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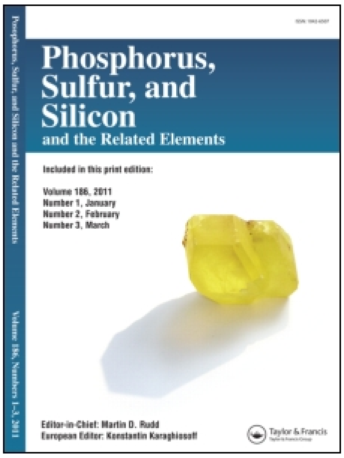

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Dynamic Crystallochemistry of Apatite

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DYNAMIC CRYSTALLOCHEMISTRY OF APATITE

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Abstract Analysis of anions ability to transfer from one structural position into another is applied for predicting the properties of apatite.

INTRODUCTION

Our laboratory is working on the exploration of structural peculiarities of apatites and dynamics of their crystallographic lattice. Let us enumerate the main results obtained while studying mineralogical, biological and synthetic apatites.

EVERY ATOM IN NATURAL APATITE IS CHARACTERIZED BY AT LEAST TWO CRYSTALLOCHEMICAL POSITIONS

Anions in the Channels on the Hexagonal Axis

There is always partial substitution of fluorine for hydroxyl ions, frequently for oxygen and sometimes for chlorine in natural apatites. Hydroxyl groups located on hexagonal axis of the structure form hydrogen bonds with other anions.

NMR ^{19}F and ^{1}H experiments revealed that formation of hydrogen bonds occured simultaneously with displacement of both - hydroxyl groups and fluorine atoms along hexagonal axis towards each other, out of symmetry plane, besides these species form clusters with the distance between fluorine and proton atoms and between two neighbouring fluorine atoms being 2.03 Å and 3.7 Å, respectively.

The polarized infrared spectra of oriented sections of single crystals of apatites established the existence of hydroxyl groups nonforming hydrogen bonds. The difference in energy between these two possible states of hydroxyl groups is 0.8 kcal/M.

Carbonate Ions in Apatite

Carbonate ions were shown to be included into apatite structure, where they can be located in two different crystallographic positions (instead of ortophosphate group and on hexagonal axis). These positions are characterized by different changes of lattice parameters and absorption bands with various frequencies and polarisation in IR spectra.

Carbonate ions are always found in natural apatites, and their quantity and distribution between mentioned above two nonequivalent crystallographic positions in the structure strongly depends upon the crystallization conditions and is different for minerals obtained from various rocks.

In the biological apatites of dental enamel preferential location of carbonate ions in the positions of orthophosphate groups is created during the maturation of teeth and disappears when carious process develops.

Phosphate Groups in Apatites

According to the ideal structural model phosphorus forms isolated orthophosphate groups in apatite. Nevertheless in the real structure of natural apatites partial condensation of orthophosphate groups to pyrophosphates also takes place. The spectroscopic indications of this condensation is the registration of weak absorption bands of vibration of bridge bonds P-O-P at the frequencies 720 and 750 cm^{-1} in IR and Raman spectra of apatites. In the polarized IR spectra of the oriented sections of single crystals the direction of the absorption bands at 720 and 750 cm^{-1} parallel and perpendicular to hexagonal axis of the structure respectively was established. Simulation of X-ray powder diffraction pattern revealed that even regular condensation of orthophosphate groups to pyrophosphates in the apatite structure doesn't change the picture, causing only pertubation of relative intensities of several lines.

Isomorphism of cations

The distribution of cations impurities between two positions depends upon the quantity of the cations and the other isomorphic substitution and defects in real structure. In the apatites of famous Chibin ores strontium is preferentially located in the position Ca II, while rare earth elements - in the position Ca I.

THE INTRINSIC MOBILITY OF ANIONS IN APATITE IS DISPLAYED DURING THERMAL TREATMENT OF THE MINERAL. FLUORINE CONTENT IS OF EXTREME IMPORTANCE FOR THIS MOBILITY.

Anions' Mobility in the Channels along Hexagonal Axis of the Structure

Thermal treatment of the apatites of sedimentary origin leads to formation of hydrogen bonds in the structure. Interesting results were obtained while studying the temperature effect on hydroxyapatite: additional "hot" absorption stretching bands of hydroxyl groups appear in the spectrum, this phenomenon being reversible.

Dynamics of Carbonate Ions

The removal of carbonate ions from the apatite structure during heating is accompanied by their decomposition resulting in the formation of CO_2, and relocation from one structural position into the other. The inhibition effect of fluorine on the relocation of carbonate ions from orthophosphate position to the hexagonal axis of the structure was shown for model synthetic compounds. The interaction of carbonate ions with nitrogen and formation of cyanate and cyanamide groups may take place during heating of an apatite.

Dynamics of phosphate groups

Condensation of orthophosphate groups in apatite is dynamic. The condensation is attributive for the apatites of high temperature origin, while in the case of the apatites of sedimentary origin it appears only after heating. The dynamics of condensations depended on the isomorphic substitution in the apatite structure. The fluorine content in the apatite plays the main role in the regulation of orthophosphate condensation.

PHYSICAL AND PHYSICO-CHEMICAL PROPERTIES OF APATITE DEPEND ON VARIOUS SUBSTITUTION IN STRUCTURE

An extreme dependency of different properties of apatite on the fluorine content was established. The ability of orthophosphate groups for condensation at first increases and then falls during elevation of fluorine content in apatites. Relative surface, crystallinity and quantity of hydrogen bonds also depends in extreme fashion on fluorine content in apatites.

Carbonate ions have a great influence on the properties of apatites, and while located in different structural positions have different influence on such properties of minerals as crystallinity and solubility. The influence of cations impurities on the properties of apatites depends on the type of ions and their distribution between two structural positions. Pyrophosphate groups have a marked effect on the apatite properties activating absorption ability of minerals.

Thus, not only the quantity of various ions in the strucutre, but their distribution between two non-equivalent crystallochemical positions as well is of great importance for the properties of apatites.

TECHNOLOGICAL CHARACTERISTICS OF APATITES ARE MARKEDLY DETERMINED BY THEIR STRUCTURAL PECULIARITIES

Flotation

The flotational properties of apatites depend on peculiarities of their real structure. Increase in condensation of orthophosphate groups, quantity of hydrogen bonds and partial substitution of calcium for strontium activate chemisorbtion of fatty acid collectors on apatite surface, while increase in substitution of phosphate groups for carbonate ions inhibits this process. Apatite is an exceptional mineral as regards interaction with N-acylated aminoacids. There can't be unambigious influence of the quantity of certain isomorphic impurity on the absorptional properties of apatite, only crystallochemical study of the mineral is suitable for prediction of its flotational characteristics.

Heating

On thermal treatment the structure of phosphate mineral in phosphorites approaches the apatite one, but sometimes heating may be accompanied by relocation of major part of carbonate ions from one structural position into the other, entry of silicon and sulphur from impurities, into apatite. Study of dynamics of phosphate mineral lattice is useful for prediction of applicability of heating for the raw material type analyzed.

Crystallochemistry of apatite has changed qualitatively: it has become dynamic. The study of the strict location of separate atoms in the apatite structure is being now accompanied by intense exploration of intrinsic mobility of ions in the lattice on the energetic treatment of minerals. Dynamic crystallochemistry possesses great possibilities in prediction of the properties of solids.