

High Temperature Dehydroxylation of Apatitic Phosphates

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$\text{Sr}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$, (Hex. $a=9.765 \text{ \AA}$, $c=7.280 \text{ \AA}$), and $\text{Ba}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$, (Hex. $a=10.177 \text{ \AA}$, $c=7.731 \text{ \AA}$), undergo cell parameter contractions at elevated temperatures in air. These can be correlated with progressive dehydroxylation, although neither can be completely dehydrated. $\text{Pb}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$, (Hex. $a=9.878 \text{ \AA}$, $c=7.432 \text{ \AA}$), also does not completely dehydrate in air.

A new apatite-like strontium phosphate, (Hex. $a=9.872 \text{ \AA}$, $c=7.199 \text{ \AA}$), was prepared at elevated temperatures in vacuum.

Key Words: Apatite, dehydroxylation, high temperature, phosphates, x-ray diffraction.

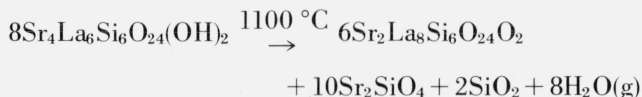
1. Introduction

The existence of the so-called oxyapatites, has been a subject of much controversy. Associated is the problem concerning the existence and nature of phases produced from the dehydroxylation of hydroxyapatite. The general cell content formula for hydroxyapatite is

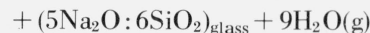
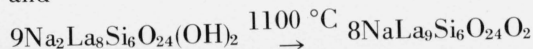


where A is a large cation distributed in 7- and 9-fold sites [1]¹ and B a small cation in tetrahedral coordination. Ideally, each $(\text{OH})^-$ is shared by three A ions. Dehydroxylation or substitution by O^{2-} for $(\text{OH})^-$ may result in the formation of true oxyapatites in a number of ways.

If two O^{2-} anions replace the two $(\text{OH})^-$ groups excess negative charge results. This necessitates either a valence change in the A or B cation sites or a change in the ratio of the constituents with the appearance of additional phases. Such compounds as $\text{Sr}_{10}\text{Cr}_6^{5+}\text{O}_{24}(\text{OH})_2$ and $\text{Ba}_{10}\text{Cr}_6^{5+}\text{O}_{24}(\text{OH})_2$ have oxyapatite counterparts which appear to be $\text{Sr}_{10}\text{Cr}_4^{5+}\text{Cr}_2^{6+}\text{O}_{24}\text{O}_2$ and $\text{Ba}_{10}\text{Cr}_4^{5+}\text{Cr}_2^{6+}\text{O}_{24}\text{O}_2$ [2]. The hydroxyapatites $\text{Sr}_4\text{La}_6\text{Si}_6\text{O}_{24}(\text{OH})_2$ and $\text{Na}_2\text{La}_8\text{Si}_6\text{O}_{24}(\text{OH})_2$ dehydrate to oxyapatites according to:



and



respectively [3]. Unit cell dimensions of all of the above oxyapatites are substantially different from those of their correspondingly related hydroxyapatites.

Theoretically, when the aforementioned mechanisms cannot operate, charge neutrality can be accomplished by the substitution of only one O^{2-} for two $(\text{OH})^-$. Such a mechanism creates vacancies in half the available positions, an unacceptable condition to some workers [4, 5]. Nevertheless, such compounds as $\text{Ba}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$, $\text{Pb}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$, and $\text{Sr}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$ have been reported to have $\text{A}_{10}\text{B}_6\text{O}_{24}\text{O}$ type oxy-analogs [6, 7, 8]. This paper deals with this class of hydroxyapatites and the question concerning the existence of oxy-analogs.

Recently, Kreidler and Hummel [8] reported that they synthesized $\text{Sr}_{10}\text{P}_6\text{O}_{24}\text{O}$ by the dehydroxylation of $\text{Sr}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$ above 1400°C in air and at 1400°C in vacuum. From phase equilibria considerations they reasoned that a series of solid solutions exists between the hydroxy and oxyapatite having the general formula



where $0 \leq x \leq 1$ and V = a vacancy. Furthermore, x-ray powder patterns of $\text{Sr}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$, synthesized below 1400°C , and $\text{Sr}_{10}\text{P}_6\text{O}_{24}\text{O}$ were said to be identical. This latter interpretation seemed untenable considering the gross "defectiveness" of the oxyapatite phase. The writers have reinvestigated in detail the behavior of $\text{Sr}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$ at elevated temperatures and extended the interpretation of these results to data obtained for barium-phosphorus and lead-phosphorus analogs.

¹ Figures in brackets indicate the literature references at the end of this paper.

2. Experimental Procedure

Starting materials of $\text{Sr}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$ and $\text{Ba}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$ were prepared in air by heating pressed pellets of the appropriate carbonate and $\text{NH}_4\text{H}_2\text{PO}_4$ (10:6 molar ratio mixture) from room temperature to 300 °C, then at 600 °C and 900 °C with intermediate grinding and pressing.² To avoid reaction of the alkaline earths, particularly barium, with platinum, syntheses were carried out on gold. The 900 °C Sr-apatite starting material was not effervescent in HCl. The 900 °C Ba-apatite, however, was weakly effervescent indicating either retention of carbonate as a structural component or free unreacted BaCO_3 . Specimens heated above 1000 °C were not effervescent in HCl. Portions of each apatite batch were mixed with distilled water, sealed in platinum capsules and reheated at 300 °C for five days in a Morey bomb. X-ray powder patterns of the phases produced in such a hydrothermal manner are identical to those synthesized in air. The strontium apatite was heated at 100 °C intervals in open gold envelopes (below 1000 °C) or platinum tubes (> 1000 °C), using small portions of the apatite previously synthesized in air. Above 1100 °C, the barium apatite could not be investigated using platinum tubes because of reaction with the metal. Instead, thin pressed wafers of the starting material were placed on two strands of fine platinum wire wrapped around an alumina dish and heated in this suspended manner.

Lead-phosphorous apatite was prepared in air and hydrothermally by the procedures described above except that the monoxide was used as the large cation source.

Specimens were heated in a platinum-wound tube-type horizontal furnace and cooled by rapid withdrawal. A number of heat treatments were made in vacuum using a modified quench furnace.

Phase analysis was accomplished predominantly by x-ray powder diffraction at room temperature using Ni-filtered copper radiation and $\frac{1}{4}$ deg 2θ per minute diffractometer scanning rate. Parameters may be considered to be accurate to ± 2 in the last decimal place listed. Supporting data were obtained by gravimetric measurements and nuclear magnetic resonance. Specimens for NMR examination were immediately transferred from the furnace to evacuated vycor tubes and sealed against contamination from atmospheric moisture.

3. Results and Discussion

3.1. $\text{Sr}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$

The x-ray powder patterns of hydrothermal and low temperature (< 900 °C) "in air" apatite are identical and can be completely indexed on the basis of an hexagonal cell having $a = 9.765$ Å and $c = 7.280$ Å.

On this basis, the 900 °C phase was considered fully hydroxylated and used as a compositional reference point for further experiments. With increasing temperature, commencing near 1000 °C, (fig. 1), unit-cell parameters continuously contract, reaching values of $a = 9.724$ Å and $c = 7.263$ Å at 1600 °C. Pertinent experimental data are given in table 1. The compound *does not* decompose with complete loss of H_2O at a fixed temperature as does, for example, $\text{Sr}_{10}\text{Cr}_6\text{O}_{24}(\text{OH})_2$ [2].

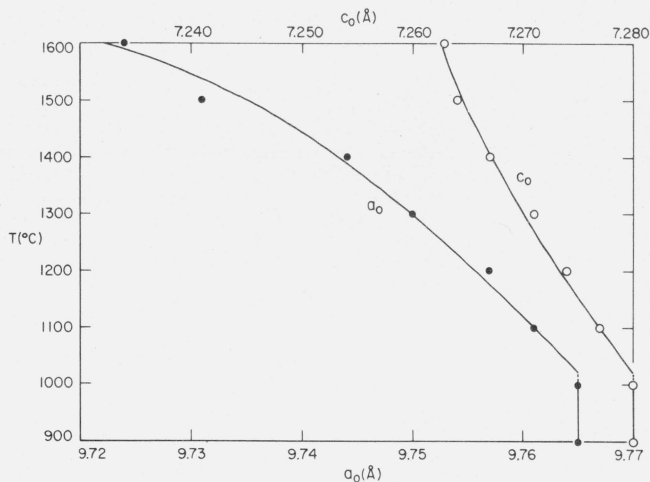


FIGURE 1. Unit-cell parameter changes of strontium-phosphorus apatite as a function of the temperature of heating in air.

Kreidler and Hummel[8] apparently failed to observe this unit cell contraction³ but on reasonable thermodynamic grounds concluded that $\text{Sr}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$ dehydroxylates in air with increasing temperature until above 1400 °C $\text{Sr}_{10}\text{P}_6\text{O}_{24}\text{O}$ exists. As shown in figure 1, cell contraction continues beyond 1400 °C and parameters *do not* attain constant values as would be expected if total dehydroxylation to $\text{Sr}_{10}\text{P}_6\text{O}_{24}\text{O}$ occurs. This suggests that even above 1400 °C a partially hydroxylated phase exists. A specimen of $\text{Sr}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$, heated 40 hr at 1500 °C lost weight and then after reheating for 50 hr on gold at 900 °C regained weight suggesting the composition of the phase at 1500 °C to be



after compensation for loss of P_2O_5 at the higher temperature. Furthermore, NMR data unequivocally established the presence of protons in a specimen heated only at 1500 °C.

² Infrared absorption analysis indicated the presence of about 0.2 percent and 0.5 percent carbonate in the starting Sr- and Ba-apatites, respectively. Personal communication, Dr. Bruce Fowler, National Institutes of Health.

³ After the completion of this manuscript, the writers received data from the dissertation of Kreidler (Ph.D. Thesis, The Pennsylvania State University, 1967). Cell contraction was observed with a conversion of hydroxy- to oxy-apatite in air at 1510 ± 15 °C.

TABLE 1. Experimental Data for the Dehydroxylation of Phosphates

Strontium-Phosphorus Apatite*				
T (°C)	Time (hrs)	a (Å)	c (Å)	Comments
800	100	9.765	7.280	NMR** Hydrothermally prepared.
900	100	9.765	7.280	
300	120	9.765	7.280	
1000	70	9.765	7.280	
1100	70	9.761	7.277	
1200	40	9.757	7.274	
1300	70	9.750	7.271	
1400	30	9.744	7.267	
1500	2, 20, 40	9.731	7.264	
1600	1	9.724	7.263	
900	5	9.765	7.280	Reversed from 1500 °C. Reversed from 1500 °C; Sr ₁₀ P ₆ O ₂₄ (OH) _{0.74} O _{0.83} V _{0.83} from weight loss and regain.
900	50	9.765	7.280	Reversed from 1400 °C. Reheat of 1500 °C specimen. Reheat of hydrothermal specimen.
900	17	9.765	7.280	Initially a 3:1 mixture of Sr ₃ (PO ₄) ₂ and SrCO ₃ . Vacuum, 10 ⁻² torr; two phases. Vacuum, 2 × 10 ⁻² torr. Vacuum, 7 × 10 ⁻³ torr. Vacuum, 10 ⁻² torr. Vacuum, 2 × 10 ⁻² torr; NMR** Vacuum; 3.8 × 10 ⁻⁴ torr. Sr ₄ P ₂ O ₉ present; NMR analysis. Reheat of 1270 °C, 7 × 10 ⁻³ torr material in air.
1400	68	9.744	7.267	
1500	2	9.731	7.264	
1500	4	9.731	7.264	
1100	70	9.84	7.21	
		9.72	7.26	
1250	113	9.729	7.240	
1270	70	9.872	7.199	
1275	110	9.872	7.199	
1350	115	9.728	7.240	
1500	15	9.726	7.246	
950	310	9.827	7.234	
Barium-Phosphorus Apatite*				
T (°C)	Time (hrs)	a (Å)	c (Å)	Comments
700	96	10.177	7.731	NMR** Hydrothermally prepared.
900	120	10.177	7.731	
300	120	10.177	7.731	
1000	50	10.175	7.728	
1200	20	10.170	7.719	
1300	20	10.164	7.714	
1400	48	10.157	7.705	
1500	20	10.148	7.696	
1500	20	10.148	7.696	
1600	2	10.153	7.696	
900	5	10.177	7.731	NMR** Partly melted? Reheat of 1500 °C specimen. Reheat of 1400 °C specimen.
900	16	10.177	7.731	
Lead-Phosphorus Apatite*				
T (°C)	Time (hrs)	a (Å)	c (Å)	Comments
300	120	9.878	7.432	Hydrothermally prepared. Reheat of hydrothermal specimen; Pb ₁₀ P ₆ O ₂₄ (OH) _{0.26} O _{0.87} V _{0.87} by weight loss.
700	65	9.825	7.421	
900	50	9.825	7.421	Reheat of 700 °C specimen; NMR** Melted and slow cooled to 950 °C in ½ hr.
925	75	9.825	7.421	
1000		9.825	7.421	

*Unless otherwise indicated, heat treatments were made in air using starting material synthesized in air at 900 °C.

**NMR analysis indicated the presence of protons.

A number of questions naturally arise at this point. Do the curves shown in figure 1 represent equilibrium conditions, i.e., for each temperature at a fixed partial pressure of H₂O does there exist a stable anion deficient apatite characterized by specific unit cell parameters, or can the data be equally interpreted as being the manifestation of a kinetic problem in which Sr₁₀P₆O₂₄(OH)₂ converts very sluggishly, yet with increasing rate with increased temperature, to Sr₁₀P₆O₂₄O through a series of defect states? If at each temperature there does exist an equilibrium phase characterized by a specific ratio of (OH)⁻:O⁻²:vacancies with unique cell parameters, a thermody-

namically possible situation, are the anions and vacancies statistically disordered resulting in a true nonstoichiometric solid solution?

Specimens, generally, were heated for periods up to 100 hr to insure sufficient time to attain reproducible results. For example, specimens held 2 hr, 20 hr, and 40 hr at 1500 °C yielded apatite phases with identical cell parameters. The 20 hr 1500 °C specimen, held 68 hr at 1400 °C, and the 100 hr 900 °C specimen, held directly at 1400 °C for 30 hr, yielded identical cell parameters. A 3:1 molar mixture of Sr₃(PO₄)₂ and SrCO₃ was heated directly at 1500 °C for 4 hr and, although it did not react completely to a single phase within this time, the predominant phase was apatite with cell dimensions identical to those previously observed at 1500 °C. High temperature phases are readily reversed by reheating at lower temperatures, as shown in table 1.

The reversibility of the process shows that a kinetic problem is not involved, however, the nature of the anion vacancy is not revealed. Thus, the best interpretation of the behavior of Sr₁₀P₆O₂₄(OH)₂ at elevated temperatures is that increasing dehydroxylation occurs with increasing temperature and is associated with unit cell contraction. Regardless of the true nature of the high temperature phase, a completely dehydroxylated Sr₁₀P₆O₂₄O definitely was not found in air.

A number of experiments, made in vacuum, also provide some interesting observations concerning the dehydroxylation of Sr₁₀P₆O₂₄(OH)₂. A specimen heated 70 hr at 1100 °C and 10⁻² torr clearly showed two phases, one having cell dimensions quite similar to the 1600 °C in air phase, the other a = 9.84 Å and c = 7.21 Å. The diffuseness of the powder pattern precluded a more precise calculation of cell parameters. Another specimen held 110 hr at 1275 °C and 10⁻² torr consisted of an apatite-like single phase whose pattern could be completely indexed on the basis of a hexagonal cell with a = 9.872 Å and c = 7.199 Å. The compound was again prepared at 1270 °C, 70 hr and 7 × 10⁻³ torr. Portions of the powder pattern of this new phase are compared to those of the 900 °C and 1500 °C in air apatite phases in figure 2.

Considering the trend established in the "in-air" experiments, that the cell contracts with hydroxyl loss, this new phase is unusual because of its rather large a and quite small c. When heated in air at 950 °C, the compound apparently reacts with atmospheric moisture very sluggishly and a contracts and c expands toward the values of the fully hydroxylated apatite. Unfortunately, the nature of this new phase could not be investigated in detail because of difficulty in the preparation of sufficiently large quantities of material for gravimetric experiments and NMR analysis.⁴ Whether or not it represents a true, ordered, Sr₁₀P₆O₂₄O oxyapatite must await single crystal structure analyses. Kreidler and Hummel [8] reported the synthesis of strontium-phosphorus oxyapatite in vacuum at 1400 °C but did not detect x-ray changes. Their

⁴ This compound was found to be (OH)⁻ and (CO₃)²⁻ free by infrared absorption. Personal communication, Dr. Bruce Fowler, National Institutes of Health.

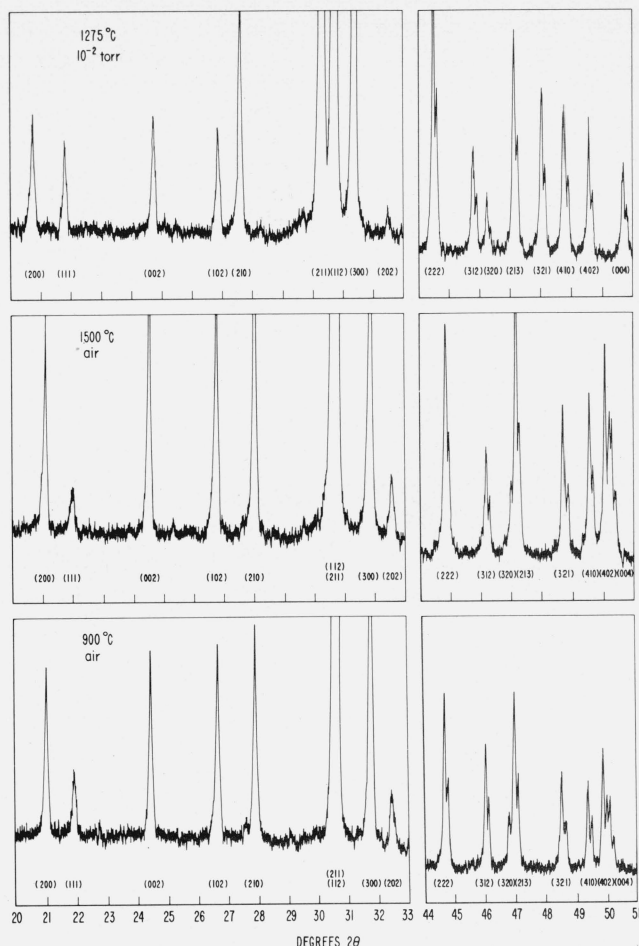


FIGURE 2. Comparison of portions of the powder patterns of $\text{Sr}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$.
 (bottom)—as prepared at 900 °C in air;
 (middle)—after heating at 1500 °C;
 (top)—heated at 1275 °C and 10^{-2} torr.

inability to observe this phase may have been due to insufficient equilibration times and/or poor vacuum. In this study, approximately 1 g specimens heated between 1250 and 1500 °C from 15 to 113 hr and less than 2×10^{-2} torr (see table 1) yielded apatite phases with powder patterns similar in appearance to the air apatites. Analysis by NMR indicated that even these phases contain protons. Although their powder patterns are not exceedingly sharp, the cell parameters indicate an expansion of a and contraction of c . Smaller specimens yield the new phase although a vacuum less than 10^{-2} torr and temperatures greater than 1100 °C are necessary.

In view of the results obtained on vacuum heated specimens another question can be raised concerning the nature of the products of high temperature in air experiments. Are the results shown in figure 1 a manifestation of stable or only metastable equilibrium? The answer to this question can only be decided after considerable experimentation with vacuum prepared starting material.

3.2. $\text{Ba}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$ and $\text{Pb}_{10}\text{P}_6\text{O}_{24}(\text{OH})_2$

A few attempts were made to correlate the high temperature "in-air" behavior of barium and lead-phosphorus apatites with that of strontium. Experimental data are given in table 1.

Hydrothermal and low temperature (700 to 900 °C) specimens of barium-phosphorus apatite are identical, with $a = 10.177$ Å and $c = 7.731$ Å. From just above 900 to 1500 °C, as shown in figure 3, cell parameters contract continuously with increasing temperature suggesting dehydroxylation as in the case of strontium. Some structural carbonate, however, may be present and the curve may represent, in reality, hydroxyl and carbonate loss. Phases can be easily reversed by reheating at lower temperatures. The 1600 °C apatite has $a = 10.153$ Å and $c = 7.696$ Å. These values do not lie on the extrapolation of the a and c curves to 1600 °C. The fact that specimens at 1600 °C show partial melting and discoloration which may be due to reaction with platinum may explain this apparent anomaly.

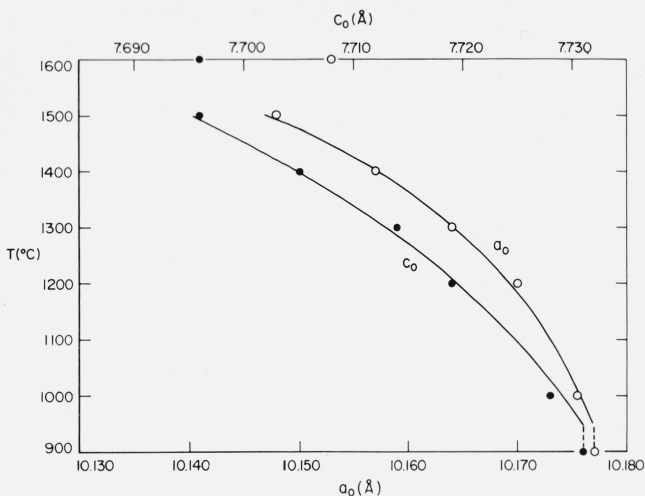


FIGURE 3. Unit-cell parameter changes of barium-phosphorus apatite as a function of the temperature of heating in air.

Alternatively, the slight increase in a at 1600 °C may reflect the same tendency observed in the strontium-phosphorus apatite heated in vacuum. Regardless of the cause, a completely dehydroxylated barium oxyapatite does not appear to exist in air. For example, NMR analysis of a specimen held at 1500 °C for 20 hr definitely established the presence of protons.

Hydrothermal and "in-air" lead-phosphorus apatites are not identical. The former has $a=9.878$ Å and $c=7.432$ Å while the latter has $a=9.825$ Å and $c=7.421$ Å. Merker and Wondratschek [7, 9] reported a doubling of the c -axis for this compound. The powder patterns made in this study do not, and perhaps cannot, reveal this doubling. A specimen of the hydrothermal apatite heated in air at 700 °C for 65 hr gave weight loss data suggesting the formula



NMR analysis of this material reheated at 925 °C for 75 hr also indicated that the phase was not totally deficient in protons. These data conflict with past reports [6, 8] regarding the synthesis of a completely dehydroxylated $\text{Pb}_{10}\text{P}_6\text{O}_{24}\text{O}$ type oxyapatite.

The "in-air" lead apatite does not show a progressive contraction of parameters with increase in temperature. In fact, crystals grown by slow cooling of the melt from 1000 to 950 °C yield powder patterns indistinguishable from lower temperature material. Significant, however, is the cell contraction of the hydrothermal apatite when partly dehydroxylated by heating in air.

4. Summary

Strontium and barium-phosphorus hydroxyapatites undergo cell parameter contractions at elevated temperatures in air. These can be correlated with progressive dehydroxylation according to



Neither, however, form the limiting $\text{M}_{10}\text{P}_6\text{O}_{24}\text{O}$ type oxyapatite in air as complete dehydroxylation does not occur. The possibility exists that such a phase can be formed at elevated temperatures in vacuo. The unit-cell dimensions of a new strontium-phosphate phase herein reported may represent those of the fully dehydroxylated apatite.

Dehydroxylation of lead-phosphorus hydroxyapatite in air does not produce a true oxyapatite but rather one which is still partially hydrated.

The writers wish to thank Thomas Farrar, National Bureau of Standards, for conducting the NMR analyses.

5. References

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