

## Some aspects of phosphorus in Precambrian sedimentation

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### ABSTRACT

The first appearance of phosphorite in sediments, at the time transitional between the Precambrian and the Cambrian, coincided with the first appearance of animals with hard parts containing calcium phosphate. At the same geological time a great change took place with regard to the phosphorus content of sedimentary iron ores, those of the Phanerozoic systems carrying normally about ten times more of this element than the Precambrian ones. Before, all during the Precambrian, the only possible sources of phosphorus in non-detrital sediments were abiotic precipitation and processes connected with the decay of the soft tissues of animals and plants. Together these sources were not adequate to produce any phosphorite deposit, or even, with extremely few exceptions, to leave more than insignificant marks in iron ores formed in an environment favourable also for phosphate deposition. With regard to abiotic precipitation, conditions must have been essentially the same in Phanerozoic sedimentation as they were during the Precambrian. The conclusion that, in the latter case, this source was of but little importance, therefore appears to be on the whole applicable also to the Phanerozoic. In the case of soft organic tissues as a source of phosphatic sediments, a similar conclusion seems justified when considering such forms of life as were in existence already at the time when the phosphorus-poor sediments of the Precambrian were deposited, but it is doubtful whether it may be extended also higher up on the evolutionary scale.

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## 1. Introduction

Contact with various problems in the Precambrian geology of Sweden has aroused the writer's interest in the role of phosphorus in Precambrian sedimentation, and the ways in which it differs from the role of the same element in the sediments of Phanerozoic times. Compilation of relevant facts, most of them already well known, brings out relations which appear to deserve attention in studies on the geochemistry of phosphorus in the sea, and related problems.

All authorities on Precambrian geology agree that the detrital sediments are essentially similar to those of the Phanerozoic. In chemical sedimentation, on the other hand, there are some general differences which, on the whole, make the Precambrian and the Phanerozoic contrasting units. This applies also to the role of phosphorus. The kinds of sediments that will be considered in the following are phosphorite, iron ores, and carbonaceous shales. It is commonly realized that phosphorite is normally found only in Phanerozoic sediments, but the conclusions—at least conjectural ones—that may be drawn from this distribution are not stated. Figures for the amounts of phosphorus in sedimentary iron ores of various ages and types are easily obtainable from the enormous number of available analyses, but no compilation of such data has, to the writer's knowledge, ever been published. Because of the importance of biogenic processes in the geochemistry of phosphorus, and the fact that the carbonaceous sediments of the Precambrian furnish important evidence of the existence of organic life at the time, certain sediments of this nature will also be considered.

## 2. Phosphorite

With regard to the occurrence of phosphorite the contrast between the Precambrian and the Phanerozoic systems is sharply marked. Nodular phosphorite is found in the Phanerozoic systems, from the Lower Cambrian upwards; continuous and extensive beds of phosphate rock first make their appearance higher up in the Paleozoic. In the Precambrian, on the other hand, sedimentary concentrations of phosphorus are virtually absent. Only two examples are known to the writer. They do not materially change the statistical picture, yet are of considerable interest for the questions studied here. Possibly a search through all literature on Precambrian geology might disclose more cases, but in all likelihood the result would not justify the time and labour spent on this task.<sup>1</sup>

The exceptions are: concretions probably related in origin to phosphorite nodules, in the Grythyttte slate in Central Sweden (Sundius 1923), and typical phosphorite nodules in the Visingsö formation of southern Sweden (Hedström 1930, Collini 1951).

The Grythyttte slate belongs to an upper part of the Svecofennian Leptite formation of Central Sweden. A number of absolute datings, by various methods, on pegmatites and granites from the concluding stage of the Svecofennian cycle give ages of about 1750–1800 m.y. The age of the slate, therefore, should be at least about 1800 m.y.; probably it is not far above this figure. The slate is a typical argillaceous deposit,

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<sup>1</sup> Once, in fact, phosphate sediments referred to the Precambrian were reported. Schists consisting of apatite, quartz, and graphite, in the Odenwald region in western Germany, were regarded as members of the Precambrian gneiss complex there (Osann 1892). Soon afterwards, however, it was shown that the rocks in question do not belong to the gneisses, but are Lower Paleozoic sediments in a comparatively high degree of metamorphism (Andrae & Osann 1896).

whose lower part regularly contains a little graphite, which imparts a dark colour to it. Phosphorus is not higher than would normally correspond to the detrital material. Thus an analysis from the Grythytte area reports C 0.55 and P 0.02 per cent (Sundius, *op. cit.*), another, from the Saxå area, has C 1.13 and P 0.05 per cent (Magnusson, 1925). Nodules of quartz, generally less than 3 cm in diameter but sometimes coalescing into bands parallel to the bedding, are characteristic of a stratigraphical level in the slate. Sundius (*op. cit.*) presents convincing arguments for the view that they were formed as concretions of amorphous silica in the sediment, before its metamorphism. At one of the places where the zone with concretions outcrops the one-time chert nodules contain in their central parts aggregates of fine-grained apatite and graphite. The interpretation presented by Sundius is that these were originally nodules of phosphorite and amorphous silica, and reference was made to occurrences of similar nodules in Paleozoic sediments in which the silica apparently was derived from sponge spicules. No traces of organic structures have been identified in the concretions of the Grythytte slate, however. Comparison may be made also with such cases of the association between phosphorite and chert, sometimes also with organic matter, which are described from Paleozoic sediments in various regions (e.g. Levat, 1899, and Raguin, 1928; Kruft, 1902; Howitt, 1928). In these deposits the silica is regarded as derived, largely at least, from radiolarians, a form of animal life hardly to be counted with for a sediment of the age of the Grythytte slate.

The alternative to Sundius's interpretation would seem to be secondary concentration of detrital apatite contained in the sediment, a process unlikely in itself and hardly compatible with the fact that the concentration occurs only locally, and not as a regular feature of the otherwise similar nodules.

The phosphorite nodules of the Visingsö formation do not require any special description: they are, in every respect, similar to such concretions occurring in Phanerozoic sediments. On the other hand, this very fact makes it necessary to describe the formation which contains them, and its place in the geological time-scale. The Visingsö formation is, on the whole, restricted to the basin of Lake Vättern in southern Sweden, with outlying remnants in the neighbourhood, at most about 60 km from it. It is generally assumed that its original extension did not go far outside the region thus indicated. The formation is chiefly built up of sandstone and pelitic sediments, the latter with limestone seams. Microfossils have long been known to occur. From a study of them Timofeev (1960) has reported the presence of a number of species, including unicellular algae and remnants of terrestrial plants. From Visingsö pelite Collini (1951) reports 0.09 per cent P, and from a limestone 0.66 per cent. The phosphorite concretions occur at several localities.

The Visingsö formation exhibits no signs of folding, beyond bucklings which may be consequences of downfaulting, and no metamorphism. The only absolute age determination is on detrital mica, therefore the figure, about 1000 m.y. (Magnusson, 1960), gives only an upper limit. Geologically, the formation is dated as pre-Ordovician, and its spatial relations to the Cambrian-Ordovician sequence in adjacent areas make it clear that this also means that it is older than the Cambrian of the region. On the other hand, a number of facts indicate that the time by which the Visingsö formation preceded the Lower Cambrian transgression in southern Sweden was probably a short one. The Visingsö has been interpreted as an early continental foreland deposit to the Caledonian geosyncline of Scandinavia (Collini, 1951), and the term "Eocambrian" has often been employed to characterize its place in geological chronology. It is, in fact, not at all improbable that it ought to be referred to the

Cambrian, since recent research on the remarkable Cambrian sediments in southern Morocco has revealed the existence of several distinct faunas before the one which represents the earliest Cambrian fauna in Sweden (Hupé, 1952).

### 3. Phosphorus in iron ores

#### 3.1. *The main ore types*

One of the most conspicuous differences between the Precambrian and the Phanerozoic lies in the enormous development in the former of siliceous "banded iron formations" or "banded ironstones" of sedimentary origin. In the Phanerozoic systems, sediments of this nature are met with only as local phases or on a small scale, in rocks of Lower Paleozoic age. Instead the characteristic marine iron sediments of the Phanerozoic are the oölitic ores. These are similar to the Precambrian banded ironstones in many respects, as in the original forms of iron minerals and the shallow-water origin, but differ, *inter alia*, by the general occurrence of oölitic texture (which is never developed on a similar scale in the banded iron formations) and their lower content of precipitated silica. In the Precambrian, throughout oölitic ores of this nature are represented only by a few occurrences, all belonging to late Precambrian stages and probably only shortly antedating the dawn of the Cambrian. It might perhaps be argued that their absence in older Precambrian sediments may be due to metamorphism which has obliterated the oölitic texture. A study of the textural development of the earlier ore deposits of the Precambrian will show, however, that this explanation cannot be valid. On the other hand, non-oölitic ores are rare in the Phanerozoic; two types (and occurrences) will be reviewed here.

In the following a survey is given of these different groups, with special regard to the percentage of phosphorus in them, its mineral form, and—in the case of banded iron formations—its distribution within the bedded ore. In order to give an objective picture it has been necessary to include most quantitatively important occurrences for which data have been available, as well as some others of special interest, and to quote a great number of analytical data. In the selection of the latter, use has often been made of the authoritative surveys in publications of the International Geological Congress ("Iron ore resources of the world", 1910, and "Symposium sur les gisements de fer du monde", 1952), without tracing the data to their original sources. Analyses reported as  $P_2O_5$  have been recalculated to P.

To emphasize already at the outset the features which this compilation brings out, a summary is presented in a diagrammatic form (Fig. 3.1.1). It is obvious that this picture must be, to some extent, a simplified one. The geological units presented vary from single deposits to provinces, and the quantities represented by an analysis range from a hand specimen to the average of many million tons. Also it has not been possible to indicate in this diagram the frequency of various values within each unit. Only the amplitude can be shown. In this, a continuous line between the extremes has been drawn whenever there are no reasons to reckon with the existence of gaps. Single analysis reported as typical of a unit have been indicated with  $\pm 0.005$  per cent P. The principles followed may be further illustrated by some examples. The enormous occurrences of banded ironstones in the Lake Superior region do not, as a rule, exceed 0.05 per cent. The formation in the Iron River and Crystal Falls district, however, throughout (with the exception of its sulfidic phase) shows much higher figures, 0.19 to 0.365 per cent. Obviously it would be misleading to indicate for this region a

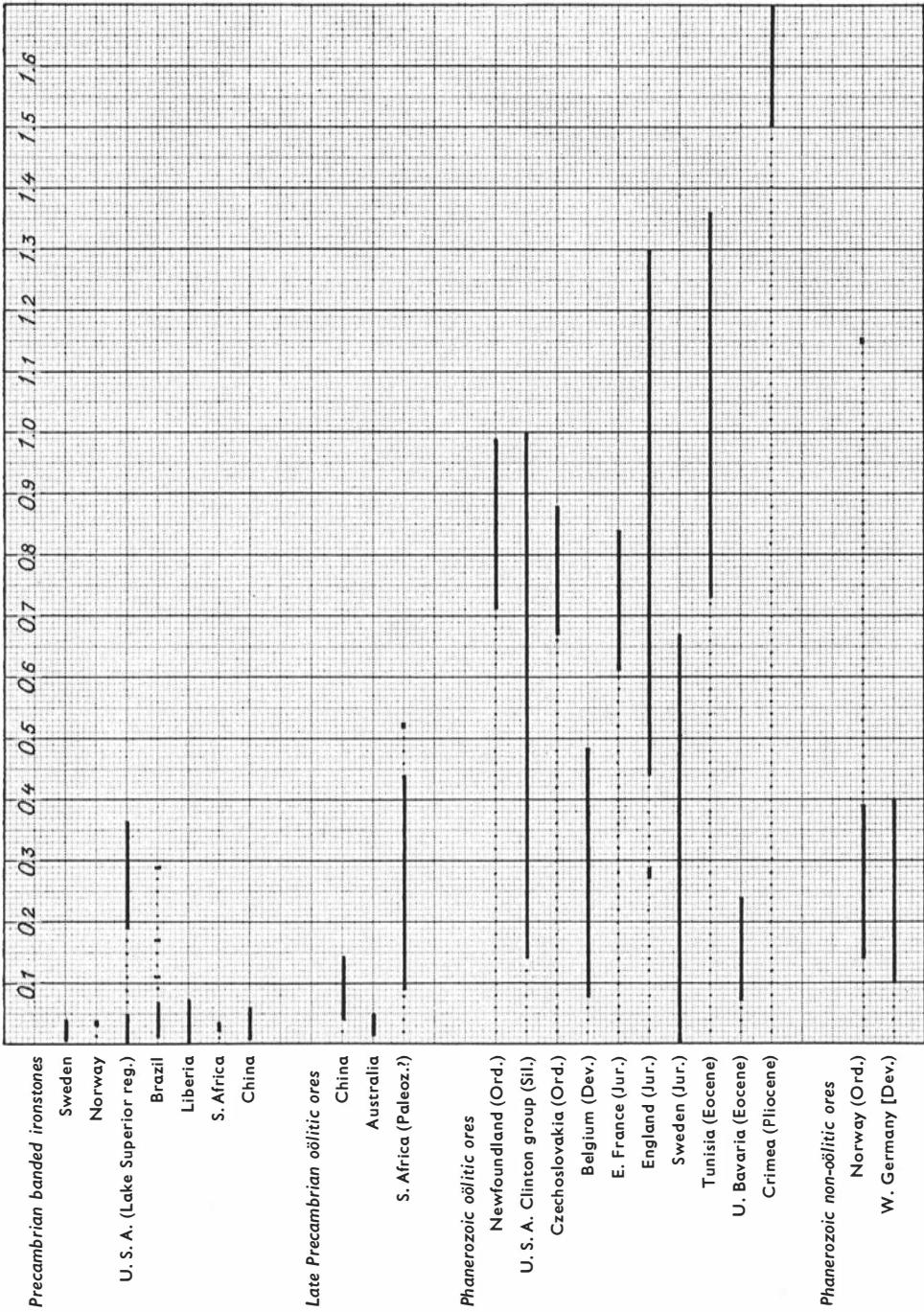


Fig. 3.1.1. Phosphorus percentages in sedimentary iron ores (see text).

continuous variation from 0 to 0.365 per cent. Special difficulties are encountered when there are reasons to suspect that the percentage of phosphorus has been increased through secondary, surficial processes. Thus the Brazilian banded ironstones are generally very low in phosphorus when unaffected by such influences, and strikingly higher figures cannot be accepted as primary features when there is no information as to possible weathering. In the diagram, therefore, three such analyses have been presented, not as an extension of the normal range, but by separate dots. For practical reasons the diagram has been ended at 1.6 per cent P; in reality the oölitic ore of Crimea ranges higher than thus shown, up to about 2.5 per cent.

A few cases which show distinct geological indications that their present content of phosphorus is due to secondary processes, have been omitted from the diagram but are duly recorded in the text. It has not been possible to indicate also percentages of iron, but such data are found in the text, in cases where they may possibly be relevant.

### 3.2. *Quartz-banded iron formations of the Precambrian*

*Sweden.* This ore type is common in Central Sweden. The ore bodies, comparatively high in iron, form beds in the lower, predominantly volcanic division of the Svecofennian Leptite formation. Their age thus is somewhat higher than that of the Grythytte slate mentioned above (p. 166). The original precipitation of the iron is held to have been in the ferric state (Geijer & Magnusson, 1944).

A great number of phosphorus determinations are available. As a rule the figure lies between 0.007 and 0.030 per cent. Although samples of hand specimen size may show considerable variations within an ore body (Geijer, 1936), from a technical point of view the phosphorus is homogeneously distributed, and different districts exhibit characteristic figures. There is no correlation between iron and phosphorus, neither in detail, as in the set of samples just mentioned, nor when comparing different occurrences. The most iron-rich deposit of this type, the main ore bed of the Stripa mine, with 50 to 54 per cent Fe, has only 0.006 to 0.007 per cent P.

The only phosphorus mineral identified in these ores is apatite. No separate analyses of hematite and quartz bands are available, to give any quantitative figure for the distribution of this mineral, and statistics from the microscopical examination of thin sections are not decisive because of the small amount of it. It may be noted, however, that the writer found, for two typical districts, Norberg and the Stripa mine (Geijer, 1936, 1938), that there is probably more apatite in the quartz seams than in those of iron minerals. In any case there has been no immediate association of iron and phosphorus in precipitation.

In a limited number of occurrences of this type higher percentages of phosphorus are found. For Utö figures of 0.08 to 0.17 per cent are recorded. The Iekorrbotten-Håksberg district has 0.085 to 0.150 per cent. All these occurrences are in zones within the migmatizing action of the Late Svecofennian granites and pegmatites, and arguments have been presented for ascribing their higher content of phosphorus to these secondary processes (Geijer & Magnusson, 1944).

In northernmost Sweden there is one large occurrence of this type, the Kallak deposit (Ödman, 1957), which also has been referred to the Svecofennian. Kallak has 35 to 38 per cent Fe and 0.04 per cent P. Like the surrounding rocks it has suffered some migmatization.

*Norway.* The large occurrences of quartz-banded ore at Sydvaranger in northeas-

ternmost Norway are geologically dated only so far that they are undoubtedly Precambrian but younger than the gneisses of the region. Their iron percentage is about 35, phosphorus is 0.035 per cent (Iron Ore Resources, 1910).

*Soviet Union in Europe.* The writer has not been able to find any analyses of unaltered iron formation from the important district of Krivoj Rog. However, numerous analyses of the rich ore bodies formed in it by secondary processes vary from 0.00 to 0.07 per cent P (Iron Ore Resources 1910), indicating a probably low percentage also in the protore.

*United States.* The Precambrian of North America, and particularly that of the Lake Superior region, represents the province with banded iron formations from which most information on the nature of these sediments has been obtained. This is due to the economic importance of the ores formed by secondary processes, and the scientific studies it has stimulated. Also, such formations occur there in at least two Precambrian systems, and they are in part only little affected by metamorphism, so that the original characters can be discerned. Much attention has been given to the distribution of phosphorus, but the concentration into workable ore bodies has, at least frequently, been accompanied by an increase in this element (Van Hise & Leith, 1911), and analyses of iron formations certainly untouched by such chemical alteration make up only a limited portion of the material at hand.

Of the iron formations of Keewatin age, which antedate the ores of Central Sweden by several hundred million years, the Soudan of the Vermilion Range, Minnesota, is reported to show, as average at Ely, Fe 28.97 and P 0.022 per cent, while one section poor in iron (16.20 per cent) has 0.042 per cent P (Van Hise & Leith 1911). It is of interest to note that there occur in the formation also seams of graphitic slate, indicating the existence of organic life in the basin of deposition.

The extensive and thick iron formations of the Animikie are considered of Proterozoic age. They were involved in the Penokean orogeny, which is dated at about 1.7 billion years ago (Goldich *et al.*, 1959). Oölitic textures are frequently encountered in these formations but do not form a regular feature.

Among these formations the Biwabik, of the Mesabi Range, is reported to contain, exclusive of the hematite and limonite ores due to secondary concentration, an average of Fe 27.0 and P 0.035 per cent (Gruner, 1946). Surprisingly, several analyses of its silicate phase show no phosphorus at all (Van Hise & Leith, 1911). Phosphorus percentages comparable to the average of the Biwabik formation are reported from other occurrences regarded to be of the same age. Thus, for the Gogebic Range the figure for the carbonate phase varies from traces to 0.030 (Irving & Van Hise, 1892). Analyses of "ferruginous chert" from the same district average 0.062 per cent P (Van Hise & Leith, 1911); however, the various forms covered by this term are generally somewhat affected by secondary alteration. Figures from the Marquette Range are 0.01 per cent in "cherty siderite", and 0.03 to 0.05 per cent in "grünerite-magnetite-schists" (Van Hise & Bayley, 1897). On the Menominee Range, typical iron formation has about 0.01 per cent (Bayley, 1904).

In a marked contrast to these always very low percentages of phosphorus stand the figures characteristic of certain occurrences of the same age, and probably originally connected with them. These are the Iron River and Crystal Falls districts, and the Cuyuna Range. Iron River has been the subject of an interesting study by James (1951, 1954). Beside the common original mineral variations of the iron formations there occurs also a sulfidic phase, a carbonaceous shale rich in pyrite. Phosphorus percentages are given by James (1954) as follows: carbonate phase 0.20–0.40,

silicate phase 0.19–0.24, and oxide phase (general sample) 0.31; the sulfidic phase has only 0.09 per cent. To judge from the descriptions, these percentages must be original features of the formation and not due to any later additions. From the neighbouring Crystal Falls district Pettijohn (1952) gives an analysis of cherty siderite with 0.365 per cent P.

The Cuyuna Range presents a more variable, and in part remarkably high content of phosphorus. Van Hise, Leith & Zapffe, writing when mining on this range had recently started, say on the subject: "Phosphorus has been concentrated with the iron during the secondary concentration of the ores. It is probable, for reasons similar to those discussed ... for the Mesabi district, that phosphorus, leached from the overlying Cretaceous rocks, has been added to the ore during its secondary concentration" (Van Hise & Leith, 1911, p. 224). Later data do not, so far as the writer has been able to find out, provide sufficient ground for any conclusion as to the phosphorus content of the Cuyuna Range iron formation before it was subjected to secondary processes. Two facts, however, indicate that perhaps the conclusion just quoted may be valid for the whole formation: the occurrence also of low phosphorus figures, comparable to those of the Biwabik formation, and indications that the Cuyuna formation may originally have been continuous with the latter (e.g. Grout & Wolff, 1955).

*Brazil* is one of the countries in which the banded iron formations reach their greatest development, with the "itabirites" of the Minas series, which consist chiefly of hematite and quartz. The series has recently been reported to be "probably younger than 1350 m.y. and definitely older than 500 m.y." (Herz *et al.*, 1961). The average iron percentage is higher than in most occurrences of this type. Rich hematite ores have been formed through secondary concentration. It is difficult to find figures which certainly represent the sediments entirely unaffected by such processes, but those available appear to give sufficiently clear indications of the magnitude of the original content of phosphorus.

From the Itabira district Sanders (1933) reports analyses representing samples of itabirite covering 8599 feet of the formation exposed in tunnels, which average Fe 49.1 and P 0.01 per cent. Scheibe (1932) publishes two analyses of moderately iron-rich itabirite, with P 0.011 and 0.017 per cent, respectively. For the Congonhas district Guild (1957) estimates the Fe percentage to average 40; ten P determinations are given, seven of which range from 0.015 to 0.07 per cent while the remaining three have 0.11, 0.17, and 0.29 per cent. It is not clear whether the higher values may be due to surficial infiltration. No phosphate mineral has been identified in the itabirites. Thus Scheibe (*op. cit.*, p. 39) states that "bisher konnten keinerlei Phosphor-Mineralien nachgewiesen werden". And Guild writes (*op. cit.*, p. 44): "The small but uniform phosphorus content is noteworthy. No phosphate minerals have ever been identified, as far as is known to the writer." If this should apply also to such a high P percentage as 0.29, it must be regarded as an indication of the presence of earthy secondary phosphate. Therefore, in Fig. 3.1.1. the three higher values have been plotted separately. The richer Brazilian ores are uniformly low in phosphorus. A production of 385000 t from one deposit had Fe 68.7 and P 0.036 per cent (Symposium, 1952, I).

*Liberia* has extensive deposits of banded ironstones, which like the Brazilian itabirites are often comparatively high in iron and contain large, secondarily formed hematite ore bodies, rich in iron and low in phosphorus. The writer is indebted to Mr. Christer Danielsson, of the Liberian American-Swedish Minerals Co. (LAMCO), for permission to quote a number of analyses, carried out at the Stråssa laboratory of



the Grängesberg company and representing various occurrences of Liberian itabirites. The low phosphorus content of the rich ores indicates that the secondary processes to which they are due were not accompanied by any appreciable increase in this element. As to the itabirites unaffected by secondary concentration of iron, which are those considered here, there is a possibility that surface processes associated with tropical weathering may have led to some secondary introduction of phosphorus (O. H. Ödman, personal communication). Therefore samples of drill cores from greater depths are of special interest.

Three ten meter sections in a tunnel near the huge Main Orebody of Nimba show 0.016, 0.021, and 0.033 per cent P. Samples from the same district which are reported to contain also limonite present higher figures, up to 0.078 per cent P. Six core samples from as many drill holes at Nimba vary from 0.002 to 0.023 per cent P; the average is 0.014. It appears probable, therefore, that the higher figures in the limonitic itabirites are due to surface processes. However, there are available also three drill core samples from Putu, seemingly unaffected by such influences, which give 0.013, 0.067 and 0.073 per cent P.

From O. H. Ödman the writer has received a drill core sample from Bong. This is a very finely quartz-banded ironstone. Microscopic examination shows it to be metamorphic in the amphibolite facies. Beside magnetite and quartz, which are the chief components, it contains an actinolitic hornblende, biotite in an amount unusual for a banded ironstone, and some apatite. A sample representing 5 cm thickness of this finely banded ironstone has 0.030 per cent P (R. Blix, analyst).

From the above data it appears that the Liberian itabirites normally are below 0.035 per cent P. However, the figures from Putu indicate the possible presence of higher percentages also in occurrences which are not affected by secondary infiltration. Therefore it has seemed correct to indicate in Fig. 3.1.1 the range of the Liberian itabirites as extending up to the maximum figure from Putu.

*South Africa* has extensive occurrences of banded ironstones, representing several stratigraphical divisions of the Precambrian. The following data are taken from the monograph by Wagner (1928). The three systems in which such sediments occur are the Swaziland ("early pre-Cambrian" according to Wagner), the Ventersdorp-Witwatersrand ("pre-Cambrian"), and the Transvaal system ("pre-Cambrian?"). The former two are treated together in Wagner's general description. Phosphorus figures are reported from Swaziland occurrences in Transvaal, three beds giving, respectively, Fe 28.4, P 0.036 per cent; Fe 29.22, P 0.02 per cent; and Fe 25.20, P 0.02 per cent. The Transvaal system, the youngest of the three and further dated only as pre-Devonian, therefore possibly of Paleozoic age, contains the enormously extensive magnetite bed of the Pretoria series. This unit is oölitic throughout, and not quartz-banded. As average figures from 43 representative samples, Wagner reports Fe 48.00, P 0.24 per cent. "Occasional detrital grains of apatite were noted under the microscope, but in what form the bulk of the phosphoric oxide, indicated by analyses, is present is not known" (Wagner op. cit., p. 83). A thinner oölitic seam higher up in the series (the Clayband or Timeball Hill horizon) is reported to have Fe 56.14, P 0.52 per cent.

*China.* In northern China—Manchuria and Chihli—a banded iron formation is developed with extensive and thick beds. To a smaller or greater extent, secondary enrichment has taken place. From the typical and important An-Shan group Tegen-gren (1921–1923) reports the following analytical data:

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Ore body	Number of analyses	Fe, per cent		P, per cent	
		Variations	Average	Variations	Average
West An-Shan	7	33.18–44.63	38.17	0.020–0.060	0.034
Ta-Ku-Shan	13	31.4–45.18	41.01	0.006–0.041	0.024
Ying-Tao-Yüan	7	48.06–62.43	57.62	0.015–0.041	0.024

Of these, the Ying-Tao-Yüan represents enriched ore throughout; in the others, relatively high iron percentages presumably are due to local enrichments. Apparently the phosphorus percentage has not been influenced by the secondary process.

*India.* Figures for the phosphorus in the large deposits of banded iron formations in India have not been available. Assuming, however, that the process which gave rise to the large bodies of secondary high-grade ores in these sediments did not essentially change the amount of phosphorus—a condition supported by evidence from Brazil and China—the character of the original sediment in this respect can be approximately judged from the phosphorus in these rich ores.<sup>1</sup>

The Noamundi deposit, according to a typical analysis, has Fe 61.94 and P 0.082 per cent, while 15 analyses of deposits in the Bastar, Drug, and Chanda districts range in iron from 62.91 to 68.85, and in phosphorus from 0.02 to 0.09 per cent, with an average of 0.065 (Symposium, 1952, I). It seems possible, from these figures, that the banded iron formations of India may be slightly higher in phosphorus than is the normal for this type.

*The mineral form of phosphorus in the banded iron formations.* Where a phosphate mineral is reported from these formations it is always apatite. It must be noted, however, that James (1951) from an analysis of cherty iron carbonate from Iron River, compared with the mineral composition found by microscopical examination, inferred that phosphorus in this case probably occurs combined with aluminium. The presence also of iron or aluminium phosphates in the secondarily enriched ores of the Lake Superior region is probable (Van Hise & Leith, 1911), but the Iron River example is from an iron formation unaffected by such processes. Since the formation of Iron River and the adjacent Crystal Falls district by its higher percentage of phosphorus forms an exception among the Lake Superior iron formations, the probable presence of an aluminium phosphate may be significant.<sup>2</sup>

### 3.3. *Oölitic ores of the Phanerozoic systems*

With the same character in all essential features these ores appear in the stratigraphical column from the Cambrian to the Pliocene, but their greatest development was in the Lower Paleozoic and the Jurassic. The range in iron content is about the same as in the quartz-banded iron formations, and the original mineral forms of the iron are the same: carbonate, silicate, and oxide (or hydrate).

The very large and iron-rich Wabana deposit of *Newfoundland* is the geologically oldest of the more important occurrences of this type, being of Ordovician age. Its geology has been the subject of a study by Hayes (1915), who also paid special attention to the distribution and way of occurrence of the phosphorus in it. From the many

<sup>1</sup> Taking into account also the change in density, the phosphorus figures here quoted are to be somewhat increased—by a factor of about 1.2–1.4—to give the percentage in the original sediment, under the above assumption.

<sup>2</sup> About lazulite compare p. 176.

analyses the following figures may be quoted as typical. Two analyses of average samples of ore from "Zone 2" ("Dominion bed") show 0.71 and 0.88 per cent P, and two from the lower and the upper part of the other ore bed of workable thickness, in "Zone 4" ("Scotia bed"), 0.99 and 0.92 per cent P, respectively. As to the source of the phosphorus, Hayes writes: "The fossil shell fragments have a composition of between 60 and 70 per cent calcium phosphate, and the lime and phosphoric acid present in the ore are derived principally from this source" (op. cit., p. 65-66).

The iron ore beds of Silurian age in the *eastern United States* ("*Clinton ores*"), with westward extensions even into Wisconsin, probably represent the most extensive horizon of such ore deposition known anywhere. It is difficult to present a fair summary of the percentage of phosphorus and its variations in these ores, but the following data may be sufficiently illustrative for this comparison. In the type district, in New York State, P is reported to vary between 0.25 and 1.0 per cent (Iron Ore Resources, 1910). For the chief province of mining based on these ores, the Birmingham district in Alabama, the following figures, taken from a report by Burchard, Butts & Eckel (1910), appear to give a representative picture. Carload lots of ore from the "Irondale Seam" vary in phosphorus from 0.14 to 0.67 per cent. Ore from other beds shows approximately the same range, and a percentage between 0.30 and 0.40 is very common. It is clear that the Clinton ores, though they are also known as "fossil ores", on the whole have a phosphorus content which is only about half the figure characteristic of the Wabana deposit.

Of the little important occurrences in the Paleozoic of Europe, the Ordovician ores in *Czechoslovakia* carry 0.67-0.88 per cent P (Iron Ore Resources, 1910). In the Upper Devonian of *Belgium* there is an extensive bed of oölitic ore, formerly worked. Data on its content of phosphorus are somewhat conflicting. Six analyses (Iron Ore Resources, 1910) report P figures from 0.076 to 0.484 per cent, with an average of 0.331. A later presentation (Symposium, 1952, II) has three analyses, with 0.04, 0.08, and 0.22 per cent P. The text comment (op. cit., p. 80) is that "the content of phosphorus is low and only rarely reaches 0.5 per cent".

The greatest development of oölitic ores in Europe is found in the Jurassic. The "minette" ores of *eastern France (Lorraine)* are remarkably uniform in their content of phosphorus. Thus thirteen representative analyses (Symposium 1952, II), varying in Fe between about 31 and 37 per cent, have P from 0.61 to 0.74 and in one case 0.84 per cent. The ores of *eastern England* exhibit somewhat greater variations in phosphorus (Iron Ore Resources, 1910). The Main Seam of the Cleveland ironstone, in the Middle Lias, is reported to vary between 1 and 3 per cent phosphoric acid (0.44 to 1.32 per cent P). Typical values for the Northamptonshire ironstone, of Lower Oölite age, are 0.65 per cent P in Northamptonshire and 0.52 in Rutlandshire. From the Frodingham ironstone of Lincolnshire, which occurs in the Lower Lias, two analyses give 0.27 per cent P. A bed in the Middle Lias of Leicestershire carries 0.60 per cent P, and two analyses from the rather iron-poor "Marlstone" of Oxfordshire give 0.28 and 0.29 per cent.

An interesting outlier of this large province of iron sedimentation is represented by the Liassic of southernmost *Sweden (Scania)* (Hadding, 1933; Palmqvist, 1935). Beside the common form of oölitic ore with siderite and chamosite, also beds of massive siderite, without any oölitic texture, occur in the sedimentary sequence. From the many analyses published in the cited works it seems that phosphorus is, on the whole, somewhat lower in the latter ore type than in the oölitic one. Thus, considering only analyses with more than 30 per cent Fe (the average for ore above this

figure is about 35 per cent), 9 analyses of oölitic ore show P varying from traces to 0.67 per cent and averaging 0.45, while 27 analyses of non-oölitic siderite beds give P from traces to 0.42 per cent, with the average at 0.10 per cent.<sup>1</sup> The difference may possibly to some extent be due to detrital apatite in the oölitic beds, as these contain an unusual proportion of "heavies" as oölite cores.

These Swedish ores are unique among Phanerozoic ones in showing a variation in phosphorus content down to only traces. It is improbable, however, that this should reflect any special nature of the occurrence. Most ore analyses are made for technical purposes and represent comparatively large samples. The Swedish occurrence, on the other hand, has been the subject of a thorough geochemical investigation which may be expected to have exposed details in the distribution of phosphorus to a greater degree than is generally attained.

Among the comparatively few occurrences of oölitic iron ores in the Tertiary, that of Djebel Ank in southern *Tunisia*, SE of Gafsa, is of special interest from the point of view considered here. It forms a bed in the Lower Eocene sedimentary sequence which contains also the very extensive phosphate beds of the Gafsa region (Berthon, 1922). Downwards only 9 meters' thickness of conformable sediments separate it from the uppermost bed of phosphate rock. According to five analyses (Berthon, op. cit.) the Djebel Ank ore, rather rich in iron for the type (Fe 46.00 to 52.60 per cent), varies in P percentage from 0.73 to 1.36.

Of Eocene age are also the lean ore beds of Kressenberg in *Upper Bavaria, Germany*. Gumbel (1893) reports their P percentage as 0.24; a later report (Symposium, II, 1952) gives only 0.07 per cent.

Younger are the extensive oölitic ore beds of the Kertsch peninsula on *Crimea*, in the Soviet Union, being interstratified in a series transitional between the Miocene and the Pliocene. Iron is mainly in the form of limonite. Manganese is present in some quantity, locally up to 8 per cent. This uneven distribution, like the mineral form of the iron, indicates the probability of surficial influences. Phosphorus is reported to be 1.5–2.5 per cent (Iron Ore Resources, 1910, p. 514). Vivianite has been identified in the ore (ibid.). It is certainly of secondary origin. Presumably a note on the occurrence of vivianite forming bivalve shells in Kertsch sediments (Piveteau, 1952, p. 26) refers to the occurrence in the ore.

Normally, phosphorus in the Phanerozoic oölitic ores is in the form of phosphorite or fossil parts, and the occurrence of vivianite at Kertsch is exceptional. Mention must be made in this connection, however, of the equally rare occurrence of lazulite in sedimentary iron ores. The Ordovician ore of Moncorvo in Portugal is metamorphic, but there are indications that it may be correlated with oölitic ores of the same age. In the Moncorvo ore, apatite is said to occur as an accessory mineral, and lazulite as a "very rare" one (Neiva, 1953). It seems possible that the appearance of the latter in this unusual environment may be due to metamorphism of a somewhat altered oölitic ore.

### 3.4. *Oölitic ores in the Precambrian*

Although oölitic textures are reported, even as occurring in some frequency, from several of the iron formations of the Lake Superior region, they cannot be regarded as any such regular and characteristic feature of the Precambrian ironstones—even

<sup>1</sup> The data here quoted are calculated from the  $P_2O_5$  figures in the analyses. In Palmqvist's thesis, analyses of ore grade also present the phosphorus as P, but these figures are consistently too low, giving only about half the amounts corresponding to the  $P_2O_5$ .

when taking into account the possible effects of metamorphism—as they are in the Phanerozoic ores. There are known, however, a few occurrences referred to the Precambrian which in this respect are wholly similar to the Phanerozoic ores.

The magnetite bed in the Pretoria series in *South Africa* ("Precambrian?") has already been mentioned (p. 173). A remarkable development of oölitic hematite ore is found in the Hsüan-Lung region of *northern China* (Tegengren, 1921–1923). These ores are, among oölitic ones, those richest in iron, and are unique also in being largely developed with a stromatolitic texture. They are interbedded in a non-fossiliferous series, which is overlain by fossiliferous Cambrian strata. It is regarded as clearly established that the ore-bearing series is Precambrian, and to be correlated with the Hu T'Ö system in the Shansi province. The age has therefore been given as Neo-Proterozoic (Tegengren, op. cit.).

The amount of phosphorus in the Hsüan-Lung ores is illustrated by the following figures (from Tegengren, op. cit.). The stromatolitic phase, according to 27 analyses from 4 occurrences, averages Fe 57.08 and P 0.093 per cent (with an amplitude of 0.04–0.17); for the purely oölitic phase the corresponding figures from 34 analyses and 6 occurrences are 55.15 and 0.143 per cent (0.05–0.42).

Approximately corresponding in age to the Hsüan-Lung deposits seen to be the recently discovered oölitic ores in *northern Australia*, at Roper Bar and Constance Range, which are referred to the Upper Proterozoic (Edwards 1958). These, too, are typically oölitic deposits, with an unusually high content of iron. Five analyses from Roper Bar quoted by Edwards show P percentages from 0.013 to 0.046, presumably the lowest figures so far recorded from any typical oölitic ore.

It is worthy of note that all these oölitic deposits are referred to a late—or even a very late—stage of the Precambrian.

### 3.5. *Non-oölitic Phanerozoic ores*

Typically oölitic ores form the overwhelmingly greater part of the iron sediments in the Phanerozoic systems, and only two other types (and provinces) need be considered here.

In the Caledonides of *northern Norway* sedimentary iron ores are widely distributed as beds of great extent. They are intercalated in a series of sediments of Cambrian to Silurian age, and are generally assumed to belong to the Ordovician. Metamorphism is rather high, and the iron minerals of these siliceous ores are hematite and magnetite. No traces of oölitic textures are reported. However, the metamorphic development is such that original features of this nature may have become obliterated. Yet it seems improbable that the ores ever have been oölitic throughout. Quartz banding occurs as a local development in several deposits (Bugge, 1948; Foslie, 1949) and is characteristic of the whole of one deposit, Naeverhaugen (e.g. Vogt, 1910). The content of phosphorus is illustrated by the following data. For the most important district, Dunderlandsdal, Bugge (op. cit.) quotes 46 analyses with an amplitude of 0.062–0.365 per cent P and an average of 0.19 per cent. About the occurrences in the Ofoten district Foslie (op. cit.) gives analyses from the Håfjell horizon with 0.23–0.39 per cent P, while sorted ore from the Sjøfjell horizon is reported to contain (with 37.3 per cent Fe) 1.15 per cent P. The only phosphorus mineral identified in these ores is apatite, which is rather common as grains of microscopical size. Its distribution in the ore beds is of interest. Thus Vogt, in a general characteristic of these ores, states that it occurs chiefly in the quartz stripes and only exceptionally in those of ore minerals.

And Foslie, in describing the quartz-banded phase of the phosphorus-rich Sjäfjell horizon, says that the apatite varies greatly in amount between the bands, and not regularly with the magnetite: "we often find a high content of apatite in light bands" (op. cit., p. 97).

An entirely different type of iron ore is represented by the hematite beds in the Devonian of the Lahn-Dill region in *western Germany*, which are interstratified in a series of volcanics and sediments.<sup>1</sup> It is generally held that the iron, and the silica which was precipitated with it, were contributed to the sea water through fumaroles or related forms of volcanic after-action. Two types of ore are discerned, viz., siliceous hematite and "Flusseisenstein". The former represents the ore precipitate when not substantially mixed with products of the normal sedimentation, the latter may be regarded as a variation diluted by contemporaneously deposited calcite. In its chief components, hematite and silica, the siliceous hematite is similar to the richest varieties of the quartz-banded ores of the Precambrian in Sweden, but there is no tendency towards the development of banding. Phosphorus is reported to vary in this type between 0.3 and 0.4 per cent, and in the "Flusseisenstein" between 0.1 and 0.2 per cent (analyses cited by Schneiderhöhn 1941). Fossils are occasionally found in the main hematite bed.

#### 4. Carbonaceous sediments in the Precambrian

The occurrences of carbonaceous rocks among sediments of Precambrian age are commonly regarded as proof of the existence of organic life in the waters in which these sediments were deposited. And "if the carbonaceous residue is a rough quantitative measure of life, the Archean seas supported as large a population as later seas, though the forms present may have been simple in structure and monotonous in kind" (Pettijohn, 1943, p. 948). It must be assumed that these organisms contained an appreciable amount of phosphorus. For instance, recent Peridineae (dinoflagellates) are known to carry C and P in the proportion 100:1.7 (Kalle, 1958). Study of the carbonaceous rocks, therefore, at least of such rich in carbon, might possibly contribute to the understanding of the role of phosphorus in Precambrian sedimentation.

"Black slates" (or shales), coloured by a low to moderate amount of evenly distributed carbon—generally graphite, but in cases of low metamorphism also organic compounds—are found in many sedimentary sequences of the Precambrian. The Grythytte slate of the Svecofennian in Sweden has already been referred to (p. 166), and it was pointed out that its content of phosphorus is not higher than what may be wholly due to detrital grains of apatite. The graphitic slates that are widespread in the Skellefte district in northern Sweden, and held likewise to belong to the Svecofennian cycle, to judge from an analysis of a typical occurrence (Gavelin 1939) appear to be similar in this respect: with 1.39 per cent C, this slate contains 0.03 per cent P. Several analyses of such rocks from the Precambrian of Finland give comparable figures, but one, from Puolanka (Väyrynen, 1928), has the notably high P percentage of 0.35. In this sample, C was not separately determined but recorded with H<sub>2</sub>O as loss at ignition, 2.93 per cent.

Of special interest in this connection is the carbonaceous and pyritic shale of the Iron River district, Michigan (James, 1951, 1954), as it forms a member of the iron

<sup>1</sup> For a clear summary of the geological conditions, see Schneiderhöhn, 1941.

formation whose phases with non-sulfidic iron—oxide, carbonate, silicate—all are remarkably rich in phosphorus (compare above, p. 171). An analysis of the shale, with 38.70 per cent pyrite, has C+org. matter 7.60 per cent (total C 7.28 per cent) and P 0.09 per cent. Lenticular bodies of anthracitic coal occur in this shale (Tyler *et al.* 1957). They are interpreted as boudins or parts of a once continuous bed. This view is supported by the fact that thin seams of shale occur locally within the coal lenses. On the other hand, the latter show considerable resemblance to the "kolm" concretions of the bituminous Cambrian shale in southern Sweden. An analysis of Iron River coal reports 16.30 per cent ash, almost all silica and with only traces of phosphorus.

It has seemed of interest to consider also the graphite occurrences of Norrbotten Län, northernmost Sweden, as they represent unusually carbon-rich sediments of Precambrian age. These deposits are held to belong to the Karelian cycle (Ödman 1957). The age of this cycle is a much-debated question, because absolute age determinations give another picture of its relation to the Svecofennian than previously assumed on geological grounds. For the present purpose it may be sufficient to state that the graphite-bearing rocks are older than the Lina granite, which latter, according to a K/Ar dating of its biotite, should have a minimum age of 1540 m.y. (Magnusson, 1960).

The graphite-bearing sedimentary formation is metamorphic, in the amphibolite facies. Amphibolites are common members, but there also occur feldspar-quartz-biotite rocks, and locally limestones. Graphitic slates, similar in their general development to the Grythytte and Skellefte slates but generally higher in graphite, occur on a considerable scale. The most interesting form of carbonaceous sediments, however, is found in a part of the region where the graphite mainly occurs in beds of lesser thickness but with a much higher concentration, commonly with 25 to 45 per cent C. These graphite occurrences (Geijer, 1918) form extensive beds, generally only some meters in thickness where not structurally deformed, but in one case (Nunasvaara Crown land) even averaging about 20 meters for a strike length approaching one kilometer. The chief mineral components, apart from the graphite, are alkaline feldspars (microcline and, less frequently, sodic plagioclase) and tremolite; quartz and biotite appear in some occurrences, and a small amount of titanite is the rule. In one deposit (Meraslinka) the plagioclase is more calcic than usual (Lundqvist, 1952). Pyrite and pyrrhotite are found in greatly varying amounts, sometimes as even impregnations but more often as diffuse veinlets. The whole mineral assemblage, and also the texture, are determined by metamorphism, but the graphite is finely granular, rarely flaky. In their original development these rocks appear to have been highly bituminous dolomitic marls or marly shales.

Following D. White's general interpretation of Precambrian deposits of graphite (White, 1908) the writer (Geijer, 1918) has assumed that unicellular algae may have been the source also of those now reviewed.

No apatite has been noted in the graphite beds. In an interbedded rock in the Nunasvaara claims<sup>1</sup> deposit the phosphate is not rare. This rock, however, consisting chiefly of oligoclase and with a little graphite, is an obviously altered one, and it is doubtful whether the apatite is of sedimentary origin.

So far only one determination of phosphorus in a Norrbotten graphite has been

<sup>1</sup> What is here called the Nunasvaara claims is a private mining property, the continuation of the adjacent large one on Crown land (compare above).

published, an analysis from the Nunasvaara Crown land with 38.1 per cent C and 0.024 per cent P (Tornedalsutredningen, II, 1960, p. 243). Five new analyses (on hand specimens) have been carried out at the Mineralogical Department of the Swedish Museum of Natural History, by R. Blix; they represent 4 different occurrences and show the following figures:

Graphite deposit	Per cent P
Palo Pöviö	0.009
Maltosrova	0.011
Airikurkkio	< 0.0005
Nunasvaara claims	< 0.0005
Nunasvaara claims	0.047

Apparently even these carbon-rich sediments never show any distinct evidence of phosphorus of chemical precipitation.

Comparing the analytical data from all these carbonaceous sediments of Precambrian age with such from deposits of analogous origin in the Phanerozoic one finds, however, that also the latter often are remarkably low in phosphorus. As examples may be cited the highly bituminous and generally pyritiferous "alum shales" in the Cambrian of southern Sweden. Two analyses of such shale from Kinnekulle show P percentages of 0.12 and 0.13 respectively (Holm & Munthe, 1901). A series of shale samples from different stratigraphical levels at Hynneberg, Närke, has been chemically investigated by Assarsson & Grundulis (1961); their data give a P percentage varying between 0.14 and 0.18. Yet these sediments were deposited in a sea which teemed with life, as is evident from their high content of organic matter (often exceeding 20 per cent) and the abundance of fossil remains. And in beds of limestone which alternate with the shale, there occur not only thin conglomerates with phosphorite pebbles but also, occasionally, thin streaks of phosphorite (Westergård, 1928). The comparatively low amount of phosphorus in the shale, therefore, must be due to circumstances unfavourable for the deposition or retention of phosphorus, and not to any lack of supply.

## 5. Discussion

Phosphorus is known to be detracted from the sea water, and deposited in sediments, in a number of ways, but there is some divergence of opinion, also among those best qualified to judge, about the relative importance of these various processes. It is neither practical nor necessary to present here an extensive review of the subject, with the arguments produced, and a brief survey will suffice.

Deposition of calcium phosphate<sup>1</sup> may result from wholly abiotic processes. Thus supersaturation in the sea water, due to special conditions, is held to be an important factor. Biogenic processes to be counted with are the forming of hard animal parts, as shells and skeletons, with a substantial content of calcium phosphate, and also the reaction between calcium carbonate and ammonium phosphate derived from decaying soft tissues of animals and plants. It is also held that the ammonia produced

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<sup>1</sup> In accordance with common usage, "calcium phosphate" is here used as a collective for the various forms of apatite and other minerals—crystallized or colloidal—closely related to it in composition.



through this decay may combine with the phosphorus in the sea water, and thus serve as an agency in the transfer of phosphorus from the water to the sediment.

Of these processes, purely abiotic precipitation due to supersaturation was not, generally, earlier regarded as a major source of phosphate deposits, but in recent years, because of Kasakov's treatment of the subject (Kasakov 1937), it has received particular attention, at least with respect to the formation of continuous phosphate beds. Hard animal parts are an obvious source of phosphorus, but the tendency nowadays appears to be to regard them as one of only restricted importance. However, in the case of present-day deep-sea sedimentation, Arrhenius (1959) maintains that all the phosphorus derives from the hard parts of fish. As to sediments formed in other environments, the prevalent opinion appears to be that the soft tissues of organisms have been the chief biogenic source. Let us now see what indications a comparison between the Precambrian and the Phanerozoic may possibly give about the subject.

*Phosphorite* is virtually absent in the Precambrian, but in the Phanerozoic it is an often recurring feature, all from the base of the Cambrian upwards through the stratigraphical column. Thus its appearance was contemporaneous with the important change in the biological geochemistry of phosphorus that is marked by the first appearance of animals with hard parts containing calcium phosphate. This coincidence is certainly suggestive, indicating a probable causal relation between these two new traits in the aspects of phosphorus in marine environment.

With regard to the content of *phosphorus in iron ores* the contrast between the Precambrian and the Phanerozoic is almost equally marked. Leaving out for the moment the exceptional case of the Iron River and Crystal Falls iron formation, the Precambrian ores generally contain only about one tenth of the phosphorus percentage that is the normal one in their Phanerozoic counterparts. It lies near at hand, of course, to correlate this fact with the evidence of the phosphorite as to the probable importance of phosphatic shells as a source of phosphate in sediments. And direct evidence in this direction, probably of more than local consequence, is presented by such examples as the Wabana deposit (p. 175).

It is necessary, however, to consider also the possibility of other causes of this difference between Precambrian and Phanerozoic iron sedimentation. The contrast that is marked by the descriptive terms "banded iron formations" and "oölitic ores" must not be overrated, for there is evidence that the conditions of formation of these two types have been essentially the same, apart from the great amount of precipitated silica that is characteristic of the former. But it is, nevertheless, possible that there have been differences which may have affected also the role of the phosphorus. No quite satisfactory explanation of the formation of the oölitic ores has been given, but all investigators agree in regarding them as wholly the products of exogenous processes: solution of iron in rocks, its transport, and final deposition, through processes still not understood in detail, on the sea bottom. In the case of the banded iron formations the final stage of the process is commonly regarded as essentially similar, but concerning the ultimate source of the iron (and silica) two different hypotheses stand against each other. One implies that this source was wholly analogous to the one assumed for the oölitic ores. The other means that the iron and silica were derived from post-volcanic sources such as fumaroles or thermal springs, thus, on the whole, as assumed for the Devonian ores in western Germany. In the writer's opinion the latter interpretation is, for many occurrences, the more likely one;<sup>1</sup> in

<sup>1</sup> A survey of the arguments for either view has recently been given (Geijer, 1957).

any case it must be seriously considered. And post-volcanic processes may have introduced factors which, also without radically changing the resulting sediment, have influenced such details as the deposition of phosphorus. One looks in vain, however, for any other indication of influences attributable to such factors. And it is of interest to note that the conditions determining the quartz-banding as such (regardless of the ultimate source of the material) are fully consistent with the deposition of an amount of phosphorus comparable even to rather high figures among the oölitic ores. Examples are found in the metamorphic Paleozoic ores of Norway, particularly in the Sjäfjell horizon (compare above, p. 177).

It seems most probable, then, that the great difference in phosphorus content between Precambrian and Phanerozoic iron ores of sedimentary origin is not caused by factors related to the possibly different sources of the iron.

There is a regrettable scarcity of absolute age determinations of sediments representing the later Precambrian stages, and the available data do not exclude that even the youngest typical banded iron formation may be considerably older than 1000 m.y. This leaves a wide gap in time between it and the oölitic ores of late Precambrian age if, as seems clear, the latter have only shortly antedated the Cambrian. Obviously the evidence that may be obtained from them is especially important. Unfortunately, the occurrences are few, and the indications they give are to some extent contradictory. The Pretoria series of South Africa shows a range in phosphorus fully comparable to that of Phanerozoic ores. But its age can be determined only so far that it is pre-Devonian, and younger than the certainly Precambrian systems of the region. Thus, a Lower Paleozoic age is not excluded. The Hsüan-Lung deposits in China have a characteristic content of phosphorus, higher than is found in any banded iron formation (the Iron River-Crystal Falls district excluded), but lower than in all Phanerozoic ores. Most important, in the writer's opinion, is the fact that the distinctly Precambrian and typically oölitic ore of the Roper Bar district in Australia differs so strikingly from all the otherwise wholly analogous Phanerozoic deposits by having a percentage of phosphorus within the low figures that are normal for the Precambrian banded iron formations. So far as the available facts indicate, therefore, it must be assumed that the great change in the phosphorus content of sedimentary iron ores took place at the time about the boundary between the Precambrian and the Cambrian. The facts that this change, like the first appearance of phosphorite, thus seems to coincide with the first development of phosphatic animal shells, and that, as at Wabana, cases are at hand which directly illustrate the importance of this source of phosphorus in iron ores, both illustrate the probability that this biogenic source is the main factor behind the great increase in the phosphorus percentage of iron ores. The statement that "the environments of phosphorite and ironstone deposition have many factors in common" (Pettijohn, 1957, p. 476) appears to contain the clue to the difference in phosphorus content between Precambrian and Phanerozoic ores. And it must be remembered in this connection that the sedimentary environment of many Precambrian iron formations must have been wholly comparable to that of the iron sediments referred to in the quotation—apart, of course, from the aspects of organic life.

The great difference in content of phosphorus between the Phanerozoic and the Precambrian ores must not lead to an overlooking of the fact that the amount of phosphorus in the latter, though very low, is a practically constant feature in them. With the exception of only one case, related above, the mineral form of this phosphorus is apatite. The total absence of any minerals of detrital origin, at least in many

Swedish occurrences, shows that the phosphate must be due to chemical precipitation. Whether this process has been a wholly abiotic one cannot be decided, but appears most probable.

Before leaving the evidence supplied by the iron ores the possibility of the precipitation of phosphorus in direct connection with that of iron must also be considered, as it is a process noted and much discussed with reference to sedimentation in fresh-water bodies. It is held (e.g., Einsele, 1936, 1938; Ohle, 1937) that oxidation of the dissolved iron may lead to the extraction of phosphorus from the water in two ways: by the forming of iron phosphate, and by the absorption of phosphorus in ferric hydrate; in the latter case the phosphorus may be soon returned in solution. For the (supposedly) marine iron ores of the Precambrian, however, this process appears not to be reckoned with. Not only is there an absence of minerals indicative of it, but there are also characteristic features incompatible with this hypothesis. One such fact is the relative distribution of the apatite on the seams of silica and those of iron minerals. For ore bodies as a whole the proportion between iron and phosphorus shows irregular variations. No relation is found between the amount of phosphorus and the form in which the iron is precipitated. This is particularly striking in the Iron River iron formation, because of its higher phosphorus percentage: no distinct difference is found between phases with ferrous iron as carbonate or silicate, and ferric oxide.

The oölitic ores do not present any indications in another direction. Thus it must be concluded that precipitation of phosphorus in direct connection with that of iron cannot have substantially contributed to the content of phosphorus in marine iron ores.

Since phosphatic shells cannot have played any role in the marine geochemistry of phosphorus during the Precambrian, and precipitation together with iron is likewise excluded as a source of this element in the sediments of the time, there only remain as possibilities the abiotic precipitation of calcium phosphate and reactions incited by the decay of soft organic tissues. Evidently, these sources together were inadequate to produce phosphorite or to impart to sedimentary iron ores more than a percentage of phosphorus very distinctly below that of later times and even that calculated to be the average figure for the earth's crust.

Of these possible processes the abiotic one must be assumed to have been regulated by essentially the same conditions during the Phanerozoic as in Precambrian time. It seems most probable, therefore, that the rather insignificant role indicated for it in Precambrian sedimentation has been, on the whole, characteristic also of the Phanerozoic.

The same applies to the "semi-biogenic" process which implies interaction between phosphorus in the sea water and ammonia derived from decaying organisms.

Somewhat different are the indications with regard to phosphorus from soft organic tissues. Certainly, phosphorus of such derivation has not left any significant traces in Precambrian sediments, in spite of the many signs of the frequency of life in the seas of the time. But this negative evidence is valid only so long as no other forms of life are counted with, than those then in existence. One would not be justified in concluding that later forms might not have offered—and still offer—conditions more favourable for a concentrated deposition of phosphorus from this source.

The percentage of phosphorus most unusual in a Precambrian banded iron formation which characterizes the Iron River and Crystal Falls parts of the Animikie, may perhaps be correlated with the uncommonly strong evidence of organic life in the waters where deposition took place. Certainly, carbonaceous slates are found also

elsewhere in association with banded iron formations—they even occur in the Keewatin, as on the Vermilion Range—but the districts in question appear to represent unusual conditions also in this respect. Alone, however, the abundance of organic matter can hardly explain the amount of precipitated phosphorus; the explanation may perhaps lie in a combination of this source and some other, incidental factor.

The *carbonaceous sediments* require few comments, as those of the Precambrian do not in their content of phosphorus exhibit any characteristic differences from the Phanerozoic ones. The low amount of phosphorus in sediments of this nature has been variously explained. Goldschmidt held that the  $H_2S$  generated by the decay of organisms has, by the formation of pyrite, detracted all the iron in solution and thus prevented the precipitation of iron phosphate (Goldschmidt, 1954, p. 530). In view of what has been pointed out above concerning precipitation of phosphorus in combination with iron, this hypothesis does not appear satisfactory. Biological processes have also been cited as possible explanations of the inability of sediments of this nature to retain phosphorus, and seem more likely factors.

*Postscript* (Sept. 1962). A recent note by C. Downie (Geol. Soc. London, Proc. no. 1600, 1962) has called the writer's attention to the occurrence of phosphorite nodules in the Torridonian of Scotland, earlier reports on such having been overlooked. According to Downie, associated microfossils indicate similarity to the Riphean of western Soviet Union; apparently also the Visingsö formation might be mentioned. Data on phosphorite nodules in the Riphean (1961) did not become known to the writer until this paper was already in proof. There are no absolute datings for anyone of these three formations, and they may extend anywhere between the approximate age limits of 600 and 1000 m.y., the latter figure being the possible maximum age at least for the Visingsö. It is possible, therefore, that formation of phosphorite in appreciable amounts from soft organic tissues began somewhat earlier, and has been of greater relative importance, than assumed above. The conclusions with regard to abiotic sedimentation of phosphorus remain unmodified, because of the evidence from the earlier Precambrian stages.

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