152 *J. Agric. Food Chem.,* Vol. 27, No. 1, 1979

Bar-On, Pelly

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

temp, °C	P_2O_5, %	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	a	a	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

a Not determined.

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

ACKNOWLEDGMENT

LITERATURE CITED

Ando, J., Matsuno, S., *Bull Chem. Soc. Jpn.* **39**, 1915–1922 (1966).
Ando, J., Hoego, K., *J. Chem. Soc. Jpn.* **12**, 2441–2442 (1972).
Baniel, M. M., Bazevi, E. L., Blumberg, R., Lavie, S., Heimann, H., *J. Agric. Food Chem.* **13**(1), 88–91 (1965).
Bar-On, P., M.Sc. Thesis, Ben Gurion University of the Negev and the Hebrew University of Jerusalem, Israel, 1975.
Bar-On, P., Pelly, I., submitted for publication to *J. Agric. Food Chem.* (1978).
Edmond, C. R., *Anal. Chem.* **41**(10), 1327–1328 (1969).
Ish-Shalom, M., Coren, S., Israel Ceramic and Silicate Institute, Technion, Haifa, Project 1015/L.T.P./0175, 1969.
Lavie, S., Magister of Science Thesis, Technion, Haifa, Israel, 1961.
Lehr, J. R., McClellan, G. H., Smith, J. P., Frazier, A. W., Proceedings of the International Colloquium on Solid Inorganic Phosphates, Toulouse, France, 1967.
Silverman, S. R., Fuyat, R. K., Weiser, J. D., *Am. Mineral.* **37**, 211–222 (1952).
Smith, J. P., Lehr, J. R., *J. Agric. Food Chem.* **14**, 342–349 (1966).
Stavski, K., *Prze. Chem.* **49**(1), 19–21 (1970).

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_2O_5 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_2O_5 by several methods tested in this study resulted in higher P_2O_5 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), $Mg_3(PO_4)_2$ (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 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_2PO_4F.

A few practical aspects are involved. It is desirable to obtain a product with as high P_2O_5 content as possible. The solubility in citric acid is about 100% of the total P_2O_5 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_2O_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, mineralogy, and mechanism of the reaction (part 1) and to try to find a method by which a product with high P_2O_5 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.

Table I. Influence of Reaction Temperatures on the Solubility of the Water-Insoluble Products in Citric Acid (Mg/Ca = 1.5, t = 20 min)

reaction temp, °C	TP	SP	RSP	SD	MP/W molar ratio (X-ray)	MP/W molar ratio (citric acid)
400	26.0	6.2[a]	24.2	43.4		
450	26.4	9.9[a]	37.5	51.8		
500	27.4	12.4	44.9	57.9	0.44	0.41
550	29.8	15.8	53.0	61.6	0.44	0.56
600	30.9	17.7	57.3	64.4	0.61	0.67
650	31.1	18.8	60.5	68.1	0.64	0.77
700	31.3	19.8	63.3	67.6	0.81	0.86

[a] The soluble phosphate is mostly apatite.

Table II. Influence of F/P Molar Ratios on the Solubility of the Water-Insoluble Products in Citric Acid (Phosphate–MgF$_2$ mixtures, Mg/Ca = 1.5, 20 min at 600 °C)

F/P	TP	SP	RSP	SD	MP/W molar ratio (X-ray)	MP/W molar ratio (citric acid)
0.41	30.9	17.7	57.3	64.4	0.61	0.67
0.75	30.2	8.8	29.2	48.7	0.13	0.21
1.0	28.9	3.1[a]	10.7	38.0		
1.25	28.1	2.3[a]	8.2	33.0		

[a] Phosphate dissolved is mostly wagnerite.

Table III. Influence of Mg/Ca Molar Ratios on the Solubility of the Water-Insoluble Products in Citric Acid (20 min at 600 °C)

Mg/Ca	TP	SP	RSP	SD	MP/W molar ratio (X-ray)	MP/W molar ratio (citric acid)
0.8	32.2	13.4[a]	41.4	53.6	0.14	(0.35)
0.9	32.6	15.7[a]	48.1	56.6	0.36	(0.46)
1.0	33.1	16.8	50.6	59.6	0.43	0.51
1.1	33.9	17.8	52.5	50.2	0.42	0.55
1.2	34.8	18.9	54.2	63.9	0.53	0.59
1.3	33.1	18.0	54.5	60.3	0.53	0.60
1.5	30.9	17.7	57.3	64.4	0.61	0.67

[a] Part of the soluble phosphate is apatite.

obtaining X-ray diffraction and IR spectra and methods of chemical analysis of several components.

The reaction products had to be thoroughly washed with water, otherwise only chlorides were identified in X-ray diffractions. So, when products are mentioned, water-insoluble products are meant.

In order to study the effect of calcination, phosphate samples were ground (250 mesh) and heated in the temperature range of 400–1000 °C. Ignition loss and solubilities were determined. After 700 °C clods appeared. Samples for reactions of precalcined phosphate with carnallite were taken without additional grinding. The standard conditions were used, i.e., Mg/Ca molar ratio 1.5, heating time 20 min, and temperature of 600 °C, since at that temperature no effects due to pregrinding are seen (see Discussion) and a possible change of behavior could be attributed to precalcination.

Solubility in citric acid was determined as follows: a few drops of alcohol were put on a 1.000-g sample (250 mesh) till all the sample was saturated; and 100 mL of 2% citric acid was added and the sample was stirred for 30 min and filtered through preweighed No. 40 Whatman filter paper. The paper and insoluble remains were dried for 3 h at 110 °C and weighed. P$_2$O$_5$ in the solution was determined spectrophotometrically (Perkin Elmer 402) using ammonium vanadomolibdate reagent.

RESULTS

The solubilities are expressed in the tables in the following forms: (a) TP, total phosphate (as P$_2$O$_5$) content

(weight percent); (b) SP, phosphate (as P$_2$O$_5$) soluble in citric acid (percent); (c) RSP, relative soluble phosphate (SP/TP) ratio of soluble phosphate (as P$_2$O$_5$) to the total phosphate (as P$_2$O$_5$); (d) SD, weight percent of sample dissolved in citric acid (i.e., including compounds other than phosphates, like periclase, brucite, calcite).

The molar ratios MP/W were calculated in two ways. One method consisted of using X-ray diffractograms (Pelly and Bar-On, 1978): MP/W ratios were calculated as the ratio of the sum of representative peak areas of each. 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 should not be taken as quantitative measurements and are given in the tables only to show order of magnitude and trend of changes of the ratios.

MP/W ratios were also calculated from the solubilities of the water-insoluble reaction products in citric acid (SP values as they appear in the various tables). It was assumed that all soluble P$_2$O$_5$ was MP and the insoluble phosphate residue was W. This is roughly correct but for low concentrations where the small solubility of apatite becomes important. This can be seen in the tables, especially in cases where no MP or W was detected, but phosphate was nevertheless in solution. Again, these ratios are given only to show magnitude and trend of changes of the ratios.

The results of experiments in which the influence of several parmeters was studied are shown in Tables I–XI.

Table IV.   Influence of Reaction Times on the Solubility of the Water-Insoluble Products in Citric Acid
(Mg/Ca = 1.5, T = 600 °C)

time, min	TP	SP	RSP	SD	MP/W molar ratio (X-ray)	MP/W molar ratio (citric acid)
0[b]	25.0	3.9[a]	15.6	39.6		
5	28.5	9.5[a]	33.3	47.0		
10	30.0	13.6	45.2	57.7	0.59	0.41
15	29.5	17.6	59.7	62.0	0.54	0.74
20	30.9	17.7	57.3	64.4	0.61	0.67
30	32.5	18.0	55.4	65.4	0.69	0.62
45	32.5	17.6	54.1	67.2	0.57	0.58
60	30.5	18.3	60.0	70.4	0.62	0.75

[a] The dissolved phosphate is mostly apatite.   [b] Raw phosphate.

Table V.   Influence of Reaction Temperature and Cooling Method on the Solubilities of the Water-Insoluble
Products of the Reaction with Ground Phosphate in Citric Acid (Mg/Ca = 1.5, t = 20 min)

temp, °C	air-cooled				water-cooled			MP/W molar ratio (X-ray)	MP/W molar ratio (citric acid)[b]
	TP	SP	RSP	SD	SP	RSP	SD		
400	24.5	9.4[a]	38.5	53.2	9.1	35.8	50.5		
450	27.8	20.0	72.0	73.8	22.1	76.4	75.7	0.30	1.29
500	29.8	17.2	57.8	65.3	18.1	60.8	68.3	0.40	0.68
550	30.6	16.2	53.0	61.0	15.4	50.6	60.0	0.39	0.56
600	30.8	17.1	55.6	63.3	17.4	54.8	63.6	0.51	0.63
650	31.3	18.7	59.7	65.9	19.8	61.3	67.6	0.62	0.74
700	31.0	19.5	63.0	68.4	20.3	62.3	71.4	0.77	0.85

[a] The dissolved phosphate is mostly apatite.   [b] Air-cooled.

Table VI.   Influence of Reaction Temperatures on the Solubilities of the Water-Insoluble Products of Fine and Coarse
Fractions of Raw Phosphate, in Citric Acid, (Mg/Ca = 1.5, t = 20 min)

temp, °C	fine fraction, –250 mesh				coarse fraction, +250 mesh			
	TP	SP	RSP	SD	TP	SP	RSP	SD
400	16.5	2.3	14.2	53.7	28.8	7.2	25.0	38.3
450	17.6	10.0	56.8	66.9	28.8	10.2	35.4	54.5
500	18.8	11.6	61.7	74.3	30.5	14.0	45.9	51.3
550	20.1	12.8	63.7	73.7	32.1	16.1	50.2	56.9
600	20.8	13.4	64.4	74.7	34.2	19.4	56.8	60.6
650	21.2	13.5	63.7	77.8	33.4	19.1	57.2	64.5
700	22.5	14.2	63.2	79.4	33.8	20.4	60.4	65.4

Table VII.   Influence of Temperatures of Calcination of
the Phosphate on Its Solubility in Citric Acid

calcination temp, °C	loss on igni- tion, %	TP	SP	RSP	SD
raw phosphate		25.0	3.9	15.6	39.6
400	1.6	24.7	3.9	15.8	39.0
500	2.6	25.0	3.8	15.2	40.3
600	4.1	25.3	3.2	12.6	39.1
700	10.8	26.8	4.0	14.9	38.5
800	11.7	27.2	4.1	15.1	37.4
900	12.8	27.4	5.2	19.0	38.8
1000	13.4	28.9	6.8	23.6	43.9

Table VIII.   Solubilities in Citric Acid of Water-Insoluble
Reaction Products Obtained from Calcined Phosphate
(Reaction with Carnallite at 600 °C, Mg/Ca = 1.5, t =
20 min)

calcination temp, °C	TP	SP	RSP	SD
400	33.1	18.0	54.4	63.6
500	33.1	17.6	53.2	63.5
600	32.2	17.4	54.1	62.6
700	33.1	17.8	53.8	64.0
800	33.1	17.2	52.0	64.4
900	33.1	17.4	52.6	62.5
1000	33.5	18.0	54.3	64.3

The parameters investigated were reaction temperatures, influence of the amount of fluorine, Mg/Ca ratio, reaction times, effect of grinding the phosphate, of precalcination of the phosphate, and of reactions with specific grain size particles of the raw phosphate.

DISCUSSION

Raw phosphate, which was an unbeneficiated grade, was used for the reactions. The presence of calcite or its calcination product CaO alters the pH of the citric acid so as to distort and obscure the solubility behavior of the apatite. In addition, the accessory minerals complicate the elucidation of the reaction mechanism. The difficulty can be removed either by Silverman extraction to remove the calcite or by using synthetic pure apatite. Nevertheless,

raw phosphate was used to make reaction conditions similar to those of industrial production. The citric acid solubility of the industrial product is also measured with the accessory minerals or their products. Moreover, calcite reacts with magnesium chloride (Baniel et al., 1965) to give an equivalent amount of MgO which is water insoluble and remains with the phosphate products so that alteration of the pH of the citric acid and lowering of the solubilities should be about equal in all the reactions of the same set. This means that SP and RSP are minimum values of the apatite–calcite system. Reactions with pure apatite should give higher values. But, since the interference is that of lowering solubilities, the fact that in spite of this solubilities arise means that the trends seen within each series are real. Moreover, there is (but for one case) a good correlation in

Table IX.   Chemical Composition and Solubilities in Citric Acid of Fractions of the Raw Phosphate

grain size, mm	% of fraction in sample	% P_2O_5 in fraction	phosphate in fraction as % of total sample	% CO_2 in fraction	SP	RSP	SD
raw phosphate		25.0			3.9	15.6	39.6
0-0.037	14.7	13.7	8.4	17.5	0.38	2.8	55.8
0.037-0.063	9.1	14.4	5.4	18.1	0.29	2.0	53.5
0.063-0.125	12.2	23.1	11.4	13.1	1.6	7.0	42.5
0.125-0.250	26.7	30.8	33.6	6.9	5.7	18.4	31.3
0.25-0.5	17.4	30.6	21.6	6.7	4.6	15.0	35.7
0.5-1.0	10.1	25.6	10.5	9.4	3.0	11.8	40.8
1.0-2.0	9.6	23.8	9.2	10.7	3.6	15.2	43.8

Table X.   Solubilities in Citric Acid of Water-Insoluble Products of Reactions with Different Grain Size Fractions of the Raw Phosphate (Mg/Ca = 1.5, T = 600 °C, t = 20 min)

grain size, mm	TP	SP	RSP	SD
0-0.037	20.5	12.4	60.6	76.6
0.037-0.063	20.6	13.0	63.0	77.2
0.063-0.125	28.4	14.8	52.2	65.5
0.125-0.25	35.1	16.5	47.1	57.2
0.25-0.5	34.1	16.1	47.3	58.1
0.5-1.0	29.2	12.0	41.2	57.4
1.0-2.0	29.3	13.2	45.2	58.8

Table XI.   Solubilities in Citric Acid after Separation of Fine Particles from the Water-Insoluble Reaction Products (Mg/Ca = 1.5, t = 20 min)

temp, °C	TP	SP	RSP	SD	P_2O_5 yield, %
550	39.0	20.4	52.2	52.4	67.3
600	40.3	21.9	54.2	57.6	63.0
650	32.8	19.4	59.2	64.3	88.6
700	34.2	20.4	59.7	66.5	88.8

the trends shown by MP/W ratios calculated from X-ray diffractions with those calculated from citric acid solubilities.

This argument is not correct in two cases: (1) Table VI since the amounts of calcite in the fine and coarse fractions are not equal, the solubilities of the two fractions should not be compared, only the influence of reaction temperatures on each fraction; and (2) Tables IX and X where different fractions contain different amounts of calcite. Changes within each table have no meaning. Only the solubilities of the same fraction in the two tables (i.e., before and after the reaction) can be compared.

It must be noted that small solubility differences may have little or no significance, so that only trends or great differences are meaningful.

It was found (Table VII) that up to about 20% of the apatite can be dissolved in citric acid, so that at low temperatures, when X-ray diffraction shows that apatite exists in the products and MP does not, there is no meaning to the calculations of MP/W from solubilities in citric acid and these ratios are not given in the tables. It was found (Table II) that in the absence of MP up to about 10% of the W can be dissolved in citric acid. This means that most of the dissolved phosphate (after the apatite is destroyed) is MP and MP/W ratios calculated this way should be at least semiquantitative. The residue which did not dissolve in citric acid was identified by X-ray diffraction and found to be W and apatite (in the cases that it was not destroyed). Because a great part of the product was dissolved, apatite was concentrated in the residue and was identified easily even if it was present in small amounts in the product. It is seen that generally there is a good correlation in the trends shown by the molar ratios MP/W calculated by the two independent methods,

so the results should be reliable. A very great discrepancy (0.30 vs. 1.29) is seen only in reactions with ground phosphates (see Discussion).

From Table I it is seen that raising the reaction temperature increases the amount of soluble phosphate in the products, but the total phosphate is only slightly above the level obtained by calcination of the raw phosphate (Table VII).

From Table II it is seen that increasing F/P ratios causes decrease in solubilities of the products in citric acid as more W is formed (Pelly and Bar-On, 1978). Also, since in all these reactions F/P ratios remain 0.41 as in the raw phosphate (Pelly and Bar-On, 1978), it means that an effective method to increase the solubility of the products would be through a reaction in which fluorine will leave the system. There are methods to remove the fluorine, but they are carried out at very high temperatures. Preliminary experiments were carried out in sort of an "Edisonian" way in which one of the following was added in turn to the reaction mixture: sodium silicate, boric acid, sulfuric acid, phosphoric acid, quartz, or quartz with sulfuric acid or phosphoric acid. It was hoped to obtain a volatile fluorine compound. Under the conditions in which the reactions were carried out, no improvement was detected, but this line of study seems to be worth further research.

From Table III it is seen that though there is only a small change of TP and SD, the increase of Mg/Ca ratio slightly increases the relative solubility of the product (for instance Mg/Ca ratios 1.0 and 1.3 where TP and SD are identical but RSP differs by 8% (relative) which shows that more phosphate was transformed into a soluble form). The reactions with low Mg/Ca ratios are the only ones in which chlorapatite was detected by X-ray diffraction (Pelly and Bar-On, 1978). Regretfully these solubilities do not shed more light on the discussion of the reaction mechanism.

Solubilities of the products of reactions with ground phosphate as a function of temperature showed a different pattern from those with unground phosphate. X-ray diffractions and IR spectra show that grinding causes acceleration of the reactions. Calcite has already disappeared at 450 °C and apatite only occurs in traces at 450 °C as against 500 and 600 °C, respectively, for unground phosphate.

The amount of chlorination and its nature are also different—d_{222} reflection peak is broader and the value is 1.946 Å, i.e., a little closer to that of chlorapatite (1.959 Å). After solution in citric acid the d_{222} peak of apatite in the residue was 1.938 Å, i.e., that of fluorapatite. It seems that the solubility in citric acid is selective; fluor-chlorapatite (or chlorapatite) is dissolved while fluorapatite is not, and the undissolved apatite residue is more homogeneous. The broadening of the peak is not the result of grinding, since in ground, unreacted raw phosphate this peak is sharp. This means that the apatite in the product

is not homogeneous; either there is a difference in the chlorination of the different crystals or only the outer surface had undergone chlorination.

There is a great difference in citric acid solubilities of water-insoluble products of reactions with ground phosphate compared to those of unground phosphate. In contrast to the constant rise in solubility (RSP) for unground phosphate, with ground phosphate there is an increase up to a maximum at 450 °C then a decrease with a minimum at 550 °C and then a rise. In the 550–700 °C range there is no difference between products of both phosphates. The values of SP, RSP, and SD at the maximum at 450 °C are the highest found in all experiments (Table V). It should be noted that at this point there is a very great discrepancy between MP/W obtained by the two methods (0.30 vs. 1.29). Since apatite is not present here, the excess solubility cannot be attributed to it. It seems that the correct ratio is given by X-ray diffraction. The high solubility may be due to the formation of a phosphate product, soluble in citric acid, other than MP, for instance chlorspodiosite, Ca_2PO_4Cl. No chlorspodiosite was identified by X-ray diffraction (Pelly and Bar-On, 1978). This negates the possibility of chlorspodiosite being formed in more than small amounts (but not the possibility of its formation as a precursor in the formation of other products). Another explanation is that at this low temperature the wagnerite is obtained in a less crystallized, more soluble form (d values of the wagnerite in the undissolved residue are changed from 2.978 Å at 450 °C to 2.967 Å at 700 °C) or that at this temperature it is formed as very small, more soluble crystals. Another possibility is that MP is formed at low temperatures, mostly in a less crystallized form and the ratio obtained by the solubility method is the correct one.

To see if during the slow cooling at room temperature there is a transformation changing soluble to unsoluble minerals, solubilities of products, cooled by quenching the products in ice–water mixture, were measured. The results (Table V) show that though at 450 °C there is a difference of about 6% (higher for water cooled), there is generally no real difference between the two cooling methods.

Experiments were done to see if the decrease in solubility between 450–550 °C is connected with heating. In one, reaction with ground phosphate was carried out at 450 °C, but for 1 h instead of 20 min. In the other, the product of the reaction with ground phosphate at 450 °C (20 min) was heated again (without carnallite) at 550 °C for 20 min. Drastic decreases in solubilities were seen in both cases (RSP was lowered from 72.0 to 57.2 and 58.5, respectively). This means that there is an effect caused by temperature (and not by the degree of reaction) which lowers the solubility.

To see if these effects are connected with grinding or are merely the result of grain size, raw phosphate was sieved into two fractions, viz. –250 and +250 mesh, and the solubilities of their reaction products were determined. While solubilities of the two fractions cannot be compared (because of a different calcite content), the results (Table VI) show that each fraction behaves in the same way as unground phosphate, i.e., rising without a maximum and a minimum and that the maximum in products of ground phosphate is the result of grinding and not of particle size.

The results in Table IV seem to be confusing. While MP/W from X-ray diffractions show maximum of 30 min, MP/W from solubilities show a maximum at 15 min. Considering the fact that prolonged heating of the products of reaction with ground phosphate caused a drastic decrease of solubility and the possibility that at the beginning

the W is obtained in a more soluble less crystallized form, these results can be reasonably interpreted. If W is obtained in a more soluble form, the solubility increases up to 15 min and further heating transforms it to a less soluble form so that a great decrease in solubility is observed. If this is correct, the value for 60 min must be an error.

Calcination is a general process of benefication of phosphates in industry. This causes transformation of francolite into fluorapatite, a decrease of surface area, a decrease of porosity, and sintering. Experiments were made to see the influence of precalcination on the phosphate and on the reaction products. Calcite disappears sharply at 700 °C, but the carbonate ion in the apatite disappears gradually and remains even at 1000 °C. As seen from Table VII, this calcination enriches the sample in P_2O_5 due to loss of volatiles. A great enrichment can be obtained by removal of the lime formed from the calcite. A decrease in solubility is seen up to 700 °C and then solubilities rise. On the other hand, solubilities of reaction products with precalcined phosphate are not different from those with uncalcined samples at 600 °C (TP a little higher RSP a little lower) (Table VIII), i.e., calcination at high temperatures has no effect on the products, probably because it does not matter if the volatiles were expelled before or during the reaction and the main factor is the reaction with the carnallite.

The value of the fertilizer depends on P_2O_5 content. Enrichment of P_2O_5 in the samples can be obtained in different ways. One mentioned above is calcination and removal of the lime formed. Calcination raises TP to 33% and removal of lime should raise it to 38–40%. In addition one saves carnallite and fuel by preremoval of volatiles and lime, but loses fuel for the precalcination which has to be a separate process. Experiments with phosphate enriched in this way were not carried out in this study.

Another way of enrichment before the reaction is presieving and using only the fractions enriched in P_2O_5. The fractions enriched in P_2O_5 are in the range of 125–500 μm (Table IX). The RSP of the fine fractions are much lower than those of the others probably due to inhibition related to high amounts of calcite dissolved in citric acid and lowering its concentration. Table X shows that there is an enrichment in total phosphate (up to 35% in the most enriched fraction). The product can be enriched in P_2O_5 by removal of the fine fractions of the raw phosphate and this also saves carnallite and fuel. The drawback (unexplained) is that RSPs of the fractions enriched in P_2O_5 are much lower than in the other reactions (though these fractions contained less calcite), so there is no reason to carry out the reactions at all.

Another method for obtaining high P_2O_5 content is enrichment after the reaction by removing the fine particles of the product. In these experiments the product was sieved wet through a 400-mesh sieve. Most of the product passed a 250-mesh sieve which shows that average grain size of the product is smaller than in the raw phosphate. Some particles greater than 400 mesh were probably broken by shaking the sieves, so there was no clear indication when to stop sieving. Sieving was stopped when it seemed that the opacity of the water did not decrease. A product richer in P_2O_5 can be obtained this way (Table XI) but at the expense of the yield of P_2O_5, and with this way more carnallite and fuel are needed for the P_2O_5 remaining in the product. Again, RSP values are relatively low (Table XI), so there seems no real reason to carry out the reaction.

It seems that enrichment in P_2O_5 can be achieved at the price of increased fuel and carnallite consumption and loss

γ Irradiation of Subtropical Fruits

J. Agric. Food Chem., Vol. 27, No. 1, 1979 **157**

of phosphate. The solubilities of the products of these enriched samples are not above those obtained from untreated raw material. High solubilities were obtained in reactions with ground phosphate at 450 °C but there seem to be two factors involved. One is catalysis of the reaction causing the production of soluble phosphate. The other is connected with raising the temperature which lowers the solubilities and is due to grinding and not to particle size. It seems that further studies should be done by adding to the reaction mixture compounds that will cause formation of volatile fluorides.

LITERATURE CITED

Baniel, A. M., Bazevi, E. L., Blumberg, R., Lavie, S., Heimann, H. H., *J. Agric. Food Chem.* **13**(1), 88–91 (1965).
Pelly, I., Bar-On, P., **26**, 000 (1978).
Stavski, K., *Przem. Chem.* **49**(1), 19–21 (1970).

γ Irradiation of Subtropical Fruits. 3. A Comparison of the Chemical Changes Occurring during Normal Ripening of Mangoes and Papayas with Changes Produced by γ Irradiation

Austin C. Thomas and Marguerite Beyers*

Changes in the concentrations of ascorbic acid, carotenes, sugars, and titratable acidity were monitored in two mango and two papaya cultivars as the fruits ripened from mature green to the edible-ripe stage, both with and without γ irradiation with doses up to 2.0 kGy. Ascorbic acid and titratable acidity changes only slightly during ripening. Virtually no difference in the total sugar content could be observed between the irradiated and nonirradiated fruits. In most experiments an apparent increase in carotene content was produced by irradiation, but this was overshadowed by the much larger increase which occurred as a result of ripening. No significant change in the nutritional value of the fruits could be detected after irradiation. Natural variation and the physiological changes produced by ripening were greater than any radiation-induced changes.

The ability of ionizing radiation to bring about chemical change in substances exposed to them is well known, and in the treatment of foodstuffs by irradiation, chemical changes undoubtedly occur. Some vitamins, in particular, are highly reactive, and it has often been stated that irradiation causes a substantial loss of essential vitamins and a consequent loss of nutritional quality of treated foodstuffs (Khan et al., 1974a). However, at the relatively low doses applied to fruits, normally in the range 0.5–2 kGy, the magnitude of these changes is small, often less than natural chemical changes which occur in the fruit (e.g., ripening) and certainly much smaller than chemical changes brought about by conventional preservation methods (e.g., heating) (Lee et al., 1976), to which very little attention has been given.

The purpose of this study was to compare changes in the concentration of selected constituents which occur during the ripening processes of some subtropical fruits with possible changes produced by irradiation. The constituents monitored were ascorbic acid, total carotenes, and total sugars. Both of these vitamins are considered relatively unstable (Rao, 1962; Snauwert et al., 1973), whereas sugars, apart from water, are by far the most abundant group of compounds present in the fruits in question (ca. 8–15% w/w). Titratable acid was also monitored during the papaya ripening studies and in the second season of mango determinations.

Chemistry Division, Atomic Energy Board, Private Bag X256, Pretoria, South Africa.

Chart I

papayas		mangoes	
Hortus Gold I	Dec 1975	Zill I	Feb 1976
Hortus Gold II	Aug 1976	Zill II	Feb 1977
Papinos I	Aug 1976	Kent I	Mar 1976
Papinos II	Oct 1976	Kent II	Feb 1977

Chart II

fruit	no./dose	total doses, kGy
papayas		
Hortus Gold I	5	0, 0.75, 1.50, 2.00
Hortus Gold II	12	0, 1.00, 1.50, 2.00
Papino I and II	30	0, 0.75, 1.50, 2.00
mangoes		
Kent I	12	0, 0.75, 1.50, 2.00
Kent II	48	0, 0.75, 1.50, 2.00
Zill I	12	0, 0.75, 1.50, 2.00
Zill II	36	0, 0.75, 1.50, 2.00

EXPERIMENTAL SECTION

Source of Fruit. All fruits were supplied by the Letaba Cooperative, Tzaneen. The timing of the various consignments of the fruits are as shown in Chart I.

Some variation occurred in the initial quality of the fruits obtained in Hortus Gold I, otherwise the fruits were received in a mature, green condition.

Heat Treatments. Fruits were heat treated and irradiated within 24 h of harvesting.

Papayas: 50 °C for 10 min and waxed. Mangoes: 55 °C for 5 min and waxed. The wax used was paraffin based