Infrared Spectra of the Hydroxyl Ions in Various Apatites

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PART I. The frequencies of the stretching and librational modes of the OH ions in 13 hydroxyapatites were measured by means of infrared spectroscopy. There appears to be no hydrogen bonding between adjacent OH groups along the channels in the apatite structure. In addition to the expected stretching bands new bands were found in the spectra of seven of the hydroxyapatites. They probably arise from OH groups in positions different from those normally occupied.

PART II. The frequencies of the stretching modes of the OH ions present in small amounts in several fluor-, chlor-, and bromapatites were determined. They provide evidence for the existence of hydrogen bonding of the type O–H . . . F, O–H. . .Cl and O–H. . .Br.

Introduction

Some time ago we published a paper on the infrared spectra of the phosphate ions in various apatites (*1*). In these compounds the coupling between the internal PO_4 vibrations and the lattice vibrations is sufficiently weak so that the internal vibrations do not lose their identity. They are, however, not unaffected by the neighbouring ions in the structure, and a measurement of their frequency values provides some useful information on these ions. In a similar way the stretching and librational vibrations of the OH ions in hydroxyapatites depend on the nature of the ions surrounding them. A study of the hydroxyl vibrations is especially interesting in view of the possibility of hydrogen bond formation in apatites. The results of such measurements will be dealt with in Part I of this paper. Part II is concerned with the vibrations of hydroxyl ions present in small amounts in fluor-, chlor-, and bromapatites. Here there is the possibility of the formation of hydrogen bonds of the type O–H...F, O–H...Cl and O–H...Br, respectively.

Part I. Spectra of Hydroxyl Ions in Hydroxyapatites

Crystal Structure of the Hydroxyapatites

The apatites examined in this paper have the general formula $M_5(XO_4)_3OH$, with M = Ca, Sr, Ba, Cd, Pb, and X = P, As, V. X-Ray powder diffraction diagrams and other data show that to a first approximation they can all be considered as being isotypic with one another. Crystal structure determinations have been carried out only on $Ca_5(PO_4)OH$, with both X-rays and neutrons (*2*, *3*). As in the case of fluorapatite (*4–7*) it has space group $P6_3/m$ with two formula units per unit cell. The OH ions lie in channels along the 6_3-axes with an orientation strictly parallel to the principal axis. This follows also from ir data (*8*). The channels have their smallest diameter at $z = \frac{1}{4}$ and $z = \frac{3}{4}$, where they are surrounded by Ca ions in a triangular arrangement. The distance from the 6_3-axes to the centre of these Ca ions is 2.36 Å. The oxygen atoms of the OH ions lie about 0.3 Å above or below the plane of the three above-mentioned Ca ions, the H atoms of the hydroxyl groups always pointing away from the plane.

The fact that space group $P6_3/m$ can be assigned to calcium hydroxyapatite (attempts to refine the structure with no mirror planes have not been successful) indicates that not all OH groups are oriented in the same way. This is in accord with one of the following models (*3*), or a combination of the two:

(1) The orientation of the OH ions within a single column is reversed at various positions;
(2) all OH ions with a single column are oriented

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in the same way, but their orientation may vary from column to column.

The exact positions of the OH ions in the other hydroxyapatites are as yet unknown.

Experimental

Preparation of the hydroxyapatites. The compounds $M_5(XO_4)_3OH$ with M = Ca, Sr, Ba, and X = P, As, V were prepared in two stages. *First stage:* In the case of the phosphates the reaction product of $(NH_4)_2HPO_4$ with the corresponding nitrate was slowly heated (under frequent regrinding) to 1000°C. In the case of the arsenates arsenic trioxide, suspended in an aqueous solution of the nitrates, was oxidized to the pentavalent state by the addition of nitric acid. After evaporation the product was heated to 1000°. The vanadates were prepared from the nitrates and vanadium pentoxide. In this case the maximum temperature was limited to 900°. *Second stage:* The products thus obtained were subjected to an aftertreatment in order to ensure that any apatites which might have been partially dehydrated to oxyapatites $M_{10}(XO_4)_6O$ (*9*) were transformed into the fully hydrated form. The Ca and Sr compounds were treated hydrothermally (425°, 1000 atm). For the Ba compounds a different treatment was chosen, since these, except for the phosphate, would under such conditions partially decompose to the *ortho*-compounds, the vanadate being the most sensitive in this respect. They were exposed to a stream of nitrogen saturated with water vapour, at temperatures of 1100° for the phosphate and arsenate, and 900° for the vanadate.

The Cd and Pb apatites were synthesized hydrothermally from material of the composition "$M_{10}(XO_4)_6O$" which had been obtained by thermal methods. The conditions (425°, 1000 atm) are described in more detail elsewhere (*10, 11*). Samples of Pb apatites which had been prepared from lead orthophosphate and lead acetate (*11*) gave X-ray powder patterns with somewhat broadened lines.

The deuterated phosphate apatites were prepared hydrothermally by substituting D_2O for H_2O.

All compounds were identified by their X-ray powder diffraction patterns, taken with a Guinier camera. According to these diagrams the compounds can be considered pure, except for $Ba_5(VO_4)_3OH$ which contained about 30 wt% of the orthophosphate. In one special sample of $Ca_5(AsO_4)_3OH$, which had been prepared with an excess of $Ca(OH)_2$ traces of the hydroxide could be detected by ir spectroscopy (band at 3644 cm^{-1}); this particular sample also showed foreign lines in the X-ray pattern.

Spectroscopic techniques. All bands were recorded on a Perkin–Elmer infrared spectrophotometer Model 225. The wave numbers are accurate to about 2 cm^{-1} relative to each other, for each of the two regions recorded. With one exception all samples were prepared as follows: A few milligrams of the substance was ground with two drops of Nujol in an agate mortar. About 50 mg of a fine polyethylene powder (VESTOLEN A 6016, Chem. Werke Huels, Germany) was added. The resulting paste was melted at about 140° and pressed between glass plates to a slightly wedge-shaped film of average thickness 0.1 mm. For recording the librational band of $Cd(PO_4)_3OH$ a conventional Nujol mull was employed because of the interfering polyethylene bands.

Results and Discussion

"Normal bands." The measured frequencies are listed in Table I. In Fig. 1 these frequencies are plotted as a function of the atomic weight of the cations. Let us note the following:

1. The frequencies of the stretching and librational modes of the OH ions in the various hydroxyapatites all differ from one another in a characteristic manner. On the whole the librational modes cover a wider range of wave numbers than the stretching modes.

2. For a given compound a relatively high stretching frequency is usually accompanied by a relatively low librational frequency, and *vice versa.* There is, however, no systematic relation between these two frequencies such that one could be calculated from the other. The lack of such a relation indicates that the effects determining the stretching modes are not identical with those determining the librational modes.

3. The cations, being the nearest neighbours of the hydroxyl groups, seemingly exert a dominant influence on the OH vibrations. The librational frequencies especially are strongly dependent on the nature of the cations. The high value of 714 cm^{-1} for $Cd_5(PO_4)_3OH$ is evidence of the strongly hindered rotation of the hydroxyl ions in that compound.

4. In comparing apatites having different tetrahedral anions but identical cations we

<center>TABLE I</center>

<center>Stretching and Librational Frequencies of the OH Ions
in Various Hydroxyapatites (in cm^{-1})</center>

	$(PO_4)_3OH$	$(PO_4)_3OD$	Wave number ratio	$(AsO_4)_3OH$	$(VO_4)_3OH$
Ca_5	3572	2634	1.356	3559	3549
	631	458.4	1.376	634	625
Sr_5	3593	2648	1.357	3575	3568
	539	404	1.334	565	559
Ba_5	3607	2659	1.357	3587	3580
	430	322	1.335	~482	476
Cd_5	3532	2606	1.355	—[a]	—[a]
	714[b]	520	1.373		
Pb_5	3559	2625	1.356	3549	3536
	~550?	405–410?		?	?

[a] Compound does not exist.

[b] In Nujol.

restrict ourselves to the alkaline earth apatites, since only for these compounds are complete data available. The data show that the stretching frequencies decrease in going from the phosphate to the arsenate to the vanadate, whereas the librational frequencies do not increase in the same order. For the Sr and Ba apatites the order of increase is phosphate–vanadate–arsenate, and for the Ca apatites it is vanadate–phosphate–arsenate, although in the latter case all three frequencies lie very close together. This behaviour is an illustration of what has been said under 2, namely that the frequencies of the stretching and librational modes are not strictly determined by the same effects.

5. According to their spectroscopic behaviour the apatites with identical anions fall into one of two classes, one comprising the alkaline earth apatites, the other one those of cadmium and lead. Within each of these two groups the stretching frequencies increase and the librational frequencies decrease with increasing atomic number of the cation. This grouping into two classes is not surprising if one thinks of the enhanced tendency of the Cd^{2+} and Pb^{2+} ions to form covalent and complex compounds, as compared to the alkaline earth ions. Evidence for this tendency is also provided by the chemical (10) and infrared spectroscopic (1) behaviour of the corresponding halide apatite in contrast to that of their alkaline earth counterparts. As further evidence for the tendency of Pb^{2+} to form covalent bonds we may mention the recently

determined structure of nasonite, Pb_6Ca_4-$(Si_2O_7)_3Cl_2$ (12). The structure of this compound is related to that of the apatites, the Cl ions also being situated in channels. This structure determination has clearly demonstrated the existence of partially covalent bonds between Pb and O on one hand and Pb and Cl on the other hand.

6. The OH stretching frequencies fall into a range which is generally regarded as being characteristic of weakly hydrogen-bonded OH groups (13). The only atoms in the apatite structure to which such bonding might be considered are the oxygen atoms of the neighbouring OH and PO_4 groups, as has been discussed by Baddiel and Berry (14) for $Ca_5(PO_4)_3OH$. In this compound the hydroxyl groups lie strictly parallel to the c-axis at equal distances from one another so that the O–O distance between neighbouring OH groups is equal to one half of the c-lattice constant, i.e., equal to 3.44 Å. Since this is too large a distance for H bond formation Baddiel and Berry were led to the assumption of a hydrogen bond of the type O–H. . .OPO_3. There are three O atoms of three different phosphate groups at a distance of 3.05 Å from the O atom of the hydroxyl group. The arrangement is that of a trigonal pyramid, with the three phosphate oxygens forming the base and the hydroxyl oxygen the apex. Baddiel and Berry make no mention of the O–H. . .O angle. A simple calculation based on the data of Kay, Young, and Posner (3) shows that this angle is
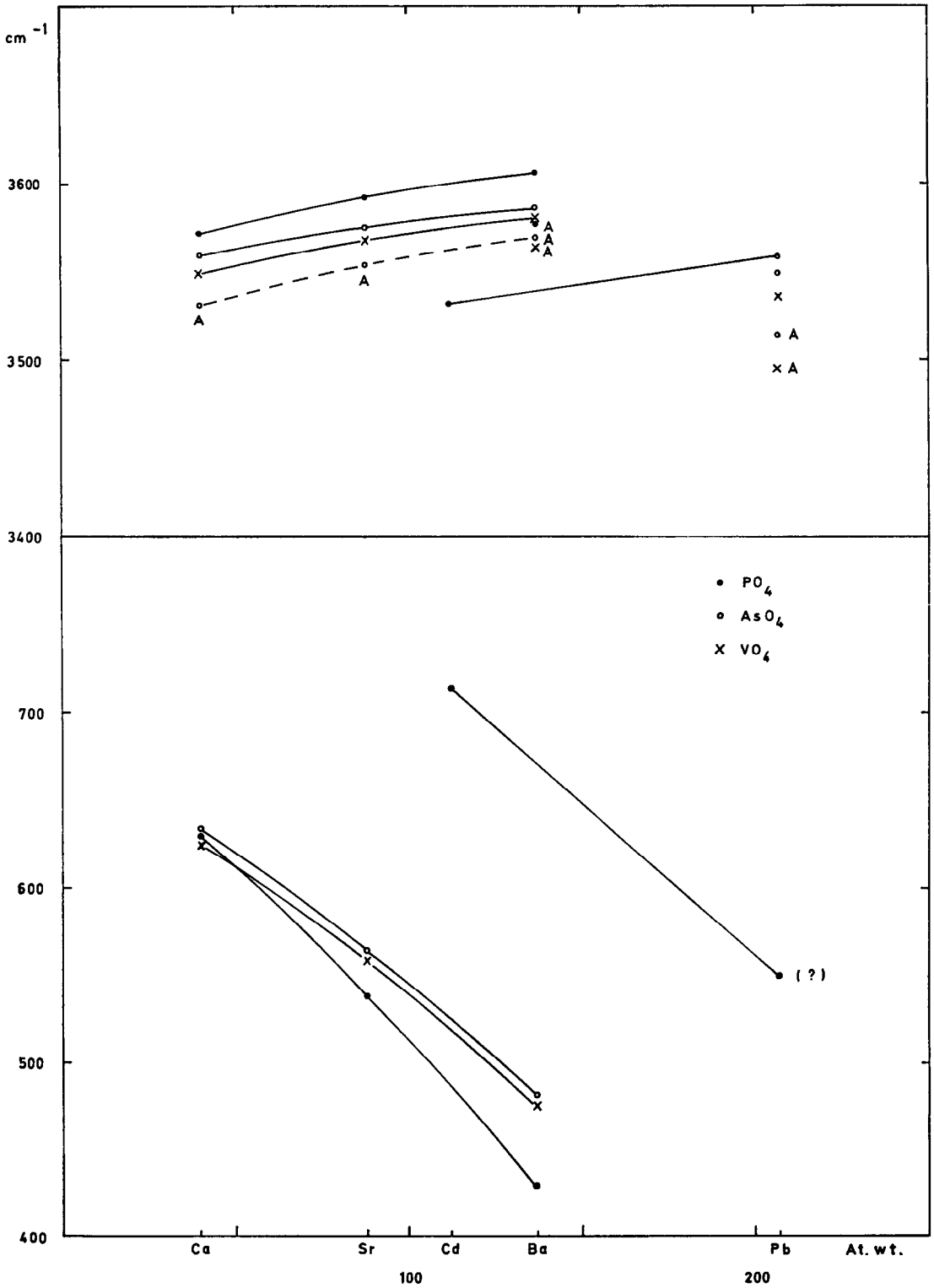
FIG. 1. Wave numbers of the stretching bands (upper part) and librational bands (lower part) of the OH ions in various hydroxyapatites (additional bands are marked with an "A").

just less than 90 degrees. One is tempted to deny the existence of an H bond under such conditions. This would mean that a lowering of the OH stretching frequency by the order of magnitude considered here is not necessarily indicative of H bond formation.

In the remaining hydroxyapatites for which the atomic positions are not exactly known we can exclude H bonding at least between neighbouring OH groups with some degree of certainty on the basis of the fact that there is no systematic relation between the OH stretching or librational frequencies and the c-lattice constants. Moreover, if one assumes that in these compounds the OH groups are arranged equidistantly along the c-axis (whether inclined to the axis or not) the magnitude of these constants—all larger than that of $Ca_5(PO_4)_3OH$, except for $Cd_5(PO_4)_3OH$ with $c = 6.64$ Å (10)—would also preclude the formation of such hydrogen bonds.

"*Additional bands.*" In addition to the bands which have been discussed so far several apatites show extra bands which are listed in Table II. These are generally of the order of 20–30 cm^{-1} lower than the normal bands. It is particularly noteworthy that the additional bands show the same general variation of frequency with change of cations or tetrahedral anions as do the normal ones. This is strong evidence against the possible explanation that the additional bands are caused by impurities. In the case of the lead apatites, which had been prepared by two different methods it was found that the intensity ratio of the additional to the normal bands was dependent on the method of preparation. Thus the estimated intensity ratios for the two compounds Pb_5-$(AsO_4)_3OH$ and $Pb_5(VO_4)_3OH$ prepared from "$Pb_{10}(XO_4)_6O$" (see above) was about $1:2$

and $1:5$, respectively, whereas for the corresponding compounds prepared with the aid of lead acetate (see above) it was about $1:1$ and $2:5$, respectively. X-Ray powder diagrams taken with a high resolution Guinier-type camera showed that the two last mentioned apatites (i.e., the ones with the higher intensity ratios) had somewhat broader lines than the other two. The positions of the lines were also slightly different, indicating a somewhat larger unit cell for the apatites prepared with lead acetate. In this connection the recently published results of Cant et al. (15) are of interest. These authors have found the appearance of a new band in the OH stretching region when spectra of stoichiometric and also of calcium-deficient calcium hydroxyapatites were taken at elevated temperatures. The intensity of the extra band increased with increasing temperature, at the expense of the intensity of the normal OH stretching band. The changes were found to be fully reversible. At a temperature of 485° the main and secondary bands of a sample of calcium-deficient apatite occurred at 3565 and 3535 cm^{-1}, respectively. The difference of 30 cm^{-1} lies within the range of the corresponding frequency differences between the normal and additional bands of our samples listed in Table II, which were all examined at room temperature. Cant et al. ascribe the extra band in calcium hydroxyapatite to hydroxyl ions in positions different from those normally occupied at room temperature. We tend to assume that the two OH bands we found for the apatites listed in Table II are also due to OH ions occupying two different sites. With regard to the question of whether nonstoichiometry plays the dominant role in these effects we note the following: (1) Cant et al. obtained practically identical

TABLE II

STRETCHING FREQUENCIES OF THE OH IONS IN VARIOUS HYDROXYAPATITES: ADDITIONAL BANDS (IN cm^{-1})

	$(PO_4)_3OH$	$(PO_4)_3OD$	Wave number ratio	$(AsO_4)_3OH$	$(VO_4)_3OH$
Ca_5	—	—	—	3531	—
Sr_5	—	—	—	~3554	—
Ba_5	3579	2639	1.356	3569	3564
Cd_5	—	—	—	—[a]	—[a]
Pb_5	—	—	—	3514	3495

[a] Compound does not exist.

results for calcium-deficient as well as for stoichiometric calcium hydroxyapatites; (2) As to our samples we can exclude a partial dehydration to compounds of the type $M_{10}(XO_4)_6[O, (OH)_2]$ at least for all of our lead apatites and one sample of $Ba_5(PO_4)_3OH$, because these were prepared hydrothermally.

We want to mention in this connection that in all strontium, barium and lead apatites discussed here the distance from the centre of the channels to the nearest oxygen atoms of the tetrahedral anions is expected to be enlarged as compared to calcium hydroxyapatite. This can be seen from a rough calculation based on a-lattice parameters. The lengths of the channels per unit cell, i.e., the c-parameters, are also enlarged, reaching an extreme value of 7.88 Å in $Ba_5(VO_4)_3OH$, compared to 6.88 Å in $Ca_5(PO_4)_3OH$. These relaxed space requirements for the OH ions may favour their orientation in different positions.

Cant et al. (15) do not mention the occurrence of any extra librational bands corresponding to the additional band in the OH stretching region, nor have we found such bands. It may well be that these bands lie so close to the normal librational band that the two are not resolved.

We believe that much useful supplementary information can be gained from a detailed study of the temperature dependence of the normal and additional bands of the compounds discussed in this paper. A study of mixed crystals between hydroxyapatites having different cations is also planned.

Part II. Spectra of Hydroxyl Ions in Halide Apatites

Structure of the Halide Apatites

As in the case of the hydroxyapatites all fluor-, chlor-, and bromapatites can be considered as being isotypic with $Ca_5(PO_4)_3F$, at least to a first approximation. The halide ions lie in the channels surrounding the 6_3-axes. In $Ca_5(PO_4)_3F$ the fluoride ions lie in the centre of the Ca triangles which surround the channels at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ (origin at centre of symmetry (4–7)). While it had been generally assumed that in $Ca_5(PO_4)_3Cl$ the chloride ions lie halfway between the calcium triangles Young and Elliott (7) present evidence that they are somewhat displaced from these positions along the c-direction. Their model also explains the lowering of symmetry from $P6_3/m$ to $P2_1/c$ found in samples of stoichiometric chlorapatites at room temperature. See also

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the discussion by Prener (16). Little is known about the exact halide positions in the remaining apatites, except for a general feeling that the fluoride ions lie at or near $z = \frac{1}{4}$ and $z = \frac{3}{4}$, and the chloride and bromide ions at or near $z = 0$ and $z = \frac{1}{2}$.

Experimental

Syntheses. The mixed crystal $Ca_5(PO_4)_3(F,OH)$ was synthesized by sintering a mixture of fluorapatite with some hydroxyapatite at 1000° for one week. $Ca_5(PO_4)_3(Cl,OH)$ was prepared hydrothermally from $Ca_5(PO_4)_3OH$, $Ca_3(PO_4)_2$, and $CaCl_2$. The chlorapatites $M_5(PO_4)_3(Cl,OH)$, M = Cd, Mn, were also prepared hydrothermally by reacting $M_3(PO_4)_2$ and MCl_2. $Cd_5(PO_4)_3$-(Br,OH) was similarly prepared. The strontium apatites $Sr_5(XO_4)_3(F,OH)$, X = P, As, V, were formed by tempering the pure fluorapatites in air at 1000° for several days. The OH content was of the order of a few per cent in all samples except $Ca_5(PO_4)_3(Cl,OH)$, which contained more hydroxyl than chloride ions.

Spectroscopic techniques. See Part I.

Results and Discussion

The frequency range of the OH stretching vibrations in the eight mixed crystals examined here (see Table III) is much larger and extends to much lower values than in the case of the pure hydroxyapatites (see Part I). Here the lowest value found is 3380 cm^{-1}, for $Mn_5(PO_4)_3(Cl,OH)$. It is natural to assume that this frequency lowering is mainly determined by hydrogen bonding of the OH ions to neighbouring halide ions along the c-axis. This assumption of O–H...F, O–H...Cl, and O–H...Br hydrogen bonds, based on the frequency values, is also supported by the fact that—in contrast to the behaviour of the pure hydroxyapatites—there seems to be a definite relation between the OH frequencies and the c-lattice constants of the halide apatites: The OH stretching frequencies of the phosphate apatites of Table III increase in the same order as the c-lattice constants. In the series Sr_5-$(XO_4)_3OH$, X = P, As, V, where a corresponding statement does not hold, the frequency variations are too small as to invalidate the above assumption, and are likely to be caused by such effects as determine the OH frequencies of the pure hydroxyapatites (see Part I).

Young et al (17) have examined a sample of synthetic calcium hydroxyapatite with 10%

Compound	OH stretching frequency (cm^{-1})	c-lattice constant of halide apatite (18, 19) (Å)
$Mn_5(PO_4)_3(Cl,OH)$	3380	6.20
$Cd_5(PO_4)_3(Cl,OH)$	3404	6.46
$Cd_5(PO_4)_3(Br,OH)$	~3405	6.46
$Ca_5(PO_4)_3(Cl,OH)$	3497	6.78
$Ca_5(PO_4)_3(F,OH)$	3537	6.88
$Sr_5(PO_4)_3(F,OH)$	3550	7.28
$Sr_5(AsO_4)_3(F,OH)$	3539	7.40
$Sr_5(VO_4)_3(F,OH)$	3537	7.43

of the hydroxyl ions replaced by fluoride ions, and also a sample of natural Holly Springs hydroxyapatite which contained both fluoride and chloride ions. In addition to the main hydroxyl band at 3572 cm^{-1} the first substance showed a band at 3545 cm^{-1}, the second sample two bands at 3540 and 3495 cm^{-1}. The bands near 3540 cm^{-1} are ascribed to O–H. . .F interactions, and the band at 3495 cm^{-1} is said to be probably due to O–H. . .Cl interactions. This is in good agreement with our results. The fact that some of their wave numbers differ a little from ours may be a consequence of the different OH content of the samples.

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