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The Constitution, Reactivity and Thermal Change of Phosphate Ores

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Tests were made on twenty-five samples of phosphate ores from all over the world deposits. All of the samples consisted of apatite, plus small amounts of calcite and other minerals. The apatite crystals of the sedimentary ores ranged in size from around 0.05 μ (Gafsa, North Carolina, etc.) to around 0.5 μ (Taiba), while those of igneous ores reached 100 μ. The difference between the ores in their reactivity with citric, hydrochloric and nitric acid was mainly due to the difference in crystal size. The decomposition of the ores by a mixture of sulfuric and phosphoric acids was seriously affected by the coating of calcium sulfate crystals on the surface of the ores, and also by the aluminum and iron present in the acids and ores. The lattice constant, a_0, of the apatite of the ores ranged from 9.340 to 9.422 Å; it was generally smaller for the ores which had larger F_2/P_2O_5 ratios. Upon calcination above 500°C, the a_0 value of the apatite which had an excess of fluorine increased and approached that of true fluorapatite. The reactivity of the ores with the acids generally decreased upon calcination due to the sintering of the grains and the crystal growth. For ease of decomposition by a mixture of sulfuric and phosphoric acids, the calcined ore should contain a small amount of carbon dioxide. Tests also were made on the amount of organic matter and its decrease upon calcination.

Phosphate ores mined from various fields differ much in their nature. Moreover, it often happens that even ores which have been obtained from the same area and which have essentially the same chemical composition are significantly different in their behavior when treated with acids; this results in trouble for phosphate fertilizer plants. The reason for such differences is not clear.

Moreover, the calcination of ores which has recently been carried out in commercial-scale plants in order to increase the grade of the ores results in a further variation in the nature of the ores. Although many investigators[1-4] have reported on the phosphate ores, there is still much to study about the constitution and the nature of the ores.

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1) J. H. Caro and W. L. Hill, *J. Agr. Food Chem.*, **4**, 684 (1961).

2) H. L. Marshall, L. F. Rader and K. D. Jacob, *Ind. Eng. Chem.*, **25**, 1253 (1933).

3) T. Noguchi, T. Hosoi and O. Kashimura, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **64**, 1892 (1961).

4) J. H. Caro and W. L. Hill, *J. Agr. Food Chem.*, **12**, 479 (1964).

TABLE I. CHEMICAL COMPOSITION OF SAMPLES

Sample	Chemical composition, %							Mole ratio		KMnO$_4$ consumption ml.
	BPL	P$_2$O$_5$	CaO	R$_2$O$_3$	SiO$_2$	F$_2$	CO$_2$	CaO/P$_2$O$_5$	F$_2$/P$_2$O$_5$	
Kola	85	39.1	51.1	1.8	3.2	2.8	0.1	3.31	0.27	2.6
Lao'Cay	87	40.2	—	0.9	—	3.7	0.1	—	0.34	—
Phallabowa	74	34.0	53.1	1.6	2.2	2.5	4.7	3.96	0.28	—
Florida	68	31.6	46.5	2.6	8.1	3.8	5.1	3.72	0.45	14.9
Florida	76	35.1	49.6	2.1	3.2	3.3	2.3	3.59	0.35	9.0
Florida	77	35.8	51.5	3.0	4.1	3.9	4.1	3.64	0.41	12.6
Calcined Florida	75	34.8	52.3	1.4	4.5	4.0	0.8	3.83	0.43	9.5
Calcined Florida	79	36.6	52.9	2.6	4.3	4.6	0.4	3.67	0.47	5.3
Calcined Florida	81	37.2	52.7	2.2	3.1	3.8	0	3.60	0.38	1.8
North Carolina	65	30.0	49.5	2.1	3.5	3.7	5.2	4.27	0.46	—
Taiba	80	36.9	50.0	2.0	3.6	—	—	3.44	—	17.3
Taiba	81	37.3	50.7	2.1	4.7	3.7	1.9	3.44	0.37	13.7
Taiba	82	37.9	52.6	2.2	2.2	3.3	1.8	3.51	0.33	—
Togo	79	36.7	53.2	1.5	3.8	3.0	1.8	3.67	0.31	—
Morocco	70	32.2	50.8	0.6	2.2	4.1	4.0	4.00	0.48	19.2
Morocco	73	33.6	51.2	0.7	1.4	4.2	6.3	3.86	0.47	10.2
Morocco	78	36.2	52.2	1.1	1.6	4.0	5.2	3.65	0.42	8.2
Kossier	61	28.4	47.3	1.5	7.9	3.4	6.3	4.22	0.45	66.0
Gafsa	55	25.5	43.2	3.4	—	3.2	4.2	4.29	0.46	—
Gafsa	64	29.8	49.1	1.2	10.8	3.7	4.2	4.17	0.46	41.5
Christmas	83	38.2	—	—	—	3.2	2.6	—	0.31	38.0
Christmas	84	38.9	—	3.0	0.2	1.1	1.5	—	0.11	18.0
Macatea	77	35.5	—	1.3	1.0	3.2	2.2	—	0.34	—
Macatea	80	37.0	52.0	1.0	0.4	3.2	2.7	3.56	0.32	43.2
Angaur	68	31.6	53.4	1.3	1.6	2.3	6.2	4.25	0.27	48.0
Synthetic HA*	89	40.9	53.8	0	0	0	0	3.33	0	0
Synthetic FHA**	89	41.1	53.9	0	0	1.8	0	3.32	0.16	0
Synthetic FA***	88	40.6	53.7	0	0	3.9	0	3.35	0.35	0
Theoretical FA	92	42.2	55.6	0	0	3.8	0	3.33	0.33	0

*Hydroxyapatite, **Fluorhydroxyapatite, ***Fluorapatite

The present authors[5-7] have recently studied many samples of ores by electron microscopy, X-ray diffraction, surface area measurement, differential thermal analysis and chemical analysis. In the present paper, the results of these studies will be summarized.

Samples

The chemical compositions of the samples of the ores and of the synthetic precipitated apatite are shown in Table I. Most of the ores were sedimentary ores; however, Kola, Lao'Cay and Phallabowa, were of igneous origin. Three ores, Christmas, Macatea and Angaur, were from ocean islands, while all of the others were from continents.

The three samples of calcined Florida ores were produced in commercial-scale plants. The reported calcination temperature was about 800°C for the BPL 75 sample and about 950°C for the others.

Three samples, FA, FHA and HA, were prepared by treating solutions of calcium chloride and sodium phosphate with or without sodium fluoride at 70°C at pH values from 8.0 to 8.6.

The principal mineral of all the ores was apatite. The F_2/P_2O_5 mol. ratios of several ores, such as Florida, Morocco and Gafsa, exceeded 0.33, which is the stoichiometric ratio for fluorapatite. As fluorite (CaF_2) was not detected in the ores, it may be considered that the excess fluorine is present in the apatite crystals, possibly in the form of CO_3F, which replaces PO_4. The ratio was smaller than 0.33 for a few ores, Kola, Phallabowa, Angaur and Christmas, this means that the shortage of fluorine ions had been covered by hydroxyl or other ions.

The ores contained more or less carbon dioxide, partly in the form of calcite and partly in the apatite as CO_3OH[8] or CO_3F, replacing PO_4^{3-}. Most of the carbon dioxide of three ores, Togo, Macatea and Taiba, seemed to be contained in the apatite,

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5) J. Ando, S. Matsuno and T. Watanabe, *J. Chem. Soc. Japan, Ind. Chem. Sect* (*Kogyo Kagaku Zasshi*), **67**, 2014 (1964).

6) J. Ando and S. Matsuno, ibid., **68**, 1195 (1965).

7) J. Ando, S. Matsuno and S. Nishiyama, ibid., **69**, 12 (1966).

TABLE II. RESULTS OF THE MEASUREMENT

Mark	Sample	BPL	Crystal size μ	Citric solubility % 100 ml.	Citric solubility % 150 ml.	X-Ray peak height (222)	X-Ray peak height (123)	Specific surface area (m^2/g.)	Lattice constants, (Å) a_0	Lattice constants, (Å) c_0
△	Kola	85	0.5—100	6.4	10.7	48	55	0.9	9.405	6.908
▲	Lao'Cay	87	0.5—100	5.7	11.7	46	54	1.1	9.388	6.896
◬	Phallabowa	74	0.1 —20	17.2	21.6	38	48	10.7	9.409	6.904
◎	Florida	68	0.05— 0.5	26.0	37.4	29	36	13.7	9.355	6.908
◉	Florida	76	0.05— 0.5	—	34.7	29	38	—	9.361	6.904
○	Florida	77	0.05— 0.5	25.2	36.4	31	40	15.7	9.364	6.906
⟁	Calcined Florida	75	0.1 — 1	—	28.0	39	47	—	9.378	6.904
⍙	Calcined Florida	79	0.1 —10	—	23.4	40	52	—	9.389	6.900
⚠	Calcined Florida	81	0.1 —10	—	20.8	43	53	—	9.391	6.899
●	North Carolina	65	0.02— 0.1	45.8	63.4	22	—	—	9.342	6.905
⊕	Taiba	80	0.05— 1	—	29.7	34	44	—	9.374	6.901
⊗	Taiba	81	0.1 — 1	20.0	29.2	33	42	12.2	9.374	6.904
⊘	Taiba	82	0.1 — 1	19.9	29.4	35	44	11.8	9.376	6.904
⊖	Togo	79	0.1 — 0.5	25.6	37.5	32	40	13.3	9.371	6.906
⊜	Morocco	70	0.05— 0.3	—	49.8	26	34	—	9.340	6.908
◐	Morocco	73	0.05— 0.2	35.5	50.2	28	37	22.0	9.355	6.910
◑	Morocco	78	0.1 — 0.5	25.7	35.6	30	38	14.6	9.364	6.906
⦶	Kossier	61	0.05— 0.2	32.4	46.5	26	35	20.6	9.359	6.907
◒	Gafsa	55	0.02— 0.1	44.7	64.4	23	31	26.4	9.344	6.911
◓	Gafsa	64	0.05— 0.2	39.7	57.5	25	32	21.8	9.345	6.911
◨	Christmas	83	0.05— 1	24.4	34.6	30	39	16.7	9.378	6.902
⬒	Christmas	84	0.05— 1.5	35.5	48.4	30	37	19.1	9.422	6.899
⧈	Macatea	77	0.05— 1	25.1	36.7	30	38	18.0	9.379	6.902
□	Macatea	80	0.05— 1	23.8	36.8	30	38	16.2	9.379	6.902
■	Angaur	68	0.05— 1	18.7	34.0	31	36	17.2	9.392	6.899
×	Synthetic HA*	89	0.05— 1.5	93.1	97.8	—	—	—	9.455	6.898
#	Synthetic FHA**	89	0.03— 1	—	62.3	—	—	—	9.429	6.902
+	Synthetic FA***	88	0.02— 0.5	44.0	57.5	—	—	—	9.406	6.904

*Hydroxyapatite, **Fluorhydroxyapatite, ***Fluorapatite

because the amount of calcite was very small in these ores.

The $KMnO_4$ (ml.) notations in Table I show the consumption of a N/10 potassium permanganate solution by 2-g. portions of the ores; this roughly indicates the relative amounts of organic matter, as will be described later.

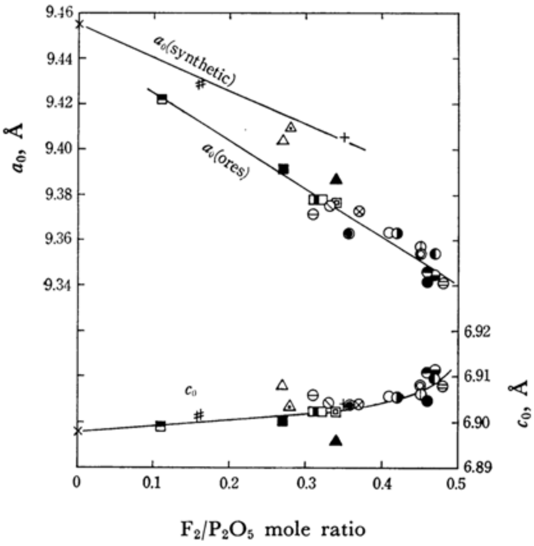

Fig. 1. Relation between the F_2/P_2O_5 ratio and the lattice constants. (The marks indicate the ores as shown in Table II.)

Results and Discussion

The Relation between the F_2/P_2O_5 Ratio and the Lattice Constants of Apatite.—The lattice constants, a_0 and c_0, determined from (140) and (004) spacings are shown in Table II. The relation between the constants and the F_2/P_2O_5 mole ratio of the samples is shown in Fig. 1.

The a_0 constant was generally smaller when the F_2/P_2O_5 ratio was larger. Fluorapatite has a smaller a_0 value than does hydroxyapatite. An excess of fluorine made the a_0 value even smaller.

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8) "DANA'S System of Mineralogy," Vol. II, (Seventh Ed.) John Wiley and Sons Inc., New York (1963), p. 882.

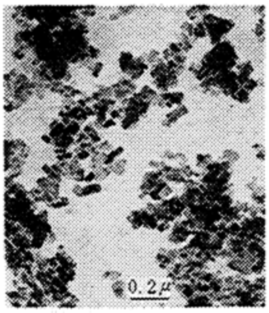

Photo. 1. Kossier
(×25000)

Photo. 2. Christmas 84
(×25000)

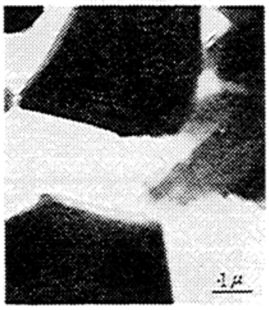

Photo. 3. Kola
(×5000)

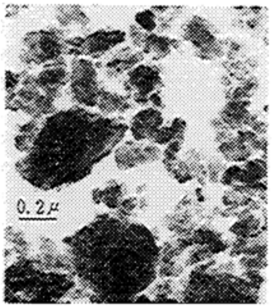

Photo. 4. Florida 77
(×25000)

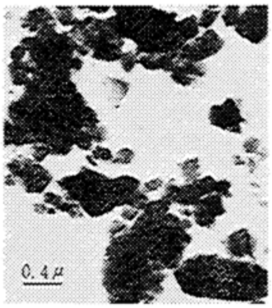

Photo. 5. Calcined
Florida 75 (×12500)

Photo. 6. Calcined
Florida 81 (×12500)

Electron microscope photographs

The constant of the ores was smaller than that of the synthetic precipitated apatite with an equal F_2/P_2O_5 ratio, presumably because of the effect of such impurities as CO_2 and R_2O_3 in the apatite. The c_0 constant increased slightly as the ratio increased from 0 to 0.33, and remarkably when the ratio exceeded 0.33, indicating the effect of excessive fluorine.

The Size and Shape of Apatite Crystals.—Apatite crystals of the samples ground to pass through 150 mesh (about 100 μ) were tested by both petrographic and electron microscopes. By the grinding, apatite crystals of the sedimentary ores were hardly destroyed at all because the crystals were generally smaller than 1 μ. The size range of most of the apatite crystals of each smaple is shown in Table II. Electron microscope photographs of typical samples are shown in Photos 1 to 6.

Most crystals of the sedimentary ores obtained from the continents (Florida, Morocco, etc.) were grainy or short-prism in shape, ranging in size from 0.02 to 1 μ. Of this sort of ores, Gafsa and North Carolina had the samllest crystal size, ranging from 0.02 to 0.1 μ, and Taiba had the largest size, ranging from 0.1 to 1 μ.

Most apatite crystals of the ores obtained from the ocean islands (Macatea, Angaur and Christmas) were prisms 0.05 to 0.2 μ in wide and 0.2 to 1 μ long. The igneous ores (Kola, Lao'Cay and Phallabowa) contained much larger crystals, up to 100 μ.

All of the synthetic apatite crystals were prism-shaped. The crystals of hydroxyapatite (HA) were much larger than those of fluorapatite (FA). Of the ores from the islands, the crystals of Christmas 84, which contained a particularly small amount of fluorine, were considerably larger than the others. Of the sedimentary ores from the continents, Gafsa and North Carolina, which had the largest F_2/P_2O_5 ratio, had the smallest crystal size. It seems that the presence of fluorine had depressed the growth of apatite crystals.

The Relation between Citric Solubility, the Height of X-ray Diffraction Peaks and the Specific Surface Area.—It has been reported that citric solubility is a good measure of the agronomic value of powdered phosphate ores.1) Table II lists the citric solublity of the samples ground to pass through 150 mesh (300 mesh, 50% pass) tested in two ways: (1) 100 ml. of 2% citric acid was added to 1 g. of the sample and shaken for 30 min., and (2) 150 ml. of the acid was added to the sample and shaken for an hour.

The citric solubilities ranged from 5.7 to 45.8% in the 100 ml. method and from 10.7 to 64.4% in the 150 ml. method; they were generally higher for those ores which had smaller crystals and which gave shorter and broader X-ray diffraction peaks.

Figure 2 shows the relation between the height of the (222) peak ($2\theta=46.7°$ by Cu$K\alpha$) and the

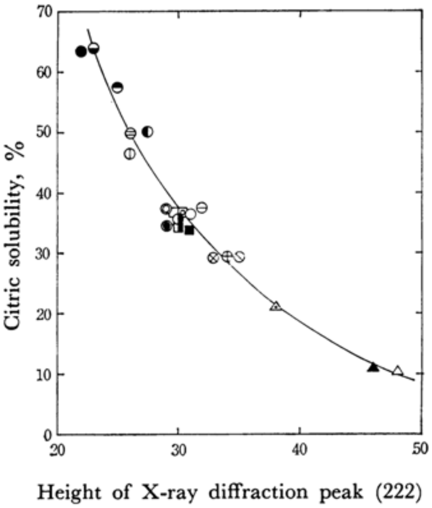

Fig. 2. Relation between the peak height and citric solubility of uncalcined ores. (The marks indicate the ores as shown in Table II.)

citric solubility as determined by the 150 ml. method. A similarly good correlation was found between the height and the solubility by the 100 ml. method, as well as found between the height of the (123) peak ($2\theta=49.5°$) and the solubility by both methods.

The peak height can be measured in several minutes; therefore, it would be useful for the rapid estimation of the nature of the ores. The peak height is related not only to the crystal size but also to the apatite content of the ore, both of which affect the citric solubility. The crystal size can be estimated more precisely by the measurement of the broadening of the diffraction peaks.

The specific surface area of the samples as measured by the nitrogen gas-absorption method is shown in Table II. The surface area was generally higher for the ores with larger citric solubilities; however, the correlation between the solubility and the X-ray peak heights was better than that between the solubility and the specific surface area⁵⁾.

Reactivity with Dilute Mineral Acids.—Tests were made on the reactivity of the ores with dilute hydrochloric, nitric, sulfuric and phosphoric acids. Figure 3 shows the relation between the decomposition ratio of the ores and the reaction time when 0.5 g. of the ore, ground to pass through 100 mesh (200 mesh, 70%; 300 mesh, 30% pass), was put into 37 to 40 ml. of N/4 hydrochloric acid (106% of the amount calculated to be needed to convert calcium, iron and aluminum into chlorides) and shaken for 10, 25 and 40 min. at 30°C.

The ease of the decomposition agreed with the fineness of the apatite crystals. The decomposition ratio of Kola was only about 70% when it was shaken for 40 min. Similar results were obtained when N/4 nitric acid instead of the hydrochloric acid was used. Tests of the decomposition of Macatea ore by N/4 sulfuric acid showed that the decomposition ratio was close to that by the hydrochloric acid. The decomposition ratio by 1/4 mol. phosphoric acid was much lower.

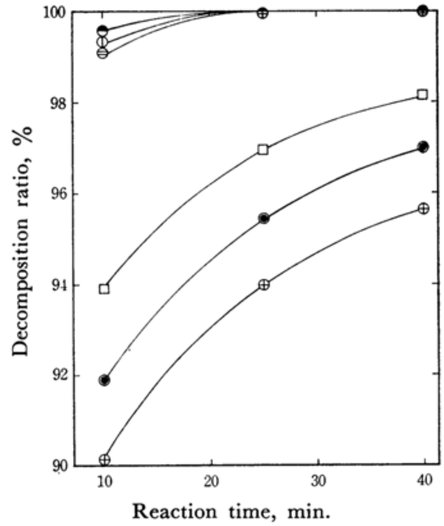

Fig. 3. Decomposition by N/4 hydrochloric acid. (30°C)
◓ Gafsa 64, ⦶ Kossier, ⊜ Morocco 70
□ Macatea 80, ◉ Florida 76, ⊕ Taiba 80

Decomposition by a Mixture of Sulfuric and Phosphoric Acids.—These decomposition tests were made using a mixture of sulfuric and phosphoric acids at 90°C in a manner similar to that used in the production of wet-process phosphoric acid by the hemihydrate-dihydrate process. For each test, 50 g. of the ore ground to pass through 100 mesh (200 mesh, 70%; 300 mesh, 30% pass) or 150 mesh (200 mesh, 90%; 300 mesh, 50% pass)was used. Reagent-grade sulfuric acid, wet-process phosphoric acid prepared with the respective ore, and water were blended in such a way that, after the decomposition and the hydration of gypsum, the weight ratio of the liquid and the gypsum would be 65 : 35 and the product acid would contain 28% P_2O_5 and 4% SO_3. The decomposition was then carried out at a stirring rate of 120 r. p. m. in a covered glass container equipped with a condenser to prevent the loss o water during the decompostion. The decomposition ratio was mersured in a way similar to that reported by Murata and Noriyama.⁹⁾

The relation between the reaction time and the ratio of the decomposition for several typical ores ground to pass through 100 mesh is shown in Fig. 4. The figure shows that Taiba was decomposed more quickly than was Morocco or

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9) A. Murata and T. Noriyama, *Sekko to Sekkai*, No. 68, 9 (1964).

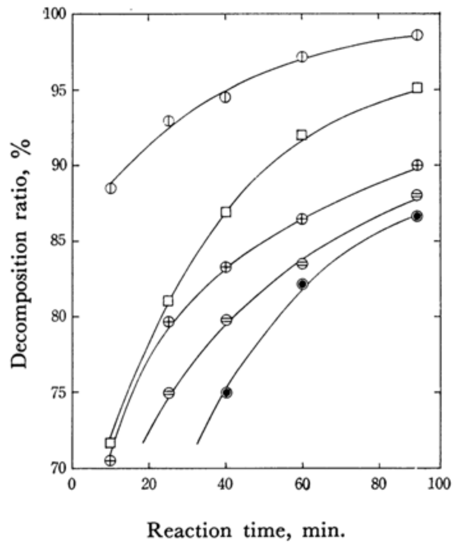

Fig. 4. Decomposition by the mixture of sulfuric and phosphoric acids. (−100 mesh, 90°C)
⦶ Kossier, □ Macatea 80, ⊕ Taiba 80,
⊜ Morocco, 70 ◉ Florida 76

Florida. The ease of the decomposition did not agree with the fineness of the apatite crystals of the ores.

Figure 4 also shows that the decomposition of the ores was much slower than when treated with dilute sulfuric or hydrochloric acid. The decomposition became still slower when an increasing amount of sulfuric acid was used. These characteristics of the decomposition by the mixed acid are mainly due to the coating by calcium sulfate hemihydrate crystals on the surface of the ores; this delays the decomposition seriously. The state of the coating differed considerably with different ores.

When the ores ground to pass through 150 mesh were treated in the same manner for 60 min., the decomposition ratio was about 98% for Kossier and Macatea (BPL 80), 95% for Taiba (BPL 80), and 93% for Florida (BPL 68 and 76) and Morocco (BPL 70). Kola was less reactive, and the decomposition ratio was 92% when the sample ground to pass through 150 mesh was reacted for 90 min.

The decomposition tests with the mixed acid were also made at 60°C, in the stable range of calcium sulfate dihydrate. The rate of the decomposition at 60°C was considerably larger than at 90°C for most ores which had been ground to pass through 100 mesh. However, for the ores which had been ground to pass through 150 mesh, the rates of the decomposition at 60°C and at 90°C were nearly equal. Presumably, the true of the reaction between the mixed acid and the ore is larger at 90°C than at 60°C; the effect of the coating by calcium sulfate is also larger at 90°C, and the effect of the coating is more remarkable when the coarser grains of the ore are used.

Carbon dioxide, especially when present in the apatite crystals, seems to promote the decomposition by breaking the calcium sulfate coating as it is released from the ore. The iron and aluminum, especially the latter, present in the ore and the acid delayed the decomposition of the ore.7) Because of the effects of these many factors, the ease of decomposition can not be predicted on the basis of only the crystal-size measurement of the ores.

The Change in Apatite Crystals by Calcination.—The phosphate ores and synthetic apatite were heated at various temperatures between 500 and 1350°C for an hour. The lattice constant, a_0, of the apatite of most ores changed remarkably upon the heating. The change in typical samples is shown in Fig. 5.

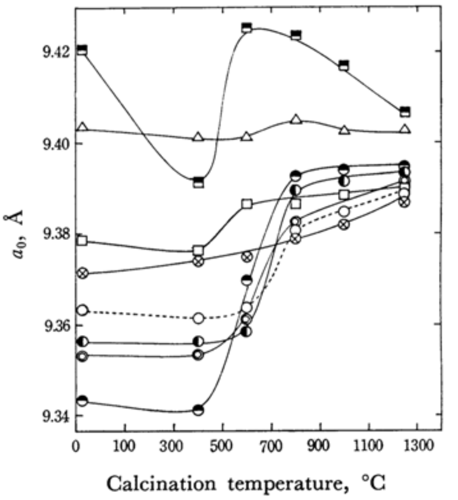

Fig. 5. Change of a_0 on the calcination. (The marks indicate the ores as shown in Table II.)

The a_0 constant of most ores increased when they were heated above 500°C. The increase was more remarkable for such ores as Morocco and Gafsa, which had larger amounts of excess fluorine and which had smaller a_0 values. The a_0 constant of synthetic apatite decreased upon the heating. After they had been heated above 900°C, the a_0 values of most ores, except Christmas 84 and Kola, were close to that of synthetic fluorapatite, 9.39 Å. Kola, which contained about 2% strontium, had larger a a_0, showing that strontium is present in the apatite, replacing calcium. The change of c_0 on the calcination was smaller.

On calcination at 500°C, the X-ray diffraction peak height of the apatite of most ores decreased by about 10%. This is probably caused by some disorder in apatite crystals which occurred prior to the reorganization and crystal growth of apatite. When the ore was heated above 700°C, a crystal growth of apatite occurred, resulting in an increase in the X-ray diffraction peak height.

Tests with an electron microscope showed that in calcined Florida 81 (Photo. 6) the fine crystals of the initial ore (Photo. 4) began to combine with each other upon calcination at about 950°C, thus forming larger crystals (up to about 10 μ) which resemble those of Kola ore (Photo. 3).

The Change in the Reactivity to Acids on Calcination.—The citric solubility, the reactivity with dilute hydrochloric acid, and that with a mixture of sulfuric and phosphoric acids were tested in ores calcined at various temperatures.

The citric solubility of most ores decreased slightly upon calcination at 500°C, presumably because of the decrease in the porocity of the ores. The decrease in the citric solubility was remarkable upon calcination above 900°C as a result of the crystal growth. After the ores had been heated at 1350°C, the citric solubility of all the ores tested by the 150 ml. method was around 10%.

The decomposition tests by N/4 hydrochloric acid also showed a decrease in the reactivity upon calcination. For example, the decomposition ratios when Florida 76 ore ground to pass through 100 mesh after it had been calcined at 500, 700, 900 and 1100°C was treated for 25 min. were 95.2, 94.5, 93.0 and 91.8% respectively, while that of the uncalcined ore was 96.2%.

The rate of the decomposition by the mixture of sulfuric and phosphoric acids also decreased upon calcination. The decrease was remarkable when the ore had been calcined at above 900°C and had so lost nearly all of its carbon dioxide. Without carbon dioxide, the powdered ore had a tendency to form lumps when mixed with the acid; this caused a further delay in the decomposition. For example, the decomposition ratios of Florida 76 ore ground to pass through 100 mesh after the calcination at 500, 700, 900 and 1100°C were 81.1, 79.8, 71.3 and 69.1% respectively when it was treated with a mixture of reagent-grade sulfuric and phosphoric acids for an hour. The above-mentioned lumps were also formed in large-scale plants.

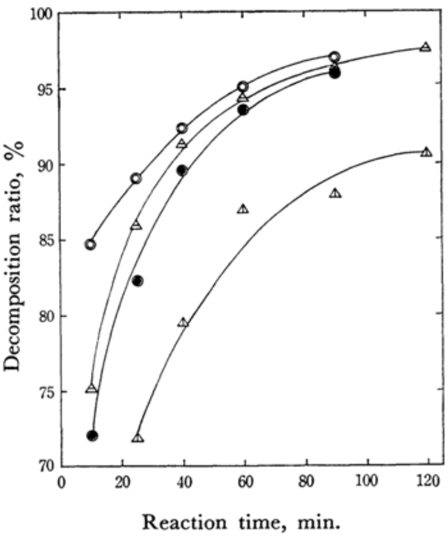

Fig. 6. Decomposition by the mixed acid of the calcined and uncalcined Florida ores.
◎ uncalcined 68, △ calcined 79
◉ uncalcined 76, △ calcined 81

The decomposition tests with the mixed acid were also made with two samples of calcined Florida ores (79 and 81) produced at commercial-scale plants. In comparison with these, two samples of uncalcined Florida ores (68 and 76) were also tested. In these tests, the ores ground to pass through 150 mesh (200 mesh, 90%; 300 mesh, 50% pass), reagent-grade sulfuric acid and the wet-process phosphoric acid prepared with the respective ores were used. The rate of the decomposition of one of the calcined ores, BPL 79, was close to that of the uncalcined samples; however, another calcined sample, BPL 81, was decomposed much more slowly, as is shown in Fig. 6. The 81 sample contained no carbon dioxide and formed a considerable amount of lumps when treated with the acid. The 79 sample had a small amount of carbon dioxide (0.4%) and had little tendency to form lumps. The decomposition of this sample was a little quicker than that of the uncalcined ore (76). It is possible that, upon calcinaton at an adequate temperature, the alumina in the ore which usually depresses the rate of the decomposition becomes less reacitve and that in this manner the decomposition is promoted.

The amount of carbon dioxide has much to do with the decomposition. Too much carbon dioxide is not desirable because of too much effervescence. Carbon dioxide present in amounts 0.5 to 1% of the ore would be most desirable for the decomposition.

The Amount of Organic Matter and Its Decrease upon Calcination.—Organic matters contained in the ores are known to affect the nature of gypsum in the production of wet-process phosphoric acid.[10] As an approximate measure of the organic-matter content, the consumption of a potassium permanganate solution was determined on uncalcined and calcined ores in the following way: To 2 g. of a sample, 100 ml. of 3N sulfuric acid was added; they were stirred until the ore had been decomposed. An excess of a 0.1N potassium permanganate solution was then added.

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10) K. Murakami and H. Tanaka, *Sekko to Sekkai*, No. 54, 207 (1961).

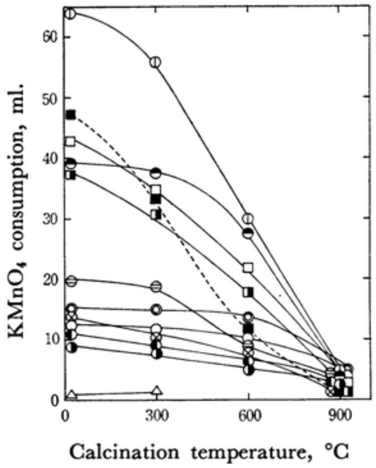

Fig. 7. Decrease of the consumption of KMnO$_4$ on the calcination. (The marks indicate the ores as shown in Table II.)

After the mixture had stood for 24 hr. at room temperature, the slurry was titrated with a 0.1 N sodium oxalate solution. The permanganate consumptions (ml.) by 2 g. portions of the samples are shown in Table I. The permanganate was mainly consumed by organic matter. The consumption by ferrous ions was minor in scale.

The samples of Kossier and Gafsa, the crystal size of which was the smallest, showed the highest consumption. The ores obtained from the ocean islands showed a relatively high consumption. The decrease in the consumption of several typical ores upon calcination is shown in Fig. 7. The manner of the decrease was considerably different for each sample. On heating at 300°C, the decrease was remarkable for Angaur, but it was only slight for the two Florida samples. Such a difference may indicate a difference in the type of organic compound.

Thermal analysis upon heating the ores showed exothermic reactions between 300 and 700°C for most ores. The amount of the exothermic heat was generally larger for those ores which consumed a larger amount of the permanganate, an indication that the exothermic reactions were mainly due to the burning of the organic matters.