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Dedicated to Prof. Menachem Steinberg on the occasion of his 65th birthday

THERMAL TRANSFORMATIONS IN PHOSPHORITES

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Abstract

The thermal transformations in phosphorites during flash calcination were investigated by FT-IR spectroscopy, X-ray diffraction and chemical analyses. During flash calcination changes occur, both in the composition of the phosphorite and in the crystallochemistry of the fluor-carbonate-apatite (francolite). The former changes include: decomposition of a great part of the calcite in the rock and oxidation of organic matter. The latter changes include: partial removal of the structural carbonate; partial relocation of the remaining carbonate ions in the apatite structure; a new arrangement of hydroxyl groups and fluorine on the hexagonal axis; partial condensation of the orthophosphate groups and increase of crystallite sizes. Isomorphous substitution of PO_4^{-3} in apatite by SO_4^{-2} and SiO_4^{-4} may take place.

Keywords: apatite, calcination, crystallinity, FT-IR, phosphorite, XRD

Introduction

Calcination is an efficient method of beneficiation of phosphorites with a high carbonate and organic matter content [1, 2]. During flash calcination the samples are heated at a high temperature for a very short time (a few seconds). In some cases calcination causes a worsening of phosphorite properties for sulfuric acid production. The reason may be connected with the differences of the real structure of apatites [1]. Comparison of analyses of products of thermal decomposition of amorphous calcium phosphates, synthetic amorphous calcium phosphates (containing carbonate) from aqueous systems, and biological apatites showed differences in the results [3]. McClellan and Van Kawenbergh, Mathews and Nathan, and Perdikatsis [4–6] have investigated the mineralogical effects of thermal treatment of sedimentary apatites. They showed that the main change in the apatite structure is the expulsion of the structural CO_2, increasing the a axis and crystallite size. This transformation is accompanied by the formation of free CaO.

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The aim of the present work is to analyze the thermal transformations in the Negev phosphorites during industry flash calcination.

Samples and methods

Samples

Phosphorite samples from the Nahal Zin deposit, Negev, Israel, were supplied by the Rotem-Amfert-Negev Company and the Geological Survey of Israel. The samples included a suite of phosphorites from the Nahal Zin deposit, before and after flash calcination at 870°C (residence time a few seconds). The whole samples and their fractions were examined. Some samples after flash calcination at 800 and 950°C were also examined. For comparison, samples were subjected to thermal treatment in the laboratory at temperatures from 600 to 900°C for 1 h. Mixtures of phosphorites with gypsum or with quartz, 10:1 *w/w*, after thermal treatment in the laboratory were also examined.

Methods

– IR spectra were recorded with a Nicolet FT-IR spectrometer. Disks were prepared using 1 or 5 mg of the sample and 150 mg of KBr. The disks were run after preparation and after drying for 24 h at 110 and 350°C. The higher temperature is needed to remove stable water bands which mask the OH stretching band. Immediately after heating, the dried disks were re-pressed (without re-grinding) in order to improve the resolution of the spectra.

– X-ray powder diffractograms were obtained with a Philips PW-1820/00 diffractometer (1720 based) using CuK_α radiation 35 kV – 40 mA, and a curved graphite monochromator with a 1° divergent slit and an 0.2° receiving slit. A semi-quantitative estimate of the structural carbonate concentration in the apatite was also carried out by XRD [4, 7].

– Chemical analyses were carried out by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES), using a Jobin-Yvon JY48 spectrometer.

Results

Changes in phosphorite

The main components of the Negev phosphorites are fluor-carbonate-apatite (francolite) and calcite [8, 9]. Minor amounts of clay minerals, quartz and opal C–T are commonly present. Most of the phosphorites contain organic matter rich in sulfur. After flash calcination at 870°C, about half of the calcite in the phosphorite is decarbonated and calcium oxide forms. The P_2O_5 content in the calcined rock increased by a little more than 10% (Table 1). The amount of organic matter decreases significantly and its composition changes, the quantity of methylene groups increases. Trace element concentrations also changed. The contents of Cd, Cr, Mo, Ni, V and Zn decrease while the contents of Ba, Eu, La, Sr and Y increases (Table 2). The changes after the flash calcination are slightly different in the various size fractions (Table 3). This may result from the differences in the actual temperatures of particles with different sizes: the tempera-

Table 1 Crystallite size (XRD), structural CO_2 (XRD), major element composition and solubility of phosphorite feed and product of flash calcination

Samples	Size of crystallite along a A^0	along c A^0	CaO %	P_2O_5 %	CO_2* %	CO_2** %	F %	F/P_2O_5	***
Feed	280	550	51.4	30.5	8.3	4.1	2.99	0.098	29.9
Product	750	1530	55.1	33.6	3.7	1.5	3.02	0.090	13.7
Feed	270	660	52.4	30.1	7.5	4.2	2.71	0.090	
Product	790	1480	55.5	33.4	3.0	1.5	2.86	0.086	
Feed	290	540	51.4	29.1	7.9	3.7	2.97	0.102	28.0
Product	830	1090	55.0	32.6	3.1	1.8	3.08	0.094	13.2
Feed	370	640	50.9	27.8	7.5	3.5	2.71	0.097	25.6
Product	840	1250	54.7	32.6	3.1	1.4	2.83	0.087	13.1
Feed	310	550	52.5	29.8	8.6	3.8	2.70	0.091	25.8
Product	820	1240	54.6	31.7	3.1	1.6	2.71	0.085	12.3

*=total CO_2; **=structural CO_2; ***=solubility in diluted citric acid

Table 2 Trace element composition of phosphorite feed and product of flash calcination

Samples	Composition/ppm										
	Ba	Cd	Cr	Eu	La	Mo	Ni	Sr	V	Y	Zn
Feed	749	29	117	0.3	16	23	46	2800	164	54	474
Product	1056	17	74	0.5	18	16	35	3076	136	60	408
Feed	430	31	119	0.2	17	38	47	2660	161	55	453
Product	736	18	70	0.4	18	25	32	2997	131	60	404
Feed	800	30	108	0.4	17	35	47	2748	159	57	471
Product	691	18	69	0.5	19	27	42	2952	127	63	411
Feed	568	31	122	0.3	16	26	57	2592	168	53	487
Product	726	20	73	0.5	18	29	42	2970	138	60	422
Feed	581	32	105	0.3	16	35	54	2562	154	54	473
Product	764	19	74	0.1	18	27	42	2898	122	58	430

Table 3 P_2O_5 and total CO_2 content in different grain-sized fractions separated from phosphorite feed and product of flash calcinatiion

Samples	Fractions	Mass	P_2O_5/	CO_2/
	(mesh)	(% of total)	%	
Feed	Whole sample		30.2	8.10
Product			33.9	3.25
Feed	+10	2.24	24.3	11.29
Product		0.07	23.7	8.67
Feed	+20	9.16	27.4	9.45
Product		3.98	30.8	6.08
Feed	+60	40.59	31.9	6.40
Product		32.92	35.0	3.37
Feed	+100	30.15	31.9	6.62
Product		33.58	35.1	2.83
Feed	+150	9.86	27.9	10.86
Product		15.25	32.7	2.90
Feed	+200	4.50	24.9	14.39
Product		9.14	30.9	2.99
Feed	–200	3.50	22.1	16.60
Product		5.06	29.5	3.24

tures within the particles in the coarse fractions are lower than those of the particles in the fine fractions.

Changes in the apatite structure

Table 1 showed that after flash calcination at 870°C, the amount of structural carbonate is drastically reduced, more than 50%. The F/P_2O_5 ratio is slightly reduced. The crystallinity of the apatites increases. The average size of an apatite crystallite along the a direction increases from 300 to 800 Å and along the *c* direction from 600 to 1300 Å. The structural changes of the apatites during the flash calcination caused changes in the properties of calcined phosphorite; the solubility of the concentrates in dilute citric acid decreases by 50%.

The changes in the apatite structure after calcination are slightly different in the various fractions. A decrease in the intensity of the ν_3 vibration of the carbonate group in the IR spectra and changes of the relative intensities of the doublet components of this vibration at 1455 and 1429 cm^{-1} are more pronounced in the spectra of fine fractions of the calcined product (Fig. 1).

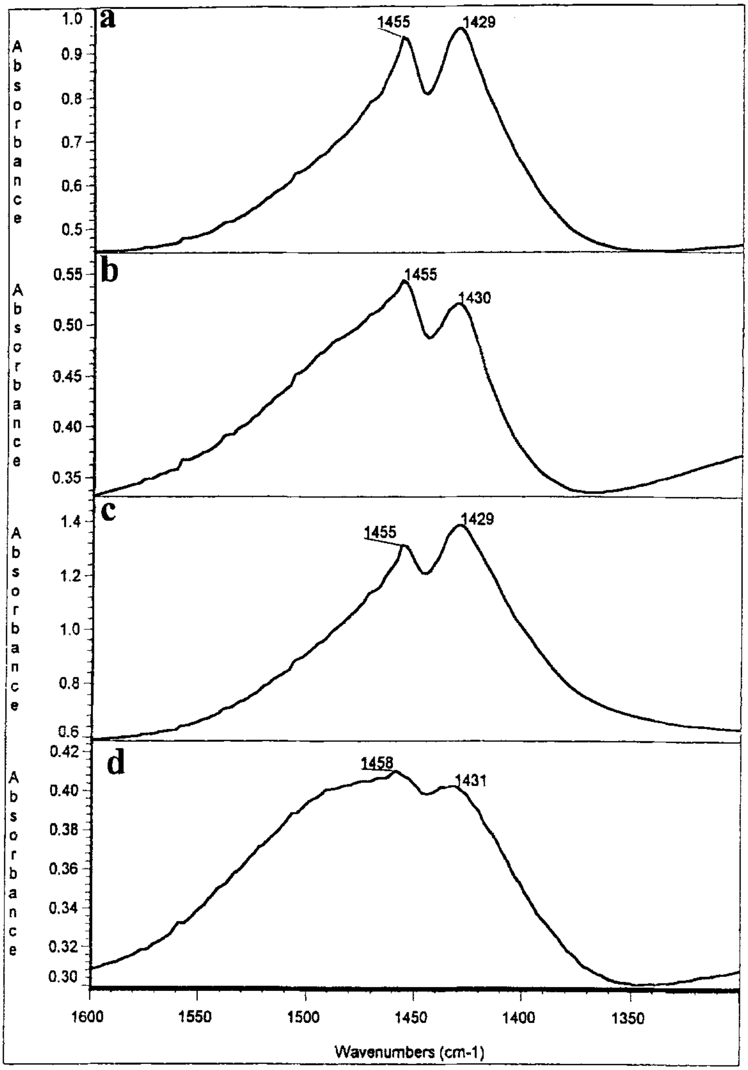

Fig. 1 The ν_3 vibrations of carbonate groups in the IR spectra of +100 (a), +200 (c) mesh fractions of phosphorite feed and +100 (b), +200 (d) mesh fractions of flash calcination product

Although the samples contain francolite, after heating at 350°C a weak OH stretching band appears in the IR spectra at 3545 cm^{-1}. After the flash calcination the frequency of the OH stretching vibration decreased to 3536 cm^{-1} (Fig. 2), indicating changes in their arrangement. A sharp, strong peak at 3643 cm^{-1} is due to the OH stretching vibrations of calcium hydroxyde [10], which is formed by the reaction of CaO with atmospheric water vapor [11]. Vibration bands at 745 cm^{-1} of the P–O–P bridge bonds [1] are observed with dif-

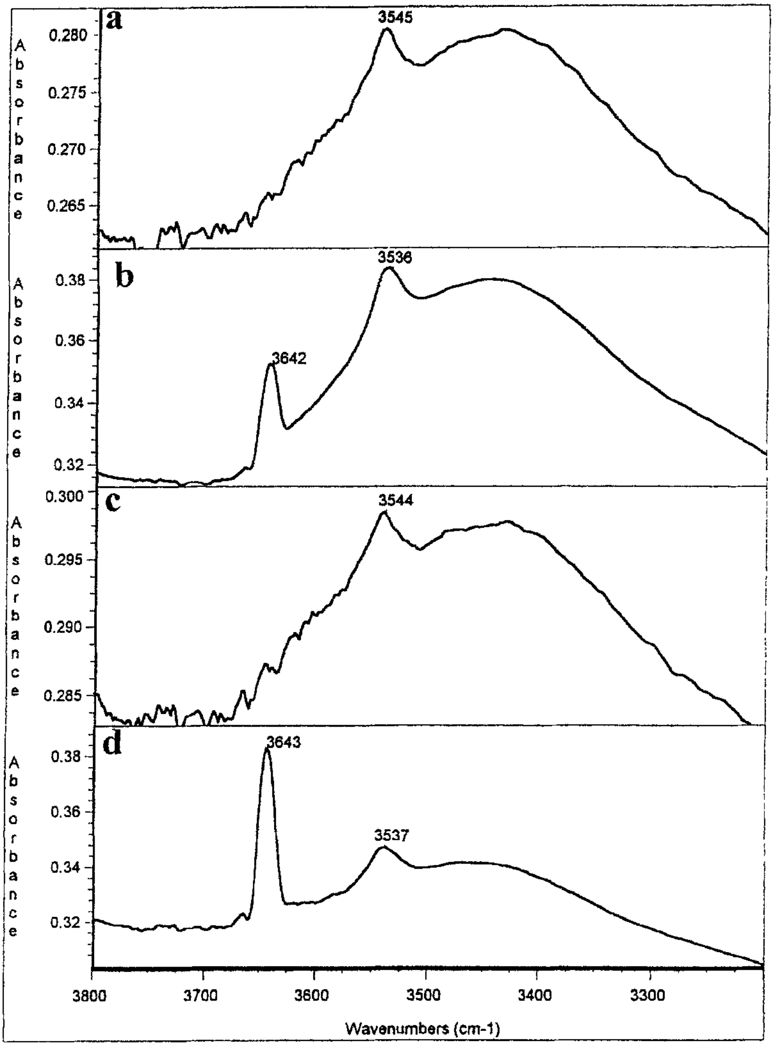

Fig. 2 The OH stretching vibrations of apatite and calcium hydroxyde in the IR spectra of +60 (a), +100 (c) mesh fractions of phosphorite feed and +60 (b), +100 (d) mesh fractions of flash calcination product

ferent intensities in IR spectra of all the fractions of the calcinated phosphorites, e.g. the band in the spectrum of the +10 mesh is much weaker than that of the average sample (Fig. 3).

Small bands were observed at 530, 930, 1150 cm^{-1} in the IR spectra of calcined apatite after flash calcination of phosphorites at 950°C (Fig. 4) and also in the spectra of the fine fractions after flash calcination at 870°C. Similar bands were observed at a lower temperature after prolonged laboratory calcination of phosphorites and their mixtures with gypsum and quartz, indicating isomor-

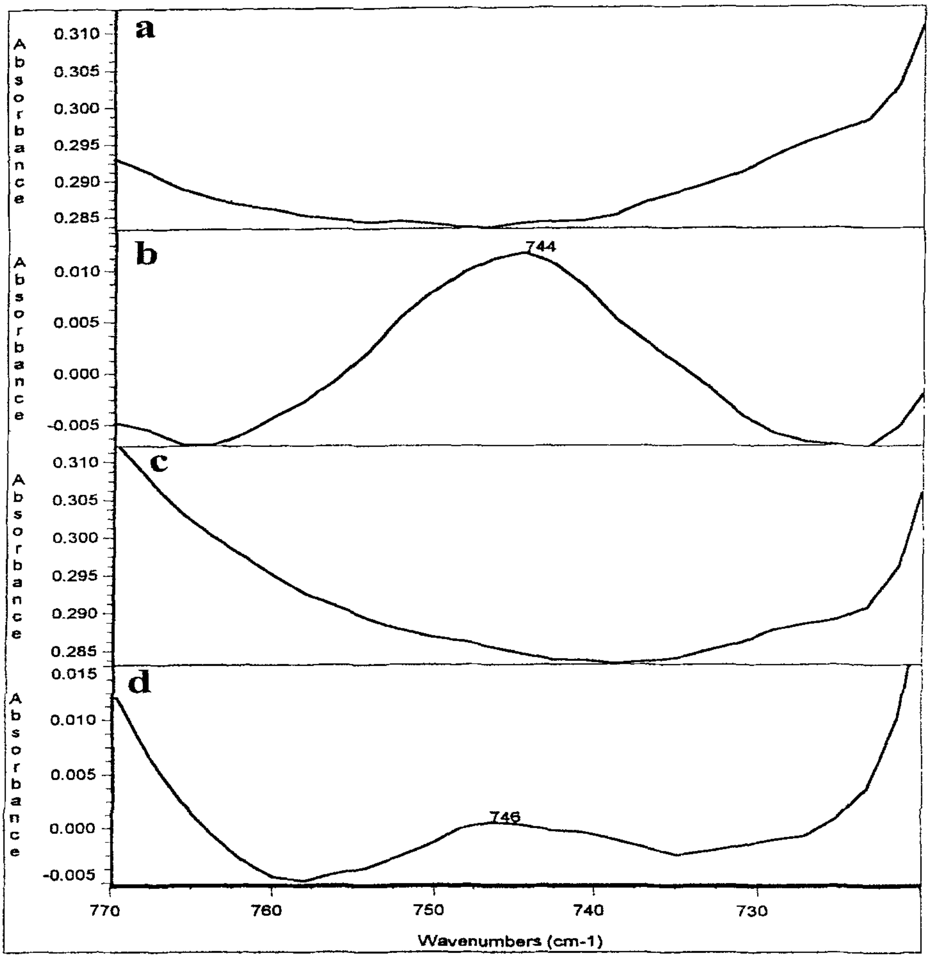

Fig. 3 The P–O–P vibration in the IR spectra of whole sample (a), +10 mesh fraction (c) of phosphorite feed and whole sample (b), +10 mesh fraction (d) of flash calcination product

phous substitution of phosphorus by sulfur and silicon. The entrance of sulfur in the apatite of the calcined product increases with the amount of organic matter in the original phosphorite.

Discussion

Changes in the structural carbonate

The carbonate ions is partly ousted from the apatite structure during the flash calcination at 870°C, as observed by the decreasing of intensities of the doublet

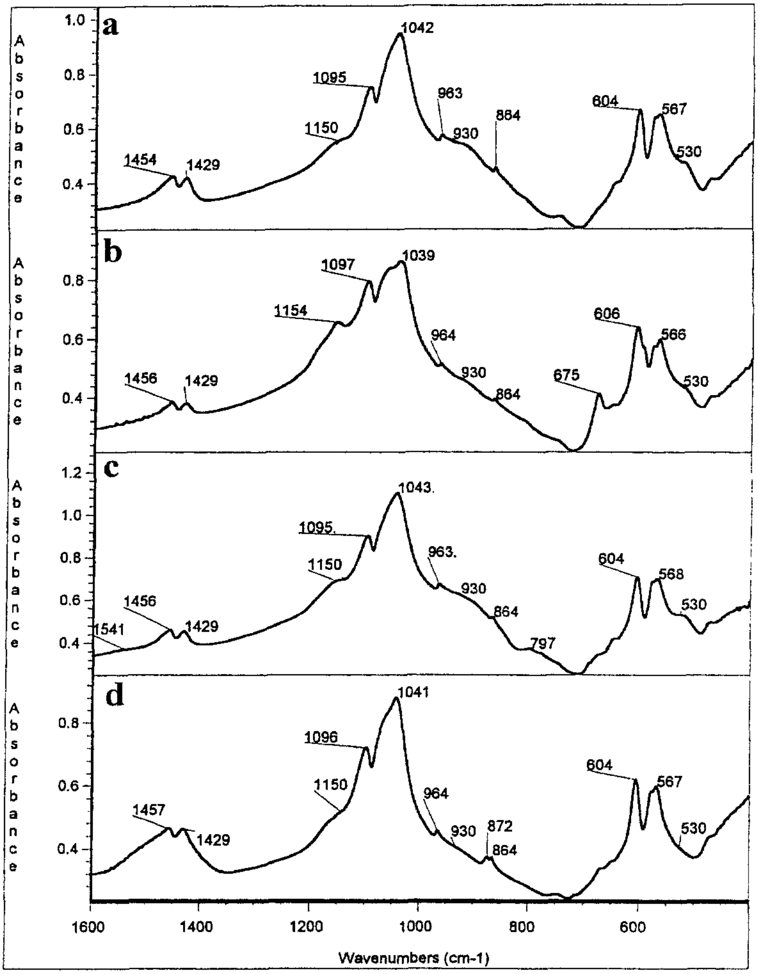

Fig. 4 IR spectra of organic-rich phosphorite (a), mixtures of phosphorite with gypsum (b) or with quartz (c) after laboratory calcination for 1 h at 900°C, compared to product of flash calcination at 950°C (d)

of the structural carbonate at 1455 and 1429 cm^{-1} in the IR spectra of the calcinated phosphorites (Fig. 1). The relative intensities of these bands are also changed after the flash calcination. The ν_3 doublet of the structural carbonate bands at 1453 and 1429 cm^{-1} in francolite is due to CO_3^{-2} ions replaced PO_4^{-3} ions (B-type substitution), whereas the location of those bands at 1548, and 1457 cm^{-1} in carbonate-apatites are due to CO_3^{-2} ions replaced OH$^-$ ions on the hexagonal axis (A-type substitution) [3]. Increase of the intensity of the 1455 cm^{-1} band relative to that at 1429 cm^{-1} indicates that some of the remaining structural carbonate relocates from the orthophosphate site to the hexagonal axis and interstitial positions. The crystallinity of the apatites and the sizes of their crystallites increase (Table 1). Increase of the a axis and crystallite size during ousting of structural carbonate were reported by Matthews and Nathan [4].

Changes in the structural hydroxyls

Structural hydroxyl groups were found in the IR spectra of all the francolites. The location of the band at 3545 cm^{-1} (Fig. 2) indicates a presence of OH...F bond [1, 3]. The decrease of the frequency of the stretching OH vibration to 3536 cm^{-1} in the IR spectra of the calcinated phosphorites indicates a new arrangement of hydroxyl groups and fluorine on the hexagonal axis. According to Elliott [3], when few OH^- ions are present in fluor-apatite, the IR band appears at 3538 cm^{-1}, which must correspond to stronger hydrogen bond. Baumer *et al.* [12] discuss the ways of arranging OH and F in a linear array. Their main criteria are the intensity and position of the two main OH stretching vibrations of hydrofluor-apatites: the band at 3573 cm^{-1} which characterizes OH–OH–OH chains and the band between 3550 and 3535 cm^{-1} which is caused by OH ions weakly hydrogen-bonded to F ions. The lower the position of this band the more F neighbours to each OH. At 600°C, the temperature at which they synthesized the apatites, the distribution of OH and F is close to statistical.

At the higher temperature used in the present work for flash calcination and laboratory calcination, there is a new arrangement of hydroxyl groups on the hexagonal axis of the apatite structure after heating. It was analyzed for low OH concentrations; whether this remains correct for higher OH concentrations has to be proved.

Changes in the orthophosphate groups

Partial condensation to pyrophosphate takes place during flash calcination at 870°C. It is observed by the appearance of vibration bands of the P–O–P bridge bonds at 745 cm^{-1} [1] in the IR spectra of the calcinated phosphorites (Fig. 3). Isomorphous substitution of phosphorus by sulfur and silicon were found after flash calcination of phosphorites at 950°C and also in the spectra of the fine fractions after flash calcination at 870°C. These substitutions were observed by the appearance of bands at 530, 930, 1150 cm^{-1} in the IR spectra of calcined apatite (Fig. 4), when no other phases are present (according to XRD). Flash calcination of organic-rich phosphorites results in more pronounced substitution. The organic matter in the Negev phosphorite is rich in sulfur (10% by weight of the organic matter [8]). Thermal oxidation and decomposition of organic matter occurs, S is liberated, mainly as SO_2, some of it enters the apatite structure as SO_4. Organic S appears to be far more active than inorganic sulfate. Substitution of PO_4^{-3} by SiO_4^{-4} takes place when silica minerals (opal C–T, clays or even quartz) are present in the phosphorite.

Similar isomorphous substitutions were found in mixtures of phosphorites with gypsum or with quartz after laboratory calcination for 1 h at 700–900°C (Fig. 4). The SO_4^{-2} and SiO_4^{-4} enter the apatite structure in the vacant orthophosphate positions produced by the ousting of the carbonate, at 800°C and sometimes already at 700°C. It appears that in general the substitution is coupled ($2PO_4^{-3} \rightarrow SO_4^{-2} + SiO_4^{-4}$). Baumer *et al.* [13] argue for the presence of a coupled substitution and assign the band at 1150 cm^{-1} to SO_4 and the bands 530 and 930 cm^{-1} to SiO_4.

The entering of sulfur and silicon in the apatite structure in the calcination process causes a worsening of phosphorite properties for sulfuric acid production [1] and is therefore of great importance. Higher temperatures and longer residence times favor such substitutions. Flash calcination reduces the residence times at the high temperature and is preferable. In this calcination the entering sulfur and silicon in the apatite structure practically takes place only at 950°C. This shows that use of flash calcination at 950°C is not desirable in spite of almost complete ousting of structural carbonate at this temperature.

Conclusions

During the flash calcination changes occur, both in the composition of the phosphorite and in the crystallochemistry of the apatite. The carbonate ions were not only ousted from the apatite structure, some of the remaining relocated from the orthophosphate site (b site) to the hexagonal axis (a site) and interstitial positions. A new arrangement of hydroxyl groups and fluorine on the hexagonal axis and partial condensation of the orthophosphate groups are found. Isomorphous substitution of PO_4^{-3} by SO_4^{-2} and SiO_4^{-4} may take place when organic matter with a high S content and silica minerals are present.

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