43	6.875	0.729
$3Ca_3P_2O_8 \cdot SrO$	9.43	6.88	0.7295
$3Ca_3P_2O_8 \cdot BaO$	9.43	6.88	0.7295
$3Ca_3P_2O_8 \cdot CaO$	9.455	6.875	0.730
$3Ca_3P_2O_8 \cdot NiO$	9.415	6.875	0.730
$3Ca_3P_2O_8 \cdot ZnCO_3$	9.451	6.875	0.730
$3Ca_3P_2O_8 \cdot SrCO_3$	9.43	6.89	0.7306
$3Ca_3P_2O_8 \cdot PbCO_3$	9.41	6.88	0.7311
$3Ca_3P_2O_8 \cdot BaCO_3$	9.43	6.90	0.7317

Apatite	a in kx	c in kx	c:a
$3Ca_3P_2O_8 \cdot CaF_2$	9.38	6.875	0.7329
Os Gabriel·$CaCl_2$ (sic)	9.61	6.875	0.7154
Hydroxylapatite (Holly Springs)	9.41	6.88	0.7311
Staffelite (Staffel)	9.375	6.875	0.7333
Hydroxylapatite (Saint-Girons)	9.34	6.88	0.7366

BFF 32

Bredig, M. A., Franck, H. H., and Fuldner, H., Beitrage zur Kenntnis der Kalk-Phosphorsäure-Verbindungen: Zeitschr. Elektrochemie 38, p. 158, 1932.

This paper presents data on the system $CaO-P_2O_5$. Three different forms of $Ca_3P_2O_8$ were found; the alpha form is stable from 600°-800°C. and gives an apatite pattern; the beta form is stable from 800° to 1180°; the gamma form is stable from 1180° to the melting point at 1500°. Beta and gamma forms can invert to the alpha form only by heating in water. The mechanism of this inversion is either the formation of a hydrate ($Ca_3P_2O_8 \cdot nH_2O$) or, by hydrolysis, a hydroxylapatite. On heating with an excess of CaO, the alpha pattern persists to high temperatures, because of the formation of oxyapatite. CaO in excess of that demanded by the apatite formula can enter into the apatite lattice at higher temperatures; the $CaO/Ca_3P_2O_8$ ratio rises to 2:3 at 1350°, and can be almost as high as 1:1. Excess CaF_2 up to 35 mol percent can also enter into the apatite lattice. Because the present writers have found enough excess Ca to satisfy this excess F, they

object to the hypothesis of Hendricks, Hill, Jacob, and Jefferson (see HHJJ 31) that this excess F is coordinated with P, substituting for O. Heating $Ca_3(PO_4)_2$ with less than enough CaO to form oxyapatite gave a mixture of $\alpha + \beta$ or γ $Ca_3P_2O_8$, but no mix-crystals. Heating $Ca_3P_2O_8$ with 20 mol percent CaO for 120 hours at 1000°C. produced a mixture of much β $Ca_3P_2O_8$, but little of the α form; heating the same mixture at 1000°C. for 500 hours gave a mixture of little of the beta form, much of the alpha form. The authors explain this apparent anomaly by the relative rapidity of the reactions of water loss and the entry of CaO into the lattice to form apatite. Oxyapatite, heated at about 100°C. below its melting point, dissociates to a mixture of γ $Ca_3(PO_4)_2$ and $Ca_4P_2O_9$. There is a eutectic point at 1325°C. for γ $Ca_3(PO_4)_2$ and $Ca_4P_2O_9$. At 1550°C. CaO and $Ca_4P_2O_9$ form, their proportions depending on the composition of the mixture. $Ca_4P_2O_9$ is prevented from forming by 2 percent CaF_2; when this is present, the apatite pattern persists at high temperatures, because of the formation of oxy- and fluorapatites.

Criticism following paper: it is actually a phase diagram of the ternary system lime-phosphate-water, as partial pressure of water vapor at room temperature and pressure is enough to form, not oxy-, but hydroxyl-apatite. In a water-free system, γ tricalcium phosphate and tetracalcium phosphate might form at lower temperatures.

BFF 33

Bredig, M. A., Franck, H. H., Fuldner, H., Beitrage zur Kenntnis der Kalk-Phosphorsäure Verbindungen: Zeitschr. Elektrochemie, 39, p. 959, 1933.

I. Structural chemistry of the apatite group

a) Phase diagram of the water-free system CaO-$Ca_3P_2O_8$--Apatite occurs only in the field previously occupied by γ $Ca_3(PO_4)_2$; $Ca_4P_2O_9$ appears throughout at 50 mol percent CaO; γ $Ca_3(PO_4)_2$ does not appear.

b) Powder patterns are given for hydroxyl-oxy- and fluor-oxyapatites synthesized by heating with less than stoichiometric water; these melt to either $Ca_4P_2O_9$ or $Ca_4P_2O_9$ + CaF_2 above 1400°C.

c) Precipitated tricalcium phosphate contains excess adsorbed P_2O_5.

d) Other apatites with bivalent radicals

1) The natural carbonate-apatites are usually more fine-grained than apatites with less or no carbonate content. Carbonate apatite was synthesized by these authors from $CaCO_3$ + $Ca(OH)_2$ + $NaHCO_3$ + Na_3PO_4 heated for a long time. The product gave an apatite pattern; crystal size was improved by heating at 700-800°C. in weak H_2CO_3.

2) Sulfate- and sulfide-apatite were produced by heating $Ca_3(PO_4)_2$ + $CaSO_4$ in a small closed iron bomb (reducing condition). It is not yet known whether this is a Ca or an Fe sulfide-apatite.

3) Cyanimidapatite was produced by heating together $Ca_3(PO_4)_2$ + $CaCN_2$. The authors suggest that N is in the F position.

4) Aluminate- and ferri-apatite were produced by heating $Ca_3(PO_4)_2$ + CaO and Fe_2O_3 or Al_2O_3. The authors suggest here the general formula:

$Ca_{10}(PO_4)_6X_{2m}Y_n$ where X is OH, F, Cl; m and n are equal to one, Y is R''.

II. The reversible inversion of tricalcium phosphate from the beta to the alpha form is affected by the presence of excess CaO and water (also perhaps by CaF_2, $CaCl_2$, or even $CaCN_2$).

BTSS 37

Belopol'skii, A. P., Taperova, A. A., Serebrennikova, M. T., Shul'gina, M. N., Physicochemical analysis in the field of sulfuric acid treatment of phosphates: I. The ternary system calcium oxide-phosphorus pentoxide-water at 80°: Jour. Chem. Ind. URSS, vol. 14, pp. 504-507, 1937.

This paper deals with the system between 0.13 and 48.9 percent P_2O_5, and gives equilibrium data for $Ca(H_2PO_4)_2$. Therefore its subject matter is not germane to the present collection of abstracts.

C 25

Carobbi, G., Richerche sulle relazioni d'isomorfismo fra i composti del samario e quelli corrispondenti del calcio, dello stronzio, del bario, e del piombo: R. accad. Napoli Fis. Mat., pp. 83-95, 1925.

The compounds $SmCl_2$ and SmI_2 are known, where Sm is divalent; Zambonini has investigated substitutions of the rare earths for the alkaline earths, and the role of samarium is here investigated further.

Compounds synthesized in this study are:

$Sm_2(MoO_4)_3$ and $Sm_2(MoO_4)_3 \cdot 15H_2O$

Mix crystals from 90% $Sm_2(MoO_4)_3$-10% $PbMoO_4$ to 10% $Sm_2(MoO_4)_3$-90% $PbMoO_4$ (9 experiments).

Mix crystals up to a maximum of 68.82% $Sm_2(MoO_4)_3$-31.8% $CaMoO_4$ (4 experiments).

Mix crystals of 46.56% $Sm_2(MoO_4)_3$-53.44% $SrMoO_4$ (1 experiment)

$SmPO_4 \cdot 2H_2O$ was prepared from hot and cold solutions of $Sm(NO_3)_3$ and Na_3PO_4.

Samariferous chlorapatite was prepared by fusing for 3 hours at 1100°C. a mixture of 0.5126 g $SmPO_4$, 3 g $Ca_3(PO_4)_2$, and 6 g $CaCl_2$. The product of this fusion was washed with water. Very small crystals, with $(10\bar{1}0)$ and $(10\bar{1}1)$ faces were obtained. They were uniaxial (-), clear and colorless, and had weak birefringence; they contained 13.63% $SmPO_4$, equivalent to 9.67% Sm_2O_3. According to the results of all these syntheses it should be possible to synthesize apatites containing even more samarium.

C 50

Carobbi, Guido, Celestina e apatite di stronzio contenenti piccole quantita di mercurio: Accad. Nazionale dei Lincei Atti, series 8, vol. 8, fasc. 2, pp. 87-93, 1950.

Mercury is widely diffused in nature, generally in the order of 10^{-8} grams per 100 grams. Trace elements in such minerals as sphalerite and apatite are a guide to their conditions of formation and genesis. The ionic radii of divalent mercury and strontium are similar, indicating the possibility of mutual substitution; mercury is known to occur in natural strontian celestite and apatite in the order of 1×10^{-4} to 17×10^{-4} percent, and in natural and synthetic barite.

Celestite was synthesized by adding 15 cc of concentrated H_2SO_4 and 100 cc of $SrCl_2$ solution (40 g per liter) to 100 cc of a concentrated solution of $HgCl_2$. The precipitate was left in contact with the liquid for some days, filtered, and washed with dilute H_2SO_4. The crystals

were rhombic, about 0.01 mm in size, and were both tabular and prismatic in habit, with refractive indices nX = 1.620, nY = 1.622, nZ = 1.629. Mercury was determined by the dithizone method: the crystals were dissolved in K_2CO_3 and HNO_3, and neutralized with NH_4OH; a 0.005-percent solution of dithizone in CCl_4 was added, and the resulting solution was titrated against a similar solution of pure dithizone by adding $Hg(NO_3)_2$. The obtained result of 0.002 percent Hg was checked spectrographically by electrolyzing the solution and checking the lines obtained on intermittent sparking against Mg lines. Under the microscope the crystals were not homogeneous, but had very small inclusions of higher index.

Two other syntheses were attempted by similar methods using $HgSO_4$ treated with HNO_3 to oxidize all the mercury. Although X-ray diffraction patterns showed nothing but celestite lines in the precipitate, microscopic examination showed that the crystals were not homogeneous.

Strontian apatite was crystallized from a mixture of $Sr_3(PO_4)_2$, $SrCl_2$, and $HgCl_2$ fused at 1000°C.; the crystals were washed with water and acetic acid. Hg escaped and sublimated during the fusion, but the crystals still contained 0.001 percent Hg. The crystals were mostly tabular, but a few were elongated along the prism; the prismatic crystals were 0.01 mm long, the tabular crystals, 0.05 mm in diameter. They had refractive indices nO = 1.658, nE = 1.664. Microscopic examination showed that no mix-crystals had been obtained, but that the crystals contained small diffused inclusions of higher refractive index.

CB 33

Clarens, J., and Bruneton, M., Contribution à l'étude des réactions mutuelles des phosphates et des sols; première note: action de la chaux sur le phosphate monocalcique: Soc. chim. France Bull. 53, pp. 1431-1435, 1933.

The authors mixed solutions 0.1 N in $CaHPO_4$ with solutions of $Ca(OH)_2$ of various concentrations. The solutions were mixed rapidly, either at room temperature or intermittently heated over steam. After precipitation, the solutions were analyzed for H_3PO_4 by titration with uranyl nitrate. The solid products are interpreted from the composition of the solutions to be mono- and tricalcium phosphates.

C 31

Clark, N. A., The system $CaO-P_2O_5-H_2O$: Jour. Physical Chemistry, vol. 35, pp. 1232-1238, 1931.

This paper gives equilibrium data for mono- and di-calcium phosphate. The material presented here has no direct bearing on the synthesis of apatite.

CW 49

Chaudron, G., and Wallaeys, R., Synthèse des apatites par réaction dans l'état solide: Soc. chim. France Bull. fasc. 3-4, mars-avril, pp. 132-134, 1949.

The authors prepared α $Ca_3(PO_4)_2$ (uncertain hydration) by reaction of Na_2HPO_4 and $CaCl_2$ in an ammoniated medium. This compound loses water gradually to 600°C., where only 0.5 molecules of water remain for 3 molecules of the anhydrous phosphate. This last water is rapidly lost on further heating, and the phosphate inverts to the beta form. At

temperatures above 1200°C., the phosphate inverts to the gamma form, and can be turned back to the beta form by heating at 600-800°C. α $Ca_3(PO_4)_2$ has a structure not far removed from that of apatite; it does not give a good X-ray diffraction pattern unless it is heated at 400°C. as it is very poorly crystallized. Preparation of apatites:

1) Fluorapatite was made from a dry mixture of α $Ca_3(PO_4)_2$ and CaF_2 heated above 600°; differential thermal curves of this reaction show a rapid but progressive water loss; the authors therefore postulate the substitution of F for OH. Fluorapatite was also produced by mixing dry β $Ca_3(PO_4)_2$ with CaF_2: this reaction takes place abruptly at 500°C.

2) Hydroxyl- and oxyapatite were produced by saturating H_3PO_4 with $Ca(OH)_2$ at 100°C. A mixture of β $Ca_3(PO_4)_2$ and CaO (dry) reacted incompletely, resulting in a mixture of β $Ca_3(PO_4)_2$ and apatite. Fusion of $Ca_2P_2O_7$ and CaO in oxyapatite proportions resulted in an unstable phase, which, reheated at 600°C., gave a good oxyapatite diagram. (If air was not excluded, this is probably hydroxylapatite. EBJ)

3) Chlorapatite was produced by heating $Ca_3(PO_4)_2$ and $CaCl_2$ in a nitrogen atmosphere. If these compounds are mixed wet or in air, their product gives a pattern which may indicate partial substitution of Cl for CaO; the powder pattern is then between those of oxyapatite and chlorapatite.

4) Mixed chlor-fluor-apatites were produced either by action of CaF_2 on chlorapatite, or by heating a mixture of CaF_2, $CaCl_2$, and $Ca_3(PO_4)_2$. These mixed apatites prove that there is a continuous isomorphous series between chlor- and fluorapatites.

Chaudron, Georges, and Wallaeys, Robert, Etude de la substitution, dans l'hydroxyapatite, du radical hydroxyle par le chlor ou le fluor, et dans la chlorapatite, du chlore par le fluor: Comptes rendus, vol. 230, number 21, May 1950.

Chlorapatite and fluorapatite were prepared by adding CaF_2 or $CaCl_2$ to anhydrous tricalcium phosphate at about 800°C. Hydroxylapatite was prepared by saturating phosphoric acid with milk of lime at 100°C., and heating the precipitate at 1100°C. to eliminate adsorbed water. All products were checked by X-ray diffraction methods.

When chlorapatite is heated at about 800°C. with calcium fluoride, its powder pattern changes to that of fluorapatite, and water-soluble calcium chloride is set free. When hydroxylapatite is heated at about 800°C. with calcium chloride in a nitrogen atmosphere, the following reaction takes place:

$$3(3CaO\cdot P_2O_5)Ca(OH)_2 + CaCl_2 \rightarrow 3(3CaO\cdot P_2O_5)CaCl_2 + CaO + H_2O$$

A similar reaction takes place between hydroxylapatite and CaF_2 to form fluorapatite. In the latter case, the X-ray diffraction patterns of fluorapatite and hydroxylapatite are very similar but may be distinguished by a difference of 0.05 A in the a dimension of the unit cell. Thermal analysis of the reaction between hydroxylapatite and CaF_2 shows that there is a quantitative water loss as the temperature rises above 600°C.; hydroxylapatite heated by itself is stable at temperatures above 1000°C.

The substitutions described above may be partial as well as complete. Under the conditions of these experiments, the compounds may be arranged in order of increasing stability: hydroxylapatite, chlorapatite, fluorapatite.

DBM 49

Dallemagne, M. J., Brasseur, H., Melon, J., La constitution de la substance minérale de l'os et la synthèse des apatites: Soc. chim. France Bull. fasc. 3-4, mars-avril pp. 138-145, 1949.

In trying to resolve the question of the mineral composition of bone, the authors discuss the reactions between α and β $Ca_3(PO_4)_2$, hydroxylapatite, brushite, and oxyapatite. They give X-ray powder patterns for all products.

1. Bone freed of organic substances has the same CO_2 elimination curve as 10:1 mixture of $Ca_3(PO_4)_2$ and $CaCO_3$. When most of the $CaCO_3$ is dissolved out of bone, leaving most of the phosphate, the Ca/P ratio is 1.94, which is equal to that of $Ca_3(PO_4)_2$. Bone alone gives a poor powder pattern; when calcined at 900°C., it gives an apatite pattern; this was previously interpreted as improvement of crystallization due to heating.

2. α $Ca_3(PO_4)_2$ has two molecules of water and gives a powder pattern similar to that of hydroxylapatite.

$Ca_3(PO_4)_2 \cdot H_2(OH)_2$ (α tricalcium phosphate)

$Ca_3(PO_4)_2 \cdot Ca(OH)_2$ (hydroxylapatite)

When α $Ca_3(PO_4)_2$ is heated to 700°C., it inverts to the beta form. This inversion is distinctive of α $Ca_3(PO_4)_2$. Bone, when treated with acid, gives an α $Ca_3(PO_4)_2$ pattern; after calcining at 700°C., it gives a β $Ca_3(PO_4)_2$ pattern. Apatite (type not specified-EBJ) treated in this way does not change its pattern.

3. α $Ca_3(PO_4)_2$ mixed with $CaCO_3$ 966:100 and heated to 900°C. gives an apatite pattern. Thermal analysis shows that the reaction CO_2-P_2O_5 takes

place within 670°-890°C. Complete dehydration of α $Ca_3(PO_4)_2$ takes place at 700°C.; therefore CO_3 replaces HOH in the alpha lattice. The same replacement of this water is possible by Cl, O, and F, and Mg may replace Ca. The inversion temperature of $CaCO_3$ is 884°C. Once fixed in the phosphate lattice, CO_2 cannot be driven off below 1050°.

4. The index of refraction measured with light of 599.1 A (sic) using the Becke line method and an Abbe refractometer is used as a control. The refractive index of ox-bone mineral substance is 1.590; that of α $Ca_3(PO_4)_2$ is 1.572; the difference is due to 10 percent adsorbed carbonate. Bone calcined at 900°C. has a refractive index of 1.645; the refractive index of β $Ca_3(PO_4)_2$ is 1.619.

5. The authors answer objections to their thesis on the basis of adsorption of CaO by bone in excess of stoichiometric proportions; this mixture, on heating, produces hydroxylapatite by the following reaction:

$$3Ca_3(PO_4)_2 \cdot H_2(OH)_2 + CaO \longrightarrow 3Ca_3(PO_4)_2 \cdot CaO + 2H_2O \text{ (sic)}.$$

The authors maintain that combination of phosphate and lime to form hydroxylapatite occurs only at high temperatures.

The tentative results of another experiment are:

$$CaCl_2 + \alpha\ Ca_3(PO_4)_2 \longrightarrow \text{chlorapatite}$$

$$CaCl_2 + \text{hydroxylapatite} \longrightarrow \text{no change in pattern}$$

A mixture of brushite and lime heated to 900°C. gives either β $Ca_3(PO_4)_2$ or apatite, depending on the proportions of the mixture.

"Conclusions:

1. Tricalcium phosphate does exist in the hydrated form which we have described, but its preparation requires definite conditions. Prepared in too acid a medium, it encloses crystals of brushite. Prepared in too alkaline a medium, it adsorbs lime. Left in the solution from which it was prepared, it decomposes. Prepared beginning with CaO, it adsorbs CaO, even if it forms in a finally neutral medium.

2. Tricalcium phosphate combines with adsorbed lime at 900°C. to form an apatite.

3. This apatite may be decomposed by brushite if the reaction proceeds at a high enough temperature.

4. Heating of brushite with lime gives rise to beta tricalcium phosphate or apatite depending on the relative amounts of the reagents."

E 24

Eitel, Wilhelm, Uber Karbonatphosphate der Apatitgruppe: Schr. Königsberger Gelehrter Gesell. Naturwiss. Kl. Jahrb. 1, Heft 4, pp. 159-177, 1924.

A. Calcium-carbonate-apatite--$3Ca_3(PO_4)_2 \cdot CaCO_3$

I. Investigations in the system $Ca_3(PO_4)_2$--$Na_2Ca(CO_3)_2$

1. 1.000 g $Ca_3(PO_4)_2$ + 5.5000 g $Na_2Ca(CO_3)_2$ under 31-32 kg/cm^2 CO_2 were heated at 1000°C. for 90 minutes and cooled very slowly; the first crystallization occurred at 840°, the second at 776°, ending at 770°C. The product showed two generations of carbonate-

apatite; at the bottom of the melt were stubby prisms of the first generation, at the top were thin prisms eutectically crystallized with $Na_2Ca(CO_3)_2$. The crystals of the first generation have a central filling of $Na_2Ca(CO_3)_2$.

2. 2.000 g $Ca_3(PO_4)_2$ + 3.000 g $Na_2Ca(CO_3)_2$, under 23 kg/cm^2 CO_2, were held at 1000-1010°C. for 30 minutes, and at 1050-1060°C. for 30 minutes, to complete melting. A reaction occurred at 755°C.; the product was similar to that of (1), but the intergrowth of carbonate-apatite and $Na_2Ca(CO_3)_2$ was poikilitic.

3. 3.000 g $Ca_3(PO_4)_2$ + 2.102 g $Na_2Ca(CO_3)_2$ under 40-43 kg/cm^2 CO_2 were heated to 1100° ± 15° for one and a half hours to complete melting. On cooling (from 1020° to 750°C. in six and a quarter hours) crystallization occurred at 755-750°C.; the product consisted of long inclusion-free crystals of carbonate-apatite in a groundmass of $Na_2Ca(CO_3)_2$ crystals.

II. Investigations in the ternary system $Ca_3(PO_4)_2$-$Na_2Ca(CO_3)_2$-$CaCO_3$.

4. 2.000 g $Ca_3(PO_4)_2$ + 1.500 g $CaCO_3$ + 1.5 g $Na_2Ca(CO_3)_2$. The first reaction took place at 770-780°C., the entire mass melted at 970°C. The melt was held at 1050°C. for 10 minutes, and raised briefly to 1220°C. under 48 kg/cm^2 CO_2. Unfortunately, slow cooling was impossible. The product consisted of skeletal carbonate-apatite crystals in a groundmass of $Na_2Ca(CO_3)_2$.

5. 2.000 g $Ca_3(PO_4)_2$ + 2 g $CaCO_3$ + 0.505 g $Na_2Ca(CO_3)_2$ on heating showed a first reaction at 820°C.; heating was continued to 1150°C. under 54 kg/cm^2 CO_2. The product consisted of carbonate-

apatite and calcite, with very little $Na_2Ca(CO_3)_2$.

6. 1.000 g $Ca_3(PO_4)_2$ + 3.003 g $CaCO_3$ + 1.011 g $Na_2Ca(CO_3)_2$ under 49 kg/cm^2 CO_2 began melting at 760-770°, was held at 850-870° for one and a half hours then heated to 1090°C. to complete melting. The product was similar to that of experiment 5, but had a great deal of primary calcite.

III. Investigations in the system $Ca_3(PO_4)_2$-$CaCO_3$

7. 3.000 g $Ca_3(PO_4)_2$ + 3.000 g $CaCO_3$ were heated to 1152°C., the temperature of the eutectic. The melt was held at this temperature for half an hour, then raised to 1202°C. The pressure was raised from 55-60 kg/cm^2 CO_2 to 81 kg/cm^2 CO_2. The apatite produced had inclusions of calcite parallel to the c axis.

8. 4 g $CaCO_3$ + 2 g $Ca_3(PO_4)_2$ under 92 kg/cm^2 CO_2 were heated to 1148-1150°, then to 1220°C. On slow cooling there was a weak thermal effect at 1130°. Again, the central hollows of the apatite crystals parallel to the c axis were filled with calcite.

9. 6.2 g $Ca_3(PO_4)_2$ + 2 g $CaCO_3$ under 98-100 kg/cm^2 CO_2 were heated at 1130° for 40 minutes and at 1000°C. for 75 minutes. The mixture showed a weak thermal reaction at 1140°. The product consisted of carbonate-apatite crystals in a groundmass of calcite. Some of the calcite reacted with the platinum.

10. 4 g $Ca_3(PO_4)_2$ + 2 g $CaCO_3$ under a pressure of 89 kg/cm^2 CO_2 were heated to 1140°, then to 1215°C. for 20 minutes, at which temperature melting was still incomplete. The maximum pressure was 97 kg/cm^2 CO_2. The melt was then held at 1050° under 80 kg/cm^2 for

50 minutes, and slowly cooled. The product was similar to that of experiment 9, but contained more calcite. The calcite again reacted with the platinum.

11. 2.5 g $Ca_3(PO_4)_2$ + 3.5 g $CaCO_3$, under 95 kg/cm^2 CO_2 were heated to the eutectic temperature (1130°), and on further heating showed a last weak melting at 1170°C. The maximum temperature was 1190°, from which the melt was slowly cooled. The product consisted of coarse crystals of both calcite and carbonate-apatite.

The system $Ca_3(PO_4)_2$ is a true binary system; the calcite-carbonate-apatite eutectic is at 1140°C., 18 mol percent $Ca_3(PO_4)_2$. Carbonate-apatite melts incongruently to $Ca_3(PO_4)_2$ and liquid at about 1475°C.

Some parts of the ternary system $CaCO_3$-Na_2CO_3-$Ca_3(PO_4)_2$ are still unknown: invariant points yet to be determined are:

$$CaCO_3 + \text{liquid} \rightleftharpoons \text{carbonate-apatite} + Na_2Ca(CO_3)_2$$

$$\text{liquid} \rightleftharpoons \text{carbonate-apatite} + Na_2Ca(CO_3)_2 + Na_2CO_3\text{-mix-crystals}.$$

IV. The physiography (sic) of carbonate-apatite

The synthetic crystals of carbonate-apatite were typically long or short prisms with $10\bar{1}0$, $10\bar{1}1$, and 0001 faces; the skeletal crystals had inclusions along central canals parallel to the c axis. The refractive indices were found to be:

$$nE_{Na} = 1.626,\ nO_{Na} = 1.635,\ nO_{Na}\text{-}nE_{Na} = 0.009\text{-}0.010.$$

Microchemical tests showed the presence of CO_2.

The synthetic carbonate-apatite is compared to natural carbonate-apatites from Tonopah, and the calcite-filled skeletal crystals are similar to those from the Fenno-Scandian pegmatites.

B. Carbonate-apatites of strontium and barium

Na_2CO_3 and $SrCO_3$ form no double salt similar to $Na_2Ca(CO_3)_2$, but have a eutectic at about 715°C. $SrCO_3$ inverts from the alpha to the beta form (the beta form is the high-temperature form) at about 926°C.

$BaCO_3$ and Na_2CO_3 form no double salt similar to $Na_2Ca(CO_3)_2$, and have a eutectic at about 705°C. $BaCO_3$ inverts from the beta to the gamma form at about 811°C. (the beta form is the high-temperature form).

a. A mixture of $Ba_3(PO_4)_2$ + $BaCO_3$ + Na_2CO_3 in the molecular proportion of 1:1:2 was heated under atmospheric pressure for one hour, then slowly cooled. The mixture was completely melted at 1040°C. The apatite produced occurred as stumpy prisms with a typical 0001 cleavage, $nO_{Na} - nE_{Na} = 0.0086$, $nE_{Na} = 1.683$, $nO_{Na} = 1.691$. The crystals had central inclusions of the carbonate-apatite groundmass.

b. A mixture of $Sr_3(PO_4)_2$ + $SrCO_3$ + Na_2CO_3 in the molecular proportion 1:1:2 was heated at atmospheric pressure to 1050°C. and held there for two hours, then slowly cooled. The melt was dark because of the presence of a little free SrO. The apatite had characteristic cleavage and prismatic habit, with nO = 1.644, nE = 1.638, nO-nE = 0.0065.

EF 40

Elmore, Kelly L., and Farr, Thad D., Equilibrium in the system calcium oxide-phosphorus pentoxide-water: Ind. and Eng. Chemistry, Anal. Ed. 32, no. 4, pp. 580-586, 1940.

Solubility and equilibrium data are given for monocalcium phosphate (monohydrate and anhydrous) and dicalcium phosphate (dihydrate and anhydrous). This material has no direct bearing on the synthesis of apatite.

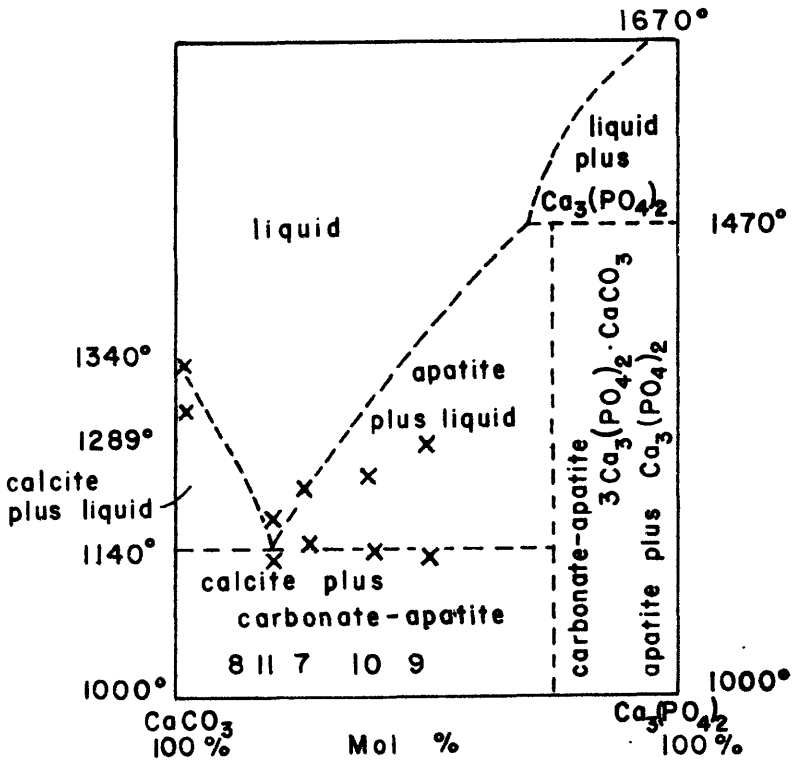


Figure 17

(Wilhelm Eitel, 1924, p. 168)

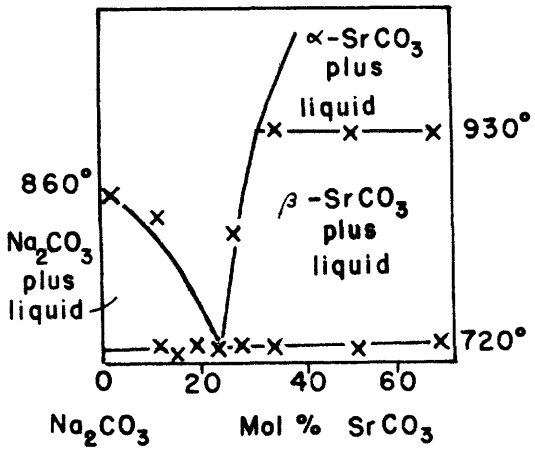


Figure 20

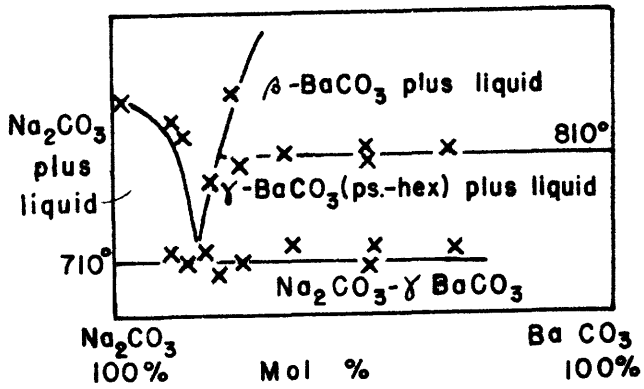


Figure 20a

(Wilhelm Eitel, 1924, p. 174.

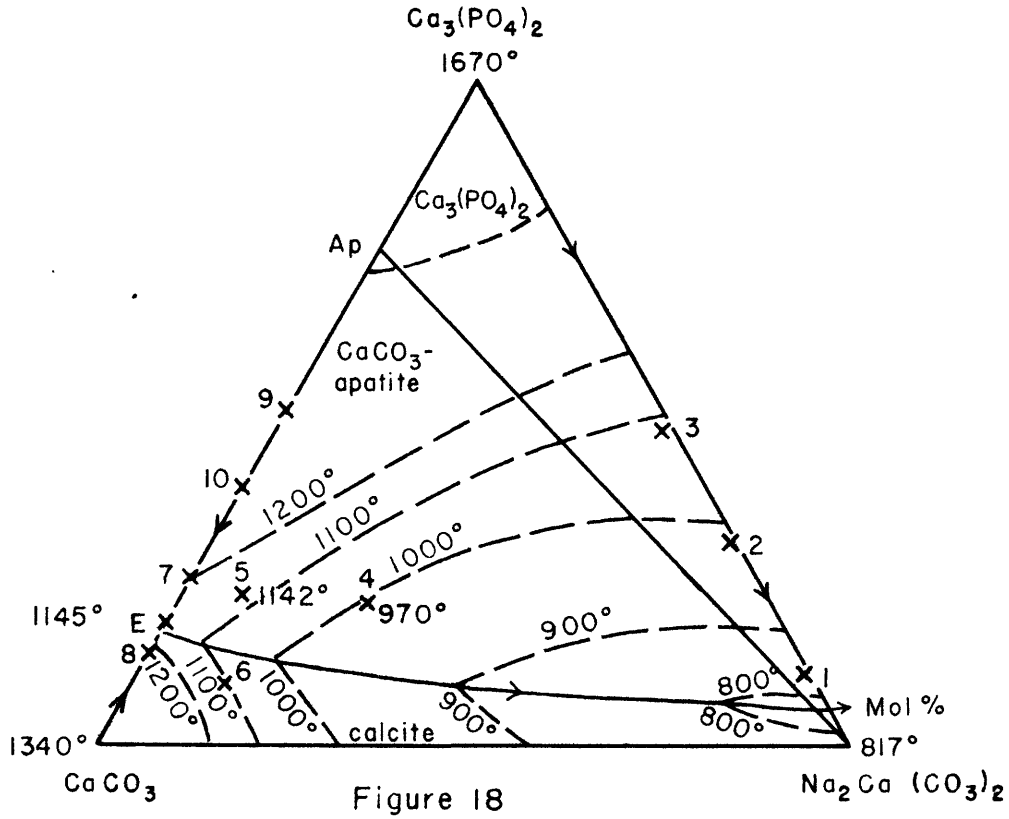


Figure 18

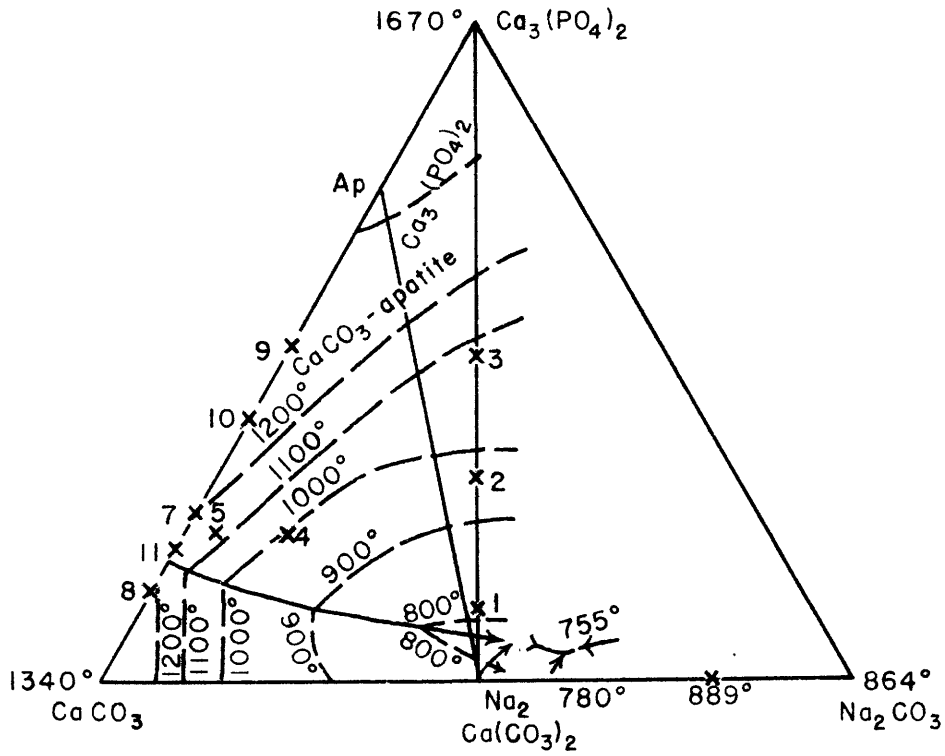


Figure 19

(Wilhelm Eitel, 1924, p.169)

ELT 40

Eisenberger, Sidney; Lehrman, Alexander; and Turner, William D.; The basic calcium phosphates and related systems. Some theoretical and practical aspects: Chem. Rev., vol. 26, pp. 257-296, 1940.

A review of the literature with 230 references. Material applicable to the synthesis of apatite is abstracted elsewhere in this paper.

Part I. Calcium phosphate systems

I. The binary system $CaO-P_2O_5$

II. The basic region of the system $CaO-P_2O_5-H_2O$

A. The phase diagram

B. The phase diagram for calcium arsenates

C. The nature of precipitated basic calcium phosphate

D. Reaction rates

III. The stability of the apatite lattice

A. Mineralogical studies

B. Basic phosphates of other metals

Part II. Practical applications

I. Phosphatic fertilizers

A. Calcined phosphate

B. Thomas meal

II. The removal of the fluoride ion from water

III. The inorganic constituents of bone

A. Carbonate apatite versus hydroxylapatite

B. Minor constituents

C. Crystal orientation

D. Physicochemical considerations

Conclusion

F 37

Fouretier, Georges, La précipitation du phosphate tricalcique et l'hydroxy-apatite: Comptes rendus 205, pp. 413-415, 1937.

Precipitates produced by rapid mixing of more or less dilute H_3PO_4 and $Ca(OH)_2$ were studied by chemical analysis of the liquid, X-ray of the solid, and determination of pH. The author theorizes that the observed fluctuation in pH is produced by metastable tricalcium phosphate slowly going over to apatite; he draws a parallel between this and the hydrolysis of brushite.

G 44

Greenwald, Isidor, Anomalous effects in the titration of phosphoric acid with calcium hydroxide: Am. Chem. Soc. Jour. 66, pp. 1305-1306, 1944.

The anomalous effect in question is, that after one equivalent $Ca(OH)_2$ has been added to a solution of H_3PO_4, further addition lowers the pH; pH rises upon standing. Previous authors explained this effect by the conversion of $CaHPO_4$ to $Ca_3(PO_4)_2$; the present author finds that this does not explain the return to a higher pH after standing.

Greenwald believes that the precipitate is not apatite or $Ca_3(PO_4)_2$, but $CaHPO_4$ and $Ca(OH)_2$ or a compound having a Ca:P ratio greater than 1.5. The first precipitate is $CaHPO_4$, which on standing goes to $Ca(OH)_2 \cdot CaPO_4$. If a crystal of $Ca_3(PO_4)_2$ is added, that compound crystallizes; otherwise the above metastable precipitate remains.

H 47

Hébert, Claude, Contribution à l'étude de la chimie des phosphates de calcium: Annales des mines Mém. 136, no. 4, pp. 5-93, 1947.

I. Qualitative spectrographic analysis of impurities in natural phosphates.

The phosphates were separated into about 10 fractions by means of specially purified reagents; the Fery spectrograph was used for the 2500-4600 A region, the Cojan spectrograph for the 3500-6800 A region.

The following elements were common to natural phosphorites, ox bones, and apatite: Pb, Cu, Fe, Cr, Al, Ti, Mn, Mg, Si, Na, K, Li, As, Sn, Zn. Cd, Sb, V, Zr, Sr were found in natural phosphorites but not in bone. Au, Ga, W, Pt, Pd, Tl, Ta, Ba were rarely found; Mo was frequently found. Rb was found in Tennessee, Lorraine, and Nassau phosphorites. Radioactivity was present as shown below; it is expressed as mg of equivalent U/g phosphate.

Morocco	0.203	Carolina	0.82
Morocco	0.336	Oceania	0.232
Gafsa	0.23	Lorraine	0.157
Constantine	0.202	Nassau	0.101
Constantine	0.262	Narlu (Somme)	0.27
Kosseir (Egypt)	0.14	Cuesmes (Belg)	0.3
Kola	0.173	Crystalline apatite	0.37
Florida	0.69	Flat ox bone	0.036
Tennessee	0.038	Long ox bone	0.029

The radioactivity is concentrated especially in fraction IV (precipitate of ammoniacal magnesian phosphate from citric acid medium), in fraction

V (precipitate of iron sulfide), and in fraction I (insoluble in hydrochloric acid).

II. Methods of measurement, analysis, and preparations.

Discussion on pH measurements and on calcium sulfite. $Ca_2H_2(PO_4)_2$ anhydride and hydrate were prepared by mixing slightly acid solutions of $Ca(OH)_2$ and H_3PO_4, acid in slight excess, and agitating for 48 hours. The hydrate was prepared from cold solutions, the anhydride from boiling solutions; the inversion point is about 80°C. $CaH_4(PO_4)_2$ is stable from pH 3.5 to pH 5.0; $Ca_2H_2(PO_4)_2$ hydrate, from pH 6.5 to pH 7.5.

III. The attack of strong acids on the calcium phosphates.

$Ca_3(PO_4)_2$ was precipitated from 12 N solutions of $Ca(OH)_2$ and H_3PO_4 and has one molecule of water. Apatite and natural phosphates are generally less attacked than is $Ca_3(PO_4)_2$. Acids used here are: oxalic, perchloric, nitric, sulfuric, and hydrochloric.

IV. The attack of medium acids (phosphoric, acetic, citric) on the calcium phosphates is similar, but less marked, than that of strong acids.

V. The attack of weak acids (boric, sulfurous) on the calcium phosphates.

Boric acid has no effect on the calcium phosphates; sulfurous acid attacks them, but the calcium sulfite oxydizes and gives an abnormal curve.

HHJJ 31

Hendricks, S. B., Hill, W. L., Jacob, K. D., and Jefferson, M. E., Structural characteristics of apatite-like substances, and composition of phosphate rock and bone as determined from microscopic and X-ray diffraction examination: Ind. and Eng. Chemistry 23, no. 12, pp. 1413-1418, Dec. 1931.

Various minerals have been thought to exist in phosphorites by Lacroix, Schaller, Rogers, and others; the mineral substance of bone has been thought to be either a carbonate-apatite or hydroxylapatite with calcite or hydrous tricalcium phosphate. An explanation of Mehmel's and Naray-Szabo's interpretations of the apatite structure follows. Hydrated tricalcium phosphate changes to the beta form by heating to constant weight at 900°C.; the hydrated form is believed to have an apatite structure and to form a complete solid solution with hydroxylapatite. As to bone, its $CaO:P_2O_5$ ratio is greater than that required for hydrated tricalcium phosphate, and it also contains CO_2. As no crystalline impurities greater than 2 percent exist even after heating, carbonate-apatite must be the essential constituent of bone. The CO_3 groups could substitute for F ions, although the carbonate-apatite structure is probably closer to that of mimetite than that of fluorapatite. The X-ray diffraction patterns of O, OH, and CO_3 apatites can be distinguished in mixtures. $Ca_3(PO_4)_2$ was made by adding Na_2HPO_4 solution slowly to a solution containing excess of $Ca(NO_3)_2$, and hydroxylapatite was prepared by hydrolysis of this $Ca_3(PO_4)_2$ with neutral ammonium citrate solution. F is present in excess in many phosphorites and eucrystalline apatite; it may be present as submicroscopic fluorite, or perhaps replacing O in PO_4

groups. Excess Na is also believed to be structural. Chlorine is usually less than 0.03 percent. In aging of recent phosphorites (Curaçao, Cenozoic deposits) both hydrated tricalcium phosphate and hydroxylapatite are changing to fluorapatite. In the fossilization of bone, carbonate-apatite also changes to fluorapatite, whose amount increases with the age of the bone. According to the rates of these changes, Pleistocene deposits should consist chiefly of fluorapatite.

Z. S. A.

HJM 32

Hendricks, S., Jefferson, M. E., Mosely, V. M., The crystal structure of some natural and synthetic apatite-like substances: Zeitschr. Kristallographie 81, pp. 352-369, 1932.

Apatite, chlorapatite, pyromorphite, mimetite, and vanadinite all have atomic arrangements derivable from space group $C_{6h}^2 - C6_{3/M}$. Pyromorphite, mimetite, and vanadinite form an extensive though incomplete solid solution series. Polysphaerite, kampylite, hedyphane, and endlichite are also members of this series. Chlor- and fluorapatite form a complete solid solution series, as do fluor- and hydroxylapatite. The occurrence of many other minerals of similar composition suggests that F in fluorapatite can also be replaced by CO_3, SO_4, Si_2O_4, O, Br, or I.

Artificial preparations:

Hydrated tricalcium phosphate was prepared by adding a solution of Na_3PO_4 slowly to a solution with excess $Ca(NO_3)_2$. The precipitate was washed with a saturated solution of $Ca_3(PO_4)_2$ until the filtrate

was free of nitrates; the salt was then dried at 50°C.

Hydroxylapatite was prepared by hydrolyzing $Ca_3(PO_4)_2$ with neutral ammonium citrate.

Oxyapatite was prepared by igniting hydroxyapatite or bone to constant weight at 50°C.

Chlorapatite was prepared from $CaCl_2$ and anhydrous $Ca_3(PO_4)_2$ fused together in platinum in stoichiometric proportions at 1400°C.

In nature chlorine seldom replaces more than one-half of the F in fluorapatite, although chlorapatite and fluorapatite form a complete solid solution. The a/c ratio decreases with increasing Cl. The reason for this limited replacement is that the ionic radius of Cl is 1.81 A, whereas that of F is 1.36 A. The authors suggest that this situation is analogous to that of dolomite and calcite, and that the structure may even be similar, with Cl and F atoms in an ordered arrangement. Pyromorphite, mimetite, vanadinite, and chlorapatite have structures similar to Mehmel's fluorapatite; fluorapatite and hydroxylapatite have Naray-Szabo's fluorapatite structure.

Z. S. A.

K 37

Kazakov, A. V., The system $CaO-P_2O_5-H_2O$ in the field of low concentration (synthesis of tricalcium phosphate and hydroxylapatite): Sci. Inst. Fertilizers and Insectofungicides Trans. 139, pp. 3-73, Leningrad 1937.

Phosphoric acid in solution in sea water at depth is brought, under certain conditions, to a shallow zone where partial pressure of CO_2 diminishes enough to allow precipitation of apatite. Work on precipita-

tion of hydroxylapatite at the isotherm 25° gave the appended diagram. Crystallization was accomplished by mixing solutions very slowly, maintaining a constant composition, and mixing constantly (the longest mixing took 17 days, at the rate of 2 mg P_2O_5 per litre per hour). The entire experiment was conducted with liquid reagents--CaO in H_3PO_4, and $Ca(OH)_2$. The solutions took one to three months to come to equilibrium; pH of the solutions was checked periodically. Kazakov criticizes Bassett for his use of solid reagents, and for mixing the reagents too quickly. Solid phases produced were: hydroxylapatite, brushite, tricalcium phosphate [given as $Ca_3(PO_4)_2 \cdot 0.5H_2O$]. See diagrams following.

The data were obtained by: X-ray of solid phases; determination of pH of liquid; chemical analysis of liquid and solid phases; differential thermal analysis of solid phases; and optical examination of solid phases.

K 39

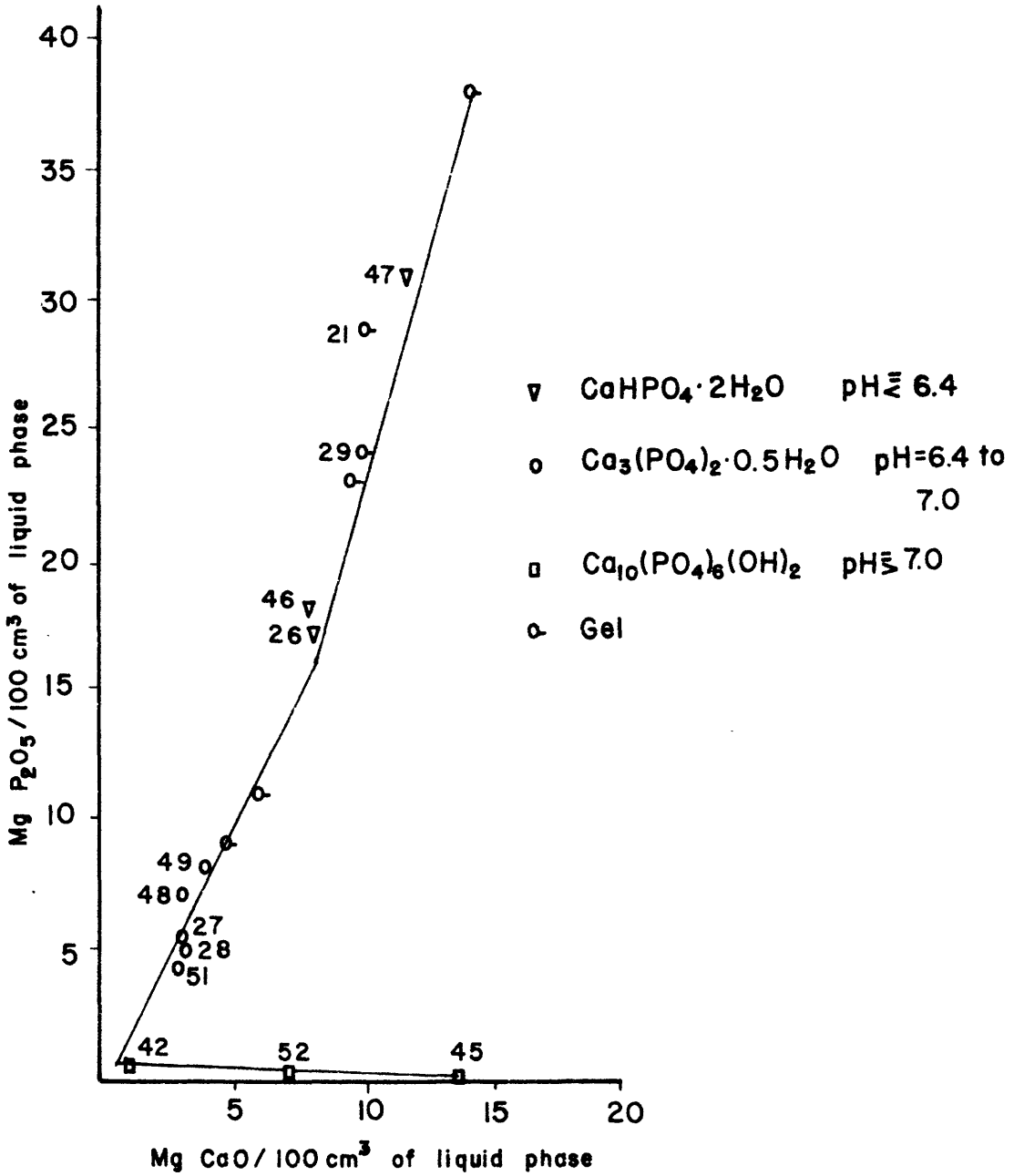
Klement, R., Basische Phosphate zweiwertigen Metalle. IV. Strontium-Hydroxylapatite: Zeitschr. anorg.u.allg. Chemie 242, pp. 215-221, 1939.

Experiments were conducted in the hydrolysis of secondary Sr phosphate ($SrHPO_4$).

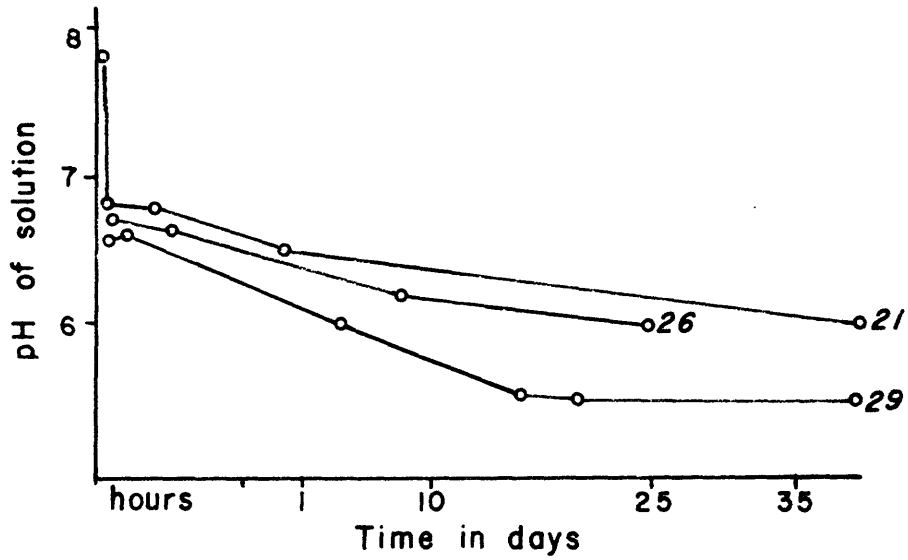
Hydrolysis for two weeks in water had no effect.

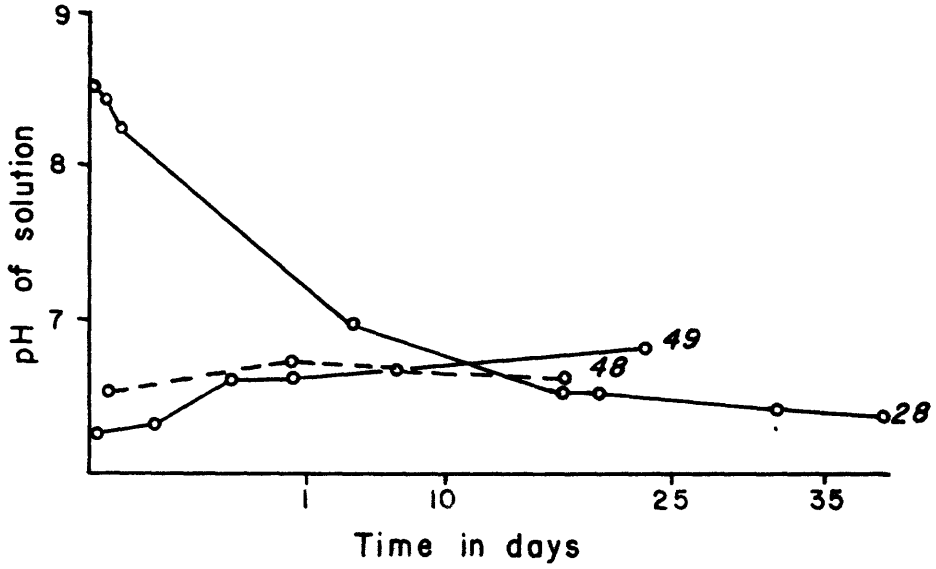
Hydrolysis in N/10 NaOH at 40°C. gave Sr hydroxylapatite; results were checked by chemical and X-ray methods.

Hydrolysis at 40°C. in phosphate buffer solutions of pH 6.8 and



Isotherm at 25°C
(Kazakov, 1937)





Change in pH with age of mixture
(Numbers are experiment numbers)

(*Kazakov, 1937*)

8.3 had no effect on the strontium salt. Klement compares this with the similar behavior of the Ba phosphate and contrasts it with the hydrolysis of Ca and Pb phosphates to apatite. Hydrolysis in a phosphate buffer solution of pH 11.0 at 40°C. resulted in incomplete conversion to Sr hydroxylapatite in four weeks. Sr hydroxylapatite was precipitated from a boiling solution of NaOH, Na_3PO_4, and $SrCl_2$. Chemical analysis of the product gave the ratio $Sr:PO_4 = 1:0.67$. Ca, Pb, and Ba hydroxylapatites may also be precipitated in this way. Adsorption of excess PO_4 throws off the $Sr:PO_4$ ratio. Pure $Sr_3(PO_4)_2$ may be made by mixing stoichiometric proportions of $Sr_2P_2O_7$ and $SrCO_3$, and heating at 1000°C.

Pure $3Sr_3(PO_4)_2 \cdot Sr(OH)_2$ may be made from a stoichiometric mixture of $Sr_3(PO_4)_2$ and $SrCO_3$, heated for seven hours in a current of steam at 1150°C. and cooled at 300°C. in a current of steam.

The unit cell of Sr hydroxylapatite is compared with those of Ca, Pb, and Ba hydroxylapatites.

	Ionic radius	a	c	c:a
$Ca_{10}(PO_4)_6(OH)_2$	1.06	9.40	6.93	0.737
$Sr_{10}(PO_4)_6(OH)_2$	1.27	9.74	7.20	0.739
$Pb_{10}(PO_4)_6(OH)_2$	1.32	9.88	7.32	0.741
$Ba_{10}(PO_4)_6(OH)_2$	1.43	10.19	7.70	0.756

K 41

Klement, R., Versuche über Isomorphie in der Wagneritgruppe: Naturw., Berlin, Jahrg. 29, Heft 20, pp. 301-302, 1941.

Synthesis by fusion of $Mg_4(Si,P,S)_2O_8F_2$ is impossible; but mix-crystals may be made by substituting Li or Na for one Mg, S for one P; the powder diagrams still give a wagnerite pattern (rhombohedral (sic)). $Ca_4P_2O_8Cl_2$ is monoclinic, and is not isomorphous with wagnerite. It may be made by fusing $Ca_3P_2O_8$ with $CaCl_2$; the arsenic analog may be similarly synthesized ($Ca_4As_2O_8Cl_2$) and has essentially the same powder pattern. By heating $Ca_4P_2O_8Cl_2$ in steam at 900°C. for 4 hours, or with NaOH in a closed tube at 100°C. for 10 days, hydroxylapatite was synthesized. The author concludes that basic phosphates and arsenates tend to crystallize as apatites rather than as wagnerites.

KD 41

Klement, R., and Dihn, P., Isomorphe Apatitarten: Naturw., Berlin, Jahrg. 29, Heft 20, p. 301, 1941.

Synthetic ellestadite $Ca_{10}Si_3S_3O_{24}F_2$ has a = 9.54, c = 6.99, c:a = 0.732, d(calc) = 3.00, d(meas) = 3.06. Hydroxyl-ellestadite produced by treating ellestadite with steam at 1000°C. has similar lattice constants. Hydroxyl-ellestadite cannot be made directly by fusion. On heating, hydroxyl-ellestadite loses water and lime and goes over to a high-temperature sodium calcium phosphate structure. Fluorellestadite retains its apatite structure on heating. Synthetic sodium calcium sulfate apatite--$Na_6Ca_4(SO_4)_6F_2$--, though it might be expected to have a smaller structure than fluorapatite, actually has

a larger structure.

	a	c	c:a	d(calc)	d(meas)
$Na_6Ca_4(SO_4)_6F_2$	9.49	6.87	0.724	2.81	2.81
$Ca_{10}(PO_4)_6F_2$	9.36	6.88	0.732		

KD 42

Klement, R., and Dihn, P., Isomorphe Apatitarten: Zeitschr. Elektrochemie 48, pp. 334-336, 1942.

The authors synthesized apatite-type minerals with Si and S replacing P by fusing stoichiometric mixtures of the various materials. The products were X-rayed and the lattice constants calculated. (See table 1.) The various fluorine compounds were converted to hydroxyl compounds by treatment with steam at 1100°C. Most of the compounds tend to form the hydroxyl compound with the water vapor in the reaction mixture. Ellestadite must be treated with steam at 1100°C. to form the hydroxyl compound from the fluorine compound.

Table 1

Lattice constants, apatite material

	a	b	c:a	calc.	meas.
$Ca_{10}P_6O_{24}F_2$ apatite	9.36	6.88	0.732	-	-
$Ca_{10}SiP_4SO_{24}F_2$	9.45	6.96	0.736	3.09	3.13
$Ca_{10}SiP_4SO_{24}(OH)_2$	9.44	6.96	0.737	3.08	3.01
$Ca_{10}Si_2S_3O_{24}F_2$ ellestadite	9.54	6.99	0.732	3.00	3.06
$Ca_{10}Si_2S_3O_{24}(OH)_2$ hydroxyl-ellestadite	9.54	6.99	0.732	3.00	3.07
$Na_6Ca_4S_6O_{24}F_2$ NaCa-sulfapatite	9.49	6.87	0.724	2.81	2.81
$Na_2Ca_8P_4S_2O_{24}F_2$	9.52	6.90	0.725	2.98	2.97

The addition of Si and S to the lattice lowers the melting point and the stability of the compound.

When Si and S are substituted for P, there must be other substitutions to balance the valences of the formulas; when Na and S substitute for Ca and P, the lattice should shrink but there is a small increase in the a axis.

Table 2

Lattice constants, apatite material,
composition different from ideal formula

	a	b	c:a	calc.	meas.
$Ca_{10}P_6O_{24}F_2$ apatite	9.36	6.88	0.732	3.19	3.2
$Ca_{10.5}SiP_5O_{24}F_2$	9.35	6.79	0.726	3.29	3.2
$Ca_{9.5}P_5SO_{24}F_2$	9.46	6.91	0.731	3.05	3.08
$Ca_{10.5}Si_2P_3SO_{24}F_2$	9.40	6.81	0.724	3.23	3.20
$Ca_{9.5}SiP_3S_2O_{24}F_2$	9.46	6.91	0.731	3.04	3.10
$Na_2Ca_9SiP_4SO_{24}F_2$	9.39	6.89	0.734	3.24	3.10

Minerals with a disordered apatite structure were synthesized by fusion of the appropriate components. X-ray examination of the products indicated that the material had lattice constants similar to those of apatite. (See table 2.) Structures with 11 and with 9 metal ions were synthesized.

Phosphorus can be replaced in the apatite lattice partly or wholly by S and/or Si without changing the lattice type; however, the metal ion must be balanced according to the charges. Therefore, the synthesis of a Na-Ca-sulfapatite is possible. The corresponding

hydroxylapatites can be prepared with the exception of the above-mentioned Na-Ca-sulfapatite.

The apatite lattice can also in certain circumstances show disorders, with excess or lack of metal ions.

T. B.

KHK 42

Klement, R., Hüter, F., and Köhrer, K., Bildet sich Carbonatapatit in Wasserigen Systemen: Zeitschr. Elektrochemie, Band 48, nr. 6, pp. 334-336, 1942.

The authors discuss the work of previous investigators and the role of the CO_3 ion in the apatite structure. Natural apatites may contain up to 10 percent CO_2, bones and teeth have less. The authors feel that C cannot substitute for P as suggested by McConnell because this substitution implies an unknown coordination (4) for carbon.

The authors precipitated calcium phosphate in the presence of sodium bicarbonate and analyzed their results. From the lack of a stoichiometric ratio of $CaCO_3$ to P_2O_5 and the direct correspondence of the amount of CO_2 in the precipitate with the amount of $NaHCO_3$ added, they conclude that carbonate apatite does not form in this manner.

They X-rayed the various precipitates and, by comparison of the reflection angles of various lines, concluded that the apatite lattice had not been changed and therefore that no carbonate had been added to the lattice. Tables of analyses and X-ray angles are given.

T. B.

KT 32

Korber, F., and Tromel, H., Untersuchungen über Kalk-Phosphorsäure und Kalk-Phosphorsäure-Kieselsäure Verbindungen: Zeitschr. Elektrochemie 38, 8a, pp. 578-582, 1932.

The authors criticize the oxyapatite concept on the ground that only one F position would be occupied; they suggest that both F positions may be taken by O, and the valence balanced by substitution of rare earths for calcium. Such a product may be made by fusion and may give an apatite pattern with intensities differing slightly from a normal apatite pattern. No other data on this synthesis are given. A melt of $Ca_3(PO_4)_2$ and $Ca_4P_2O_9$ at about 1100°C. gives an apatite pattern; the product of this is hydroxylapatite made by reaction with the humidity of the air. Hydroxylapatite was also made by mixing Na_3PO_4 + $Ca(NO_3)_2$ with excess NH_4OH. This hydroxylapatite contained adsorbed PO_4 which gave it a $CaO:P_2O_5$ ratio smaller than the ratio characteristic of pure hydroxylapatite. The authors present the same objections to the carbonate-apatite concept as to oxyapatite.

L 35

Larson, H. W. E., Preparation and properties of mono-, di-, and tricalcium phosphates: Ind. and Eng. Chemistry, Anal. Ed., 7, no. 6, pp. 401-406, 1935.

Monocalcium phosphate monohydrate ($CaH_4(PO_4)_2 \cdot H_2O$) was prepared from a 5:1 = P_2O_5:CaO mixture (as $Ca(OH)_2$ and H_3PO_4 solutions). The solutions were evaporated slowly and the supernatant liquid decanted; the crystals were filtered, then washed with alcohol and ether. The yield was 66 percent of the theoretical yield. The CaO and P_2O_5 content

of the crystals was within 0.5 percent of that required by the formula. The crystals were white, rhomboidal, and finely twinned; petrographic study showed that they were optically (-), 2V = 70°, and had the following refractive indices by sodium light: nG = 1.5292, nM = 1.5176, nP = 1.4392. Optical and X-ray study showed that the crystals were triclinic. When the crystals were heated at 100°C. for a long time, they lost 1 mol H_2O; heating at 200-205°C. for 10 weeks caused a loss of 2.5 mols H_2O, which the author accounts for by the following reaction:

$$2CaH_4(PO_4)_2 \cdot H_2O \longrightarrow Ca_2P_2O_7 + 2HPO_3 + 5H_2O$$

Other dissociations take place under varying temperature conditions. Solubility data for this salt in CO_2-free and CO_2-saturated water are given.

Dicalcium phosphate tetrahydrate ($CaHPO_4 \cdot 4H_2O$) was prepared by recrystallizing commercial dicalcium phosphate. Analysis for CaO and P_2O_5 checked within 0.5 percent of the amount required by the formula. The crystals were pale-yellow rhomboidal plates, monoclinic, optically (-), with refractive indices by sodium light nG = 1.5516, nM = 1.5457, nP = 1.5394. One mol H_2O was lost at 108°C., one more at 150°, and two more from 150° to 185°. Solubility data are given for this salt in CO_2-free and CO_2-saturated water.

Tricalcium phosphate monohydrate ($Ca_3(PO_4)_2 \cdot H_2O$) was prepared from solutions of $Na_2HPO_4 \cdot 12H_2O$ and $CaCl_2$, mixed with constant stirring over 48 hours at 65-70°C.; pH was kept between 7 and 8 by addition of dilute NH_4OH. The precipitate was filtered, washed free of chlorides with a small amount of water, air-dried, and ground. CaO and P_2O_5 were within 0.5 percent of the amount required by the formula. The crystals were too small for petrographic study; X-ray diffraction patterns of the

freshly prepared salt and of the salt heated at 950-970°C. showed that the lines of the heated salt were closer together and more prominent than those of the freshly prepared salt; both patterns differed from those of oxy- and hydroxylapatite. The crystals lost very little water on heating between 65 and 100°C.; heating between 950° and 970°C. drove off one molecule of water. Solubility data for this salt in CO_2-free and CO_2-saturated water are given.

LTW 29

Lorah, J. R., Tarter, H. V., Wood, L., A basic phosphate of calcium and strontium and the absorption of calcium phosphate by tricalcium phosphate: Am. Chem. Soc., Jour. 51, pp. 1097-1106, 1929.

Tricalcium phosphate was prepared from $CaH_4(PO_4)_2 \cdot H_2O$ by adding carbonate-free ammonia until the solution was alkaline; the precipitate was washed with water.

Tricalcium phosphate prepared in this way contained small amounts of a more basic phase. Tristrontium phosphate was prepared in the same way. Tribarium phosphate was prepared by dropping $BaCl_2$ into a solution of Na_2HPO_4, and alkalizing with carbonate-free NaOH.

Hydrolysis: the hydrolysis of $Ca_3(PO_4)_2$ in water or 0.5 or 0.05 M NaOH produced hydroxylapatite after several days of carbonate-free boiling with removal of supernatant liquid. A similar but slower reaction occurred with $Sr_3(PO_4)_2$.

Ba or $CaCl_2$ + Na_2HPO_4 + H_2O + NaOH produced apatite plus tribarium or tricalcium phosphate.

Adsorption: Apatite prepared by hydrolysis of $Ca_3(PO_4)_2$ was placed

in contact with $Ca(OH)_2$ solution for 3 days to 6 months; it showed a normal adsorption curve, except that after 6 months it showed greater-than-usual adsorption. The authors suggest that this may be due either to slow penetration of $Ca(OH)_2$ into the interstices of colloidal apatite, or to solid solution (agreeing with Bassett, Cameron, and Bell).

Adsorption experiments with $Ca_3(PO_4)_2$ were limited to 16 hours, to prevent formation of apatite. The adsorption curve was normal and stronger than that of the more basic salt. The authors conclude that equilibrium between the two "basic" phosphates is on the acid side of neutrality.

M 41

Minguzzi, Carlo, Apatiti sintetiche con cromo trivalente ed esavalente: Periodico Miner. anno 12, no. 3, pp. 343-378, 1941.

I. History of the study of substitutions in the apatite group. Borgstrom (1931) found a complete series from chlorapatite to $3Ca_3(PO_4)_2 \cdot NaCl$ with 2.91 percent Na_2O (by synthesis from $Ca_3(PO_4)_2 + CaCl_2 + NaCl$).

Larsen and Shannon (1931) found 4.34-7.11 percent Na_2O in lewistonite, dehrnite, (crandallite?).

K substitution is possible only in very small amounts.

Substitution of rare earths is possible, and occurs in natural apatites up to 5 percent.

MgO substitution is possible in limited quantities, probably around 2 percent.

There may be complete substitution of SrO; there is more SrO in pegmatitic than in magmatic apatites.

Substitution of BaO is possible; its limits are unknown.

There is probably very limited solid solution of apatite and pyromorphite.

There is more MnO in pegmatitic than in magmatic apatites. Its oxidation state in apatite is uncertain.

Fe and Al may substitute in very small quantities.

Cd, Be, St, are present in spectrographically perceptible amounts in natural apatites.

The substitution of CO_3 in apatites is under as yet unresolved discussion.

The substitution of V and of As is possible, as is that of S and Si. SO_3 may substitute in small quantities.

In britholite, Ce and Si substitute for Ca and P. MO_4 and WO_4 may substitute in mimetite, vanadinite, and pyromorphite; their substitution in apatite may therefore be possible. F and Cl can substitute freely for each other; traces of Br and I have also been found.

OH is a well-established substitution; the possible substitution of O is under discussion.

The possibility of substituting Cr_2O_3, CrO_3, or both, has been described in natural apatites and demonstrated for synthetic mimetite, vanadinite, and pyromorphite.

II. Synthesis

In the first four syntheses, simple chromo-chlorapatites crystallized at the top of the melt as long fragile needles, at the bottom as

shorter prisms with bipyramids; maximum length of needles was 2 cm. The crystals are green, the color intensifying to blue green with increase in chromium; the deepest-colored crystals have a very slight biaxial character. Pleochroism of chromo-chlorapatites is E = clear yellow green, O = deep blue. The trivalent chromium in the apatites was formed by reduction of hexavalent chromium by HCl from the combination of $CaCl_2$ with absorbed water. It was not possible, even in the presence of NH_4NO_3, to form crystals free of Cr^{+++}. Procedure of crystallization in all cases was to fuse reagents for 6 hours at 1100°C., cool slowly, and wash with water and dilute acetic acid, in which excess of reagents dissolved. In an attempt to form crystals containing only Cr^{+++} a mixture of 18 g $CaCl_2$, 8 g $Ca_3(PO_4)_2$, and 1 g $CrPO_4$ was fused; this produced some colorless, transparent crystals with 0.06 percent Cr^{+++}, indices by red light nO = 1.670, nE = 1.669, by yellow light nO = 1.667, nE = 1.666, by green light nO = 1.653, nE = 1.651; some very fine green crystals were also formed, due to partial oxidation of trivalent chromium. A complete analysis of the crystals formed in experiment III led to the formula

$$Ca_{10}(P,Cr^{+3},Cr^{+6})_6O_{24}Cl_2.$$

Unit-cell dimensions calculated from powder patterns of products of experiment IV are: c = 6.73, a = 9.56, c:a = 0.704. Calculated from this cell and from the molecular weight derived from the analysis of the product of experiment III is the specific gravity 3.22; the measured specific gravity is 3.21.

The soda-chromo-chlorapatites resembled the chromo-chlor-apatites except for being a little more yellow green. Chemical analysis of them showed an excess of Ca over the theoretical formula. Substitution of Cr in apatites might be accounted for by: $3P^{+5} = 2Cr^{+6} + Cr^{+3}$; this is not borne out by the variable $Cr^{+3}:Cr^{+6}$ ratios obtained. The author suggests that, where $Cr^{+6}:Cr^{+3}$ is greater than 2:1, some oxyapatite forms to compensate the excessive charges.

Experiment number	Reagents (grams)				Cr^{+3} %	Cr^{+6} %	Red light		Yellow light		Green light		Na light	
	$CaCl_2$	$Ca_3(PO_4)_2$	$CaCrO_4$	Na_2CrO_4			nO	nE	nO	nE	nO	nE	nO	nE
Chlorapatite	---	---	---	---	---	---	1.670	---	1.667	---	1.653	---	---	---
	27	12	1	---	0.20	0.18	1.672	1.670	1.668	1.666	1.655	1.652	---	---
I	27	12	3	---	0.14	0.66	1.683	1.681	1.676	1.674	1.665	1.663	---	---
II	27	10	5	---	0.51	0.96	1.688	1.686	1.682	1.680	1.670	1.668	---	---
V	27	7	5	---	0.14	2.92	---	---	1.710	1.707	---	---	---	---
VIII	27	9	---	3	0.54	2.20	---	---	---	---	---	---	1.693	1.690
X	27	6	---	6	0.30	2.84	---	---	---	---	---	---	1.701	1.698

M 47

Müller, Marcel, Die Fällung und die röntgenographische Untersuchung des Mischkristallsystems $Ca_{10}(PO_4)_6(OH)_2$ -- $Pb_{10}(PO_4)_6(OH)_2$: Helv. Chim. Acta, vol. 30, fasc. 7, pp. 2069-2080, 1947.

A series of hydroxylapatites ranging in composition from 100 percent $Ca_{10}(PO_4)_6(OH)_2$ to 100 percent $Pb_{10}(PO_4)_6(OH)_2$ was synthesized by precipitation followed by hydrolysis according to the method described below.

Ca or Pb nitrates (or a mixture of the two), KH_2PO_4, and 0.1 normal NaOH(CO_2-free) were dropped together from 3 burettes in stoichiometric proportions, and reacted in this way:

$$10MeX_2 + 6\ KH_2PO_4 + 2HOH \rightleftharpoons 3Me_3(PO_4)_2 \cdot Me(OH)_2 + 6KX + 14HX,$$

where Me is a divalent metal and X is a monovalent anion.

100 cm^3 of KH_2PO_4 solution were dropped into one liter of boiling water containing 10 cm^3 of bromo-cresol purple (0.1%). This excess of phosphate was added first so that $Pb(OH)_2$ would not precipitate. Then 0.5 cm^3 of Ca or Pb solutions (or mixture) and more KH_2PO_4 were added, and the solution neutralized with NaOH to red violet (pH about 6.5). After stirring for one minute, the solution was again neutralized. This process was repeated until the desired amounts of Me^{++} and PO_4 ions were in solution. The volume of the solution was kept at one liter by addition of distilled water. Precipitates were filtered out, hydrolyzed for 15 hours in one liter of boiling water, filtered out, and dried at 110°C. CO_2-free water was used throughout.

The products of these syntheses were analyzed for Ca, Pb, and PO_4. X-ray diffraction patterns show a progressive change in spacings from

100 percent Ca to 100 percent Pb, proving that actual mix-crystals were formed. Crystal size was improved by heating the products at 600°C. for 4 hours, and cooling quickly. Spacings of crystallographic planes were calculated for the pure end members, and for $Ca_5Pb_5(PO_4)_6(OH)_2$, as well as the following lattice dimensions.

	$\lim_{\theta \to 90} \lambda^2/\alpha^2$	a	c
$Ca_{10}(PO_4)_6(OH)_2$	2.680	9.40	6.92
$Ca_5Pb_5(PO_4)_6(OH)_2$	2.650	9.62	7.08
$Pb_{10}(PO_4)_6(OH)_2$	2.425	9.89	7.28

In general, the lines on the X-ray diffraction patterns broaden as the reflection angle increases. In the series from $Pb_5Ca_5(PO_4)_6(OH)_2$ to $Pb_{10}(PO_4)_6(OH)_2$, the splitting of the K_α doublet can be seen with difficulty, but from $Ca_7Pb_3(PO_4)_6(OH)_2$ to $Ca_{10}(PO_4)_6(OH)_2$ it disappears completely. In the last instance, the broadening of lines with increasing reflection angles is so great that only lines with reflection angles of 25°-33° can be measured, whereas in the series $Ca_5Pb_5(PO_4)_6(OH)_2$ to $Pb_{10}(PO_4)_6(OH)_2$, the lines with reflection angles greater than 41° can be measured precisely. This broadening may be caused by the variation in lattice constants owing to inhomogeneity in the chemical composition of these apatites. It is possible that homogeneous single layers of different composition may precipitate one above the other, or that a single mix-crystal may have some such inhomogeneity as a zonal structure. As this broadening of the lines is apparent to the same extent in the pure end-members as it is in the intermediate members of this series, the broadening may be explained

by variation of lattice constants owing to defective structure in microcrystals, and especially by the very small size of the individual crystallites. The d spacings of the same lines decrease with increasing Pb.

NNMM 49

Neuman, W. F., Neuman, M. W., Main, E. R., and Mulryan, B. J., The deposition of uranium in bone. IV. Adsorption studies in vitro: Jour. Biol. Chemistry 179, pp. 325-334, 1949.

The first three papers of this series are concerned with in vivo studies of uranium metabolism in rats.

Adsorption studies described in this paper were carried out on bone ash, prepared from the shafts of long bones (of rabbits) boiled in a three percent solution of KOH in ethylene glycol, and on fresh bone, ground and dried to constant weight. Particle size had no perceptible effect on the adsorptive capacity of fresh bone or bone ash. The fluid medium was 0.025 M $NaHCO_3$; its pH remained between 7.2 and 7.3 throughout the experiments. The solutions were prepared by diluting aliquots of a saturated stock solution of U containing equimolar amounts of $UO_2(CH_3COO)_2$ and sodium acetate with a concentrated solution of $NaHCO_3$. The final solutions were equilibrated at atmospheric pressure with a mixture of 5 percent CO_2, 95 percent O_2; one ml of solution was added to 2 mg of bone ash, reequilibrated with the CO_2-O_2 mixture, and shaken for 48 hours to equilibrium. The solutions were then analyzed for U, Ca, and P. The initial U concentration was varied from 5 to 1500 γ per ml. See figure 1.

Eighty to 400 γ per ml of uranyl acetate were added to uranium-free solutions saturated with bone ash. Precipitation was erratic; the solutions were therefore salted out with NaCl. The precipitates thus obtained had a molecular ratio of U:P = 1:1. Assuming 3 molecules of water per molecule of U, their composition corresponded to a mixture of $Na(UO_2)(PO_4)$, $Ca(UO_2)_2(PO_4)_2$, $Mg(UO_2)_2(PO_4)_2$ in the molecular ratio 23:2.7:1.

Synthetic bone ash solutions were prepared using 6γ/ml each of $CaCl_2$ and $NaHPO_4$ in 0.025 M $NaHCO_3$. 80 to 400γU/ml were added to this solution. The solutions were equilibrated as before with the CO_2-O_2 mixture, centrifuged after standing, and the supernatant liquid analyzed. U remained soluble up to 80 γ/ml, but exchanged for Ca; from 80 to about 450 γ/ml, uranyl phosphate precipitated on bone. Above 450 γ, both the U and P present in solution show an apparent increase, probably due to the formation of colloidal uranyl phosphates.

All the processes described above are shown to be reversible. It is shown that fresh bone has less adsorptive capacity than bone ash.

Below 80 γ/ml, U remains soluble under the conditions described above; however, the U content of bone increases. As the amount of U fixed by bone depends on the relative amounts of the phases present, a surface-limited reaction is suggested. Particle size does not affect the adsorptive capacity of bone, because the surface of bone ash is not a function of particle size. A plot of U initially in solution against U finally present in bone ash suggests a dissociation reaction. The uranyl group, therefore, probably replaces Ca, and is bound by phosphate, the only group present on the surface in large enough concentration.

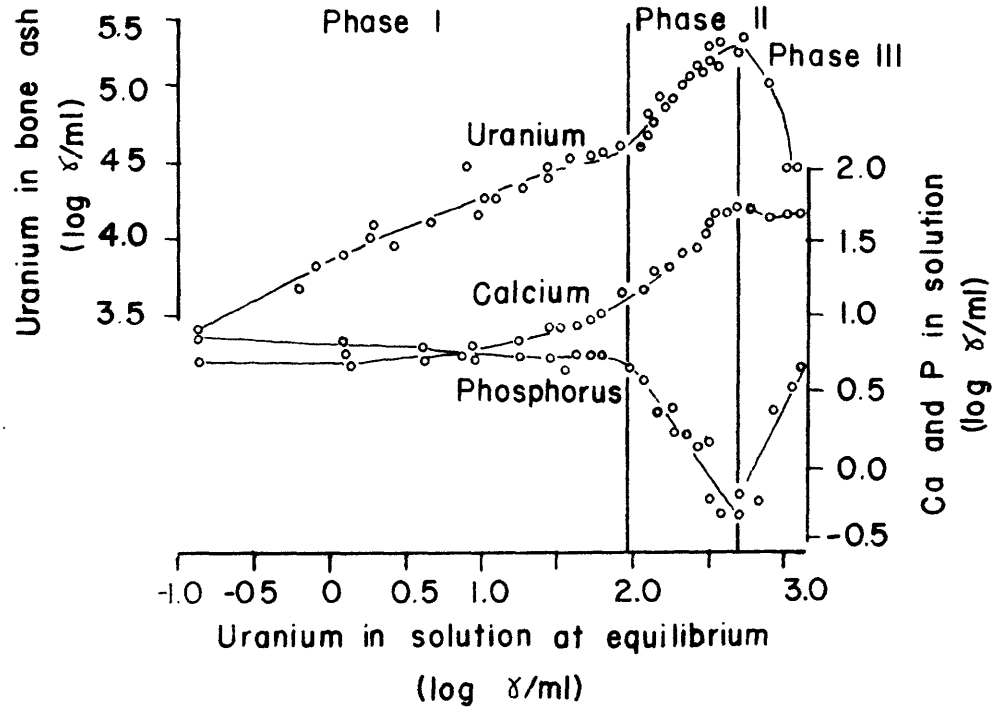


Fig. I. The adsorption of uranium on bone ash

(Neuman, Neuman, Main and Mulryan, 1949, p. 32

NNMM 49

Neuman, W. F., Neuman, M. W., Main, E. R., and Mulryan, B. J., The deposition of uranium in bone. V. Ion exchange studies: Jour. Biol. Chemistry 179, pp. 335-340, 1949.

The bone used in these experiments consisted of: bone ash, boiled in alkaline glycol; fresh bone dried and ground; and glycol ash heated in a muffle furnace at 400°C. for 6 hours and at 700°C. for 6 hours. Solutions were prepared as described in the preceding article. Exchange capacity of bone relative to Ca and P was studied by means of P^{32} and Ca^{45}. Bone ash prepared by boiling in alkaline glycol showed a greater exchange and adsorption capacity than fresh bone, but glycol ash heated in a muffle furnace had practically no exchange or adsorption capacity. Saturating glycol-ashed bone with U reduced its capacity to exchange Ca and P; the adsorption of 1 mol of U reduced exchangeable Ca and P each by 2 mols.

About twice as much Ca as P is exchangeable, indicating a surface concentration of Ca in bone. Non-phosphate anions must therefore be associated with surface Ca. (Heating bone ash at a high temperature may convert it to a different structure, and thus inhibit or prevent adsorption by exchange of Ca. EBJ)

NNMM 49

Neuman, W. F., Neuman, M. W., Main, E. R., and Mulryan, B. J., The deposition of uranium in bone. VI. Ion competition studies: Jour. Biol. Chemistry 179, pp. 341-348, 1949.

Bone ash prepared by heating in alkaline glycol at 200°C. was used for these experiments. Using 87 γU/ml and increasing concentrations of $NaHCO_3$, the capacity of bone ash to adsorb U fell off with

increasing pH. Using 45 γ U/ml and an 0.025 M solution of $NaHCO_3$, concentrations of $CaCl_2$ or $NaHPO_4$ were varied. Excess Ca reduced the concentration of P in solution and the adsorption of U. The concentrations of Ca and P in solution showed an inverse relationship. At pH 8, addition of U to the system increased the Ca in solution but did not decrease P; therefore at pH 7.3 the effect of varying Ca:P ratios on U adsorption are due to variations in the Ca ion. Variations in the P ion may be due to the limited solubility of some compound of Ca and P. There is a linear relationship between Ca and U present in solution at equilibrium, and an inverse relationship between Ca in solution and U in bone; these facts show that there is direct competition between Ca and U for the surface phosphate groups of bone.

A discussion of uranium metabolism follows.

Uranium might be fixed in the skeleton in three different ways: by binding with protein carboxyl groups, with carbonate groups, or with phosphate groups. There are too few protein carboxyl groups in bone to account for its adsorptive capacity relative to U; these groups are not present in bone ash, which shows a higher adsorptive capacity than fresh bone; protein-bound U is highly dissociated. There are likewise too few carbonate groups in bone; the complexes UO_2-O-CO-R are too highly dissociated; although the groups $UO_2(CO_3)_2^{=}$ and $UO_2(CO_3)_3^{\equiv}$ form in solutions with excess carbonate or bicarbonate, they are too large for the apatite lattice. There is a good correlation between exchangeable phosphate groups

and their affinity for U. Uranyl pyrophosphate is only slightly dissociated. As one mol U inactivates two phosphate groups, it is possible that U combines with two adjacent PO_4 groups to form a structure similar to uranyl pyrophosphate. The maximum capacity of uranium adsorption by bone is equivalent to 40 percent of the surface PO_4 groups. There is direct competition of Ca and U for these positions. At high $NaHCO_3$ concentrations, both the bicarbonate and PO_4 groups compete for U. At a high pH, OH and PO_4 groups compete for U.

P 32

Pallu, R., Étude du système H_3PO_4--$Ca(OH)_2$--CO_2--H_2O: Comptes rendus 194, no. 5, pp. 458-461, 1932.

The author plotted a curve of conductivity against composition in the system H_3PO_4--$Ca(OH)_2$--CO_2--H_2O. He obtained the curve by measuring the conductivity at equilibrium at 15° of a series of mixtures of $CaCO_3$ in an 0.5 N solution of H_3PO_4, bubbling CO_2 through the solution until equilibrium was reached. The curve had a single break at the mixture 0.587 P_2O_5, 0.464 CaO, where the solid phase had the composition $CaHPO_4 \cdot 2H_2O$. In more basic mixtures, $CaCO_3$ also precipitated out. In the absence of CO_2, mixtures of 0.5 N H_3PO_4 with 0.5 N $Ca(OH)_2$ in various proportions showed a break in the curve at the composition $CaHPO_4 \cdot 2H_2O$, at the composition P_2O_5/CaO = 0.30-0.28 (for the liquid phase). The precipitate at this second break was colloidal, and the result is therefore uncertain. The author suggests that the rise of conductivity at the basic end may imply that either a more basic phase than $Ca_3(PO_4)_2$ has formed, or that excess CaO has been absorbed by $Ca_3(PO_4)_2$.

P 47

Pieruccini, R., Sulla possibilita di introdurre alluminio, ferro, piombo o molibdeno nel reticolo delle apatiti: Soc. toscana sci. nat. Atti 54, pp. 256-67, 1947.

The author discusses the various substitutions reported to take place in apatites and apatite-like minerals. The possibility of introducing Al, Fe, Pb, and Mo into the apatite lattice was investigated; these elements were expected to substitute only in small quantities.

The minerals were synthesized in all cases by fusion of salts at high temperatures and checked by measuring the refractive indices of the resulting material. In all cases small crystals were formed.

Aluminian apatite was synthesized with 1.88 percent Al_2O_3;1/ its composition was checked by chemical analysis: CaO = 53.70 percent, Al_2O_3 = 1.88, P_2O_5 = 39.73, Cl = 5.76, H_2O = 0.33, total = 101.40, less (O for Cl_2 = 1.30) = 100.10. nO_{Na} = 1.6681, nE_{Na} = 1.6643, nO_{Na}-nE_{Na} = 0.0038. Maximum amount of Al_2O_3 is probably 2 percent.

Iron-bearing apatite was synthesized in a closed metal tube.2/ The product obtained was never homogeneous; some of the crystals were clear; some were violet colored. With slow cooling magnetite was formed. The uncolored crystals had nO_{Na} = 1.6720, 1.6745; uniformly colored areas of violet crystals gave nO_{Na} = 1.6745, 1.6736, 1.6738, nE_{Na} = 1.6711, 1.6704, 1.6705. Fe_2O_3 determined by visual spectrograph was

---

1/ By fusing a mixture of aluminum phosphate, calcium phosphate, and calcium chloride at 1100° for one hour and cooling slowly.

2/ By fusing mixtures of iron phosphate, calcium phosphate, and calcium chloride for 45 minutes to 6 hours and cooling slowly.

0.03 - 0.05 percent; violet crystals contained about 2 percent Fe_2O_3.

As Ca substitutes for Pb in some minerals, a mixture of Pb phosphate, Ca phosphate, and Ca chloride was fused at 1100°C. for one hour and treated to remove other products. Elongate crystals gave nO = 1.6693. Other mixtures containing lead were fused and indices measured. Elongate crystals contained 0.07 percent PbO.

An attempt was made to synthesize Mo apatite. Calcium molybdate was one of the fusion products; some apatite with 0.01 percent MoO_3 determined spectrographically, and nO = 1.6640, nE = 1.6615, was obtained by fusing calcium phosphate, calcium chloride, and calcium molybdate.

T. B.

R 41

Rivière, André, Recherches expérimentales sur la sédimentation phosphatée en milieu marin: Comptes rendus, vol. 212, pp. 1038-1041, 1941.

$(NH_4)_3PO_4$ liberated from decayed organic matter can coprecipitate with carbonates as calcium diphosphate and ammonium magnesium phosphates; this can happen only in concentrated solutions and with a pH of about 6. The first precipitate is rich in ammonium magnesium phosphate. In the presence of $CaCO_3$ this salt produces phospho-carbonates in equilibrium with mono- and di-phosphates in solution, the relative amounts depending on the pH. Precipitation is almost complete at pH 8 (normal alkalinity of seawater). The solubility of $Ca_3(PO_4)_2$ is also linked to the pH. This salt dissolves mostly as dicalcium phosphate.

The following experiments were performed at atmospheric pressure and room temperature.

1) Seawater was shaken for several hours with excess dicalcium phosphate, then filtered; the pH fell from 7.7 to 7.4, the P_2O_5 in solution increased sharply. The dicalcium phosphate substitutes for the bicarbonates normally present in seawater, whereas the CO_2 thus liberated lowers the pH. No dicalcium phosphate can precipitate in seawater unless more than 1000 times the normal concentration is present.

2) The preceding experiment was carried out with CO_2 bubbling through the solution; the amount of phosphate in solution increased as the pH fell to 5.8.

3) Some of the solution from experiment 2 was filtered and freed of CO_2 by bubbling CO_2-free air through it; there was an abundant precipitate of calcium and magnesium diphosphate plus a small amount of carbonate (probably as a phosphocarbonate). The filtrate had a pH of 7.2. In such an environment, a rise of pH would cause precipitation of diphosphates, which would then convert to tricalcium phosphate by diagenesis.

4) Another part of the solution from experiment 2 was filtered and left in contact with excess $CaCO_3$ in a closed system. The pH rose to 6.2 without any perceptible change in the amount of P_2O_5 in solution. CO_2 was then eliminated as in experiment 3. After filtration, the solution had a pH of 7.32, and the phosphate in solution had diminished. The phosphate probably precipitated on the excess $CaCO_3$ as "tricalcium phosphocarbonate (dahllite)". Thus, phosphatic solutions can phosphatize $CaCO_3$ if the pH rises because of algal

activity or simple agitation. This replacement can take place with much less phosphate in solution than can simple precipitation.

Variations of pressure seem to have little influence on the reactions described above; variations in temperature affect the solubility of CO_2 and thus affect these reactions.

S 33

Sanfourche, A., Recherches sur l'acide phosphorique et les phosphates. I. La formation des phosphates alcalino-terreux basiques: Soc. chim. France Bull. 53, pp. 951-963, 1933.

Experiments were made with 0.1 N H_3PO_4, plus basic solutions of Ba, Sr, and Ca.

In the case of Ca, the author used a saturated solution at 20°C. (0.44 N) -- crystallization was much slower than with the Ba or Sr salt. The author postulates a series of more and more basic phosphates, tending towards $Ca_4P_2O_9$ (purely chemical study of precipitates-EBJ).

SH 33

Sanfourche, A., and Henry, J., Recherches sur l'acide phosphorique et les phosphates. V. Les réactions d'hydrolyse des phosphates dicalcique et tricalcique: Soc. chim. France Bull. 53, pp. 1210-1217, 1933.

The hydrolysis of brushite is questionable, because, according to these authors, it must be seeded with $Ca_3(PO_4)_2$. Once started, it proceeds until $Ca_3(PO_4)_2$ is present as a solid phase, and hydrolysis of this last ensues. For large quantities of brushite relative to water, equilibrium is rapidly attained. The discontinuity in the temperature curve at 75°C. means that the solid phase inverts here to

monetite. $Ca_3(PO_4)_2$ was prepared from $Ca(NO_3)_2$ and Na_2HPO_4 with excess of ammonia. During washing to remove ammonia, hydrolysis began, giving a more basic product. According to these authors, the normal products of this hydrolysis are apatite and brushite.

SSK 32

Schleede, A., Schmidt, W., and Kindt, H., Zur Kenntnis der Calciumphosphate und Apatite: Zeitschr. Elektrochemie, Band 38, Nr. 8a, 1932.

Experiments:

1) Brushite, hydrolyzed in warm water for 500 hours, gave a hydroxylapatite pattern.

2) Commercial triphosphate (sic) gave a hydroxylapatite pattern and, in one case, brushite lines, before hydrolysis; after hydrolysis it gave a hydroxylapatite pattern only.

3) Tetracalcium phosphate made by fusing a mixture of commercial triphosphate and CaO gave a pattern close to but not exactly like apatite. On heating, this gave apatite and CaO lines; on hydrolysis, it gave a simple apatite pattern.

4) Silicocalciumphosphate was made by fusing commercial triphosphate, CaO, and quartz. When this was hydrolyzed in cold water, the pattern changed only slightly. These authors believe that no real tricalcium phosphate exists. They synthesized hydroxylapatite from 30 g phosphate (tricalcium ? EBJ) and 500 cc KOH (.5 N) boiled for 67 hours in 12 days in CO_2 atmosphere; the product was decanted to neutrality with water, washed with ether and alcohol, dried in air; it gave an apatite pattern. This product was then dried at 1050°C. for analysis;

its $CaO:P_2O_5$ ratio was too low and water too high for apatite; when heated to fusion, the $CaO:P_2O_5$ ratio approached that of apatite, but water was lost gradually. At about 900°C. the amount of water and the $CaO:P_2O_5$ ratio corresponded to those of hydroxylapatite rather than to those of the oxyapatite which has been supposed by previous authors to exist at this temperature. These authors do not believe in the existence of carbonate- or sulfate-apatites, and are doubtful about chlorapatites. At temperatures above 1500°C., hydroxylapatite dissociates to a mixture of tricalcium and tetracalcium phosphate.

T 32

Tromel, Gerhard, Untersuchungen über die Bildung eines halogenfreien Apatits aus basischer Calciumphosphaten: Zeitschr. physikal. Chemie, Band 158, Abt. A, pp. 422-432, 1932.

Oxyapatite is not likely to exist, because it is at the eutectic $CaO \cdot P_2O_5$ and $4CaO \cdot P_2O_5$, and because of the substitution of 1 oxygen for 2 F. Nevertheless, an apatite does exist in the system $CaO-P_2O_5$ below 1400°C. When $4CaO \cdot P_2O_5$ was heated under a pressure of 0.3 - 0.5 mm Hg, no apatite formed; however, when this same compound was heated in air, hydroxylapatite formed. When it was heated in dry air or oxygen, no apatite formed. X-ray diffraction patterns suggest that $4CaO \cdot P_2O_5$ may have a deformed apatite structure.

Z 16

Zambonini, Ferrucio, Quelques observations sur la composition des apatites: Comptes rendus 162, pp. 919-921, 1916.

Fusion of $Ca_3(PO_4)_2$ and $CaCl_2$ produced a chlorapatite with very weak birefringence. Fusing $Ca_3(PO_4)_2$ with excess NaCl gave crystals with a birefringence of 0.0050-0.0058, averaging 0.0053, analysis of which gave the formula $4.34\ Ca_3(PO_4)_2 \cdot CaCl_2$ (but these crystals had 1.56 percent Na, 4.85 percent Cl). The author lists other apatite analyses leading to the formula $mCa_3(PO_4)_2 \cdot Ca[O,(OH)_2, F_2,Cl_2,CO_3]$ where m is greater than 3; but all these analyses show an excess of CaO.

Z 23

Zambonini, Ferrucio, Uber die Mischkristalle, welche die Verbindungen des Calciums, Strontiums, Bariums, und Bleis mit jenen der seltenen Erden bilden: Zeitschr. Kristallographie Band 58, pp. 226-292, 1923.

The author discusses histories of syntheses of various compounds, and substitutions of Ca, Sr, Ba, Pb, for some of the "rare earths"(sic).

Synthesis was attempted from the following mixtures with the results noted:

$BaCl_2 \cdot 2H_2O$ and $CeCl_3$ - successful

$Ca(NO_3)_2$ and $Y(NO_3)_3$ - mix with difficulty

$Sr(NO_3)_2$ and $Y(NO_3)_3$ - with difficulty

$PbSO_4$ and "Di_2"$(SO_4)_3$ - unsuccessful

$Ce_2(MoO_4)_3$ and $PbMoO_4$ - successful

$Ce_2(MoO_4)_3$ and $CaMoO_4$ - successful

$Ce_2(MoO_4)_3$ and $SrMoO_4$ - successful

$Nd_2(MoO_4)_3$ and $PbMoO_4$ - successful

$Pr_2(MoO_4)_3$ and $PbMoO_4$ - successful

"$Di_2^{II}(MoO_4)_3$ and $PbMoO_4$ - successful

$La_2(MoO_4)_3$ and $PbMoO_4$ - successful

$La_2(MoO_4)_3$ and $CaMoO_4$ - successful

$La_2(MoO_4)_3$ and $SrMoO_4$ - successful

$La_2(MoO_4)_3$ and $BaMoO_4$ - successful

$Y_2(MoO_4)_3$ and $PbMoO_4$ - successful

$Y_2(MoO_4)_3$ and $CaMoO_4$ - successful

$Y_2(MoO_4)_3$ and $CaMoO_4$ and $Ce_2(MoO_4)_3$ - successful

$Ce_2(WO_4)_3$ and $PbWO_4$ - successful

$Ce_2(WO_4)_3$ and $CaWO_4$ - successful

$CePO_4$ and $Pb_3(PO_4)_2$ - successful

Pure $Pb_3(PO_4)_2$ was opt. (-), had no anomalies; $(10\bar{1}0):(01\bar{1}0)$ had an average value of 60°1'; it was uniaxial and melted at 1015°C.

The maximum mixture contained 3-5 percent $CePO_4$ by weight: at 5 percent $CePO_4$, a eutectic occurred at 1008°C.

Mix-crystals with 2 percent $CePO_4$ resembled the pure $Pb_3(PO_4)_2$ crystals, but had a slightly lower nE, and higher birefringence; dispersion was anomalous in yellow and green.

Indices of refraction:	nO	nE	nO-nE
Pure $Pb_3(PO_4)_2$	1.9549-1.9994	1.9232-1.9618	0.0317-0.0376
Mix-crystals with 2 percent $CePO_4$	1.9587-1.9999	1.9227-1.9600	0.0360-0.0399

Cerium-bearing apatite

1.37 g $Ca_3(PO_4)_2$ and 3 g $CaCl_2$ were fused at 1150°C., washed with water after slow cooling; the crystals were 1.5 X 0.3 mm in size, colorless to greenish, opt. (-); they had a birefringence of 0.0008 (Na) and sp. gr. = 3.14. 4 g $Ca_3(PO_4)_2$ and 9 g $CaCl_2$ were heated 6 hours at 1100°C.; the crystals were 2.5 X 1.0 mm in size, colorless or sky blue; a:c was 1:0.7038; the birefringence was 0.0009-0.0006; crystals were zoned parallel and perpendicular to c; nO was 1.6642-1.6747.

2 g $Ca_3(PO_4)_2$ and excess NaCl were heated 5 hours at 900°C.; the birefringence was 0.0053 and analysis led to the formula 4.34 $Ca_3(PO_4)_2 \cdot CaCl_2$; the author suggests solid solution with $Ca_3(PO_4)_2$.

A mixture of $Ca_3(PO_4)_2$, $CePO_4$, and NaCl was heated for 5 hours but the product showed only traces of Ce; however, mixtures made with excess $CaCl_2$ instead of NaCl were successful.

1.37 g $Ca_3(PO_4)_2$ and 0.08 g $CePO_4$ and 3 g $CaCl_2$ were heated to 1150°C., cooled slowly, and washed with H_2O. This produced a mixture of chlorapatite with minor amounts of chlorspodiosite and monazite. The chlorapatite was uniaxial (-), birefringence = 0.0005, sp. gr. = 3.165, waterclear, homogeneous, and contained 1 percent $CePO_4$. Mixing 5.48 g $Ca_3(PO_4)_2$, 0.8 g $CePO_4$ and 12 g $CaCl_2$ and heating to 1200°C. gave a colorless chlorapatite with a birefringence of 0.001 containing 1.6 percent $CePO_4$.

A mixture of 1.37 g $Ca_3(PO_4)_2$, 0.49 g $CePO_4$, and 3 g $CaCl_2$ heated to 1400°C. produced a mixture of violet needles and short crystals;

the birefringence was 0.001, and $n0_{Na}$ = 1.6672. The crystals richest in $CePO_4$ had a sp. gr. of 3.166--all the above products had, in addition, crystalline $CePO_4$. A mixture of 3 g $Ca_3(PO_4)_2$ and 2 g $CePO_4$ and 6 g $CaCl_2$ heated for 6 hours at 1100°C. produced small colorless apatite crystals, birefringence = 0.004, $n0_{Na}$=1.6703, sp. gr. = 3.3-3.18, and containing 8 percent $CePO_4$.

A mixture of 2 g $CePO_4$ and 3 g $Ca_3(PO_4)_2$ and 6 g $CaCl_2$ heated at 1100°C. for 24 hours produced colorless apatite crystals with n0 = 1.666-1.673, nE = 1.665-1.672, and 13 percent $CePO_4$. Apatites containing 8 percent and 13 percent $CePO_4$ turn yellow on heating.

"Didymium"-bearing chlorapatite and chlorspodiosite

1.37 g $Ca_3(PO_4)_2$, 0.1 g "Di"PO_4, and 3 g $CaCl_2$ heated to 1180°C. produced a mixture of chlorapatite and chlorspodiosite. The apatite was transparent, colorless, sp. gr. = 3.135-3.170, contained 3 percent "Di"PO_4, and had the same optics as the pure synthetic chlorapatite.

1.37 g $Ca_3(PO_4)_2$, 0.2 g "Di"PO_4 and 12 g $CaCl_2$ heated to 1000°C. produced pale-violet crystals of chlorspodiosite.

3 g $Ca_3(PO_4)_2$, 2 g "Di"PO_4, and 6 g $CaCl_2$ heated 6 hours at 1100°C. gave "Di"PO_4, a little chlorapatite, and chlorspodiosite with 9 percent "Di"PO_4.

Yttrium-bearing chlorapatite

3 g $Ca_3(PO_4)_2$, 0.7 g YPO_4, and 6 g $CaCl_2$ heated for 15 hours at 1100°C. after washing with water produced chlorapatites with n0 = 1.669 (therefore yttrium-bearing), and yellowish crystals (not investigated) with 6.3 percent YPO_4.

Theoretical discussion

When absolute differences in molecular volume are considered, most of these isomorphous substitutions are not permissible, but when the difference in molecular volume is taken relative to the smallest molecular volume in question, this relative difference does not exceed that in certain natural series. This difference can further be reduced by considering the compound of smallest molecular volume as a double or triple salt--e.g. $CaCl_2$--$(LiCl)_2$; $(SnS)_3$--Sb_2S_3.

The change in interfacial angles is not a straightline function of percent substitution.

SECRET

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D. C.

DEC 27 1950

[illegible] OF 1 [illegible] PAGE(S)
NO. 48 OF 55 COPIES, SERIES A

AEC-330/1

Dr. Phillip L. Merritt, Assistant Manager
Raw Material Operations
U. S. Atomic Energy Commission
P. O. Box 30, Ansonia Station
New York 23, New York

Dear Phil:

Transmitted herewith for your information and distribution are copies 3 through 10 of Trace Elements Investigations Report 132, Part II, "Abstracts of the literature on synthesis of apatites and some related phosphates, Part II," by Elizabeth B. Jaffe, December 1950.

This part of the report is being issued separately because it deals with classified material.

Other copies are being distributed as shown on the attached distribution sheet.

Sincerely yours,

/s/ W. H. Bradley

W. H. Bradley
Chief Geologist

When separated from enclosures, handle this document

as unclassified
(Insert proper classification)

SECRET

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

ABSTRACTS OF THE LITERATURE

ON

SYNTHESIS OF APATITES AND SOME RELATED PHOSPHATES

PART II

by

Elizabeth B. Jaffe

December 1950

Trace Elements Investigations Report 132, Part II

USGS-TEI Rept. 132, Part II
Consisting of 10 pages
Copy No. 48 of 52 copies
Series A
Issued to (see below)

The distribution (Series A) of this report is as follows:

Copies 1 and 2 ..... AEC, Washington (J. C. Johnson)
Copies 3 - 10 ..... AEC, New York (P. L. Merritt)
Copy 11 ..... AEC, Washington (J. O. Hosted)
Copy 12 ..... AEC, Washington (E. F. Wilson)
Copy 13 ..... AEC, Washington (F. W. McQuiston)
Copy 14 ..... AEC, Denver (C. C. Towle, Jr.)
Copy 15 ..... AEC, Spokane (E. E. Thurlow)
Copy 16 ..... AEC, Grand Junction (T. W. Oster)
Copy 17 ..... IMC, Mulberry, Fla. (I. M. LeBaron)
Copy 18 ..... Dow Chemical Co., Pittsburg, Calif. (G. L. Allen)
Copy 19 ..... MIT, Watertown, Mass. (John Dasher)
Copy 20 ..... ORNL, Y-12, Oak Ridge (Glenn Clewett)
Copy 21 ..... USGS, Washington (Mineral Deposits Branch)
Copy 22 ..... USGS, Washington (Fuels Branch)
Copy 23 ..... USGS, Washington (Alaska Branch)
Copies 24 - 45 ..... USGS, Washington (Geochemistry and Petrology Branch)
Copy 46 ..... USGS, Plant City, Fla. (J. B. Cathcart)
Copy 47 ..... USGS, Grand Junction (R. P. Fischer)
Copy 48 ..... USGS, Denver (L. R. Page)
Copy 49 ..... USGS, Spokane (A. E. Weissenborn)
Copies 50 - 52 ..... USGS, Washington (TEPCO)
(including master copy)

CONTENTS

TABLE

ABSTRACTS OF THE LITERATURE ON SYNTHESIS OF APATITES AND SOME RELATED PHOSPHATES, PART II

by

Elizabeth B. Jaffe

DISCUSSION AND SUGGESTIONS

The U. S. Geological Survey's present interest in the phosphorites centers mainly around their uranium content. Several problems connected with both the northwest and southeast phosphate projects may be solved through synthesis:

1. A study of the mode of occurrence of uranium in phosphorites and of the limits of its miscibility in the various end members of the apatite series.

2. The conditions of and reasons for enrichment of phosphorites in uranium.

3. The effects of postdepositional alteration of the phosphorites on their uranium content, and the relative stability of uranium and phosphate under natural conditions both of precipitation and diagenesis.

The program for synthesis by wet and dry methods outlined in Part I, Discussion and Suggestions, can be followed in attempts to make uraniferous apatite; this program should be supplemented by the following leaching and absorption studies:

1. Leaching of synthetic uraniferous products by weak acids, bases, and neutral solutions.

2. Study of the absorption by pure synthetic products of ions from acid, basic, and neutral solutions; among these should be uranium ions in different valence states.

3. Similar leaching and absorption studies on Florida and western phosphorites.

ABSTRACTS

BAT 48

Battelle Memorial Institute-Progress and Topical Reports on Phosphates. Identification of the mode of occurrence of uranium in phosphate rock--H. R. Nelson, Supervisor.

Progress report for March 1948

Apatite was synthesized and identified by X-ray, in the following ways:

1. Ca_2HPO_4 + CaF_2 + $CaCO_3$ were fused at 200°C. in a stainless steel bomb.

2. Ca_2HPO_4 + CaF_2 + $CaCO_3$ and acetic acid (mixture had a pH of 6) were fused in a stainless steel bomb at 200°C.

3. Ca_2HPO_4 + CaF_2 + $CaCO_3$ and enough acetic acid to dissolve all of the $CaCO_3$ were fused at 200°C. in a stainless steeel bomb. This synthesis produced apatite and Ca_2HPO_4.

Progress report for April 1948

Syntheses similar to those done in March 1948 were run for a longer time at 300° and 400°C.; the higher temperatures and longer

time resulted in more successful syntheses.

Adsorption experiments with uranyl acetate solutions were done at 30° and 40°C. Synthetic apatite adsorbed 0.096 millimoles U/g from an 0.010M solution of uranyl acetate and 0.530 millimoles U/g from an 0.100 M solution of uranyl acetate.

Progress report for May 1948

Adsorption experiments. Synthetic apatite adsorbed U equivalent to 1.2 percent of its own weight from a solution containing 0.05 percent U in the form of uranyl acetate; leaching of this product with 10 percent HNO_3 solution removed half of the apatite, but only 1 percent of the U present in the apatite. Synthetic apatite in an 0.1 M solution of uranyl acetate at 200°C. adsorbed 8.3 percent of its own weight of uranium; leaching as above took out only 2 percent of the U in the apatite.

Progress report for June 1948

Heating UF_4, $CaCO_3$, Ca_2HPO_4, Na_2CO_3 at 400°C. for 12 hours produced apatite, UF_4, and a third minor phase; 11 percent U was present in the product. Similar syntheses using uranyl acetate or uranyl phosphate instead of UF_4 produced apatite plus a second phase; the product contained about 18 percent U.

The lattice constants of the natural apatite were: $a = 9.330 \pm 0.005$, $c = 6.890 \pm 0.005$; lattice constants of the synthetic apatite were: $a = 9.352 \pm 0.003$, $c = 6.890 \pm 0.005$.

Topical report June 1948

A water suspension of $CaHPO_4$, CaF_2, $CaCO_3$, at 167°F., produced apatite in 8 hours. Products were autoclaved at 752°F. for 6 to 12

hours in order to produce better crystals for X-ray work. Synthesis with UF_4 equivalent to 11 percent U produced apatite plus UO_2 plus a third phase.

Progress report for July 1948

Apatite was synthesized with 2 percent U as UF_4 at 400°C. for 6 hours; this produced apatite plus UO_2. Synthesis with uranyl acetate instead of UF_4 was done under the same conditions. Synthetic apatite removed 90 percent of the U from a 0.010 percent uranyl acetate solution: the apatite then contained 0.072 percent U. Leaching with enough HNO_3 to dissolve half the apatite removed 58 percent of the uranium in it.

Progress report for August 1948

Apatite was synthesized with 2 percent U as uranyl acetate; it gave the same powder pattern as natural apatite. Synthetic apatite absorbed 0.0205 percent of its own weight of U from a 0.002 percent solution of uranyl acetate; leaching away 50 percent of the apatite with HNO_3 extracted 48 percent of the U in the apatite. With a 0.014 percent uranyl acetate solution, apatite absorbed 0.207 percent of its own weight of U; dissolving 57 percent of the apatite with HNO_3 extracted 16 percent of the uranium from the apatite.

Progress report for September 1948

It is suggested that meta-autunite II is the extra phase observed in attempts to synthesize apatite with uranium.

Progress report for October 1948

Adsorption work in the range 0.075M -- 0.002M confirms previous results in the range 0.1M -- 0.01M. The adsorption is not physical,

because the normal Freundlich isotherm is not obtained. The solubility of synthetic autunite at room temperature in water is 0.00113 g/cc. The apparent solubility of autunite in 17 percent HNO_3 is 8.6 g/cc.

Autunite was mixed with synthetic apatite to give mixtures of 0.07, 0.20, and 1.00 percents U; when 50 percent of the apatite was dissolved in 17 percent HNO_3, solutions contained 0.030-0.079 mg U/cc. This removal of U agrees with previous data on adsorption and leaching of U. 56 percent U was removed from the 0.07 percent mixture; 19.5 percent U from the 0.20 percent mixture; and 1.5 percent from the 1.00 percent mixture. Similar results were obtained with mixtures of apatite and uranyl phosphate. Uranyl phosphate, not autunite, was observed to be in equilibrium with the HNO_3 leach solution. A 50:50 mixture of apatite and autunite was held in water suspension for 8 days at 50°C.; no change in the mixture was perceived by X-ray methods.

Progress report for December 1948

Further study of the occurrence of uranium in apatites will be made by using small natural crystals as seeds in a mixture of Ca_2HPO_4, CaF_2, and $CaCO_3$.

Topical report for March 1949 - prepared by C. M. Schwartz and A. E. Austin.

Attempts at synthesizing apatites containing uranium indicate that, at a uranium concentration greater than 1 percent, conditions are favorable for a second phase. Synthetic apatite which has adsorbed uranium in low concentrations from uranyl solutions responds to leaching as do the natural ores.

It is suggested from spatial considerations that uranium can substitute for calcium in the apatite lattice; this would have to be on the threefold axis as tetravalent uranium, or on the reflection planes as the uranyl group with O replacing F; the formula would then probably be $Ca_{17}Na_2U(PO_4)_{12}F_4$ or $Ca_7Na_2(UO_2)(PO_4)_6$. The uranyl group is linear, and, although apatite contains no linear groups, autunite does. The adsorption curve for synthetic apatite in solutions of uranyl acetate and uranyl phosphate is not a normal Freundlich curve; the leaching experiments suggest a chemical equilibrium. The phosphate ion dissolving from apatite suppresses the solubility of the uranyl phosphate, which is in true equilibrium, or the autunite, which is not. The coprecipitation of uranium phosphates and apatite is impossible because of their relative solubilities.

Table 1.--Attempts by workers at Battelle to synthesize apatites containing uranium

Mineral	Method	Reagents	Time and temp in °C	Checked by	Reference
Fluorapatite		Ca_2HPO_4, CaF_2, $CaCO_3$ in stainless steel bomb	200°,300° and 400°	X-ray	BAT 48
Fluorapatite	pption	Ca_2HPO_4, CaF_2, and $CaCO_3$	167°F, 8 hrs	X-ray	BAT 48
2% U? apatite		Ca_2HPO_4, CaF_2, $CaCO_3$, and uranyl acetate	400°	X-ray	BAT 48

SECRET