APPLICATION OF THE PEAK FITTING PROGRAM "GALACTIC" FOR FTIR ANALYSIS OF OH⁻ IONS IN APATITE

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Abstract. The results of the FTIR analysis of the vibration of OH⁻ ions in magmatic, sedimentary, and synthetic apatites obtained with the Peak Fitting Program "Galactic" are presented. Comparative analysis of the dependence of the OH stretching mode vibrations at 3600–3500 cm^{-1} depending on the composition of apatite, particularly on the content of CO_3^{2-} and F⁻ ions, is performed. This domain of FTIR spectra of apatites can be used for revealing the peculiarities of their structure.

Key words: apatite, magmatic, sedimentary, synthetic, FTIR analysis, peak fitting, OH stretching mode.

INTRODUCTION

Natural apatites similar by composition to $Ca_{10}(PO_4)_6(F,OH,Cl)_2$ vary largely in their F, OH, and Cl contents. These ions form linear chains parallel to the c-axis of the apatite structure. Pure end members of the fluorhydroxyapatite series are uncommon in nature, though fluorine usually dominates both in magmatic and sedimentary apatites. Sometimes also the presence of oriented water has been identified in apatites as structural rather than absorbed water on the internal surface of apatite. For sedimentary apatites (phosphorites), beside the substitutions on the c-axis, the replacement of PO_4^{3-} by CO_3^{2-} also occurs. Properties of the apatites strongly depend on the substitutions in their crystal lattice. As a rule incorporation of fluorine into the structure of apatite increases its strength, the carbonate ion, on the contrary, makes it weaker.

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Fourier transform infrared (FTIR) spectra of apatites give valuable information on their structural peculiarities, but often the bands of different origin get covered like on the occasion of the OH bands. For a better differentiation of the OH bands in FTIR spectra a special study, in which the computer Peak Fitting Program (PFP) "Galactic" was used, was performed.

By the literature data the most intensive OH band (stretching mode) in the IR spectrum of hydroxyapatite (OHAp) is located at about 3570 cm^{-1}, the libration OH band at 630 cm^{-1}. The half-width of the band at about 3570 cm^{-1} is changed by various methods of OHAp synthesis [1]. This band is narrower and the corresponding extinction coefficient is larger in the case of non-stoichiometric OHAp than in the stoichiometric one [2].

An additional OH stretching band from OH...F hydrogen bond at lower frequencies (about 3540 cm^{-1}) and an additional OH libration band at higher frequencies (about 670 cm^{-1}) appear when a part of the OH groups are substituted by fluorine [3–15]. The frequency of the OH stretch band in the OH...F hydrogen bond increases from 3535 to 3545 cm^{-1} if the content of fluorine decreases [4]. The line shape of this band changes in the IR spectra of synthetic apatites [15]. The stretching OH band at 3498 cm^{-1} has been assigned to a hydrogen bond of OH...Cl [16].

An additional OH stretch at 20 to 30 cm^{-1} below the main OH IR band in OHAp (without any additional OH librational mode) was detected in some synthetic compounds with an apatite structure having various substitutions for calcium and phosphate ions [11]. An additional OH band of uncertain origin was seen at 3544 cm^{-1} in calcium-rich (Ca/P molar ratios from 1.67 to 1.83) OHAp [17].

The spectra of OH^- ions in mineral fluorapatites (FAp) have been investigated in the range of 4000 to 3000 cm^{-1}. The bands were determined at about 3540 cm^{-1} and in some cases also at about 3570 and 3500 cm^{-1}. Sometimes a number of OH stretching bands with frequencies exceeding 3600 up to 3850 cm^{-1} were also detected and these had not always strict orientation [7,11,12].

In the IR spectra of magmatic apatites the OH stretching mode is always registered in the interval of 3500–3600 cm^{-1} on the background of the band of the water at about 3400 cm^{-1}. In the IR spectra of sedimentary apatites the detection of OH^- ions is problematic because they are masked by a significant quantity of water. Water slightly oriented in the apatite structure was identified by the polarized IR spectra of the oriented sections of apatite single crystals [4, 7]. Structural water distinguished from adsorbed water was determined also in OHAp synthesized by the wet method [1].

MATERIALS AND METHODS

Magmatic apatites from various deposits were analysed: Kola (Russia), Kovdor (North Karelia), Siilinjärvi (Central Finland), Kiruna (North Sweden),

and Sokli (North Finland). The apatite from Kola apatite rock is typical igneous FAp relatively well corresponding to the ideal apatite formula $Ca_{10}(PO_4)_6F_2$. The other analysed apatites represent fluorhydroxyapatites with the formula $Ca_{10}(PO_4)_6F_n(OH)_{2-n}$. The content of fluorine in Siilinjärvi and Kiruna apatites is higher ($n = 1.3$–1.5), in Sokli apatite medium ($n = 0.9$–1.0), in Kovdor apatite much lower ($n = 0.6$–0.7). Detailed data on the magmatic apatite samples used in the experiments have been published in [18–20].

Phosphorite samples of Egor'evsk (Russia), Rakvere (Estonia), Arad and Nahal Zin (Israel) deposits as well as a sample of metamorphic apatite of Karatau phosphorite basin (Kokdgon deposit, Kazakhstan) were studied. According to the data of chemical analyses (Table 1) the content of fluorine in the samples ($n = 1.89$–2.06) is close to the theoretical value for FAp, except the Egor'evsk phosphorite in which it is much higher ($n = 2.31$). This indicates a possibility of the incorporation of CO_3F^{3-} ions into the apatite structure [21]. The phosphorite samples differ in the amount of the CO_3^{2-} ions substituting the PO_4^{3-}: in the Egor'evsk phosphorite sample the molar ratio of CO_3/PO_4 is the highest (0.29), in the Kokdgon phosphorite the lowest (0.11).
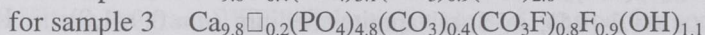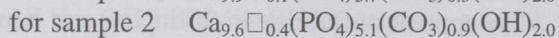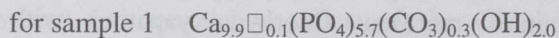
Table 1

Amounts of the main constituents in the phosphorite samples* (%)

Constituent	Sample				
	Arad	Nahal Zin	Egor'evsk	Rakvere	Kokdgon
P_2O_5	33.4	36.7	29.1	32.1	27.2
CaO	51.4	52.8	49.0	50.1	42.6
F	3.0	3.1	3.0	2.7	2.5
CO_2	3.9	2.8	5.2	3.0	1.8
Mole ratio CO_3/PO_4	0.21	0.13	0.29	0.15	0.11
n in apatite formula	2.01	1.89	2.31	1.89	2.06

* The samples were treated with triammonium citrate solution (pH = 8) to eliminate calcite and dolomite from the phosphorite concentrate [22, 23].

Three samples of synthetic apatite with different composition were also investigated to compare the data on OH groups with the results for natural apatites. Apatites were synthesized by precipitation from solutions at 80 °C and pH = 9 by the method described in [24]. Synthetic apatites were identified by XRD and IR as B-type carbonateapatites (CO_3^{2-} substitutes for PO_4^{3-}). On the basis of the data of analysis and the principle of electroneutrality, the

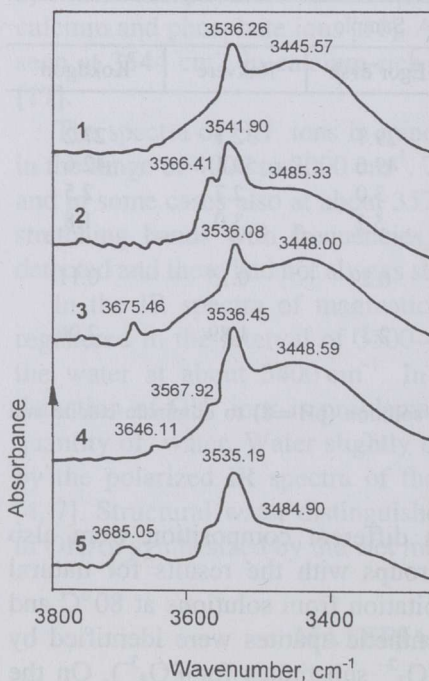composition of the samples obtained can be expressed by the following formulas:

for sample 1 $Ca_{9.9}\square_{0.1}(PO_4)_{5.7}(CO_3)_{0.3}(OH)_{2.0}$
for sample 2 $Ca_{9.6}\square_{0.4}(PO_4)_{5.1}(CO_3)_{0.9}(OH)_{2.0}$
for sample 3 $Ca_{9.8}\square_{0.2}(PO_4)_{4.8}(CO_3)_{0.4}(CO_3F)_{0.8}F_{0.9}(OH)_{1.1}$

The squares ($\square$) in the formulas indicate that the synthesized apatites belong to the Ca-deficient type of apatites.

The FTIR spectra of mineral and synthetic apatites were recorded with Nicolet ZDX FTIR spectrometer. The samples were pressed into KBr pellets (5 mg of sample per 300 mg KBr) under vacuum at pressure 0.1 Pa.

An analysis of the line shape of the OH bands in the FTIR spectra was carried out by means of PFP "Galactic". This program enables fitting peak shapes and the baseline of the experimental spectra with various functions, estimating the number of the peaks and their positions and the amplitudes on the spectra. It also enables to study the residuals [25]. The best line shape function for the approximation of FTIR data was Lorentzian–Gaussian mixture.

RESULTS AND DISCUSSION

Fig. 1. OH and H$_2$O bands in the FTIR spectra at 3300–3800 cm^{-1} of magmatic apatites from Kola (1), Kovdor (2), Kiruna (3), Siilinjärvi (4), and Sokli (5) deposits.

The OH stretching modes in the FTIR spectra of magmatic apatites are shown in Fig. 1. In the interval from 3500 to 3600 cm^{-1} only two OH bands can be seen. An analysis of the line shape of these bands by means of the program "Galactic" shows a more complicated picture. Decomposition of the bands and the residual trace are shown in Fig. 2. The results of the analyses are shown in Table 2.
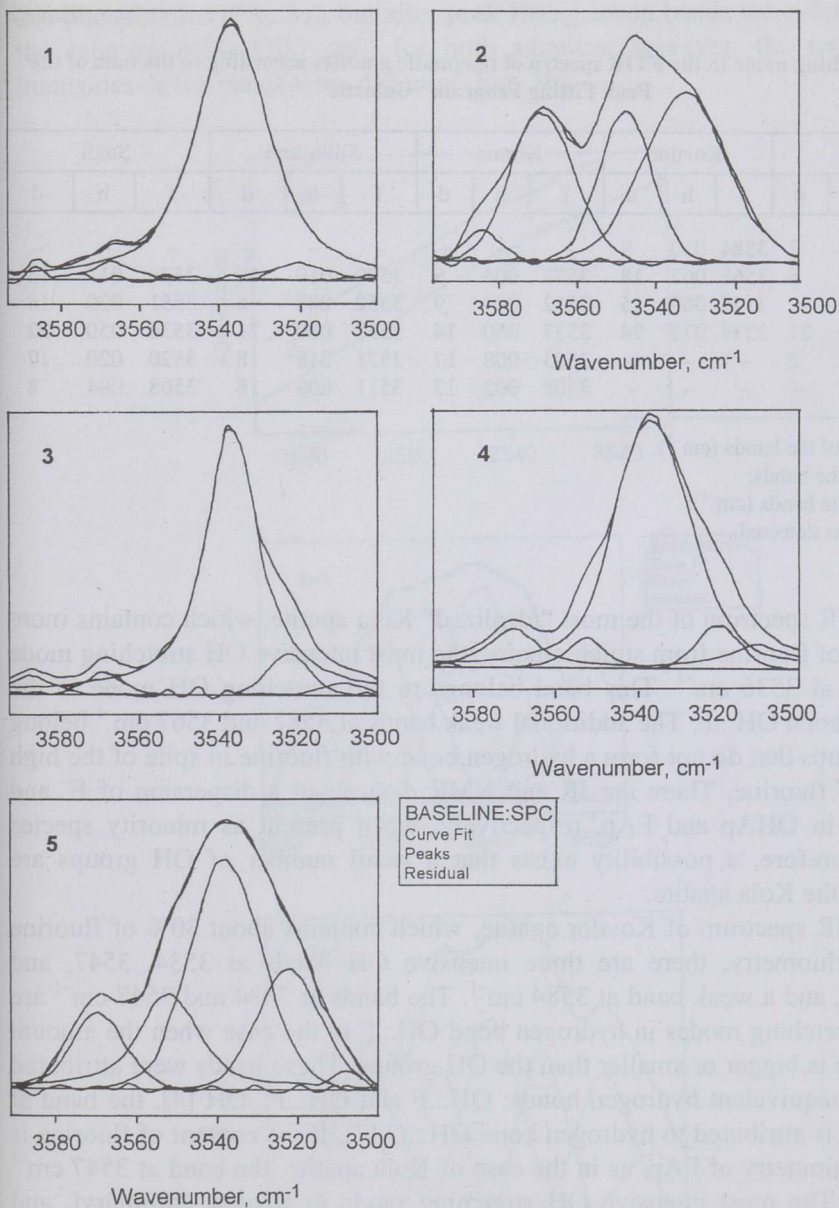
Fig. 2. Decomposition of the OH stretching mode and the residual trace after Peak Fitting Program "Galactic" in the FTIR spectra of magmatic apatites from Kola (1), Kovdor (2), Kiruna (3), Siilinjärvi (4), and Sokli (5) deposits.

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Table 2

OH stretching mode in the FTIR spectra of magmatic apatites according to the data of the Peak Fitting Program "Galactic"

Kola			Kovdor			Kiruna			Siilinjärvi			Sokli		
f	h	d	f	h	d	f	h	d	f	h	d	f	h	d
3587	003	2	3584	010	9	–	–	–	–	–	–	–	–	–
3567	002	5	3568	067	18	3572	004	9	3570	010	10	3570	017	15
–	–	–	3547	067	15	3552	004	9	3552	007	6	3551	020	18
3536	040	21	3534	075	24	3537	050	14	3537	080	21	3536	050	22
3520	003	2	–	–	–	3523	008	17	3521	018	18	3520	020	17
–	–	–	–	–	–	3508	002	12	3511	008	18	3508	004	8

f, frequence of the bands (cm^{-1});
h, height of the bands;
d, width of the bands (cm^{-1});
– no peak was detected.

In the IR spectrum of the most "idealized" Kola apatite, which contains more than 90% of fluorine from stoichiometry, the most intensive OH stretching mode is located at 3536 cm^{-1}. This band belongs to the stretching OH mode in the hydrogen bond OH...F. The additional weak bands at 3587 and 3567 cm^{-1} belong to OH groups that do not form a hydrogen bond with fluorine in spite of the high content of fluorine. There are IR and NMR data about a dispersion of F$^-$ and OH$^-$ ions in OHAp and FAp, respectively, when present as minority species [4, 7]. Therefore, a possibility exists that a small number of OH groups are present in the Kola apatite.

In the IR spectrum of Kovdor apatite, which contains about 30% of fluorine from stoichiometry, there are three intensive OH bands at 3534, 3547, and 3568 cm^{-1}, and a weak band at 3584 cm^{-1}. The bands at 3534 and 3547 cm^{-1} are the OH stretching modes in hydrogen bond OH...F in the case when the amount of fluorine is bigger or smaller than the OH groups. These bands were attributed to two nonequivalent hydrogen bonds: OH...F and OH...F...OH [4], the band at 3568 cm^{-1} is attributed to hydrogen bond OH...O [7]. If the content of fluorine is near stoichiometry of FAp, as in the case of Kola apatite, the band at 3547 cm^{-1} is absent. The most intensive OH stretching mode in Kiruna, Siilinjärvi, and Sokli apatite spectra is located at about 3537 cm^{-1}. The other bands, including the band at 3552 cm^{-1} lacking in the spectra of Kola apatite, also coincide, but the ratios of their intensities differ greatly. The spectrum of Sokli apatite, containing more OH$^-$ ions and also CO$_3^{2-}$ groups, includes four intensive bands.

We have emphasized that the OH bands in the IR spectra of sedimentary apatites are masked by water. However, the use of PFP allowed us to see the OH stretching mode in the spectra of sedimentary apatites on the background of the water band. We did not see any OH bands in the IR spectra of Arad and Nahal

Zin phosphorites (Fig. 3a), but after peak fitting seven bands were determined in the interval 3600–3500 cm^{-1} for both samples; however, the ratios of the intensities of the bands were different (Fig. 3b).
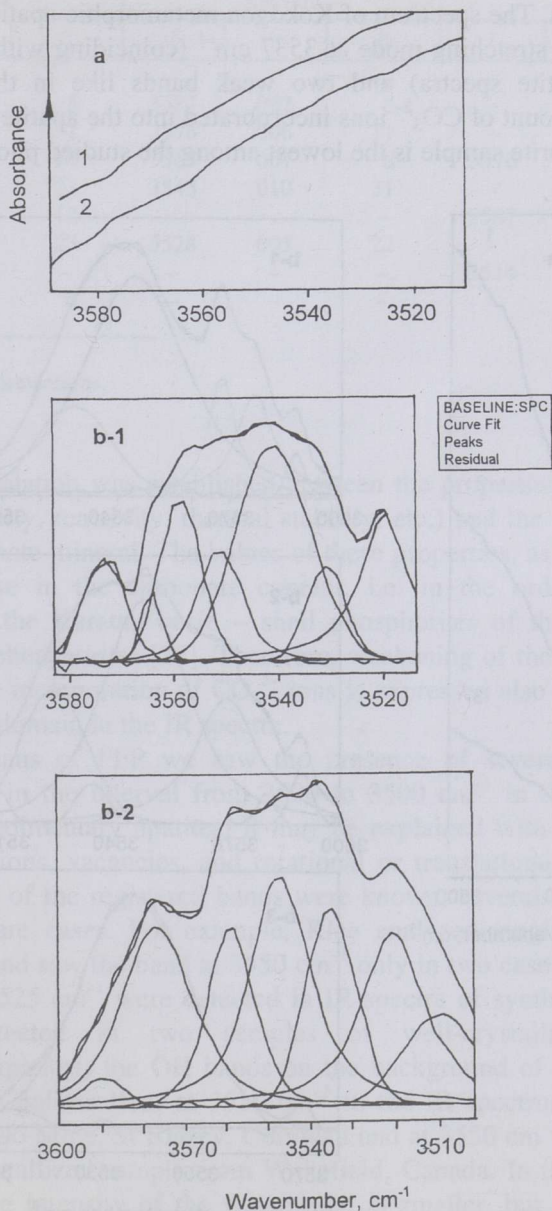

Fig. 3. OH bands in the FTIR spectra of Israel sedimentary apatites: 1, Arad and 2, Nahal Zin deposits. a, initial spectra; b-1 and b-2, decomposition of the OH stretching mode and the residual trace after Peak Fitting Program "Galactic" in the FTIR spectra.

The spectra of other phosphorites in this interval are presented in Fig. 4, the numerical data in Table 3. In the peak-fitted spectrum of Egor'evsk phosphorite, in which the content of carbonate and fluorine are the highest, seven bands can be established. The stretching modes in the Rakvere phosphorite spectrum include five bands. The spectrum of Kokdgon metamorphic apatite contains only one intensive OH stretching mode at 3537 cm^{-1} (coinciding with the main band in magmatic apatite spectra) and two weak bands like in the Kola apatite spectrum. The amount of CO_3^{2-} ions incorporated into the apatite structure of the Kokdgon phosphorite sample is the lowest among the studied phosphorites.
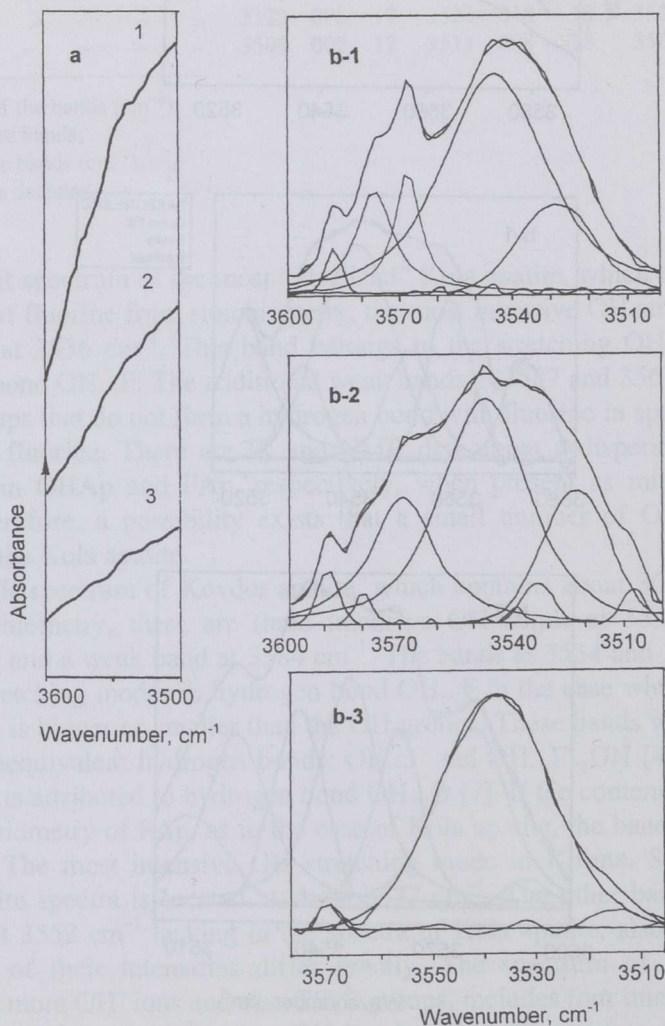

Fig. 4. OH bands in the FTIR spectra of phosphorites from Rakvere (1), Egor'evsk (2), and Kokdgon (3). a, initial spectra; b-1–b-3, decomposition of the OH stretching mode and the residual trace after Peak Fitting Program "Galactic" in the FTIR spectra.

Table 3

OH stretching mode in the FTIR spectra of phosphorites according to the data of the Peak Fitting Program "Galactic"

Egor'evsk			Rakvere			Kokdgon		
f*	h	d	f	h	d	f	h	d
3589	003	5	3587	002	5	–	–	–
3579	001	2	3576	006	11	–	–	–
3568	008	24	3567	007	8	3570	001	2
3547	012	24	3545	010	31	–	–	–
3534	003	12	–	–	–	3537	007	25
3523	008	23	3528	005	22	–	–	–
–	–	–	–	–	–	3514	0005	9
3507	002	6	–	–	–	–	–	–

* See Table 2 for abbreviations.

Earlier a correlation was established between the properties of phosphorites (porosity, solubility, reactivity, thermal stability, etc.) and the content of CO_3^{2-} ion in the phosphate mineral. The values of these properties, as a rule, are rising with the increase in the carbonate content, i.e. in the order: metamorphic phosphorites of the Karatau basin – shell phosphorites of the Baltic basin – Russian pebble phosphorites [25]. Therefore, weakening of the apatite structure as a result of the incorporation of CO_3^{2-} ions is expressed also in the OH bands stretching mode domain in the IR spectra.

Thus, by means of PFP we saw the presence of several bands of OH stretching mode in the interval from 3600 to 3500 cm^{-1} in the IR spectra of magmatic and sedimentary apatites. It may be explained with the existence of various substitutions, vacancies, and rotational or translational disorder in the structure. A part of the registered bands were known, several bands have been determined in rare cases. For example, Klee analyzed single crystals of 25 natural apatites and saw the band at 3550 cm^{-1} only in two cases [12]. Shoulders near 3585 and 3525 cm^{-1} were detected in IR spectra of synthetic apatites [2]. Elliott [4] detected in two samples of well-crystallized francolites (fluorcarbonate apatites) the OH bands on the background of the water in the parallel to c-axis polarization: at 3510 cm^{-1} in the IR spectrum of the sample from Fowey Conso Mine, St Blazey, Cornwall and at 3550 cm^{-1} in the spectrum of the better crystallized sample from Wakefield, Canada. In the case of better crystallization the intensity of the water band is smaller, but the band of OH groups has a higher frequency and intensity [4].

The effect of the chemical composition of apatites on the OH bonds can also be demonstrated for synthetic apatites. An analysis of the OH stretch in the spectra by means of PFP testified the existence of various OH clusters in the

presence of carbonate and fluorine ions (Fig. 5). The rise of the content of CO_3^{2-} ions and the entering of fluorine into the apatite structure causes an increase in the number of the peaks and a change in their intensities.

Therefore, spectra of natural apatites, particularly of sedimentary apatites, in the domain of OH stretching modes are affected by CO_3^{2-} ions in the apatite structure. It is valid also for Kovdor and Sokli apatites where the presence of CO_3^{2-} ions in the apatite structure was established by selective dissolution [22, 23] and chemical analysis.
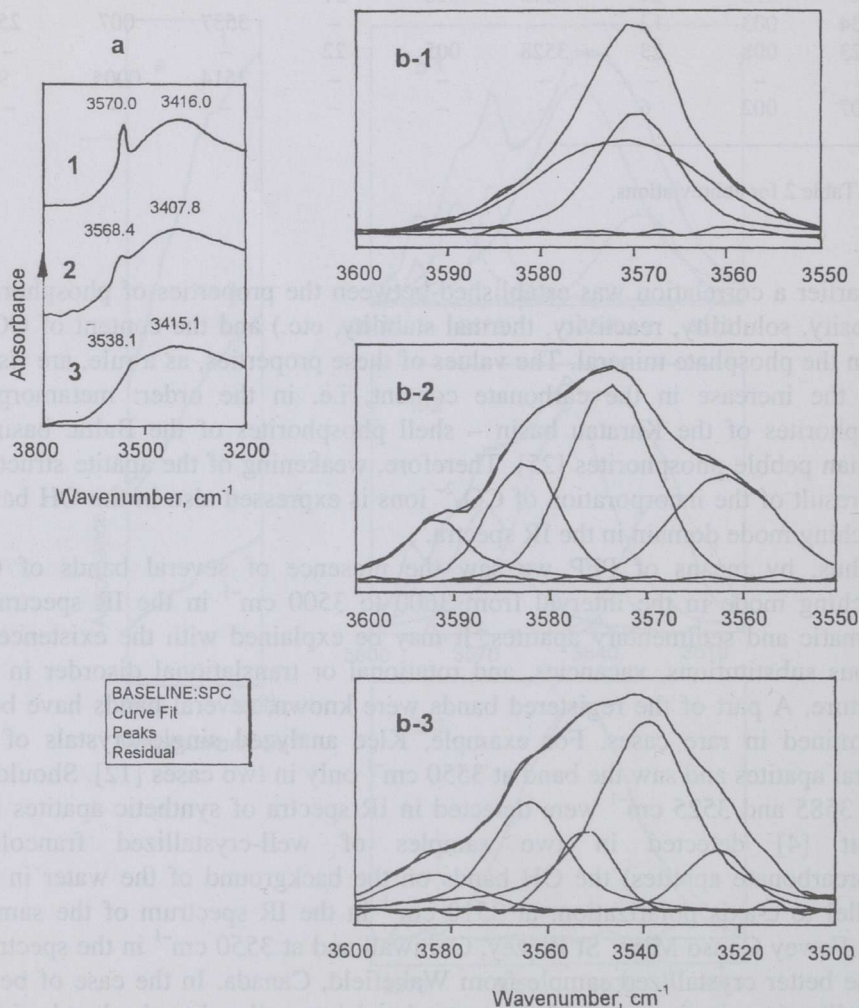

Fig. 5. OH and H_2O bands in the FTIR spectra of synthetic apatites at 3800–3200 cm^{-1}: a, initial spectra; b-1–b-3, decomposition of the OH stretching mode and the residual trace after Peak Fitting Program "Galactic" in the FTIR spectra.

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CONCLUSIONS

The multiplicity of OH groups in magmatic, sedimentary, and synthetic apatites was determined by means of the Peak Fitting Progam "Galactic". The dependence of the OH stretching mode in the FTIR spectra on the composition of apatites, particularly on the content of CO_3^{2-} and F^- ions, was shown for the synthetic samples. The use of the Peak Fitting Program "Galactic" makes it possible to determine the OH stretching mode in the FTIR spectra of sedimentary apatites on the background of the water band. Deconvoluted FTIR spectra of the apatites in the domain of OH stretching mode can be used as one of the characteristics of apatites to bring out their peculiarities in the structure and properties.

ACKNOWLEDGEMENT

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PIIGISOBITUSPROGRAMMI "GALACTIC" RAKENDAMINE APATIIDIS SISALDUVATE OH⁻-RÜHMADE FTIP-ANALÜÜSIS

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On esitatud magmaatiliste, setteliste ja sünteetiliste apatiitide FTIP-spektrites OH⁻-ioonide võnkumistele vastavate piikide lahutamise tulemused vahemikus 3600–3500 cm⁻¹. Piikide lahutamiseks kasutati programmi "Galactic". Analüüsiti apatiidi OH-rühmade venitusvõngete sõltuvust apatiidi koostisest, peamiselt CO_3^{2-}- ja F⁻-ioonide sisaldusest. Apatiitide FTIP-spektrite abil saab esile tuua apatiitide struktuurierinevusi.