THE RÔLE OF FLUORINE IN PHOSPHATE DEPOSITION.[1]

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CONTENTS.

ABSTRACT. In earlier studies of phosphate deposition attention has centered on the accumulation of phosphorus. In this paper it is shown that some agent, probably fluorine, is necessary to render the phosphate insoluble enough to be preserved through geologic ages. Although fluorine is steadily supplied to the oceans by the weathering and erosion of rocks containing fluorine-bearing minerals, additional large supplies are furnished from time to time by volcanism. It appears significant in this connection that volcanic products accumulated in great quantity in proximity to the regions where the principal phosphate deposits of the United States were laid down and at the time when these deposits were formed. Thus it is thought that volcanism, as a source of fluorine, may have been an indirect though determinative factor in their origin. Volcanism and unconformities are no doubt related to deep-seated causes within the earth. The principal phosphate deposits of the United States lie above unconformities of greater or less extent.

INTRODUCTION.

THE genesis of phosphate rock is a chemical process usually involving organic agencies. In many deposits marine or fluviatile processes of sedimentation are also utilized. The original deposits are primary but with notable exceptions, the western phosphate for example, are likely to be of too low grade to be of commercial interest. Secondary processes, that is re-solution and redeposition, play an important part in the formation of most deposits and in some, notably the Florida hard rock, they appear to have been dominant. Recent studies seem to show that volcanism is more intimately associated with phosphate deposition, especially the accumulation of great

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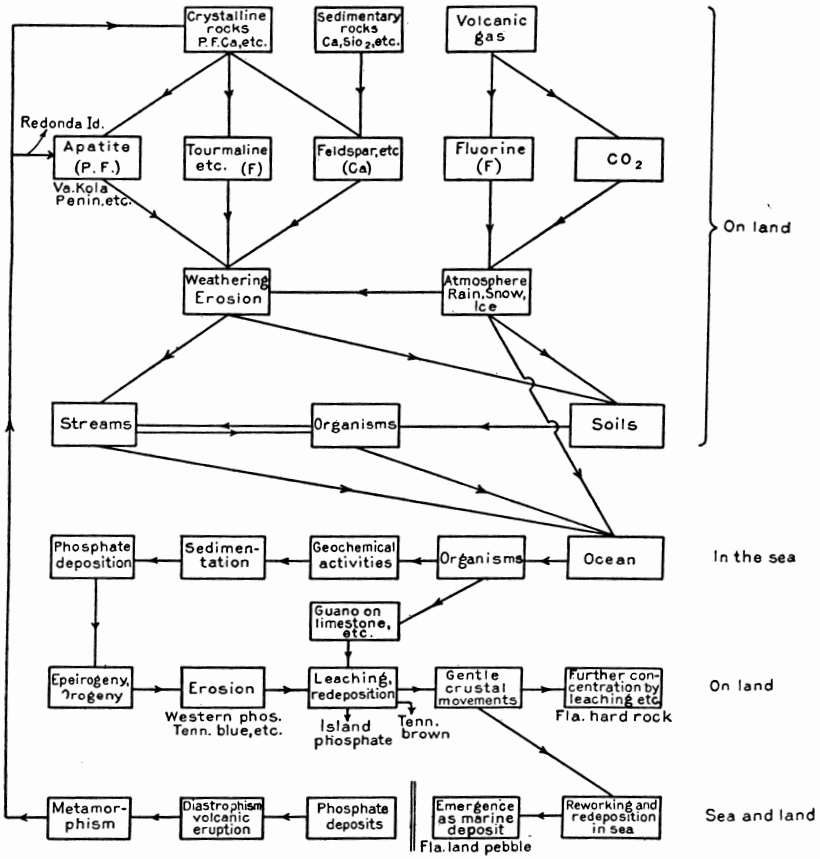
deposits, than has hitherto been supposed. This paper is a preliminary account of an investigation undertaken in collaboration with K. D. Jacob, Bureau of Plant Industry, U. S. Department of Agriculture, relating to the presence and geological importance of fluorine in phosphate rock.



GENESIS OF PHOSPHATE . TENTATIVE FLOW SHEET

Fig. 1.

THE PHOSPHATE CYCLE.

More than twenty years ago, in an illuminating essay, Blackwelder[2] pointed out the essentially cyclic nature of phosphate deposition. He discussed the different means by which phosphate deposits may be formed on land and in the sea and empha-

[2] Blackwelder, Eliot: The Geologic Rôle of Phosphorus: This Journal, 42, pp. 285-298, 1916.

sized the part that anaerobic conditions on the sea bottom may have played in the formation of many deposits that are now located in continental areas. The phosphate cycle in modified form is illustrated by the accompanying diagram, Fig. 1. Blackwelder's paper goes into the subject so thoroughly that it is not necessary here to consider other phases of it than the contribution of volcanism, which seems now to supplement Blackwelder's account and to shed new light on the problem of phosphate genesis. The probable connection of volcanism with phosphate rock deposition is through fluorine, an element recognized as present to some extent in all commercial phosphate deposits and considered an integral part of the chemical composition of phosphate rock, where it is firmly bound with the other constituents.

FLUORINE IN PHOSPHATE ROCK.

According to Jacob, Reynolds, and Marshall[3] "All types of commercial phosphate rock produced throughout the world contain fluorine in quantities ranging from approximately 0.4 to 1.3 per cent in the Curaçao and Christmas Island phosphates to 3.1 to 4.2 per cent in the phosphates of the United States and North Africa. For a given type of rock, the fluorine content is usually roughly proportional to the phosphorus content." These authors cite other workers to the effect that chemical and X-ray diffraction studies show fluorapatite—$Ca_{10}F_2(PO_4)_6$—to be the essential phosphatic constituent of phosphate rock. However, it seems that different commercial types of domestic phosphate rock usually contain from 12 to 52 per cent more fluorine than theoretically is required to form fluorapatite with all the phosphorus. This condition has been explained by Bredig, Franck, and Füldner[4] as the result of the formation of a solid solution between fluorapatite and calcium fluoride in which the calcium fluoride may amount to as much as 70 per cent of the quantity required theoretically by the apatite formula. This suggestion has been neither substantiated nor disproved. On the other hand the work of McCon-

[3] Jacob, K. D., Reynolds, D. S., and Marshall, H. L.: Phosphate Fertilizers by Calcination Process—Volatilization of Fluorine from Phosphate Rock at High Temperatures: Amer. Inst. Min. and Met. Engrs. Tech. Pub. 695, 1936.

[4] Bredig, M. A., Franck, H. H., and Füldner: Beiträge zur Kenntnis der Kalk-Phosphorsäure-Verbindungen: Ztsch., Elektrochem. 38, pp. 158-164, 1932.

nell[5] indicates that the excess fluorine may be due to the replacement of phosphorus by sulphur, silicon, carbon, and perhaps other elements. Some excess fluorine may be due to the presence of fluorite independently in the phosphate rock. Gale and Richards[6] report the occurrence of fluorite in phosphate rock from Cokeville, Wyoming, and the writer has himself observed fluorite in a hand specimen of phosphate rock from Montana.

Fluorine in phosphate rock has been a source of trouble to fertilizer manufacturers since the beginning and various methods of driving out all or part of it have been adopted. In making the widely used superphosphates sulphuric acid is the reagent employed. Different types of furnace treatment have been tried and the electric furnace is now able to separate the fluorine from the fluorapatite molecule and produce elemental phosphorus and other phosphate products. In the last few years experiments by Jacob[7] and his associates have demonstrated that fluorine can be driven out of phosphate rock by heating it in the presence of silica and water vapor at 1,400° C. Usually the rock contains enough silica for the purpose. The high temperature appears to be necessary to insure breaking up the fluorapatite molecule, which is the essential feature of all methods of treating phosphate for fertilizer use. Another method of accomplishing this result is by heating with an alkali salt.

The expulsion of fluorine though desirable is not essential to the production of phosphate suitable for fertilizer use. Usually not more than 30 per cent of the fluorine is removed in the manufacture of superphosphates. The electric furnace is more successful and removes practically all the fluorine. Under some, but not all, conditions of alkali-salt treatment the fertilizing value of the product seems to be dependent on the removal of the fluorine. However, with the steam and silica treatment the fertilizing value of the product seems always to

[5] McConnell, D.: Substitution of the SiO_2 and SO_4 Groups for PO_4 Groups in the Apatite Formula: Ellestadite, the End Member: Am. Mineralogist 22, pp. 977-986, 1937.

————: A Structural Investigation of the Isomorphism of the Apatite Group: Am. Mineralogist 23, pp. 1-19, 1938.

————: The Problem of the Carbonate-Apatites; A Carbonate Oxy-Apatite (dahllite): This Journal, 36, pp. 296-303, 1938.

[6] Gale, H. S., and Richards, R. W.: Preliminary Report on the Phosphate Deposits in Southeastern Idaho and Adjacent Parts of Wyoming and Utah: U. S. Geol. Survey Bull. 430, p. 464, 1910.

[7] Idem.

be directly related to the proportion of fluorine removed. Thus manufacturing experience and experimental evidence show that fluorine is an essential constituent in phosphate rock and that its tendency is to lock up the phosphorus. This fact has important geologic bearing, as it suggests that fluorine is the agent by which phosphate deposits have been preserved through successive geologic ages.

SOURCES OF FLUORINE.

Fluorine is a constituent of such common minerals as apatite, tourmaline, and some of the micas. Clarke[8] points out its relation to magmas as indicated by the minerals named. He also notes its occurrence in volcanic sublimates, spring waters, mineral veins, and as a constituent of igneous and metamorphic rocks.[9] The fluorite deposits of southern Illinois and northwest Kentucky are believed to have been derived from igneous sources.[10] Fluorine is also found in some ground waters. In the western and southwestern parts of the United States fluorine has been reported in waters from many wells and in some localities the quantity present is sufficient to cause the dental malady known as mottled enamel.[11]

Fluorine in ground water is probably the principal source of

[8] Clarke, F. W.: The Data of Geochemistry: U. S. Geol. Survey Bull. 770, p. 307, 1924.

[9] Idem., pp. 193, 273, 339, 357, 358.

[10] Bastin, E. S.: The Fluorspar Deposits of Hardin and Pope Counties, Ill.: Illinois State Geol. Survey Bull. 58, p. 68, 1931.

[11] Churchill, H. V.: Occurrence of Fluorides in some Waters of the United States: Ind. Eng. Chem. 23, 996, 1931.

Smith, H. V., and Smith, M. C.: Mottled Enamel in Arizona and its Correlation with the Concentration of Fluorides in Water Supplies: Ariz. Agr. Exp. Sta., Tech. Bull. 43, pp. 213-287, 1932.

Willis, W. R.: The Source of Fluorine in some Waters: Colo. State Dental Assn. Bull. 12 (4), 39, 1934.

Abbott, G. A.: The Fluoride Content of North Dakota Ground Waters: N. Dakota Geol. Survey Bull. 9, 1937.

Andrews, D. A.: Ground-Water in Avra-Altar Valley, Ariz.: U. S. Geol. Survey Water-Supply Paper 766-E, pp. 177-179, 1937.

Abbott, G. A., and Voedisch, F. W.: The Municipal Ground Water Supplies of North Dakota: N. Dakota Geol. Survey Bull. 11, 1938.

Jordan, B., and Frary, G. G.: Fluoride Content of South Dakota Water Supplies: S. Dakota Acad. Sci. Proc. 18, pp. 86-94, 1938.

Lohr, E. W. and Knechtel, M. M.: Geology and Ground-Water Resources of the Valley of Gila River and San Simon Creek, Graham County, Arizona: U. S. Geol. Survey Water Supply Paper 796-F, pp. 220-222, 1938.

Marshall, H. A., and Eckel, E. B.: Ground-Water Resources of the Holbrook Region, Arizona: U. S. Geol. Survey Water-Supply Paper 836-B, pp. 62-64, 1939.

supply for streams which in turn deliver it to the ocean. This fluorine has been derived in part from the breakdown of fluorine-bearing minerals by processes of weathering and erosion but in some areas contributions direct or indirect from volcanism may supply a larger portion. Allen and Day[12] report the presence of fluorine in the hot spring waters of the Yellowstone National Park and ascribe it to magmatic sources.

Volcanic gases are probably an important source. Zies,[13] for example, estimates that the Valley of Ten Thousand Smokes at the time of his visit was contributing fluorine to the atmosphere at the annual rate of 135,000 metric tons.

FLUORINE IN THE PHOSPHATE CYCLE.

As shown in Fig. 1, fluorine may enter the phosphate cycle from both mineral sources and volcanic gases. That from mineral sources enters through the usual channels of weathering, erosion, and transportation by ground water and streams with customary stopovers in soils and organisms and with various secondary activities. The supply in the soils and streams is doubtless augmented locally by fluorine contributed from magmatic sources to ground water and regionally by gases discharged into the atmosphere where fluorine is dissolved in rain or snow. Fluorine from volcanic gas is also supplied directly to the ocean by the same means.

Clarke[14] cites Gautier and Clausmann as having determined fluorine (fluoride) in several river waters, the fluorine content ranging from 0.02 to 0.6 milligram per liter and being highest in waters emerging from primitive rocks. Though these figures were reported in 1914, Howard[15] states that on the basis of his work on the Colorado River they are probably still applicable. The same authors reported 0.3 milligram of fluorine per liter in the Atlantic Ocean. Later work by Thompson and Taylor[16] shows a concentration of 1.0 to 1.4 milligrams of fluorine per

[12] Allen, E. T., and Day, A. L.: Hot Springs of the Yellowstone National Park: Carnegie Inst. Washington Pub. 466, pp. 119-120, 1935.

[13] Zies, E. G.: The Valley of Ten Thousand Smokes; I, The Fumarolic Incrustations and Their Bearing on Ore Deposition; II, The Acid Gases Contributed to the Sea During Volcanic Activity: Nat. Geog. Soc. Cont. Tech. Papers, Vol. 1 Katmai Ser. No. 4, p. 66, 1929.

[14] Clarke: Ref. cit., p. 73, 122.

[15] Howard, C. S.: Personal Communication.

[16] Thompson, T. G., and Taylor, H. J.: Determination and Occurrence of Fluorides in Sea Water: Ind. and Eng. Chemistry, Anal. Ed. 5, pp. 87-89, 1933.

liter in waters from the Pacific Ocean. These figures show that the proportion of fluorine normally present in the sea is small and that correspondingly small proportions of phosphorus would be locked up by it in forming fluorapatite. Hence it would be expected that under ordinary conditions insufficient phosphate would be deposited to form either primary or secondary deposits of sufficient concentration to have commercial interest.

Blackwelder in the paper cited calls attention to certain special geographic or paleogeographic conditions that seem necessary for the production of large phosphate deposits. The writer,[17] too, in his account of the western phosphates emphasized the importance of paleogeographic conditions. Blackwelder[18] in discussing the effect of deficiency of oxygen on the sea bottom as a factor in phosphate formation writes as follows:

"In order to account for the oceanic phosphate deposits, therefore, we must apparently discover those rare areas of the sea bottom where this circulation [of oxygen] is not effective. Deep inclosed gulfs or seas, such as the Black Sea, today afford some of the conditions, but not all of them. The bottom sediment of the Black Sea is now a lifeless mud blackened by hydrocarbons and charged with hydrogen sulphide. There is, however, some condition lacking, for the deposition of phosphates in the Black Sea is not indicated by the dredgings thus far reported."

The Phosphoria formation of Idaho and adjacent States[19] has many similarities with the Black Sea muds, but in addition contains thick and widely extended phosphate deposits. Why is it that apparently similar geographic conditions have led to phosphate deposition in one region and not in the other? Can deficiency in fluorine have anything to do with it?

Shepherd,[20] who has assembled many analyses showing the fluorine content of rocks, points out that this content is much greater than was formerly supposed and averages about 0.04

[17] Mansfield, G. R.: The Geography, Geology, and Mineral Resources of Part of Southeastern Idaho: U. S. Geol. Survey Prof. Paper 152, pp. 187, 188, 361-367, 1927.

[18] Blackwelder, Eliot: ref. cited, p. 293.

[19] Mansfield, G. R.: ref. cit., pp. 75-81.

[20] Shepherd, E. S.: Note on the Fluorine Content of Rocks and Ocean Bottom Samples: This Journal, Vol. 238, 2, pp. 117-128, 1940.

per cent. Efforts to find corresponding amounts in sea-bottom deposits have been disappointing. He asks what has become of all this fluorine. Possibly the tendency of fluorine to unite with phosphorus compounds to form phosphate deposits may provide a partial answer. Both Blackwelder and the writer in the publications cited have discussed different paleogeographic conditions, such as climatic changes, restriction of oceanic circulation, character and erosion stage of neighboring land masses, and other features that might affect phosphate deposition. Such conditions tend to favor deposition in some areas and not in others. As phosphates and fluorine seem to have great affinity for each other, any condition affecting phosphate deposition might tend also to localize the trapping of fluorine and account for the spotty occurrence of it in sea-bottom deposits noted by Shepherd.

In his study of Idaho phosphates and their accompanying bedded cherts the writer has become impressed by the great extent of volcanic activity, which, as noted further on, took place in regions relatively close to those in which the western phosphates were formed. The work of Zies already cited and the fact that, with some exceptions to be noted later, most of the commercial phosphate deposits contain noteworthy amounts of fluorine have suggested the possibility that volcanism may be intimately connected with the problem of the origin of at least some of the deposits. The purpose of this paper is to consider what bearing, if any, volcanism may have on phosphate deposits in general and whether it may not be a major factor in their formation.

K. D. Jacob[21] suggests that three possibilities with respect to the relation of fluorine to phosphate deposits may logically be considered, namely:

(1) That at the time of the formation of most of the deposits the conditions and the fluorine-phosphorus relationships in the medium were such as to bring about direct precipitation of fluorapatite having such a high content of fluorine that little or no further absorption of fluorine could take place. That is, the ratio of fluorine to phosphorus in the fluorapatite was at or near its maximum value at the time the phosphate was originally deposited. An abundant supply of fluorine, such as might arise from volcanic activity in the region at the time of deposition, would favor this possibility.

[21] Jacob, K. D.: Personal Communication.

(2) That the deposits were originally laid down in the form of calcium phosphates that contained little or no fluoride and that gradual absorption of fluorine from percolating waters took place with the ultimate formation of fluorapatite in which the fluorine-phosphorus ratio reached its maximum value. That such a procedure is possible is shown by the fact that such insoluble materials as bone and hydroxyapatite ($Ca_{10}(OH)_2$-$(PO_4)_6$) readily absorb fluorine from very dilute solutions. Also, we know that when fossil bones and teeth have been exposed to water, their relative age can usually be correlated with the ratios of the fluorine to phosphorus in their contained materials. The ratio of fluorine to phosphorus is very low in modern bones and also in fossil bones that have been protected from water. The geologically young phosphates of Curaçao and Christmas Islands seem to be examples of deposits that have had insufficient time to permit the attainment of the maximum fluorine content.

(3) That at the time of the formation of the deposits the conditions and the fluorine-phosphorus relationships in the medium were such as to bring about direct precipitation of phosphate with an intermediate fluorine content and that the fluorine-phosphorus ratio was subsequently augmented by the gradual absorption of fluorine from percolating waters.

These suggestions seem to offer satisfactory means for attaining the maximum fluorine-phosphorus ratio in the fluorapatite of the phosphate deposits but leave unexplained the presence of the additional 12 to 52 per cent of fluorine already noted as usually present in most domestic deposits. If, as previously suggested, some of the phosphorus has been replaced by silica or carbon the relative proportion of fluorine in the resulting compound may thereby have been increased. The presence of fluorite in some deposits, which would have the same effect, has already been noted.

The decay of fluorine-bearing minerals under weathering and erosion would probably yield a fairly steady supply of fluorine to the ocean. The amount supplied by volcanism on the other hand would probably fluctuate according to the intensity of volcanic activity at different times and places. It is thought that at times of unusual volcanic activity the normal supply of fluorine may have been sufficiently augmented to induce at places where conditions were otherwise favorable an unusual rate and amount of primary phosphate deposition.

Mr. Jacobs[22] further notes that hydroxyapatite, an analogue of fluorapatite, is also highly insoluble in water and that in fluorine-free systems it is the solid end product of the action of water on mono-, di-, and tricalcium phosphates and tetracalcium phosphate. In the absence of fluorine, therefore, it could presumably act in the same way as is here postulated for fluorapatite in preserving phosphates through geologic time. However, the widespread occurrence of fluorine in water and the ease with which hydroxyapatite is converted into fluorapatite have prevented the occurrence of low fluorine deposits of calcium phosphate except in a few instances such as the geologically young formations on some of the oceanic islands. Given sufficient time, and equal opportunity for contact with fluorine-bearing water, even these deposits would be likely to increase in fluorine content and ultimately attain the maximum fluorine-phosphorus ratios.

The ease and rapidity with which tricalcium phosphate takes up fluorine to form fluorapatite has recently been demonstrated by Adler, Klein, and Lindsay,[23] who have been working on the problem of defluorinating potable waters.

VOLCANISM AND PHOSPHATE DEPOSITS.

To consider the phosphate deposits of the world in relation to volcanism would be a task too great for the scope of this paper. Probably sufficient information may be obtained from those of the United States to indicate the trend of the evidence.

The sedimentary phosphates of the United States begin with the Ordovician. To this group belong the phosphatic limestones that gave rise to the brown rock phosphates of Tennessee, Kentucky, and northwest Alabama. The Arkansas phosphate is also of Ordovician age. Mississippian time is represented by certain phosphates near Logan, Utah, and in parts of southeastern Idaho. The blue phosphate rock of Tennessee may also belong here though it is associated with the Chattanooga black shale, which is considered by the Geological Survey as Devonian or

[22] See footnote 21.

[23] Adler, H., Klein, G., and Lindsay, F. K.: Removal of Fluorides from Potable Water by Tricalcium Phosphate: Ind. and Eng. Chem. 30, pp. 163-165, 1938.

Mississippian. The great bulk of the western phosphates is of Permian age. Certain beds of Upper Cretaceous age in the coastal plain, in Mississippi and Alabama, for example, are phosphatic, and finally the Miocene Hawthorn formation of Florida, Georgia, and South Carolina is phosphatic. This is the parent rock, from which have been derived the land and river pebble and the hard rock phosphates, the principal commercial types of phosphate rock in Florida, as well as the South Carolina phosphates. Other phosphate occurrences in the United States might be mentioned to amplify the argument, but they are small and scattered and to include them would probably confuse rather than clarify the discussion.

The postulated connection of volcanism with phosphate deposition seems most suggestive for the Ordovician, Permian, and Miocene phosphates. These with their secondary derivatives include most of the phosphates of prospective commercial importance in the United States. For the other deposits the connection is apparently more remote, but some of them deserve brief mention.

Evidence of volcanic activity in Ordovician time in the Tennessee-Kentucky area was discovered in the form of bentonite by Nelson[24] some years ago. Information about this and other similar discoveries has been summarized by Ross.[25] According to Ross the most widespread bentonites of the eastern United States occur in Tennessee, Kentucky, and Alabama. In Tennessee they are recognized at five different horizons. The two more widespread beds occur at the top of the Lowville limestone and at the base of the Trenton. It happens that the Bigby limestone, the most important source of Tennessee brown phosphate, and the underlying Hermitage formation (also a source of brown phosphate) are of Trenton age. Ross goes on to say:

"Ordovician volcanic materials have been found by different geologists at many places in six of the eastern United States and have been examined by petrologists and their volcanic nature confirmed. When all the evidence is considered there can be no doubt that great volcanic eruptions occurred in Ordo-

[24] Nelson, W. A.: Volcanic Ash Beds in the Ordovician of Tennessee, Kentucky, and Alabama: Geol. Soc. America Bull. 33, 605-615, 1922.

[25] Ross, C. S.: Altered Paleozoic Volcanic Materials and Their Recognition: Am. Assoc. Petroleum Geologists, 12, 2, pp. 143-164, 1928.

vician time, and deposits hundreds of miles apart show that thousands of square miles were at this time covered with ash."

The Permian was a period of world-wide change culminating in mountain building on a tremendous scale. In the region adjacent to and now occupied by the Western phosphate field volcanic activity was a noteworthy feature of the period. Gilluly[26] reports that in eastern Oregon the Clover Creek greenstone, consisting of altered volcanic flows, pyroclastics, and subordinate conglomerate, limestone, and chert, contains Permian fossils. It covers many square miles, extending into Idaho, and has a minimum thickness of at least 4,000 feet. On the Idaho side of the Snake River canyon Livingston and Laney[27] twenty years ago described andesitic tuffs and limestone apparently of generally similar character to those of the later described Clover Creek greenstone. More recently fossils identified as Permian by J. Steele Williams have been collected by Cannon[28] from limestones overlying the tuffs of this sequence. Cannon states that no base for these rocks has been seen and that their minimum thickness must be at least a mile. Ferguson[29] has found in the Toyabe Range, Tonopah quadrangle, Nev., a Permian sequence containing two divisions. The lower, 2,000 feet thick, is fossiliferous at the base and consists of grit, conglomerate, sandstone, etc. The upper, more than 4,000 feet thick, is principally volcanic with some interbedded material similar to that of the conformably underlying division. These rocks are cut by felsitic intrusions also considered Permian. Ross[30] has described as the Casto volcanics, Permian (?), a thick sequence of tuffs and lavas with some associated conglomerates and a little limestone. These rocks cover more than 231 square miles in the Casto quadrangle in central Idaho and have a thickness that in places may exceed 5,000 feet. In the Phosphoria formation of southeastern Idaho the writer has seen volcanic shards. Extensive volcanic activity in the South-

[26] Gilluly, James: Geology and Mineral Resources of the Baker Quadrangle, Oreg.: U. S. Geol. Survey Bull. 879, pp. 21-27, 1937.

[27] Livingston, D. C., and Laney, F. B.: The Copper Deposits of the Seven Devils and Adjacent Districts: Idaho Bur. Mines and Geology Bull. 1, pp. 18-23, 1920.

[28] Cannon, R. S.: Personal Communication.

[29] Ferguson, H. G.: U. S. Geol. Survey (unpublished manuscript).

[30] Ross, C. P.: Geology and Ore Deposits of the Casto Quadrangle, Idaho: U. S. Geol. Survey Bull. 854, pp. 28-35, 1934.

west and adjoining parts of Mexico during Permian time is indicated by the work of Lang[31] and King.[32]

Volcanic activity was fairly widespread in the Gulf Coastal Plain region in Upper Cretaceous time[33] as indicated by water-laid deposits of volcanic origin, plugs, and other phenomena. Bentonite beds of this period have been recognized in Mississippi, Alabama, Texas, and Louisiana. Phosphate deposits of this age have been recognized in Mississippi[34] and Alabama.[35] They are composed chiefly of nodules and casts of shells and have no present commercial value, though some farmers have used them advantageously for direct application to their farms. As noted further on phosphate deposits of this age in Europe are well known.

In Miocene time volcanic activity again caused the deposition of thick and extensive accumulations of volcanic ash in the Coastal Plain region. These are represented by beds of bentonitic clay and of fuller's earth in Florida and Georgia.[36] The fuller's earth is being exploited on a large scale in both these States. Both the fuller's earth and the bentonitic beds are in the Hawthorn formation, which is phosphatic and is the parent formation of the Florida land and river pebble and hard rock phosphates as already stated.

The Mississippian phosphates of the West and the blue phosphate of Tennessee, the latter rated as potentially commercial, are not apparently related to volcanic activity in any adjacent region, though the available record indicates that such activity did occur on a considerable scale at some places comparatively remote from those areas of deposition at what was or may have

[31] Lang, W. B.: The Permian Formations of the Pecos Valley of New Mexico and Texas: Am. Assoc. Pet. Geols. 21 (7), p. 874, July, 1937.

[32] King, R. E.: The Permian of Southern Coahuila, Mexico: This Journal, Vol. 27, pp. 106-108, 1934.

[33] Ross, C. S., Miser, H. D., and Stephenson, L. W.: Water-Laid Volcanic Rocks of Early Upper Cretaceous Age in Southwestern Arkansas, Southeastern Oklahoma and Northeastern Texas: U. S. Geological Survey Prof. Paper 154, pp. 175-202, 1929.

Lonsdale, J. T.: Igneous Rocks of the Balcones Fault Region of Texas: Univ. Texas Bull. 2744, 1927.

[34] Stephenson, L. W., and Monroe, W. H.: Stratigraphy of Upper Cretaceous Series in Mississippi and Alabama: Am. Assoc. Petroleum Geologists Bull. 22, no. 12, pp. 1639-1657, 1938.

[35] Smith, E. A.: The Phosphates and Marls of Alabama: Trans. Amer. Inst. Mining Engrs., 25, pp. 819-820, 1895.

[36] Bay, H. X., and Munyan, A. C.: In Clay Investigations in the Southern States: U. S. Geol. Survey Bull. 901, pp. 251-333, 1940.

been approximately that time. Such activities have been noted in southeastern Canada,[37] New England,[38] and Scotland.[39] To what extent these activities may have influenced phosphate deposition elsewhere it is impossible to state with any assurance. Under ordinary conditions any fluorine emitted by these eruptions might be supposed to have made its way into the oceans and have been dissipated without notably increasing their fluorine concentration.

However, the Western phosphates of Mississippian age are relatively thin and of low concentration, except perhaps locally, and afford little promise of commercial development. They apparently represent one or more local basins of small extent as compared with those of Permian age. With other physiographic conditions favorable, the supply of fluorine in the ocean may have been sufficient to produce the observed effects without recourse to additional supplies from volcanic sources.

The Tennessee blue phosphate represents in large part a concentration by marine agencies in Devonian or Mississippian time of phosphatic material deposited originally in Ordovician time. Hayes and Ulrich[40] state that it never forms a valuable deposit where it does not rest directly upon the Leipers formation, being of low grade and shaly—never oolitic—where the Clifton limestone and Fernvale formations intervene. The Leipers is one of the principal phosphate-bearing formations of Ordovician age.

Thus the Mississippian or Devonian phosphates in the United States are equivocal. Though not directly supporting the hypothesis here presented they do not convincingly oppose it.

RELATION OF PHOSPHATE DEPOSITS TO UNCONFORMITIES.

Some years ago Cayeux[41] thought that the phosphate deposits of the Upper Cretaceous in Europe were formed as a re-

[37] Ross, C. S.: Altered Paleozoic Volcanic Materials and Their Recognition: Am. Assoc. Petroleum Geologists, 12 (2), pp. 161-162, 1926.
Pirsson, L. V., and Schuchert, Charles: A Textbook of Geology, p. 737, 1915.

[38] La Forge, Laurence: Geology of the Boston area: U. S. Geol. Survey Bull. 839, pp. 28-37, 1932.

[39] Geikie, Archibald: Textbook of Geology, 4th Ed., Vol. 2, pp. 1043-44, 1903.

[40] Hayes, C. W., and Ulrich, E. O.: Description of the Columbia Quadrangle: U. S. Geol. Survey Folio 95, p. 6, 1903.

[41] Cited by Collet, L. W.: Les Depots Marins: Encyclopédie scientifique, pp. 212-213, Paris, 1908.

sult of great disturbances of the equilibrium of the sea. These disturbances bring in their train changes in ocean currents and in the depth of the sea. Such changes cause the destruction of great numbers of organisms, which furnish in abundance the phosphoric acid that passes into the sediments. This view places phosphate beds in close relationship with unconformities and other stratigraphic breaks. Great unconformities are no doubt related to deep-seated causes within the earth's crust, which may well give rise to or be accompanied by volcanic activity on a more or less extensive scale. They also mark epochs of stimulated erosion, during which the contributions of fluorine from mineral sources as well as of other erosion products would be increased to some extent.

To trace the possible connection between volcanism and unconformities is beyond the scope of this paper. It is interesting, however, to note that submergence during the Upper Cretaceous was of wide extent in many parts of the globe. Also the events that led to and culminated in the eruption of the Deccan basalts and tuffs, which, according to Geikie,[42] cover more than 200,000 square miles in India and attain a thickness of 6,000 feet or more, took place in Upper Cretaceous time. Similarly the great outpouring of the Columbia River basalts, comparable in area and thickness to those of the Deccan, took place in Miocene time. It is perhaps noteworthy, too, that the phosphate deposits described in this paper lie above and apparently in close connection with unconformities representing stratigraphic breaks of shorter or longer duration.

ESSENTIALS OF PHOSPHATE DEPOSITION.

Reference has already been made to the importance of paleogeographic conditions at the time of primary phosphate deposition. Two things seem to stand out as essential; first, a combination of circumstances favorable to the accumulation of phosphoric acid, and, second, the presence of some agent to fix that phosphoric acid in relatively insoluble form. It is here suggested that this agent may be fluorine. Fluorine is a noteworthy product of volcanism at different times and places and volcanic products on a considerable scale accumulated in proximity to the principal phosphate fields of the United States at the times when their primary deposits were being laid down. It

[42] Geikie, Archibald: Ref. cit. pp. 346, 1209.

is thought, therefore, that volcanism may have been a determinative though indirect factor in the accumulation of these deposits.

Though the great Permian deposits of the West appear to have been little affected by secondary activity and are being used in their primary form, such activity has played a large part in converting the Ordovician phosphatic limestones of Tennessee and the Miocene limestones of Florida into the brown rock and hard rock of commerce. Though the blue rock of Tennessee and the land and river pebble of Florida are in a sense secondary deposits, as they are largely the products of the reworking of earlier formed deposits, they are primary in the sense that the reworking agents were chiefly marine or fluviatile rather than chemical. The fact that the island phosphates, which generally contain less fluorine than the continental types, are younger than those types, indicates that secondary enrichment may be a factor in accumulating fluorine as well as phosphorus. These phosphates have been formed in general on the land rather than in the sea and under conditions that permitted only limited access to waters containing fluorine. With increased time and further opportunity to acquire fluorine their fluorine-phosphorus ratio may be expected to increase.

Many accumulations of organic remains are found in nature, which do not yield phosphate deposits. Undoubtedly phosphatic material was once present, but it may be that without volcanism no adequate supply of fluorine was available to fix the phosphorus and preserve it for future use. On the other hand, many periods of volcanism are known, for which no corresponding phosphate deposits have been found. In such examples it would seem that the supply of fluorine may have been inadequate or, if adequate, that no accumulations of phosphorus were present in sufficient magnitude to utilize the available fluorine. Instead it became dissipated in widespread and dilute combinations.

SUMMARY.

It has been shown that fluorine is an essential constituent of phosphate rock and tends to keep it relatively insoluble. Volcanic activity is recognized as a major source of fluorine. It is logical to suppose that during periods of marked volcanicity, when paleogeographic conditions are otherwise favorable for the accumulation of phosphorus, the unusual amounts of fluor-

ine available may so combine with the available phosphorus as to produce noteworthy or great deposits of phosphate. As crustal disturbances, such as those which produce marked unconformities, may give rise to or be accompanied by volcanic disturbances, it is logical to suppose that phosphate deposits may bear some definite relation to unconformities.

A review of the phosphate deposits of the United States shows that volcanic activity on a considerable scale occurred at approximately the same time as the deposition of the primary phosphates and that these phosphate deposits in general lie above unconformities. Thus it would appear that a close relation may obtain between periods of volcanism and the formation of great phosphate deposits.

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