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Impact of anionic substitutions on apatite structure and properties

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Abstract

A review of the results of the authors on single and coupled substitutions of F for OH, and of CO_3 and SO_4 for PO_4 in synthetic and natural apatites, their influence on apatite structure and properties, studied by peak fitting FTIR, XRD, TG/DTA and TG/EGA methods, is presented. Calcination of carbonate and sulphate substituted apatites leads to the formation of stable stoichiometric apatite.

Keywords: Apatite; Fluorhydroxy-; Carbonate-; Sulphate-; FTIR; XRD; TG/DTA; TG/EGA

1. Introduction

Apatite is a basic mineral of phosphate ores as well as a component of bones and teeth of vertebrates. Apatites have found use in several applications such as sorbents, catalysts, and biomaterials. The structure and chemistry of apatites is thoroughly reviewed by Elliot [1,2].

Apatites may contain several different substituents in their structure. The properties of apatites depend on the nature of monovalent anion, substitutions for PO_4 groups and cationic sites (especially in Ca II position) [3].

In this paper the results of a research of the authors on the impact of anionic substituents, singly and coupled, on the structure and properties of natural and synthetic calcium apatites are presented.

2. Fluorhydroxy-apatites and hydrogen bond

Natural apatites (in particular the magmatic ones) are usually fluorhydroxy-apatites (FOHAp) with variable F:OH ratio: $Ca_{10}(PO_4)_6F_n(OH)_{2-n}$. Anomalies in the behaviour of natural and synthetic FOHAps in thermal, dissolution and adsorption processes have been established, manifested by their lower reactivity in comparison with pure F- or OH-apatites. For example, the studies on the hydrothermal processing of FOHAp revealed that in the course of the reaction the degree of defluorination remains lower than the decomposition rate of the apatite, thus fluorine is remained in the structure [4]. These phenomena are explained by the existence of strong OH–F hydrogen bonding in apatite structure.

The presence of OH bonding can be detected by IR spectroscopy in the domain of the OH stretching mode at 3500–3600 cm^{-1} and the libration OH mode at 630 cm^{-1}. Shifts in the frequencies of these vibrations and the appearances of the additional ones, as well as their overlapping and masking by water molecule vibrations, complicate the interpretation of apatite spectra. For a better differentiation of the OH bands in FTIR spectra the Peak Fitting Program "Galactic" [5–8] was used.

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Samples investigated were distributed into three groups: (1) synthetic apatites obtained by precipitation from solutions as described in [6]; (2) magmatic apatites from Northern Europe; and (3) sedimentary apatites (phosphorites) of different deposits.

The effect of the chemical composition of apatites on the OH bonds can be easily demonstrated for synthetic non-stoichiometric carbonate apatites with different CO_3:PO_4 and OH:F mole ratios, containing also vacancies. The increase in the content of CO_3 groups and fluorine in apatite structure causes an increase in the number of the peaks and a change in their intensities (Fig. 1). Analysis of the OH stretching vibrations in the apatite spectra testified the existence of various OH clusters in the presence of carbonate and fluorine ions [6].

In magmatic apatites the highest content of fluorine is in Kola apatite ($n = 1.9$), the lowest in Kovdor apatite ($n = 0.6$). Sedimentary apatites are B-type carbonate apatites with mole ratio of CO_3/PO_4 in the range from 0.1 for metamorphic Karatau phosphorite to 0.3 for pebble phosphorite from Jegor'evsk deposit. The last named sample occurs as an exception, containing excess of fluorine regarding the stoichiometry, which may be explained by an existence of coupled ionic group of CO_3^{2-} and F^- [1,9].

The OH stretching mode in FTIR spectra of magmatic apatites are shown in Fig. 2(a). In the interval of 3500–3600 cm^{-1} only two OH bands are found. However, the line shape of these bands obtained by peak fitting reveals a more complicated picture (Fig. 2(b)). In the IR spectrum of the most "idealized" Kola fluorapatite, the intensive OH stretching mode is located at 3536 cm^{-1}. The weak bands at 3587 and 3567 cm^{-1} belong to OH groups that do not form a hydrogen bond with fluorine. In the spectra of Kovdor apatite three intensive OH bands at 3534, 3547 and 3568 cm^{-1} and a weak band at 3584 cm^{-1} have been found. The bands at 3534 and 3547 cm^{-1} belong to the OH stretching mode in hydrogen bond OH···F in case the amount of fluorine is, respectively, bigger or smaller than that of OH groups. The band at 3568 cm^{-1} belongs to hydrogen bond OH···O [1]. The most intensive OH stretching mode in Kiruna and Siilinjärvi (for both $n = 1.5$) apatite spectra, as well as in Kola apatite, is located at about 3537 cm^{-1}.

The IR spectra of sedimentary apatites are much more complicated (Fig. 3). In the peak-fitted spectrum of Jegor'evsk phosphorite, in which the contents of carbonate and fluorine are the highest, seven bands were

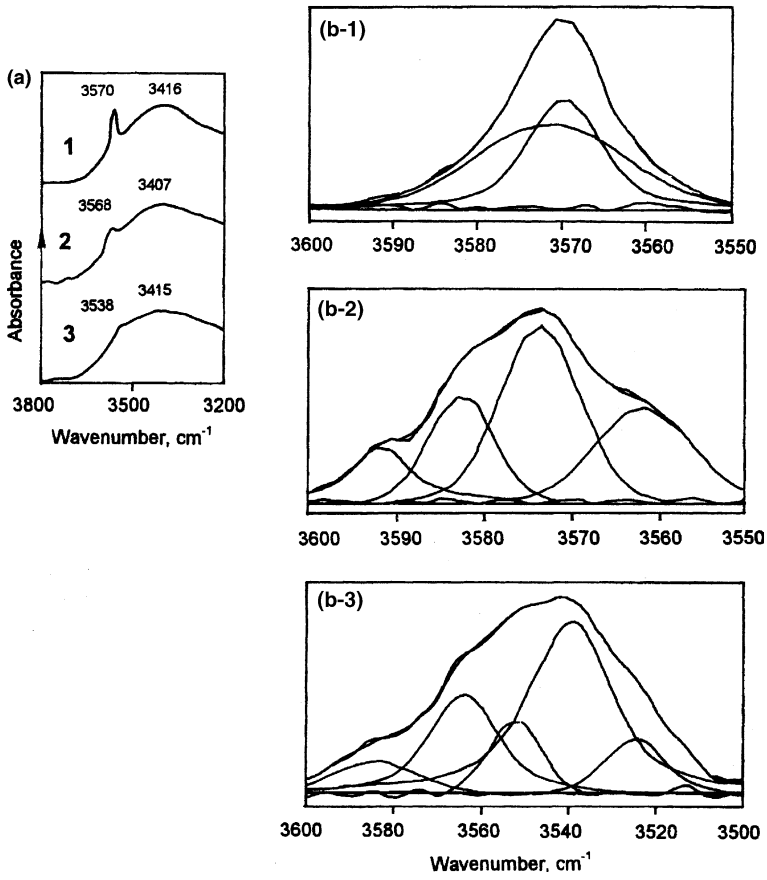

Fig. 1. FTIR spectra of synthetic apatites: 1, $Ca_{9.9 \pm 0.1}(PO_4)_{5.7}(CO_3)_{0.3}(OH)_2$; 2, $Ca_{9.6 \pm 0.4}(PO_4)_{5.1}(CO_3)_{0.9}(OH)_2$; 3, $Ca_{9.8 \pm 0.2}(PO_4)_{4.8}(CO_3)_{0.4}$-$(CO_3F)_{0.8}F_{0.9}(OH)_{1.1}$. (a) OH and H_2O bands. (b) decomposition of the OH ν_1 mode by peak fitting.