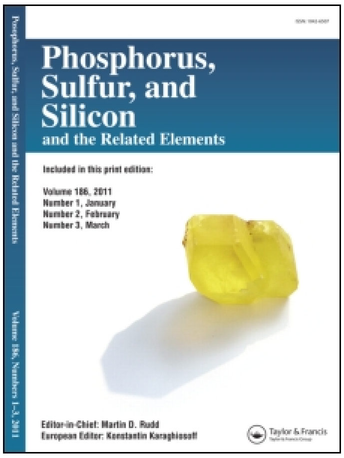

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Fluorhydroxyapatites of Northern Europe and Their Thermal Transformations

Mihkel Veiderma; Rena Knubovets; Kaia Tônsuaadu

To cite this Article Veiderma, Mihkel , Knubovets, Rena and Tônsuaadu, Kaia(1996) 'Fluorhydroxyapatites of Northern Europe and Their Thermal Transformations', Phosphorus, Sulfur, and Silicon and the Related Elements, 109: 1, 43 — 46
To link to this Article: DOI: 10.1080/10426509608545086
URL: http://dx.doi.org/10.1080/10426509608545086

ORAL PRESENTATIONS

Phosphorus, Sulfur, and Silicon, 1996, Vols. 109–110, pp. 43–46
Reprints available directly from the publisher
Photocopying permitted by license only

FLUORHYDROXYAPATITES OF NORTHERN EUROPE AND THEIR THERMAL TRANSFORMATIONS

MIHKEL VEIDERMA*, RENA KNUBOVETS**, KAIA TÔNSUAADU*
* Tallinn Technical University, Tallinn, EE0026, Estonia
**The Open University of Israel, Ramat Aviv, Tel Aviv 61392, Israel

Abstract Peculiarities in the composition, structure and thermal properties of fluorhydroxyapatites of Northern Europe have been studied by XRD, FTIR, chemical and thermal analyses.

Key Words: Phosphate rock, fluorhydroxyapatite, properties, thermal transformations.

A belt of apatite containing rocks in Northern Europe is known mainly from Kola apatite rock which is a typical igneous fluorapatite relatively well corresponding to the ideal formula $Ca_{10}(PO_4)_6F_2$. The apatites of Kovdor (North Karelia), Siilinjärvi (Central Finland) and Kiruna (North Sweden) deposits being already exploited and of Sokli deposit (North Finland) discovered recently represent fluorhydroxyapatites (F,OHAp) $Ca_{10}(PO_4)_6F_{2-n}(OH)_n$.

As a result of rock enrichment apatite concentrates (ApC) containing 32-37 % of P_2O_5 are obtained. They differ, to some extent by the composition and structure of the apatitic mineral, but essentially by the origin and quantity of the accompanying minerals (Table). In spite of a higher reactivity these ApC are more complicated raw materials for processing in comparison with the high quality Kola ApC. Nevertheless, Siilinjärvi ApC is used for the production of phosphoric acid by wet method, Kovdor ApC for obtaining feed phosphates by thermal processing.

The content of fluorine in Siilinjärvi and Kiruna Ap is approximately the same ($n = 0.5$-0.7), in Kovdor Ap much lower ($n = 1.3$-1.4). The main accompanying minerals in Kovdor ApC are calcite, dolomite and forsterite, in Siilinjärvi ApC calcite and flogopite, and in Kiruna ApC calcite, talc and magnetite.

Differences in the structure and thermal properties of the Ap have been studied by the methods of XRD (DRON-4), IR spectroscopy (Nicolet FTIR with FSD), thermal (MOM) and chemical analyses. For XRD and IR studies the ApC were previously treated by triammonium citrate solution for the elimination of calcite and dolomite.

TABLE Characteristics of apatite concentrates

Chemical composition, %	Kola	Kiruna	Siilinjärvi	Kovdor
P_2O_5	39.6	31.5	36.4	36.5
CaO	52.0	51.5	53.1	51.1
MgO	0.2	0.8	1.4	2.7
F	3.3	2.1	2.4	1.0
SiO_2	0.7	3.0	0.5	1.4
CO_2		6.5	4.4	3.4
Fe_2O_3	0.4	1.9	0.5	0.5
Molar ratio F/6P	1.87	1.49	1.48	0.61
Unit cell parameters, Å				
a, ±0.002	9.384	9.403	9.402	9.403
a*,±0.005		9.394	9.398	9.400
c, ±0.005	6.893	6.904	6.904	6.884

* calcined at 1350 °C in air.

The XRD patterns of the apatites are typically apatitic, with slight shifts in peak positions and intensities. The unit cell parameter *a* changes from 9.421 to 9.376 Å in accordance with the increase in fluorine content in the Ap (Table). Changes in the unit cell parameters are influenced also by the other substitutions and by differences of the ion positions in the Ap structure, specified by means of IR spectra.

In IR absorption spectra of the igneous Ap beside the typical bands of PO_4^{3-} asymmetric deformation v_4 at 605, 570 cm^{-1}, symmetric valence v_1 oscillation at 963 cm^{-1} and asymmetric valence v_3 oscillation at 1042, 1093 cm^{-1}, also other bands are usually revealed, belonging to the OH-groups on the hexagonal axis of the Ap crystal, to P-O-P bond and to CO_3^{2-} group in the PO_4^{3-} position or on hexagonal axis.

A comparison of the Ap spectra in the domain of valence oscillations of OH-group testifies that the maximum spreading of OH...F (3543 cm^{-1}) and OH...O (3566 cm^{-1}) bonds occurs in Kovdor Ap (Fig.1a). The half-width of these bands gives an evidence of a lower regularity of the ions on the hexagonal axis and of the presence of defects. In Siilinjärvi Ap also OH...F and OH...O bonds were detected, but the integral intensity of the bands is lower and the bands are narrower and thus the regularity of the structure is higher. In Kola and Kiruna Ap where the fluorine content is higher, only OH...F band occurs. These data are in agreement with the data of libration oscillations of the OH-group in the studied Ap (Fig.1a). Only in the Kovdor Ap spectrum the

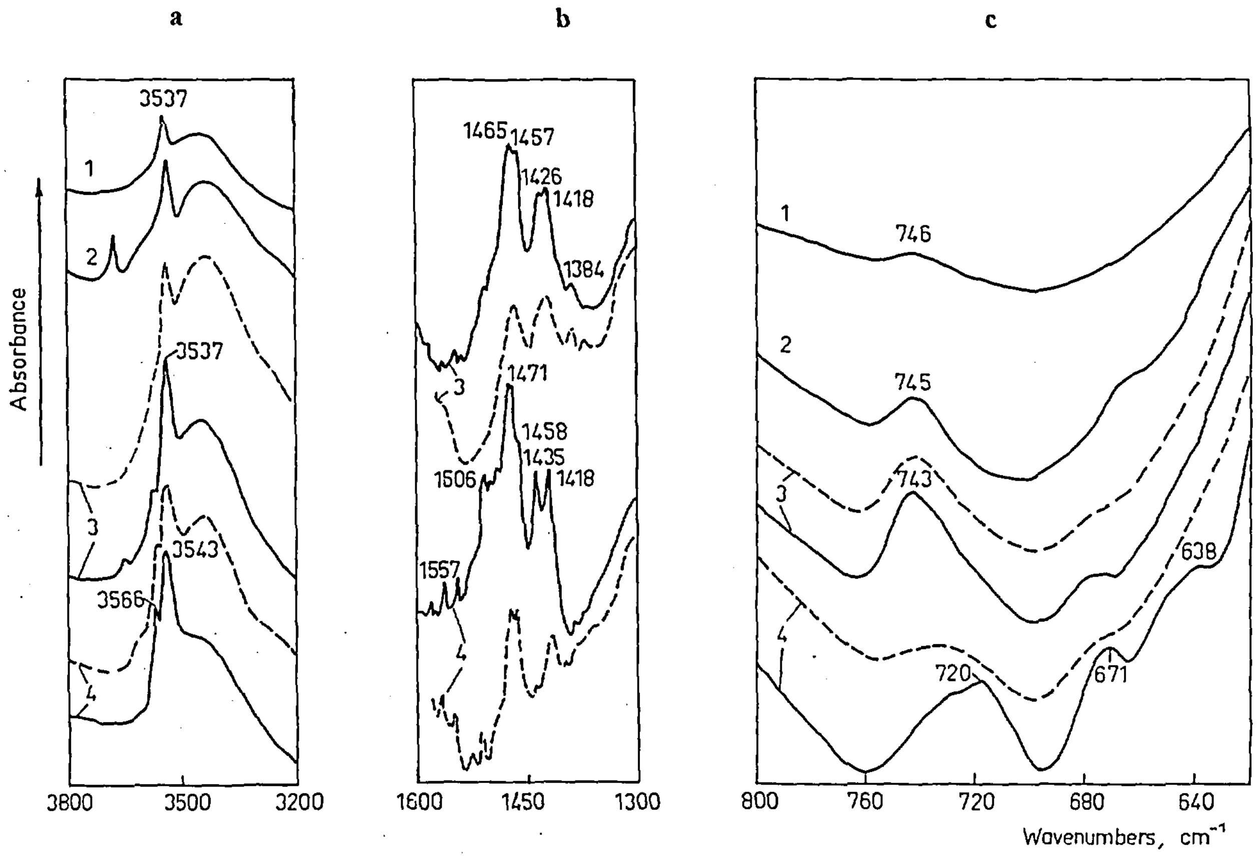

FIGURE IR spectra of Kola (1), Kiruna (2), Siilinjärvi (3) and Kovdor (4) apatites.
—— initial sample; - - - - - sample calcined at 1350 C

bands at 671 and 638 cm^{-1} belonging to librations of the OH-groups in the OH...F and OH...O bonds, respectively, were both distinctly fixed. In the spectra of the other Ap only weak bands at 671 cm^{-1} were seen.

In Fig.1c the bands at 720 and 745 cm^{-1} belonging to the symmetric valence oscillations of P-O-P bridge bonds, formed by the condensation of PO_4^{3-} tetrahedron, are also well seen. The band at 720 cm^{-1} is well expressed only in case of Kovdor Ap. In Kola Ap spectrum only the band at 745 cm^{-1} exists and the P-O-P bond oscillation has the lowest intensity.

Due to the low content, identification of CO_3^{2-} group in Ap structure and its belonging to the A or B type of carbonateapatite (substitution for OH-groups or for PO_4^{3-} ions, respectively) is more complicated. Fig.1b. represents baseline corrected spectra of the Ap studied in the domain of CO_3^{2-} ion oscillations. There are probably at least 7 bands: at 1559, 1540, 1506, 1471-1465, 1458-1456, 1434-1426 and 1417-1419 cm^{-1} from which can be concluded that they all contain CO_3^{2-} ions both at A and B positions. The Kovdor Ap contains CO_3^{2-} ions as well as OH^- ions, to a maximum extent.

On calcination of ApC the main thermoeffect with the maximum at 860 °C is connected with decomposition of carbonates. Thereafter, at 1100 °C, decomposition of Ap begins, fixed by a weight loss in TG curves. The weight loss at 700-900 °C is the biggest for Kiruna ApC, at temperatures higher than 1000 °C for Kovdor ApC, which corresponds to the highest content of carbonates and OH group.

The XRD patterns of Kovdor and Kiruna Ap calcined at 1350 °C show the appearance of β-$Ca_3(PO_4)_2$ formed as a result of decomposition of F,OHAp. The decrease in the unit cell parameter *a* (Table) indicates that the Ap structure is changing into FAp structure. This phenomenon is confirmed also by the decrease in the band intensity at 720 cm^{-1}, that belongs to the P-O-P bond, and by relocation of this band to 736 cm^{-1}. The decrease in the band intensities at 3543 and 3566 cm^{-1} (Fig.1a), and the appearance of a new band at 435 cm^{-1} is an indication of a decrease in OH...F and OH...O bonds and the appearance of molecular oxygen in the channels of Ap structure. The intensity of CO_3^{2-} bands has sharply decreased as a result of calcination, especially of those at B position (at 1471, 1458, and 1435 cm^{-1} for Kovdor Ap and 1465, 1457, and 1426 cm^{-1} for Siilinjärvi Ap, Fig.1b.). That conforms with the higher endurance of A type CO_3^{2-} group substitution in Ap on calcination.

Similar changes in the F,OHAp structure occur during thermal processing of ApC for obtaining feed phosphates or fertilizers.