

OCCURRENCE OF SELENIUM IN NATURAL PHOSPHATES, SUPERPHOSPHATES, AND PHOSPHORIC ACID¹

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INTRODUCTION

The occurrence, origin, and distribution of selenium in soils, its absorption by plants, and the toxicity of the plants to animals have been discussed in several recent papers (3, 7, 8, 9, 13, 18).³

With regard to the limits in the quantities of selenium that may be present in soil and vegetation without injury to animals, Byers (3, p. 44) states:

In general it would appear that any soil containing upwards of 0.5 p. p. m. of selenium, and any vegetation containing 5 p. p. m. is potentially dangerous.

More than a decade ago Stoklasa (22) pointed out that the selenium content of soil may be greatly increased through heavy fertilization with superphosphate and ammonium sulphate. That the quantities of selenium occurring in fertilizers and soil amendments is sufficient to alter the amount the plant would otherwise absorb from the soil appears possible, when due consideration is given to the fact that these agents are applied to the layers of soil most readily accessible to the roots of the plant during its growing period, and often, particularly in the case of fertilizers, in relatively large quantities very near the root system. For example, let it be supposed that a fertilizer containing 50 p. p. m. of selenium is applied to the soil at the rate of 1,000 pounds per acre within 3 inches of the plant rows which are 3 feet apart. Then, assuming the customary figure, 2,000,000 pounds of topsoil to a depth of 6 inches per acre, the increase in the selenium concentration of the entire soil layer would be 0.025 p. p. m., and the increase in the concentration in a 6-inch layer of topsoil extending 3 inches on either side of the row, if all the selenium were retained therein, would be about 0.15 p. p. m. Under certain conditions the latter figure may represent a significant increase in the selenium content of the soil.

Results are given in this paper for selenium in 96 representative samples of phosphate rock and 3 samples of apatite from various deposits of the world, 8 typical samples of domestic superphosphate, and 4 samples of crude phosphoric acid manufactured by the sulphuric acid process. The results for selenium in natural phosphates reported herein represent an extension of the studies of this Bureau on the composition of phosphate rock (11, 16).

PROCEDURE AND REAGENTS USED

The procedure used in the determination of selenium was substantially the same as that developed by Robinson, Dudley, Williams, and Byers (19) for selenium in soil and in sulphide-bearing rocks

¹ Received for publication Sept. 27, 1935; issued February 1936.

² The authors are indebted to K. D. Jacob, who suggested the investigation and rendered valuable aid during the course of the work, and to H. G. Byers and K. T. Williams, Division of Soil Chemistry and Physics, Bureau of Chemistry and Soils, for helpful suggestions in the application of the analytical methods.

³ Reference is made by number (italic) to Literature Cited, p. 1082.

and minerals, according to which the selenium is separated and concentrated by distillation with hydrobromic acid in the presence of bromine and is determined in the distillate by gravimetric methods, or by a colorimetric procedure when the absolute amount of selenium is less than 0.5 mg. Three distillation procedures are described for inorganic materials: (1) Direct distillation of the sample, applicable to soil and nonpyritiferous rocks and minerals; (2) distillation after the sample has been pretreated with nitric acid to destroy sulphides, and finally with concentrated sulphuric acid to eliminate the nitrate radical which otherwise would decompose the hydrobromic acid in the subsequent distillation, applicable to materials containing pyrite and other sulphides; and (3) integrated distillation, a method of concentration in which the distillate from one portion of the sample is added in the distillation of a fresh portion and so on, which is especially adapted to the determination of traces of selenium.

Phosphate rock presents some difficulties in the application of these methods. As a result of the presence of considerable quantities of fluorine and silica, relatively large quantities of gelatinous silica are rapidly deposited in the condenser during the early stages of distillation, and when more than about 10 g of the samples are used, the condenser often becomes clogged. Furthermore, the amount of gelatinous silica that separates in the distillate when large samples are used is sufficient seriously to retard subsequent filtration. These difficulties are intensified in the integrated distillation. For a calcium-rich material like phosphate rock, sulphuric acid is not satisfactory for the expulsion of the nitrate radical following the preliminary treatment of pyritiferous samples, because the relatively insoluble calcium sulphate causes serious bumping during subsequent distillation. Phosphoric acid is recommended for this purpose.

Selenium can be removed from dry soil by distillation with hydrobromic acid with a specific gravity as low as 1.2.⁴ Accordingly, acid sufficiently concentrated for use in the distillation can be readily recovered by redistilling the filtrates and solutions from the estimation of the selenium. The specific gravity of the recovered acid used by the writers ranged between 1.35 and 1.40. When 10 g of 100-mesh pyrite-free rock was distilled with 100 ml of acid of this strength, all the selenium passed into the first 50 ml of the distillate. In samples that carried only small amounts of acid-insoluble sulphides, selenium was detected in the second 50 ml of the distillate but not thereafter. In view of these findings the volume of distillate collected was 75 to 150 ml, depending on the character of the sample. It should be mentioned that the difficulties with the separation of gelatinous silica are less marked when the more dilute acid is used.

Bromine often contains impurities capable of imparting to the distillate a color which, since it persists after the solution is reduced with sulphur dioxide, interferes in the colorimetric comparison. The interfering substance can be eliminated by dissolving the bromine in hydrobromic acid, filtering off the flocculent precipitate,⁵ and distilling the filtered solution.

⁴ BYERS, H. G. Private communication.

⁵ The nearly white, waxy substance (0.232 g of air-dried material) obtained by adding 30 ml of bromine to 600 ml of water-white hydrobromic acid (48 percent), allowing the mixture to stand an hour, filtering, and washing the precipitate with cold water, was soluble in alcohol and ether. Somewhat more than one-half of the substance melted at 136° to 140° C.; the remainder did not melt at 160° C. When it was subjected to steam distillation about two-thirds of the wax passed over with the steam.

In order to compare the performance of the three distillation methods mentioned, these procedures were used to determine the selenium in several typical phosphate rocks. The results (table 1) indicate that, even though the rock contains relatively large quantities of organic matter, pretreatment of the sample is not necessary, unless acid-insoluble sulphides are present and then only when the highest accuracy is desired. Unless it is stated otherwise, the results for selenium reported in this paper were obtained by distilling the samples without pretreatment.

TABLE 1.—Selenium in typical phosphate rocks as determined by three different distillation procedures

Sample no.	Type or source of phosphate	FeS ₂	Organic carbon	Selenium determined by—		
				Distilling 10 g of sample		Integrated distillation of untreated sample ¹
				Un-treated	Pre-treated	
		Percent	Percent	P. p. m.	P. p. m.	P. p. m.
973	Idaho.....	0.00	2.34	28	28	(?)
948	Wyoming.....	.97	3.47	48	48	(?)
449	Tennessee blue rock.....	2.39	(?)	11.8	1.0	(?)
930	do.....	3.90	.20	2.0	3.0	(?)
1139	South Carolina land rock.....	.36	(?)	14	16	(?)
912	Florida land pebble.....	.00	.38	8	(?)	0.8
908	Tennessee brown rock.....	.00	.11	8	(?)	<.1
916	Tennessee phosphatic limestone.....	.73	(?)	8	(?)	<.1
917	do.....	1.89	(?)	8	(?)	.2

¹ 100 g of the sample was distilled in 10-g portions.

² Not determined.

Under the conditions prescribed (19) for the colorimetric estimation, the threshold sensitivity of the method is about 0.008 mg of selenium. For 10 g of sample this figure corresponds to 0.8 p. p. m., and accordingly the results are reported as ≥ 0.8 p. p. m. in those cases where the coloration was barely perceptible and as < 0.8 where no color was noted. When 100 g of the sample are used (integrated distillation) the detectable concentration of selenium is thereby reduced to approximately 0.1 p. p. m.

SELENIUM IN NATURAL PHOSPHATES

Results for selenium in domestic and foreign phosphates are given in tables 2 and 3, respectively. All the samples from Florida, Tennessee (except Tennessee blue rock), Kentucky, Arkansas, Oklahoma, and Australia, the light-colored phosphates from the western part of the United States, and the apatites from Virginia and Canada contained 1 p. p. m. or less of selenium. The results for the dark-colored phosphates of the western part of the United States and Canada, the majority of the Tennessee blue-rock and South Carolina samples, and the African and Palestinian phosphates ranged between 1 and 55 p. p. m. A few of the samples from European and insular deposits contained as much as 1 to 2 p. p. m. of selenium.

TABLE 2.—Selenium content of domestic phosphates

FLORIDA PHOSPHATES

Sample no.	Type of phosphate	Location of deposit	P ₂ O ₅	Se
			Percent	P. p. m.
910	Land pebble.....	Mulberry.....	31.09	<0.8
947	do.....	Brewster.....	31.28	<0.8
790	do.....	Not known.....	31.40	<0.8
912	do.....	Mulberry.....	35.37	1.8
771	Hard rock.....	Not known.....	31.25	<0.8
589	do.....	Floral City.....	34.68	<0.8
932	do.....	Dunnellon.....	35.99	<0.8
1091	Soft.....	Bartow.....	25.47	<0.8
728	do.....	Juliette.....	31.80	<0.8
915	Waste pond.....	Dunnellon.....	23.63	<0.8

SOUTH CAROLINA PHOSPHATES

495	Not known.....	Not known.....	16.07	<0.8
1139	Land rock.....	Bulow mines, Johns Island.....	26.92	216.0
1138	do.....	Lamb's mine, near Charleston.....	27.85	8.5
650	do.....	Not known.....	28.86	5.0

TENNESSEE PHOSPHATES

56	Brown rock.....	Not known.....	31.28	<0.8
906	do.....	Wales.....	34.39	<0.8
908	do.....	Mountpleasant.....	34.44	1.1
772	Blue rock.....	Glover.....	30.45	1.8
930	do.....	Gordonsburg.....	30.97	23.0
448	do.....	Glover.....	32.03	2.5
449	do.....	Gordonsburg.....	32.03	21.0
1049	Kidney phosphate.....	Boma.....	31.22	1.8
1048	White rock.....	Toms creek.....	30.20	<0.8
1031	do.....	Godwin.....	35.80	<0.8
916	Phosphatic limestone.....	Mountpleasant.....	11.22	1.1
917	do.....	Gordonsburg.....	11.68	1.2

WESTERN PHOSPHATES

550	Light colored.....	Idaho, Paris.....	32.21	<0.8
1412	do.....	do.....	35.39	1.0
1011	do.....	Montana, Garrison.....	27.63	<0.8
1018	do.....	do.....	29.11	<0.8
1019	do.....	do.....	31.47	<0.8
1017	do.....	do.....	34.92	<0.8
1012	do.....	do.....	36.07	<0.8
1252	do.....	do.....	36.38	<0.8
1010	do.....	do.....	37.47	1.0
1407	do.....	do.....	37.93	<0.8
1411	Dark colored.....	Idaho, Georgetown.....	30.29	50
489	do.....	do.....	31.97	6.0
973	do.....	Idaho, Conda.....	31.97	28
1253	do.....	do.....	32.13	8.0
454	do.....	do.....	32.24	40
1408	do.....	do.....	32.26	23
494	do.....	Idaho, Georgetown.....	34.96	8.0
1280	do.....	Montana, Maxville.....	24.95	6.0
1410	do.....	Utah, Devils Slide.....	11.90	38
1409	do.....	Utah, Logan.....	31.50	10
467	do.....	Wyoming, Cokeville.....	26.60	35
469	do.....	do.....	29.75	50
468	do.....	do.....	29.79	55
948	do.....	do.....	30.19	248

OTHER PHOSPHATES

1267	Arkansas, Independence County.....	31.98	<0.8
1235	Brown rock.....	Kentucky, Wallace.....	21.19	<0.8
1242	do.....	Oklahoma, Cotton County.....	24.31	<0.8
1295	Apatite.....	Virginia, Amherst County.....	39.58	<0.8

¹ Result obtained by integrated distillation.

² Result obtained by distillation of pretreated sample.

³ National Bureau of Standards sample no. 56.

TABLE 3.—Selenium content of foreign phosphates

AFRICAN PHOSPHATES

Sample no.	Location of deposit	P ₂ O ₅	Se	Sample no.	Location of deposit	P ₂ O ₅	Se
		<i>Per-cent</i>	<i>P. p. m.</i>			<i>Per-cent</i>	<i>P. p. m.</i>
560	Algeria, Dyr.....	23.39	18.0	453	Morocco.....	33.47	5.0
551	Algeria, Tebessa.....	26.10	2.5	563	do.....	34.30	1.5
558	Algeria, Rebiba.....	26.84	3.0	1162	do.....	35.11	1.0
562	Algeria, M'Zaita.....	28.59	7.5	552	Tunis, Gafsa.....	26.91	18.0
557	Algeria, Tocqueville.....	29.38	18.0	556	Tunis, Kalaa-Djerda.....	27.55	30.0
559	Algeria, Bordj-Redir.....	32.34	55.0	561	Tunis, M'Dilla.....	28.66	3.5
555	Egypt, Kosseir.....	30.60	1.0	553	Tunis, Gafsa.....	29.13	1.0

EUROPEAN AND ASIAN PHOSPHATES

1226	Belgium, Liège.....	18.13	<0.8	1263	U. S. S. R., Saratov.....	18.40	<0.8
1155	Estonia, Tallinn.....	25.68	<.8	1266	U. S. S. R., Egoriev.....	19.50	1.5
1228	France, Somme.....	22.02	1.5	1264	do.....	22.37	1.0
1240	do.....	24.66	<.8	1262	U. S. S. R., Vyatka.....	27.88	1.8
1241	France, Pyrenees Mountains.....	26.87	2.0	1260	U. S. S. R., Kola Peninsula.....	39.08	<.8
1239	France, Quercy.....	34.74	1.0	1258	Palestine, Neby Musa.....	8.14	1.5
1151	Portugal, Marvão.....	27.14	<.8	1255	do.....	16.60	1.0
1152	U. S. S. R., Volga River region.....	13.40	<.8	1256	do.....	17.50	1.5
1265	U. S. S. R., Aktyubinsk, Siberia.....	17.42	<.8	1257	do.....	20.40	15.0

INSULAR PHOSPHATES

1223	Angaur Island.....	40.00	<0.8	943	Curaçao Island.....	40.66	1.0
452	Christmas Island.....	39.46	<.8	1159	Makatea Island.....	38.22	<.8
904	Grand Connetable Island.....	54.51	2.0	450	Nauru Island.....	38.92	<.8
985	Curaçao Island.....	38.59	1.5	451	Ocean Island.....	40.32	<.8

OTHER PHOSPHATES

1157	South Australia, Kapunda.....	30.18	<0.8	2582	Canada, British Columbia.....	24.11	3.0
1158	South Australia, Port Clinton.....	33.53	<.8	1905	Canada, Quebec Province.....	40.30	<.8

¹ Apatite.² A dark-colored phosphate from Crow's Nest Pass.

SELENIUM-BEARING CONSTITUENTS

In general, selenium is found in nature associated with sulphur, particularly the sulphides (4, 5, 17) and in a number of rare selenide minerals analagous to the sulphides (17, pp. 693-695). Byers (3) concluded that the selenium in soils came from sulphide minerals in the soil parent materials. Since selenium under certain conditions is absorbed by growing plants and is associated with the protein (18), organic matter originating from vegetation may be regarded as a potential source of selenium in sedimentary rocks. If the organic matter represents the remains of plant life that grew on seleniferous soil under climatic conditions favorable to selenium absorption, it may easily be the principal carrier of selenium.

In view of the foregoing some relationship may be expected to exist between the selenium content of phosphate rock and the quantities of sulphide sulphur, organic carbon, and nitrogen present. According to the comparative data (table 4), larger amounts of selenium occur in pyritiferous than in pyrite-free samples from the same region, and as a rule rocks containing the greater amounts of organic matter also carry the larger quantities of selenium. The latter relationship is best shown by the Permian phosphates of the western part of the

United States, and at least in the case of these phosphates it may be regarded as evidence that the organic matter is seleniferous. The nitrogen figures show somewhat less correlation with the selenium results than do the figures for organic carbon. The sample of Tennessee kidney phosphate is a notable exception to these general relationships.

TABLE 4.—Comparative results for selenium, organic carbon, nitrogen, and pyritic sulphur in phosphate rock

Source or type of phosphate	Organic carbon	Se	N	FeS ₂
Western part of the United States:	<i>Percent</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>Percent</i>
Dark-colored pyritiferous rock.....	1 3.90	1 30.0	1, 100	1 1.92
Dark-colored pyrite-free rock.....	1 2.60	1 13.0	1, 1,000	.0
Light-colored rock.....	1.16	1 < .9	80	.0
Tennessee kidney phosphate.....	1.46	≧ 8	2,600	1.5
Tunis, Gafsa.....	.86	18.0	470	.0
South Carolina.....	.51	8.5	510	.3
Florida ¹31	< 8	170	.0
Grand Connetable Island.....	.28	2.0	490	.0
Tennessee blue rock.....	.28	≧ 1.4	280	3.0
Curacao Island.....	.17	1.5	130	.0
Morocco.....	.17	1.0	180	.0
Tennessee brown rock and Tennessee white rock.....	.16	< .8	160	(²)

¹ Average of results for 3 or more samples.

² Average of results for 2 samples.

³ The 1 pyritiferous brown rock, National Bureau of Standards standard sample no. 56, contained sulphide equivalent to 0.89 percent of FeS₂.

Results for organic carbon and selenium in mechanical separates of ground phosphate rock are given in table 5. The correlation between the results for selenium and organic carbon is probably as close as could be expected, particularly in the sample of Wyoming phosphate. In the Idaho sample the results indicate considerable loss of selenium occasioned by suspension of the material in water incident to mechanical separation into fractions.

TABLE 5.—Distribution of selenium among mechanical separates of ground phosphate rock

Mechanical fraction ¹	Idaho phosphate no. 973			Wyoming phosphate no. 948			
	Fraction of original material	Organic carbon	Se	Fraction of original material	Organic carbon	Se	FeS ₂
	<i>Percent</i>	<i>Percent</i>	<i>P. p. m.</i>	<i>Percent</i>	<i>Percent</i>	<i>P. p. m.</i>	<i>Percent</i>
"Sand".....	26.0	2.22	33	49.8	2.96	36	0.62
"Silt".....	45.5	2.03	20	43.6	4.25	56	1.17
"Clay".....	27.9	3.03	18	6.6	8.29	64	.42
Solution loss.....	.6	-----	1 5	.0	-----	1 2	-----
Original material.....	100.0	2.34	28	100.0	3.47	48	.97

¹ The mechanical fractions of these phosphates were prepared by Alexander and Jacob (1) from material ground to pass a 100-mesh sieve.

² Calculated.

PRIMARY AND SECONDARY DEPOSITS

Following Blackwelder's division (2) of the world's phosphate deposits into six genetic varieties, comprised in two broad groups (primary and secondary deposits), Mansfield (15, p. 362) has partially

classified a number of the deposits. Accordingly, as far as possible the results for selenium in phosphate are summarized under the two general groups in table 6.

TABLE 6.—Selenium content of phosphate rocks from primary and secondary deposits

Type of deposits and location	Samples analyzed	Selenium	
		Range	Average
Primary:	<i>Number</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
Western part of the United States and Canada.....	25	<0.8-55	<16.7
Algeria, Tunis, and Egypt.....	11	1.0-55	14.3
Tennessee (blue rock) and Arkansas.....	5	<.8-3.0	<1.6
Average.....			<10.9
Secondary:			
South Carolina.....	4	<.8-16	<7.6
France.....	4	<.8-2.0	<1.3
Islands.....	8	<.8-2.0	<1.1
Florida.....	10	<.8	<.8
Tennessee and Kentucky (brown rock and white rock).....	6	<.8	<.6
South Australia.....	2	<.8	<.8
Average.....			<2.0

Byers' conclusion (3) that selenium is leached from soil by percolating waters, which is supported by the presence of considerable amounts of this element in drainage water (table 8), and the fact that a considerable part of the selenium in one phosphate rock (table 5) was removed when the material was treated with water incident to mechanical analysis, afford good reasons to expect primary deposits, having been protected from the action of water, to carry larger quantities of selenium than secondary deposits. Considering the average figures for the groups (table 6), the primary deposits show about five times as much selenium as the secondary deposits, and the expectation is, in general, thus confirmed. It should be pointed out, however, that this criterion fails when it is applied to certain individual deposits. For example, South Carolina phosphate, a secondary deposit, carries about fivefold as much selenium as does Tennessee blue rock, a primary deposit. In this connection special interest attaches to the experimental finding (9) that the absorption and retention of added selenium is much more pronounced in some soils than in others, and to the suggestion that this difference in the behavior of the selenium might be due to the difference in the composition of the soil colloids.

GEOLOGIC AGE AND SELENIUM CONTENT

In table 7 the results for selenium in natural phosphates are grouped, as far as possible, according to the geologic age of the deposits (10). Of the deposits for which the average result is greater than 1 p. p. m., the Permian phosphates show the largest amount of selenium and the post-Tertiary the least. In the descending order of selenium content, the Miocene, Cretaceous (or Jurassic), Eocene, and Devonian phosphates are between these extremes.

TABLE 7.—Geologic age as correlated with selenium content of natural phosphates

Period or epoch	Source or type of phosphate	Samples analyzed	Selenium	
			Range	Average
Post-Tertiary-----	Island phosphates-----	Number	<i>P. p. m.</i>	<i>P. p. m.</i>
Tertiary-----	Florida, South Carolina, Morocco, Australia, and Russia.	8	<0.8-2.0	<1.1
		20	<.8-16	<2.4
	Florida land pebble-----	4	≅.8	<.8
Pliocene-----	South Carolina land rock-----	3	5.0-16	9.8
Miocene-----	Florida hard rock and soft phosphate-----	6	≅.8	<.8
Oligocene-----	Morocco-----	3	1.0-5.0	2.5
Eocene-----	France, Russia, Algeria, Tunis, and Egypt.	19	<.8-55	<8.8
Cretaceous (or Jurassic)---	Western United States and Canada-----	25	<.8-55	<16.7
Carboniferous-----	Dark-colored phosphates ¹ -----	15	3.0-56	27
Permian-----	Light-colored phosphates ² -----	10	<.8-1.0	<.8
Do-----	Tennessee kidney phosphate-----	1	-----	≅.8
Mississippian-----	Tennessee blue rock-----	4	≅.8-31	≅1.8
Devonian-----	Tennessee and Kentucky brown rock ³ -----	8	<.8	<.8
Ordovician-----	Apatite from Virginia and Canada-----	2	<.8	<.8
Pre-Cambrian-----				

¹ From Canada; Georgetown, Idaho; Maxville, Mont.; Cokeville, Wyo.; and British Columbia.

² From Paris, Idaho; and Garrison, Mont.

³ Also 2 samples of Tennessee phosphatic limestone, 1 sample of Arkansas phosphate, and 1 sample of Estonian phosphate.

In view of previous discussion, it is hardly necessary to remark that other factors may play a greater part than geologic age in limiting the amounts of selenium that occur in any given deposit. As to the geologic age, a comparison of primary deposits is most logical. Accordingly, the geologic periods during which the primary phosphate deposits were laid down are, in the increasing order of average selenium content of the phosphates, Devonian, Cretaceous, and Permian.

PHOSPHATES COMPARED WITH OTHER ROCKS, MINERALS, SOIL, AND WATER

The available results for selenium in rocks, minerals, soils, and waters of the United States are summarized in table 8. The analyses of all the materials other than phosphates were recently published by Byers (3) and Williams and Byers (25). Since the data are by far the most extensive for certain localities west of the Mississippi River, mainly parts of Colorado, Montana, Nebraska, South Dakota, and Wyoming, the results have been classified under two geographic divisions of the country, the Mississippi River being used as the dividing line. The results of Goldschmidt and Hefter (4) and Goldschmidt and Strock (5) for selenium in certain genetic varieties of rocks and minerals, particularly sulphides, are summarized in table 9, in which the results for phosphates (table 6) are also included for convenience in comparison.

According to the available data (table 8), phosphate rock from deposits east of the Mississippi River contains less selenium than does that from deposits in the West. Aside from a crude sulphur from Colorado showing 8,350 p. p. m., pyrite, as would be expected, contained the largest quantities of selenium. The selenium content of phosphate rock from the western division of the United States agrees very well with that of other sedimentary deposits in this region. In the ascending order of the average results, shale, chalk, Permian phosphate, and limestone lie between the values (9 and 20 p. p. m., respectively) for ironstone (and mudstone) and bentonite.

TABLE 8.—Selenium in rocks, minerals, soils, and waters of the United States west and east of the Mississippi River

Location and material	Samples analyzed	Selenium	
		Range	Average
West of Mississippi River:	<i>Number</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
Phosphate rock (Permian only).....	24	<0.8-55	<17.2
Limestone.....	6	1.5-46	19
Sandstone.....	14
Chalk (Niobrara).....	17	6.0-30	15
Gypsum.....	4	1.0-10	4.6
Gypsum sand.....	12
Sulphur (crude from Colorado).....	1	8,350
Pyrite.....	6	5.0-320	123
Ironstone and mudstone.....	4	4.0-14	9.0
Shale.....	80	.0-103	11
Bentonite.....	6	2.0-76	20
Soil.....	446	.0-41	2.0
Well water.....	12	.02-.2	.06
Creek and drainage water.....	6	.00-1.2	.2
East of Mississippi River:			
Phosphate rock.....	25	<8-16	<2.7
Apatite.....	1	<.8
Pyrite.....	20	.0-250	70
Marcasite (from clay).....	2	.3-.6	4.5
Pyrrhotite.....	1	5.0
Chalcopyrite.....	1	10
Mispickel.....	1	(¹)
Shale.....	5	.15-.6	.25
Clay bed.....	26	.0-.4	.18

¹ Trace.² Samples of surface soil, sand, and clay.

TABLE 9.—Selenium in certain genetic varieties of minerals and rocks, nitrate beds, and waters

Material	Samples analyzed	Selenium	
		Range	Average
	<i>Number</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
Meteorites (iron, troilite, and chondite).....	5	1.5-132	47
Sulphides:			
Primary magmatic ¹	7	17-65	44
Pneumatolytic and hydrothermal ²	12	.8-190	29
From sedimentary deposits ³	13	.1-32	12
Oxides of iron and manganese ⁴	5	.5-5.4	2.0
Phosphates: ⁵			
Primary deposits.....	41	<8-55	<10.9
Secondary deposits.....	34	<8-16	<2.0
Limestone, Devonian.....	(⁶)1
Argillaceous-arenaceous rocks.....	(⁷)6
Chilean nitrate beds, caliche.....	(⁸)	5.2
Water from North Sea.....	2	.0033-.0044	.0038
Water from La Roche-Posay.....	32

¹ Pyrrhotite from Germany, Norway, South Africa, and Ontario, Canada.² From Norway, Germany, England, California, and Colorado.³ I sample from Newfoundland, others from Germany.⁴ I sample was a deep-sea nodule of manganese ore, others from Germany, Finland, and Newfoundland.⁵ Results from table 6.⁶ Composite sample representative of 32 limestones of Germany.⁷ Composite sample representative of deposits in Germany and Japan.⁸ Composite sample representative of 14 localities.⁹ Analyses by Taboury (23).

When all the data are considered, it appears that sedimentary deposits, in general, carry less selenium than other deposits. Furthermore, larger quantities of selenium occur in primary than in secondary deposits.

SELENIUM IN SUPERPHOSPHATE AND PHOSPHORIC ACID

In view of the occurrence of selenium in phosphate rock in amounts ranging from <0.1 to 55 p. p. m. (tables 2 and 3), notable quantities of this element would ordinarily be expected in superphosphate and phosphoric acid manufactured from rock from certain phosphate deposits. Furthermore, selenium may be introduced into superphosphate and phosphoric acid as an impurity in the sulphuric acid used to decompose the rock. Considerable quantities of selenium are often present in sulphuric acid manufactured from pyrite or produced as a byproduct of the smelting of other sulphide ores; acid from these sources is used extensively in the fertilizer industry, particularly in the manufacture of superphosphate. Stoklasa (22) reported 26 to 58 p. p. m. of selenium in Glover tower acid and 15 to 42 p. p. m. in chamber acid. A sample of byproduct sulphuric acid (60° B.) from a copper-smelting operation in Tennessee contained 52 p. p. m. of selenium (6). The presence of selenium in sulphuric acid has also been noted by others (20, 24). Inasmuch as selenium occurs in coal (12) and also in coke (21), phosphoric acid produced by the electric-furnace and blast-furnace processes, particularly the latter, may also carry selenium as the result of using coke as a reducing agent and as fuel.

Stoklasa (22) found 15 to 36 p. p. m. of selenium in European superphosphate. Much smaller quantities were found in American superphosphates by the authors. The results (table 10) range from <0.8 to 4.0 p. p. m. As the samples were typical commercial superphosphates recently made from phosphate rock representing the principal deposits in this country, it appears that these results may be regarded as a fairly accurate range for the selenium content of superphosphate manufactured in the United States at the present time.

TABLE 10.—Selenium in superphosphate and phosphoric acid

ORDINARY SUPERPHOSPHATE				
Sample no.	Type or source of phosphate rock	Source of sulphuric acid	P ₂ O ₅	Se
			Percent	P. p. m.
1315	Florida land pebble.....	Pyrite.....	19.20	1.5
1370	do.....	do.....	21.06	.8
1316	Tennessee brown rock.....	Sulphur.....	18.86	$<.8$
1414	Florida land pebble.....	Sludge acid from petroleum refining.....	17.85	$<.8$
1402	do.....	do.....	20.60	1.0
DOUBLE SUPERPHOSPHATE				
1337	Florida land pebble.....	Sulphur.....	46.21	<0.8
1362	Tennessee brown rock.....	(1).....	48.37	1.5
1372	Idaho.....	Copper-smelting operation in Montana.....	47.33	4.0
CRUDE PHOSPHORIC ACID				
1200	Idaho.....	Copper-smelting operation in Montana.....	20.26	<0.07
1199	do.....	do.....	37.80	$<.07$
1058	Tennessee brown rock.....	Copper-smelting operation in Tennessee ²	16.04	.14
1057	do.....	do.....	41.38	.5

¹ Phosphoric acid manufactured by the blast-furnace process was used.² A sample of acid (60° B.) from this smelting operation contained 52 p. p. m. of selenium (6).

The results in table 10 present a few additional points of special interest. Only a very small part of the selenium in the raw materials was found in the superphosphate or phosphoric acid. For example, the phosphoric acids produced from Idaho phosphate by the sulphuric-acid process carried less than 0.07 p. p. m. of selenium, despite the fact that the rock (Conda, Idaho) contains 8 to 40 p. p. m. (table 2) and the copper ore from which the sulphuric acid was produced as a by-product was probably also seleniferous. On processing phosphate rock from Conda, Idaho, it is the practice to calcine the rock at about 700° C. (14), in order to eliminate most of the organic matter which otherwise would seriously foul the acid and apparatus. At least a portion of the selenium of the phosphate rock is probably volatilized by this treatment.⁶ Doubtless a part of any selenium that is present in the mixture of rock and sulphuric acid remains with the sludge and is thus eliminated from the phosphoric acid. Furthermore, selenium may be lost by volatilization during concentration operations, although such a loss is not indicated by the results for the Tennessee acids. It may also be noted in this connection that, whereas a sample of sulphuric acid from the same source as that used in the manufacture of the Tennessee brown-rock acids carried 52 p. p. m. of selenium, the concentrated phosphoric acid contained only 0.5 p. p. m. and the dilute acid considerably less. Therefore, it would appear that, under the conditions of manufacture in this country, only a small part of the selenium occurring in the raw materials, in general, finds its way into the finished phosphate products.

SUMMARY

Results are given for selenium in 96 samples of phosphate rock and 3 samples of apatite from various deposits of the world, 8 representative samples of commercial superphosphates manufactured from domestic rock, and 4 samples of crude phosphoric acid produced by the sulphuric-acid process.

The results for selenium in natural phosphates range from <0.1 p. p. m. in a Tennessee brown rock to 55 p. p. m. in Wyoming and Algerian phosphates. The occurrence of selenium in natural phosphates is discussed from the following points of view: (1) Selenium-bearing constituents; (2) primary and secondary deposits; (3) geologic age of deposits; and (4) a comparison of phosphates with other geologic formations. Accordingly, the data indicate (1) that organic matter and, to a less extent, inorganic sulphides are important carriers of selenium in phosphate rock, (2) that primary deposits are in general richer in this element than are secondary deposits, (3) that deposits belonging to the Permian and Cretaceous ages contain the most selenium, and (4) that the selenium content of phosphate deposits is about the same as that of other sedimentary deposits in the same region.

The quantity of selenium in superphosphate ranges from <0.8 to 4.0 p. p. m., and in phosphoric acid is 0.5 p. p. m. or less. According to the available data only a small fraction of the selenium occurring in the natural materials from which superphosphate and phosphoric acid are made finds its way into the finished product.

⁶ According to the results of a single experiment with Wyoming rock no. 948, a highly seleniferous phosphate (table 2), selenium was completely volatilized when the phosphate was calcined in the presence of water vapor at 1,400° C. for 30 minutes.

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