

interferences. The accuracy and precision of the AAS technique make it very attractive for measuring high concentrations of phosphorus, such as those existing in fertilizers. Because of these advantages, it is conceivable that this method may someday be used on a routine basis for these determinations.

Furthermore, since our studies were conducted, two ways of improving both sensitivity and detection limits for phosphorus determination have been demonstrated. Barnett et al. (1976) have shown that the detection limit can be improved respectively 2.8- and 5-fold by the use of electrodeless discharge lamps (EDL) with either flame AA or nonflame graphite furnace technique. In addition, Ediger (1976) has demonstrated that sensitivity and detection limits can be further improved substantially by the use of a combination of EDL with graphite furnace and the addition of 1% lanthanum as nitrate. Using this combination and the Perkin-Elmer Model 603 atomic absorption spectrophotometer, Ediger obtained sensitivity and detection limit values of 7500 pg and 10 ng (0.1  $\mu\text{g}/\text{mL}$ ), respectively. Therefore the use of either of these

methods for phosphorus determinations would substantially reduce the sample sizes and the concentrations of samples used in general. The application of these techniques to fertilizer analysis should make AA even more advantageous to use than the existing methods.

#### ACKNOWLEDGMENT

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## Production of Magnesium Phosphate from Apatite and Carnallite. 1. Chemistry and Mineralogy

Ithamar Pelly\* and Petahia Bar-On

Magnesium phosphate was produced from Oron phosphate and carnallite. Chemical and mineralogical aspects were studied as a function of reaction temperatures, F/P ratios, Mg/Ca ratios, reaction times, and grinding the phosphate. Although two reaction mechanisms are suggested in the literature, it appears that no clear-cut conclusion can be reached and that neither explains all the observed facts. The most likely mechanism seems to be one in which the first step is the formation of chlorapatite and  $\text{MgF}_2$ . The chlorapatite reacts to give magnesium phosphate which reacts with  $\text{MgF}_2$  to form wagnerite. Magnesium phosphate and wagnerite are in equilibrium; the higher the temperature, the higher is the magnesium phosphate yield in the product.

Most of the phosphate fertilizers are manufactured from phosphate rocks. In phosphate sedimentary rocks the major mineral is usually francolite (fluorcarbonate-apatite). Its composition varies but can be summarized as  $(\text{Ca}, \text{Na}, \text{Mg})_{10}(\text{PO}_4)_{6-x}(\text{CO}_3)_x\text{F}_y(\text{F}, \text{OH})_2$ , where  $y$  is the range of  $0.33x-0.5x$ .

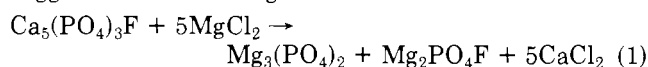
The mole ratio F/P in Israeli phosphates is about 0.41 and is higher than in fluorapatite (0.33). It is suggested (Ando and Matsuno, 1966; Smith and Lehr, 1966) that in such cases some of the phosphate ions are replaced by  $\text{CO}_3\text{F}^{3-}$  ions.

Apatites containing fluorides are only slightly soluble in water and in organic acids so that the phosphate is not readily available to plants. In the fertilizer industry the apatite is destroyed (there are several methods) to create more soluble compounds. For comparison purposes the availability to plants is measured by the solubility in citric acid or in ammonium citrate.

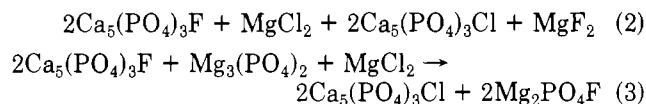
Magnesium phosphate (MP),  $\text{Mg}_3(\text{PO}_4)_2$  (which is soluble in citric acid), is produced in Japan by reacting the phosphate with olivine or serpentine at 1400 °C. MP can also be produced in a reaction between apatite and magnesium chloride brine (Lavie, 1961).

Baniel et al. (1965) suggested the use of carnallite,  $\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ , for this reaction.  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  cannot be used because on drying it reacts with its own water to form MgO (periclase) which does not react with apatite. Carnallite is more stable on drying (at about 180 °C). The reaction between carnallite and apatite is carried out at 600 °C. The product is washed with water and up to 80% of the potassium can be recovered, thus the reaction can be carried out at almost no loss of potash yield.

Only a few studies (Ando and Hoego, 1972; Stavski, 1970) have been done to investigate the mechanism and mineralogical changes involved in the reaction. The main phosphate minerals formed are wagnerite (W) ( $\text{Mg}_2\text{PO}_4\text{F}$ ) and magnesium phosphate (MP). Stavski (1970) studied the influence of the amounts of Ca, Mg, and F and the temperature, but he used mixtures of  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{CaF}_2$  instead of apatite so the results may not hold for the apatite case. He found that chlorapatite,  $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ , and  $\text{Ca}_2\text{PO}_4\text{Cl}$ , calcium chlorwagnerite, can also be formed. Ando and Hoego (1972) did a semiquantitative analysis (using X-ray diffractograms) of products of reactions at several temperatures. They found that chlorapatite was a major reaction product (together with MP and W) and suggested the following mechanism:

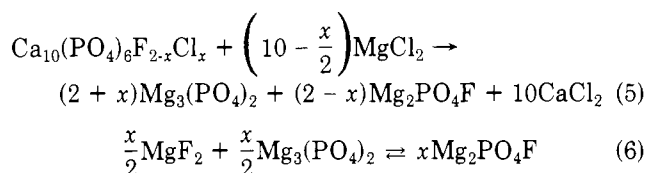
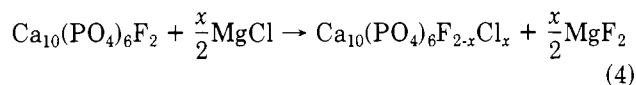


\*Department of Geology and Mineralogy, Ben Gurion University of the Negev, Beer Sheva, Israel.



Accordingly the amount of chlorapatite should rise as the reaction proceeds.

Bar-On (1975) suggested the formation of fluorchlorapatite (by partial chlorination of the apatite) and  $\text{MgF}_2$ . This chlorinated apatite reacts with  $\text{MgCl}_2$  to give MP and W. In addition, there is a reaction (6) by which  $\text{MgF}_2$  is destroyed forming wagnerite.



If  $\text{MgF}_2$  is destroyed completely by the last reaction, the overall reaction is the same as 1.

A few practical problems are involved. One is to obtain a product with as high  $\text{P}_2\text{O}_5$  content as possible. Another problem is that the solubility in citric acid is about 100% of the total  $\text{P}_2\text{O}_5$  when the reaction is carried out at 1000 °C range (Stavski, 1970). At 600 °C solubilities are lowered to about 50% of the total  $\text{P}_2\text{O}_5$ , mainly because large amounts of wagnerite (W), insoluble in citric acid are formed, so that the value as a fertilizer is lowered. From the industrial point of view the reaction at high temperatures causes high corrosion (chloride melt) and requires a very high fuel consumption, thus making the process unprofitable. The aim of this research was to study the chemistry and mineralogy of the reaction and to try to find a method by which a product with high  $\text{P}_2\text{O}_5$  content and a high citric acid solubility could be produced at lower temperatures than in the standard process.

#### EXPERIMENTAL SECTION

**Materials.** *Apatite.* Obtained from Negev Phosphates Ltd., from field 5, Oron. It includes quartz, calcite, gypsum, and sodium chloride.

*Carnallite.* Obtained from Dead Sea Works Ltd., Beer Sheva, Israel, manufactured from Dead Sea brines. It contained sodium chloride which lowered its melting point to about 410 °C.

**Methods and Instrumentation.** *Apatite.* The phosphate was sieved and only grain size less than 2 mm was used after homogenization with a splitter. Samples were dried at 110 °C for 3 h before reactions. For some experiments the sample was ground in an agate grinder to 250 mesh and dried after sieving.

*Carnallite.* Samples were dried at 110 °C, ground quickly, and dried (as a thin layer) at 180 °C and kept in a dessicator (180 °C is the optimum temperature for an effective drying on one hand and limiting the decomposition on the other).

**Reactions.** For each experiment, 6.0 g of phosphate was taken. The amount of carnallite taken was according to a predetermined Mg/Ca ratio (calculated on basis of  $\text{MgCl}_2$ , i.e., total Mg in the carnallite minus magnesium oxide). The phosphate was shaken with the carnallite in a closed vessel and put (in a ceramic crucible) in the furnace at the desired temperature. A small temperature decrease was observed for 3–5 min and time measurements started when the temperature returned to the desired level. At the end of the reaction the crucible was cooled at room

temperature, water was introduced, and the contents were broken down in water with a spatula, transferred into a beaker, stirred for a few minutes, and kept overnight. After filtering, the product was washed with water (until the water was chloride free) and dried at 110 °C for 3 h.

To check the influence of temperature, phosphate-carnallite mixtures with Mg/Ca molar ratio 1.5 were used. Mixtures were heated for 20 min in the temperature range 400–700 °C.

To check the influence of fluoride, phosphate- $\text{MgF}_2$  mixtures with F/P molar ratios between 0.75–1.25 were used (taking into account the ratio 0.41 existing in the phosphate) and carnallite added to give a Mg/Ca molar ratio 1.5. Reactions were carried out for 20 min at 600 °C.

To check the influence of Mg/Ca molar ratio, phosphate-carnallite mixtures with different ratios were heated at 600 °C for 20 min.

To check the influence of reaction times, mixtures with Mg/Ca molar ratio 1.5 were heated at 600 °C for different times (5–60 min).

**Calcite Removal.** In order to obtain a purer apatite for IR absorption measurements and X-ray diffractions, the method suggested by Silverman et al. (1952), which enables removal without damage to the apatite, was used.

**Fluoride Determination.** A potentiometric method was used (Edmond, 1969), using a specific fluoride electrode (Orion 94-049A) and a calomel reference electrode.

**Chloride.** The Vollhard method was used.

$\text{CO}_2$  was determined gasometrically.

$\text{P}_2\text{O}_5$  was determined with a Perkin-Elmer Model 402 spectrophotometer using ammonium vanadomolybdate reagent.

**Calcium.** A Varian Techtron Model AA6 atomic absorption spectrophotometer was used using acetylene- $\text{N}_2\text{O}$  flame with addition of  $\text{K}^+$ . It was found that even so, with high  $\text{P}_2\text{O}_5/\text{Ca}$  ratios (30/1), low Ca results were obtained. Therefore, matching amounts of  $\text{P}_2\text{O}_5$  were added to the standards.

**Magnesium.** A sample was dissolved in water and another sample in nitric acid, and magnesium was determined in each using EDTA.  $\text{MgCl}_2$  content was obtained from the first sample and MgO from the difference of the two.

**X-Ray Diffractions.** Rich-Siefert Iso Debyflex 2000 instrument was used using  $\text{Cu K}\alpha$  radiation. Intensities were calculated by multiplying the peak's height by mid-height width. The reflections chosen for each mineral were not always the strongest but were those which were strong enough and as isolated as possible from other reflections. For  $d$  value determinations, the sample was mixed with quartz and  $2\theta$  values were corrected according to the nearest quartz reflections.

**IR Absorption.** A Perkin Elmer Model 457 IR spectrophotometer was used. Samples were measured in KBr discs. This way it is possible to differentiate between francolite, fluorapatite, and calcite carbonates (Ish-Shalom and Coren, 1969; Lehr et al., 1967).

#### RESULTS

Analysis showed that the optimal drying conditions could not prevent a partial decomposition of carnallite into magnesium oxide. The decomposition varied between 2–7 weight percent.

The results of experiments in which the influence of several parameters on the insoluble reaction products was studied are shown in Tables I–VIII. The parameters investigated were: reaction temperatures, influence of fluoride, Mg/Ca ratio, reaction times, and the effect of grinding the phosphate.

**Table I. Influence of Reaction Temperatures on the Chemical Composition of the Insoluble Products (Ratios Given Are Molar, Mg/Ca = 1.5,  $t = 20$  min)**

temp, °C	P <sub>2</sub> O <sub>5</sub> , %	F, %	F/P <sup>a</sup>	insol- uble Cl, %	Cl/P	CaO, %	Ca/P
400	26.0	2.73	0.39	1.19	0.092	37.0	1.80
450	26.4	2.77	0.39	2.11	0.160	25.0	1.19
500	27.6	2.99	0.40	1.02	0.073	13.7	0.50
550	29.8	3.16	0.39	0.70	0.047	2.67	0.11
600	30.9	3.34	0.40	0.53	0.035	0.90	0.029
650	31.1	3.36	0.40	0.67	0.043	1.03	0.033
700	31.3	3.38	0.40	0.70	0.045	0.84	0.027

<sup>a</sup> This ratio in the raw phosphate is 0.41.

Attempts to prepare known mixtures of MP and W for determining the ratio from X-ray diffractions resulted in a calibration curve with a low precision. MP/W ratios were calculated as the ratio of the sum of representative peak areas of each, as they appear in the tables. Since these two minerals have almost the same atomic composition and their mass absorption is about the same, this ratio could be taken as proportional to their weight ratio. From this the molar ratio was calculated. These ratios, of course, should not be taken as quantitative measurements and are given here only to show order of magnitude and trend of changes of the ratios.

MP/W ratios were calculated also from the solubilities of the products in citric acid (Bar-On and Pelly, 1978). It was assumed that all soluble P<sub>2</sub>O<sub>5</sub> is MP and the insoluble is W. This is roughly correct, but for small concentrations where the small solubility of apatite becomes important. Again, these ratios are given only to show magnitude and trend of changes of the ratios.

#### DISCUSSION

To make conditions similar to those of industrial production, raw phosphate rather than pure apatite was used, though this added many complications to the investigation.

The reaction products were kept overnight in water and then washed. This step at first seems to complicate the objective of elucidating the overall, thermally promoted reaction mechanisms. Compounds can slowly dissolve or react (hydrolyze), MgF<sub>2</sub> can precipitate, etc. In previous works (Baniel et al., 1965; Stavskii, 1970), soluble products also were leached before analysis of the products. Tests carried out during this study show that in the X-ray diffraction pattern of unwashed reaction products, only chlorides are identified, probably because the chloride melt

forms a coat on the phosphate particles. The main peaks are those of NaCl and KCaCl<sub>3</sub> with small peaks of carnallite and magnesium chloride. But for one small peak of MP, no phosphate compound can be detected. This means that in order to identify the minerals, the product has to be washed. When the products were stirred in water for 3 min, only peaks of MP, W, MgF<sub>2</sub>, and magnesium oxide (periclase) were detected. After keeping the products overnight in water, no changes were seen, but for the partial transformation of magnesium oxide into hydroxide (brucite).

It seems that although two reaction mechanisms of decomposition are suggested in the literature, no clear-cut conclusion can be reached. From the following discussion it seems that neither explains all the observed facts.

From Table II it is seen that calcite reacts with carnallite at lower temperatures than apatite does even at 400 °C, i.e., below the melting point of carnallite. The reaction products are CO<sub>2</sub>, CaCl<sub>2</sub>, brucite, and periclase. Periclase can be formed also by reaction of carnallite with its own remaining water, while brucite can be formed from periclase during washing of the products. The increase of periclase and brucite above 550 °C is attributed to fast decomposition of carnallite at high temperatures before it reacts.

Apatite is almost entirely decomposed at 500 °C (at 550 °C only traces remain and could be seen only after concentration by dissolving a great part of the product in citric acid). IR absorption peaks of the francolite carbonate, at 865, 1430, and 1455 cm<sup>-1</sup> (Lehr et al., 1967) remain as long as there is apatite left in the sample. Hence, at least part of the carbonate ion remains in the apatite structure till its decomposition.

From Tables II, IV, VI, and VII it is seen that the molar ratio MP/W is always below 1 and the ratio increases as temperature rises. The increase of this ratio is not a result of fluoride leaving the system since the molar ratio F/P (Table I and VIII) is the same as for the raw material.

The raw material contains 0.81% chloride, all of which is dissolved in water. In the products, however, chloride is found even after prolonged washing. It is seen (Table I) that Cl/P (molar ratio) has a maximum at 450 °C. At higher temperature, after 20 min, the apatite is destroyed and most of the chloride disappears. From Table VI it is seen that Cl/P at 600 °C is highest after 5 min and then decreases. From A.S.T.M. cards,  $d_{222}$  of carbonate apatite is 1.929 Å, of fluorapatite, 1.937 Å, and that of chlorapatite, 1.959 Å. Before the reaction,  $d_{222}$  of the apatite was 1.931

**Table II. Diffraction Intensities of Insoluble Products Formed at Various Temperatures (Mg/Ca = 1.5,  $t = 20$  min)**

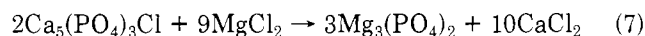
mineral	representative $d$ , Å	400 °C	450 °C	500 °C	550 °C	600 °C	650 °C	700 °C
		apatite	14	14	8			
	1.94	15	16	10				
	1.84	14	14	8				
wagnerite (W)	3.32			20	33	30	16	11
	3.15			20	56	51	16	14
	2.99			28	100	90	35	33
magnesium phosphate (MP)	4.35			11	42	47	15	19
	4.11			18	24	41	16	24
	3.85			20	80	81	39	33
brucite	4.77	7	12	13	42	25		
	2.37	9	9	19	79	63		
periclase	2.11				59	100	100	100
calcite	3.04	29	21					
calcite/apatite <sup>a</sup>		0.67	0.48					
MP/W molar ratio (X-ray)				0.44	0.44	0.61	0.64	0.81
MP/W molar ratio (citric acid)				0.41	0.56	0.67	0.77	0.86

<sup>a</sup> This ratio in the raw phosphate is 1.95.

**Table III. Influence of the Molar Ratios F/P on the Unsoluble Reaction Products (Phosphate-MgF<sub>2</sub> Mixtures, Mg/Ca = 1.5, 20 min at 600 °C)**

initial F/P	% P <sub>2</sub> O <sub>5</sub> in the product	MP/W molar ratio (X-ray)	MP/W molar ratio (citric acid)
0.41	30.9	0.61	0.67
0.75	30.2	0.13	0.21
1.0	28.9		0.06
1.25	28.1		0.04

Å and after the reaction this reflection went up to 1.937 Å. This means only that the structure of fluorcarbonate-apatite was changed to the structure of fluorapatite (though not all the carbonate ion left the system). In all experiments carried out under standard conditions (see Experimental Section), no chlorapatite was detected even as an intermediate in reactions carried out for shorter times. But, in experiments with Mg/Ca, lower than 1.5 (Table IV) chlorination was well advanced and the remaining apatite was chlorapatite with  $d_{222} = 1.959$  Å. From Table V it is seen that Cl/P decreases as Mg/Ca increases and in parallel MP/W increases (Table IV). This takes place in spite of the fact that increasing Mg/Ca means actually increasing chloride content in the reaction mixture (chlorapatite formation was not observed also in reactions with KCl instead of carnallite, but this is a solid-solid reaction). It can be concluded that chlorapatite can exist only if the amount of magnesium is too small to obtain high amounts of MP. If this is correct it may indicate that the formation of chlorapatite (eq 2) is the first step of the reaction. The chlorapatite is then destroyed by excess MgCl<sub>2</sub> forming MP, probably by the reaction:



If chlorapatite is formed by side reactions (eq 2 and 3), the fact that it is not found means that it is destroyed by excess MgCl<sub>2</sub> (reaction 7). This means that, if not all, at least part of the MP is formed from chlorapatite. The alternative is to say that chlorapatite is not formed during normal reactions and when magnesium is present in small amounts the reaction goes through a totally different mechanism in which chlorapatite is formed. This does not seem plausible. The question remains—what is the insoluble chloride remaining in the products? This could be chlorapatite formed by chlorination of the apatite in such small amounts that it is not seen in X-ray diffractograms. Calculation shows that the chloride remaining is enough

to transform up to 50% of the initial apatite to chlorapatite and not only a small amount. It seems, therefore, that the chloride remains in small amounts (up to about 2%) as an insoluble compound other than apatite, probably some sort of magnesium oxy or hydroxy chloride. If this is the case, Cl/P really has no meaning. Ando and Hoego (1972) found by semiquantitative analysis using X-ray diffractions that chlorapatite is seen in great amounts in the products. According to the mechanism suggested by them (eq 2 and 3), the amount of chlorapatite should rise as the reaction proceeds. This seems contrary to our experience that no chlorapatite is found. But, they carried all their experiments with Mg/Ca = 1.1 and noticed that hydrolysis took place, i.e., part of the magnesium was transformed to the unreacting oxide so that Mg/Ca is even lower. Now, these cases with low Mg/Ca are the cases in which chlorapatite was also found in this study, but these cases are the exception and not the rule.

In reactions with ground phosphate, insoluble chloride was also found and again in amounts high enough to chlorinate a great part of the initial phosphate (higher than for the reaction with Mg/Ca = 0.8). The  $d_{222}$  peak of the apatite is broader than in the standard cases (this is not due to grinding since the peak of ground unreacted apatite is sharp). The value of this reflection is 1.946 Å, i.e., closer to that of chlorapatite. After solution in citric acid the  $d_{222}$  peak of apatite in the residue was 1.938 Å, i.e., that of fluorapatite. In this case the interpretation might be that during the reaction partial chlorination took place to form chlorfluorapatite with intermediate dimensions between the two components.

The possibility of the formation of Ca<sub>2</sub>PO<sub>4</sub>Cl (chlorospodiosite) as a reaction product was checked. It is difficult to identify this compound by X-ray diffraction as the main peaks overlap those of wagnerite, apatite, and chlorapatite. The only intense peak which can be used,  $d_{111} = 4.25$  Å, overlaps one of the main peaks of quartz ( $d_{100}$ ) which is present in the samples. As chlorospodiosite dissolves well in citric acid, this peak should disappear in diffractograms of the undissolved residue. In all cases where this peak was seen clearly it remained after solution in citric acid, so it may be due to quartz. This negates the possibility of chlorospodiosite being formed in more than small amounts but not the possibility of its formation as a precursor in the formation of other compounds.

The increase of MP/W with temperature is not the result of fluoride leaving the system.

MgF<sub>2</sub> is formed during the reaction and its appearance can be detected by X-ray diffraction by its strongest peak

**Table IV. Influence of Initial Mg/Ca Molar Ratios on the Diffraction Intensities of the Unsoluble Products (20 min at 600 °C)**

mineral	representative $d$ , Å	0.8	0.9	1.0	1.1	1.2	1.3	1.5
	apatite (chlor-)	2.62	5	4	weak	tr		
	1.96	20	15	15	tr			
	1.84	27	19	20	tr			
wagnerite	3.32	14	21	30	38	43	46	
	3.15	24	30	38	46	42	51	
	2.99	37	54	69	90	93	100	
magnesium phosphate	4.35	tr	16	29	34	38	46	
	4.11	tr	13	19	22	31	30	
	3.85	17	32	48	62	83	87	
brucite	4.77	23	47	38	33	18	37	
	2.37	30	36	46	49	33	49	
periclase	2.11	22	31	41	63	100	97	
MP/W molar ratio (X-ray)		0.14	0.36	0.43	0.42	0.53	0.53	0.61
MP/W molar ratio (citric acid)		(0.35) <sup>a</sup>	(0.46) <sup>a</sup>	0.51	0.55	0.59	0.60	0.67

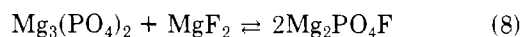
<sup>a</sup> Part of the soluble phosphate is apatite.

Table V. Influence of Initial Mg/Ca Molar Ratios on the Composition of the Unsoluble Products (All Ratios Are Molar, 20 min at 600 °C)

Mg/Ca	P <sub>2</sub> O <sub>5</sub> , %	insoluble Cl, %	Cl/P	CaO, %	Ca/P
0.8	32.2	2.28	0.141	17.6	0.69
0.9	32.6	1.61	0.099	13.2	0.51
1.0	33.1	1.26	0.076	8.3	0.32
1.1	33.9	1.03	0.061	5.8	0.22
1.2	34.8	0.73	0.042	2.5	0.091
1.3	33.1	0.58	0.035	1.3	0.05
1.5	30.9	0.53	0.035	0.90	0.029

at  $d = 3.27 \text{ \AA}$  (as a shoulder on W's peak at  $d = 3.32 \text{ \AA}$ ), getting stronger with the rise in the reaction temperature. This is a small shoulder, and in no experiment was a separate peak obtained. MgF<sub>2</sub> can be formed in two ways. Ando and Hoego (1972) suggested the formation of MgF<sub>2</sub> (as a side reaction) by reaction of fluorapatite with MgCl<sub>2</sub> (eq 2). According to Bar-On (1975) the formation of MgF<sub>2</sub> and chlorapatite is the first step of the main reaction.

The MgF<sub>2</sub> can react with MP to form W:



where W and MP are in equilibrium. With temperature increase, less W is formed, which explains the rise of

MP/W (and MgF<sub>2</sub> diffraction peak) with temperature. Without adding MgF<sub>2</sub> there is an equilibrium concentration of MgF<sub>2</sub>. The equilibrium was checked by adding MgF<sub>2</sub> to the system. It is seen (Table III) that this addition caused a drastic decrease in MP/W ratio, i.e., the equilibrium was such that the production of W was favored. Stavski (1970) checked the influence of F/P ratio [on reactions with Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>] and found the change in MP/W ratio but did not report finding MgF<sub>2</sub> in the reaction products.

The assumption was made (Ando and Hoego, 1972; Bar-On 1975) that either reaction 1 or 5 and 6 are the main reactions in which MP and W are formed, but there is really no proof. Other reactions may exist. The mechanism of decomposition of the reactants and the formation of the various products can be described by various equations. Regretfully, from the existing data (previous works and this work), one cannot choose among them and it cannot be ascertained whether the mechanism goes through one of the suggested reactions or a combination of two or more of them.

The most likely mechanism seems to be one in which the first step is the formation of chlorapatite and MgF<sub>2</sub> (reactions 2 or 4). The chlorapatite reacts to give MP (reaction 7) and MP reacts with MgF<sub>2</sub> to give W (reaction 8). MP and W are in equilibrium. At higher temperatures

Table VI. Influence of Reaction Times on Diffraction Intensities and Chemical Composition of the Unsoluble Products (Mg/Ca = 1.5, T = 600 °C)

d(A)	time, min								raw material
	5	10	15	20	30	45	60		
apatite	2.62	14	8	6					
	1.94	16	10	12					
	1.84	16	8	9					
wagnerite	3.32	tr	10	17	30	29	33	30	
	3.15	tr	13	26	51	43	43	40	
	2.99	tr	27	56	90	80	100	100	
magnesium phosphate	4.35	tr	13	22	47	40	40	45	
	4.11	tr	10	19	41	33	31	33	
	3.85	tr	25	45	81	96	90	94	
brucite	4.77	12	22	28	25	50	42	60	
	2.37	18	32	44	63	80	72	100	
periclase	2.11			24	100	85	97	82	
calcite	3.04	31							
MP/W molar ratios (X-ray)			0.59	0.54	0.61	0.69	0.57	0.62	
MP/W molar ratio (citric acid)			0.41 <sup>a</sup>	0.74 <sup>a</sup>	0.67	0.62	0.58	0.75	0.09
P <sub>2</sub> O <sub>5</sub> %		28.5	30.0	29.5	30.9	32.5	32.5	30.5	25.0
Ca O %		29.4	13.7	4.34	0.90	2.31	1.17	0.72	50.0
insoluble Cl, %		0.89	0.57	0.46	0.53	0.39	0.43	0.43	0
Cl/P molar ratio		0.062	0.038	0.031	0.035	0.024	0.026	0.023	0

<sup>a</sup> Part of the dissolved phosphate is apatite.

Table VII. Influence of Reaction Temperatures on Diffraction Intensities of the Unsoluble Products of the Reaction with Ground Phosphate (Mg/Ca = 1.5, t = 20 min)

mineral	representative d, Å	temperature, °C						
		400	450	500	550	600	650	700
apatite	2.62	7	tr					
	1.94	13	tr					
	1.84	15	tr					
wagnerite	3.32		36	35	35	17	13	10
	3.15		43	45	40	22	18	14
	2.99		100	100	100	55	47	40
magnesium phosphate	4.35		20	31	32	19	19	20
	4.11		15	18	18	14	15	16
	3.85		51	68	61	45	44	44
brucite	4.77		44	40	38	4	tr	
	2.37		67	52	64	4	tr	
periclase	2.11		26	19	31	100	100	100
calcite	3.04	22						
MP/W molar ratios (X-ray)			0.30	0.40	0.39	0.51	0.62	0.77
MP/W molar ratios (citric acid)			1.29	0.68	0.56	0.63	0.74	0.85

**Table VIII. Influence of Reaction Temperatures on the Insoluble Products of Reactions with Ground Phosphate (All Ratios Are Molar, Mg/Ca = 1.5,  $t$  = 20 min)**

temp, °C	P <sub>2</sub> O <sub>5</sub> , %	F, %	F/P	CaO, %	Cl, %	Cl/P
400	24.5	2.72	0.42	33.7	2.26	0.184
450	27.8	3.02	0.41	5.1	1.11	0.080
500	29.8	3.21	0.40	1.0	0.45	0.030
550	30.6	3.32	0.41	0.57	0.52	0.034
600	30.8	<i>a</i>	<i>a</i>	0.49	0.56	0.036
650	31.3	3.38	0.40	0.38	0.59	0.038
700	31.0	3.40	0.41	0.41	0.59	0.038

<sup>a</sup> Not determined.

the equilibrium of reaction 8 is such as to favor the formation of more MP.

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## Production of Magnesium Phosphate from Apatite and Carnallite. 2. Solubility in Citric Acid

Petahia Bar-On and Ithamar Pelly\*

Magnesium phosphate was produced from Oron phosphate and carnallite. Solubilities of the product in citric acid were studied as a function of reaction temperatures, F/P ratios, Mg/Ca ratios, reaction times, grinding the phosphate, particle size of the raw phosphate, and precalcination of the phosphate. Enrichment in P<sub>2</sub>O<sub>5</sub> was studied. Reactions with ground phosphate showed a maximum solubility at 450 °C (the highest obtained under all conditions) and a minimum at 550 °C, after which there is no difference between ground and unground phosphate. Two factors seem to be involved. One is catalysis of the reaction causing the production of soluble phosphate and is due to grinding and not to particle size. The other is connected with raising the temperature, which lowers solubilities. Enrichment in P<sub>2</sub>O<sub>5</sub> by several methods tested in this study resulted in higher P<sub>2</sub>O<sub>5</sub> content but low solubilities of the product in citric acid.

Apatites containing fluorine are only slightly soluble in water and in organic acids, so that the phosphate is not readily available to plants. In the fertilizer industry the apatite is destroyed (there are several methods) to create more soluble compounds. For comparison purposes the availability to plants is measured by the solubility in citric acid or ammonium citrate under specified conditions.

Magnesium phosphate (MP), Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (which is soluble in citric acid), is produced in Japan by reacting the phosphate with olivine or serpentine at 1400 °C. MP can also be produced in a reaction between apatite and magnesium chloride or with carnallite (Baniel et al., 1965). The reaction between carnallite and apatite is carried out at 600 °C. The product is washed with water so that most of the potash can be recovered.

The chemistry, mineralogy, and the mechanism of this reaction are discussed in part 1 of this paper (Pelly and Bar-On, 1978). The main phosphate minerals formed are magnesium phosphate (MP) and wagnerite (W), Mg<sub>2</sub>PO<sub>4</sub>F.

A few practical aspects are involved. It is desirable to obtain a product with as high P<sub>2</sub>O<sub>5</sub> content as possible. The solubility in citric acid is about 100% of the total P<sub>2</sub>O<sub>5</sub> when the reaction is carried out at the 1000 °C range (Stavski, 1970). At 600 °C solubilities are lowered to about 50% of the total P<sub>2</sub>O<sub>5</sub>, mainly because large amounts of wagnerite (W), insoluble in citric acid, are formed, so that the value as a fertilizer is lowered. From the industrial point of view, the reaction at high temperatures causes high corrosion (chloride melt) and requires a very high fuel consumption, thus making the process unprofitable.

The aim of this research was to study the chemistry, mineralogy, and mechanism of the reaction (part 1) and to try to find a method by which a product with high P<sub>2</sub>O<sub>5</sub> content and a high solubility in citric acid could be produced at lower temperatures than in the standard process.

#### EXPERIMENTAL SECTION

The materials and the procedure of the various reactions for studying the influence of the reaction temperature, amount of fluorine, Mg/Ca molar ratio, reaction times, and of grinding the phosphate are described in part 1 (Pelly and Bar-On, 1978), together with details of procedures for

\*Department of Geology and Mineralogy, Ben Gurion University of the Negev, Beer Sheva, Israel.