Stratigraphic Significance and Petrology of Phosphate Nodules at Base of Niobrara Formation, East Flank of Black Hills, South Dakota

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By HARRY A. TOURTELOT *and* W. A. COBBAN

SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

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Phosphate replaces marlstone in microenvironments formed by mollusks

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STRATIGRAPHIC SIGNIFICANCE AND PETROLOGY OF PHOSPHATE NODULES AT BASE OF NIOBRARA FORMATION, EAST FLANK OF BLACK HILLS, SOUTH DAKOTA

By Harry A. Tourtelot and W. A. Cobban

ABSTRACT

In the Black Hills region, phosphate nodules are concentrated in a thin bed at the base of the Niobrara Formation where the Niobrara rests sharply on the underlying Carlile Shale. Identifiable fossils, mostly internal molds of inocerams and ammonites, have been found in phosphate nodules at a single locality near Fairburn, Custer County, S. Dak., and record a part of Turonian time (Late Cretaceous) not previously known to be represented in the region. In addition to small gastropods, shark teeth, and ray teeth, the fauna includes the following forms: *Inoceramus* sp., *Ostrea* sp., *Veniella* cf. *V. goniophora* Meek, *Baculites* aff. *B. mariasensis* Cobban, *Allocrioceras* sp., *Scaphites* cf. *S. mariasensis* Cobban, *Scaphites* cf. *S. preventricosus* Cobban, *Scaphites* cf. *S. corvensis* Cobban, *Scaphites sagensis* Cobban, and *Scaphites frontierensis* Cobban. The late Turonian age is assigned to the assemblage inasmuch as *Allocrioceras* and the baculite are known only from Turonian rocks, and the inocerams and scaphites more closely resemble Turonian species than later ones.

At most localities, the phosphate nodules seem to be scattered along the basal plane of the Niobrara Formation. At some localities, however, the nodules lie in a bed an inch or so thick. The bed is cemented by pyrite, much of which is oxidized to iron oxides and gypsum. The nodules consist of carbonate fluorapatite that contains preexisting material such as quartz, clay, biotite, and constituents of organic origin such as radiolarians, foraminifers, and *Inoceramus* prisms, the latter two of which have been replaced by barite. The carbonate fluorapatite makes up the groundmass of the nodules and also occurs in ooids with concentric structure distributed in the nodule in such a random way that the ooids cannot be detrital in origin.

Pyrite occurs in ooids and in the groundmass of the nodules, as well as in the matrix of the nodule bed, and is inferred to have been formed prior to the cementation of the nodule bed. Some of this early pyrite is included in barite that replaces parts of the groundmass and ooids. Barite does not occur in the matrix of the nodule bed. The pyrite, which formed later than the barite, extends from the bed matrix into veins in the nodules and is locally mixed in the veins with calcite. A few small patches of calcite, partly replaced by barite, seem to represent recrystallization or diagenetic segregation of calcite of organic origin at the time of nodule formation.

The nodules are interpreted to have been formed by the replacement of marlstone by phosphate in microenvironments created by the closed or semiclosed systems resulting from the rapid burial of ammonites and of pelecypods with their shells naturally articulated or accidentally opposed. Laboratory investigations by L. L. Ames, Jr., outline the conditions under which carbonate can be replaced by phosphate to form carbonate fluorapatite. We infer that similar conditions prevailed in a marlstone unit that was a precursor to the Niobrara Formation. This unit was eroded, leaving the nodules concentrated along the sharp contact at the base of the Niobrara Formation, where they are typical remanié fossils.

The pyrite in the nodules is a normal diagenetic mineral and was formed from sulfide resulting from the probable bacterial reduction of sulfate at the time of nodule formation. The pyrite in the matrix of the nodule bed was formed from bacterially reduced sulfate from the pore water of the marlstone that covers the bed. The origin of the barite is difficult to interpret. Barite could have formed during the erosion of the precursor unit of the Niobrara Formation by the mixing of sulfate-rich sea water and barite-rich pore water in and around the nodules. The mechanics of formation of barite in this way are not clear, but under the conditions outlined, the solubility product of barite would be exceeded. Other possible explanations of the origin of the barite are less satisfactory.

INTRODUCTION

Phosphate nodules occur at many localities at the base of the Niobrara Formation in the Black Hills area. Cephalopods and pelecypods can be recognized in some nodules from these localities, but the traces of the fossils are so obscure that ordinarily they cannot be identified. Phosphate nodules discovered at a single locality (8 miles south of Fairburn) on the east flank of the Black Hills preserve identifiable ammonites that afford a basis for dating the lower part of the Niobrara Formation more precisely than was possible before. The well-preserved fossils are of particular importance because the Niobrara in this area contains few megafossils.

The good preservation of fossils makes these nodules unusual among those that generally are found at the base of the Niobrara Formation. It is useful to publish together the results of the paleontologic and petrologic studies inasmuch as both are concerned with the same material. The paleontologic and petrologic interpretations are so interrelated that a much more complete account can be given of the stratigraphic significance, origin, and geologic history of the interesting nodules than would otherwise be possible.

STRATIGRAPHY AND PALEONTOLOGY

By W. A. Cobban

The Niobrara Formation, of Late Cretaceous age, is chiefly soft calcareous shale and marl in its outcrop area along the flanks of the Black Hills uplift in South Dakota, Wyoming, and Montana. The formation is thin in this area and rests sharply on the Carlile Shale, also of Late Cretaceous age. Megafossils, other than vertebrate remains and fragments of *Inoceramus* with attached *Ostrea congesta* Conrad, are almost unknown from the Niobrara in this area. The recent discovery of ammonites at the base of the Niobrara is of much interest as it provides a means of dating the base of the formation and evaluating the sharpness of the boundary between the Niobrara and Carlile Formations.

The ammonites shown on plate 1 are in the United States National Museum in Washington. The photographs were made by Robert E. Burkholder.

NIOBRARA FORMATION

The Niobrara Formation consists largely of medium- to dark-gray calcareous shale and marl that weather light gray, pale yellow, and orange. It contains tiny white calcareous specks that represent clusters of coccoliths and rhabdoliths (Goodman, 1951). Some noncalcareous shale is present in the uppermost part of the formation and, in places, near the base. Limestone concretions, which are scarce, weather light gray and contain white specks. Thin layers of bentonite are common especially near the base and in the upper part of the formation.

The Niobrara Formation is 150–225 feet thick on the northwest flank of the Black Hills (Robinson and others, 1964, p. 74) and 217 to about 300 feet thick on the south and southeast flanks (Rothrock, 1931, p. 8; Connor, 1963, p. 114). It thickens southward away from the Black Hills to more than 600 feet in western Nebraska (Fuenning, 1942, fig. 4) and westward across the Powder River Basin to nearly 800 feet on its west flank (Hose, 1955, p. 62).

The contact of the Niobrara Formation and the overlying Pierre Shale is gradational in the Black Hills area, with interfingering of calcareous and noncalcareous shale. In contrast, the contact of the Niobrara and underlying Carlile Shale is sharp in most places and is commonly marked by a thin layer of phosphatic nodules (Cobban, 1952, p. 87; Connor, 1963, p. 114; Robinson and others, 1964, p. 74). The nodules are scattered thinly along the contact; concentrations of nodules into pockets were not observed. A few nodules at many localities show traces of fossils but only those in the collections described here can be identified. The occurrence of the nodules is discussed in more detail on page L7.

FOSSILS REPORTED

Ostrea congesta Conrad attached to pieces of *Inoceramus* shells are common in much of the Niobrara Formation. Darton recorded *O. congesta* in almost all of his works on the Black Hills and illustrated one cluster of shells many times (for example, Darton, 1909, pl. 12, fig. A). Scattered fish bones, teeth, and scales are also common. Mosasaur bones have been found at two localities on the north flank of the Black Hills (Robinson and others, 1964, p. 74). Other macrofossils are scarce, and little is known concerning them. Darton and O'Harra (1909, p. 5) stated that "several small ammonites were obtained from large limestone concretions near the top of the formation at a point several miles east of Twin Buttes [Butte County, S. Dak.]." The whereabouts of this collection is unknown. Darton (1919, p. 3) found that "some hard layers in the upper beds of the formation exposed on the east bank of the Belle Fourche a mile north of Butte Hall [Butte County, S. Dak.] contain many fossil shells of undescribed species." The collection made here by Darton (USGS Mesozoic loc. 7825) consists of *Nucula* sp., numerous specimens of a small high-spired gastropod, *Dentalium pauperculum*, Meek and Hayden, *Baculites* sp., *Scaphites* sp., and *Haresiceras* sp.

FOSSILS AT BASE OF NIOBRARA FORMATION

Fossils were discovered in 1961 in the phosphatic nodule bed at the base of the Niobrara Formation at USGS Mesozoic loc. D3757, 8 miles south of Fairburn, Custer County, S. Dak. (NE¼NW¼SW¼ sec. 36, T. 5 S., R. 7 E., Fairburn SW 7½-minute quadrangle). The fossils occur as phosphatic nodules and in phosphatic nodules. Most of the fossils are small inocerams or bits of large inocerams. Baculites are next in abundance followed by scaphites. Other fossils are small oysters, gastropods, uncoiled ammonites, shark and ray teeth, and a single specimen of the pelecypod *Veniella*. The gastropods are bits of internal molds too incomplete for specific identification. The pelecypods and ammonites are as follows:

Inoceramus sp.
Ostrea sp.
Veniella cf. *V. goniophora* Meek
Baculites aff. *B. mariasensis* Cobban
Allocrioceras sp.
Scaphites cf. *S. mariasensis* Cobban
  cf. *S. preventricosus* Cobban

cf. *S. corvensis* Cobban
sagensis Cobban
frontierensis Cobban

SYSTEMATIC DESCRIPTIONS

Class CEPHALOPODA
Order AMMONOIDEA
Family SCAPHITIDAE Meek, 1876
Genus SCAPHITES Parkinson, 1811

Scaphites cf. S. preventricosus Cobban

Plate 1, figure 15

1951 [1952]. *Scaphites preventricosus* Cobban, U.S. Geol. Survey Prof. Paper 239, p. 26, pl. 8, figs. 1–6; pl. 9, figs. 1–16; pl. 10, figs. 18–25.
1955. *Scaphites preventricosus* Cobban. Cobban, Billings Geol. Soc. Guidebook 6th Ann. Field Conf., p. 201, pl. 1, fig. 9; pl. 2, fig. 5.
1961. *Scaphites preventricosus* Cobban. Brown, Discoveries in ancient life, New York, Science Materials Center, p. 72, text-fig. 84.

Scaphites preventricosus is a moderately large species that has well-defined primary and secondary ribs of which the secondaries are equally spaced along the venter. The younger part of the body chamber is considerably freed from the phragmocone, and the suture is fairly complex. The species occurs in two forms, a large stout type (typical form) and a smaller and more slender form (var. *sweetgrassensis*). Three fragments of body chambers from the phosphatic nodule bed could represent the inflated or typical form of this species.

Figured specimen.—USNM 153063.

Scaphites cf. S. corvensis Cobban

Plate 1, figures 21–23

1951 [1952]. *Scaphites corvensis* Cobban, U.S. Geol. Survey Prof. Paper 239, p. 26, pl. 7, figs. 6–17.

Scaphites corvensis differs from *S. preventricosus* by being a little smaller and a little more coarsely ribbed. It occurs as two forms, a large inflated one (typical form) and a smaller and more slender form (var. *bighornensis* Cobban). Three fragments of body chambers from the phosphatic nodule bed suggest the typical form. The best preserved fragment is the older part of a body chamber (pl. 1, fig. 23). Four fragments of body chambers suggest the var. *bighornensis*, and the best preserved of these specimens is illustrated (pl. 1, figs. 21, 22).

Figured specimens.—USNM 153064, 153065.

Scaphites cf. S. mariasensis Cobban

Plate 1, figures 10–12

1951 [1952]. *Scaphites mariasensis* Cobban, U.S. Geol. Survey Prof. Paper 239, p. 28, pl. 8, figs. 7–17.

Three fragments of body chambers strongly suggest *Scaphites mariasensis*, which is characterized by numerous high sharp primary and secondary ribs. This species occurs as a large inflated form (typical form) and as a smaller and more slender form (var. *gracillistriatus*). The holotype of the var. *gracillistriatus* has a depression along the middle of the venter near the base of the body chamber, and such a feature is also present at the base of the body chamber of a specimen from the phosphatic nodule bed (pl. 1, fig. 11).

Figured specimen.—USNM 153059.

Scaphites sagensis Cobban

Plate 1, figures 13, 14, 16–20

1951 [1952]. *Scaphites sagenis* Cobban, U.S. Geol. Survey Prof. Paper 239, p. 30, pl. 10, figs. 7–10.

The body chamber of *Scaphites sagensis* has two rows of nodes on the primary ribs. The more conspicuous nodes are along the ventrolateral margin, where they have circular bases and rise into sharp points. The other row of nodes consists of bullate nodes on the middle of the flank. Secondary ribs are uniformly spaced where they cross the venter. The holotype, from the Frontier Formation near Lander, Wyo., is distorted; a better specimen that was recently collected at the type locality is illustrated (pl. 1, figs. 18–20). Four fragments of body chambers from the phosphatic nodule bed near Fairburn seem referable to this species.

Plesiotypes.—USNM 153060–153062.

Scaphites frontierensis Cobban

Plate 1, figures 3–9

1951 [1952]. *Scaphites frontierensis* Cobban, U.S. Geol. Survey Prof. Paper 239, p. 30, pl. 10, figs. 1–4.

Scaphites frontierensis is a small species that resembles *S. sagensis* by having two rows of nodes on the body chamber. It differs, however, by the presence of dense ventral ribbing which becomes widely spaced near the aperture. Two fragments of body chambers from the phosphatic nodule bed seem assignable to *S. frontierensis* (pl. 1, figs. 3–9). The older part of the body chamber of a very small adult may also belong to this species although the fragment seems to have periodic constrictions (pl. 1, figs. 1, 2).

Plesiotypes.—USNM 153056–153058.

Family BACULITIDAE Meek, 1876
Genus BACULITES Lamarck, 1799

Baculites aff. B. mariasensis Cobban

Plate 1, figures 27–33

1951. *Baculites mariasensis* Cobban, Jour. Paleontology, v. 25, no. 6, p. 818, pl. 118, figs. 10–12; text-figs. 4–7.
1955. *Baculites mariasensis* Cobban. Cobban. Billings Geol. Soc. Guidebook 6th Ann. Field Conf., p. 204, p. 2, fig. 1.

Baculites mariasensis is a small species that has a very low degree of taper, ovate cross section with fairly narrow venter, smooth flanks, weakly ribbed venter, and rather simple suture. Baculites from the phosphatic nodule bed closely resemble *B. mariasensis* except for the cross section which is more elliptical owing to a broader venter.

Figured specimens.—USNM 153069–153071.

Family ANISOCERATIDAE Hyatt, 1909
Genus ALLOCRIOCERAS Spath, 1926

Allocrioceras sp.

Plate 1, figures 24–26

Allocrioceras is a loosely coiled ammonite in which the earlier part is coiled helically, whereas the later part is coiled in a plane (Wright, 1957, p. L220). Ventrolateral nodes are present on some ribs. The genotype, *Allocrioceras woodsi* Spath (Woods, 1896, p. 84, pl. 3, figs. 8–10), is an upper Turonian species from England that has whorls with an elliptical cross section, ventrolateral nodes on every second or third rib, and suture with broad saddles and narrow lobes. Four fragments of a loosely coiled ammonite genus are present in the collections from the phosphatic nodule bed. They resemble *A. woodsi* in the density of ribbing and in the presence of nodes on every third rib on at least one specimen (pl. 1, fig. 26). They differ, however, by their more circular section and by the suture with shorter and broader lobes.

Figured specimens.—USNM 153066–153068.

AGE

Inoceramus is the commonest fossil in the phosphatic nodule bed. Most specimens represent small individuals 15–30 mm in height; these resemble *Inoceramus perplexus* Whitfield (1880, p. 392, pl. 8, fig. 3; pl. 10, figs. 4, 5) from the Turner Sandy Member of the Carlile Shale of the Black Hills as well as some of the variants of *I. costellatus* Woods from the upper Turonian of Germany as illustrated by Fiege (1930, pl. 5, figs. 5–9). Some pieces of the larger specimens resemble *I. inaequivalvis* Schlüter from the Turonian as figured by Fiege (1930, pl. 5, fig. 1) and Heinz (1934, pl. 18, figs. 1a–c).

Allocrioceras is known only from rocks of Turonian age (Wright, 1957, p. L220), and all recorded American species are of this age (Swensen, 1962, p. 60).

Baculites aff. *B. mariasensis* is the species referred to in my earlier papers as *Baculites* cf. *B. besairiei* Collignon (for example, Cobban, 1951a, p. 2188, 2190–2192). In the Black Hills area, *Baculites* aff. *B. mariasensis* has hitherto been known only from the upper half of the Carlile Shale in which it is associated with *Prionocyclus* and other fossils of unquestioned Turonian age.

The scaphites are either closely related or identical to species in the upper part of the Carlile Shale and basal part of rocks equivalent to the Niobrara Formation. The scaphite that has the oldest appearance in the phosphatic nodule bed is *Scaphites* cf. *S. corvensis*. *Scaphites corvensis* has been recorded only from the Carlile Shale Member of the Cody Shale in south-central Montana (Richards, 1955, p. 53) and north-central Wyoming (Hose, 1955, p. 97) and from the Sage Breaks Member and uppermost part of the underlying Turner Sandy Member of the Carlile Shale of the Black Hills (Cobban, 1951a, p. 2188, 2190). At these localities the species is associated with *Prionocyclus* and considered as late Turonian in age. In recent years *Scaphites corvensis* has been discovered in the Ferdig Shale Member of the Marias River Shale in northwestern Montana a little below strata containing the *Scaphites mariasensis* fauna.

Scaphites sagensis and *S. frontierensis* have been known only from the uppermost part of the Frontier Formation of western Wyoming (Cobban, 1951b, p. 30), where they are associated with *Baculites* aff. *B. mariasensis* and an early form of *Scaphites preventricosus*. The specimens of *S. sagensis* from the phosphatic nodule bed have the venters rounded a little more than those on specimens from the Frontier Formation, possibly reflecting a slight age difference.

Scaphites mariasensis occurs with an early form of *S. preventricosus* in the basal beds of the Kevin Shale Member of the Marias River Shale of northwestern Montana (Cobban, 1951a, p. 2194). Recently *Baculites* aff. *B. mariasensis* has been discovered in these basal beds. *Scaphites mariasensis* and associated fossils were assigned to the lower part of the *Scaphites preventricosus* zone and considered as early Coniacian (Cobban 1951a, p. 2197). The *S. mariasensis* assemblage probably should be assigned to the upper Turonian in light of the Turonian aspect of the ammonites from the phosphatic nodule bed.

In summary, a late Turonian age seems consistent with the fossils from the phosphatic nodule bed. An age that old is surprising, considering the sharp boundary between the Carlile and Niobrara Formation.

PETROLOGY AND ORIGIN OF NODULES

By Harry A. Tourtelot

GENERAL STATEMENT ON PHOSPHATE NODULES

The history of the growth of concepts and knowledge of phosphate nodules in general is usefully reviewed in connection with this study of the nodules at the base of the Niobrara Formation. The history is basically interesting in itself, but in addition, it allows the conceptual paths by which we have arrived at our present ideas to be understood. The history also supplies a background that helps to orient our thinking about phosphate nodules within the broadest possible range of information and ideas.

HISTORY OF STUDY OF PHOSPHATE NODULES

Fossiliferous phosphate nodules such as those described by Cobban, and other kinds as well, have long been of interest because they record the history of biological processes in marine sedimentation. Nodules also seem to have been the first mineral phosphate used for fertilizer. The following brief account of the growth of knowledge about phosphate nodules in England illustrates the change in status of the nodules from early objects of curiosity to, later, deposits of economic worth and, now, markers of unconformities (Goldman, 1922; Adams, Groot, and Hiller, 1961; Diggens, 1966, p. 270–271; and Brown, 1966). The growth of knowledge about phosphate nodules in France has a similar history.

The first notice of phosphate nodules seems to have been in a paper by Fitton (1836, p. 111) which was read before the Geological Society of London in 1827. He described nodules from the Gault Formation of Cretaceous age in southeastern England. The nodules contained fragments of shells or filled the interior of ammonites. He recognized the similarity in apparent composition to coprolites, which by 1837, when Fitton's paper was published, had been shown by Buckland (1829, 1835) to be phosphate. Buckland and Conybeare (1824, p. 302) had noticed nodules in the Lias beds in southwest England. Most of these nodules were interpreted as coprolites by Buckland (1829, 1835) and found to be phosphate by Prout (1835) at the time of Buckland's 1829 note. Some phosphatic nodules, however, were recognized as having a different origin (Buckland, 1835, p. 236).

Curiously, the first coprolite for which an illustration was published came from New Jersey. Buckland had read his paper on coprolites to the Geological Society of London on February 6, 1829, and an abstract of it was published in July 1829 in Magazine of Natural History (Buckland, 1829, p. 258). This abstract was seen by J. E. Dekay in New York who recognized that the collections of the Lyceum of New York contained an object from the "ferruginous sands" of New Jersey that probably was a coprolite. He sent a sketch to Buckland in January 1830, and Buckland published it, along with Dekay's letter and some additional comments, in May 1830 (Buckland, 1830).

Phosphatic nodules that were casts and molds of fossils were specifically described in 1843 by Mantell (1843, 1846). The specimens were illustrated in the 1846 paper. Mantell thought that the nodules were derived from the phosphatization of the soft parts of the mollusks and extended this interpretation to include nodules that neither showed any traces of fossils nor were coprolites. He had analyses made that seemed to show that the nodules contained organic carbon and probably nitrogen (Mantell, 1843, p. 246). He named the material molluskite.

Before 1845, most of the phosphatic nodules that had been recognized came from the Lias or from Cretaceous strata; after 1845, phosphatic nodules were discovered in other rocks and at many more localities in Cretaceous rocks. In 1845, Henslow (1846) reported nodules in the Red Crag of Pliocene age in southeastern England and cited opinion that some of them, at least, had been eroded from the London clay of Eocene age. Jenyns (1866) credited Henslow with the suggestion that these nodules, along with accompanying glauconite, would be useful as fertilizer. In 1848, however, Austen (1848) reported experiments in using nodules as fertilizer and discussed their occurrence in the rocks of Cretaceous age below the Chalk in a way that was useful for further prospecting. He also commented on the occurrence of abundant molds and casts of mollusks now known to consist of aragonite and implied the replacement of calcitic shells by phosphate (Austen, 1848, p. 259). He recognized that the casts had to form and that the replacements had to take place after the mollusks were buried (Austen, 1848, p. 261).

In 1849, Buckland (1850), by then elevated to be the Dean of Winchester, credited Liebig (without reference) as being the first to suggest that fossil phosphates could be put to the same uses in agriculture as recent bones and guano. Apparently, the nodule deposits in the Red Crag already were being worked. He also mentioned the occurrence of phosphate in the "air chambers" of ammonites from the Kimmeridge beds of Jurassic age. The widespread occurrence of phosphate "adsorbed," as he put it, by clay, marl, and lime led him to suggest that these materials might be used to deodorize and combine with the phosphates in sewage.

Leckenby (1859, p. 10) mentioned nodules in the Speeton Clay in Yorkshire that, according to Judd (1868, p. 220), Leckenby recognized as being phosphatic. Mackie (1859), editor of "The Geologist," in a reply to an inquiry from a reader, stated that nodules in Cambridgeshire had long been profitably utilized in agriculture. He also mentioned other occurrences of nodules in the Greensand at localities in Europe. Seeley (1866) describe the method of digging phosphate nodules in Cambridgeshire and recognized that mollusks with shells of aragonite are represented only by internal casts. Many of the casts showed signs of abrasion and

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supported epifauna, evidence indicating the exposure of the nodules on the sea floor (Seeley, 1866, p. 306–307).

Phosphate nodules of Paleozoic age were found in North Wales in 1864 and were analyzed in 1865 by Voelcker (1866). Davies became interested in the commercial possibilities of the bed of nodules and published a brief note in 1867 and a fuller account in 1875 about the bed, the nodules, and the origin of the nodules. He conjectured that phosphate was gathered into nodules by a "dull crystallization" that took place after shallow burial of the bed. (Davies, 1875, p. 363). Davies made no mention of the better known nodules of Cretaceous age, a good summary description of which had been published by Fisher (1873).

Examination of the Speeton Clay in Yorkshire by Judd (1868, p. 221) was hampered by debris, from the mining of phosphate nodules, which had concealed many cliff sections that were available for study in earlier years.

The account of the phosphatic nodules in the Cambridge Greensand by Fisher (1873) is remarkably complete even though it lacks petrographic data. He made many pertinent observations on the relation between fossil form and phosphate nodules; some of his conclusions seem valid today. He recognized, for example, that the nodules were derived from a preexisting rock (Fisher, 1873, p. 53) and that this rock was similar to the overlying Chalk rather than to the underlying Gault.

In 1872 the great voyage of the *Challenger* began, which was to result in much of the present knowledge about phosphate nodules on the sea floor. Phosphate nodules, however, were not mentioned by Murray (1876, p. 491) in brief descriptions of bottom sediments, even though samples from the Agulhas Bank were described. Material from the Agulhas Bank and nodules from other localities were described in detail, however, in the final report (Murray and Renard, 1891, p. 391–400). The first phosphate nodules to be described from the present sea floor were collected on a cruise of the *Blake* in 1880 and were described by Murray in 1885. By this time, the phosphatic nodules collected by the *Challenger* had been recognized as such even though a description of them had not been published (Murray, 1885, p. 41).

Murray and Renard (1891, p. 397) concluded that the phosphate nodules on the present sea floor formed in situ and implied that they are forming at the present time. They paid little attention to the data on phosphate nodules from the older geologic record. It should be noted, however, that the conclusions of Murray and Renard were based largely on the nodules from the Agulhas Bank. The fact that the Agulhas Bank nodules were shown by Cayeux (1934) to have been derived from some environment other than where they are found has not received much attention.

Cayeux's monographic study of sedimentary phosphates (1939) illustrates types of phosphate rocks and provides much data on the range of characteristics of phosphate rocks that can be seen in thin section.

SUMMARY DESCRIPTION OF PHOSPHATE NODULES

The following general description of the nature and composition of phosphate nodules is based for the most part on references already cited. This general description gives a background against which the characteristics of the nodules at the base of the Niobrara Formation can be considered.

The word "nodule" is defined in Howell (1957, p. 199) as follows: "A general term for rounded concretionary bodies, which can be separated as discrete masses from the formation in which they occur * * *. Nodules are generally small structures of hand-specimen size." Phosphate nodules in marine sedimentary rocks are such bodies composed of phosphate minerals. The nodules generally contain resistant detrital minerals such as quartz and glauconite, traces of microfossils such as foraminifers, radiolaria, and diatoms, and diagenetic minerals such as pyrite. The tests of the microfossils may be replaced by phosphate minerals or other minerals, or they may retain their original composition. Bands or irregular patches of different colors are present in some nodules and have been interpreted as indicating accretionary growth of the nodule or as reflecting the distribution of different nonphosphate mineral phases within the nodule. The exterior surfaces of the nodules can be highly variable. Some that have been reworked are smoothly rounded and may be polished; others that obviously have not been reworked have similar surfaces. Many nodules have irregularly spherical to elliptical shapes with warty surfaces. It is very common for the nodule to be an internal or external cast of a fossil such as a mollusk, a brachiopod, a bryozoan, or an arthropod. Fossil wood sometimes is replaced with phosphate. Nodules have been found in rocks of nearly all ages and some dredged from the ocean floor have been interpreted to be forming today.

Nodules can be formed in sandstone, shale, or limestone but perhaps are most abundant in calcareous rocks. Nodules can be reworked to form pebble beds in sandstone or at the base of other kinds of stratigraphic units. Nodules can be concentrated at the tops of stratigraphic units by weathering without transportation in either the present cycle or some previous one.

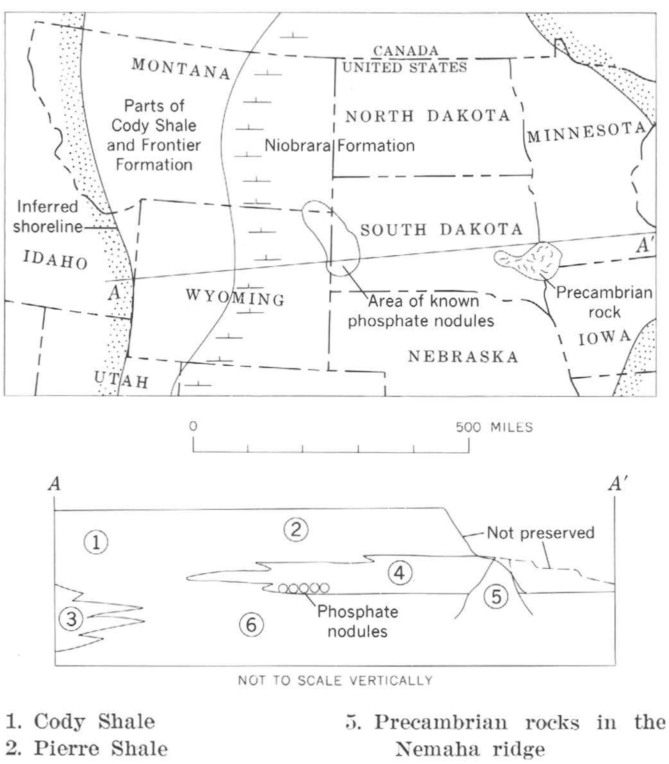
The phosphate mineral that forms phosphate nodules most often is reported as collophane, a petrographically amorphous apatite (McConnell, 1958). Bushinsky (1945, p. 129) listed collophane, francolite, kurskite, dahllite, and fluorapatite as the minerals forming nodules and bedded phosphates. Altschuler, Cisney, and Barlow (1952) determined the existence of carbonate fluorapatite as a distinct variety of apatite, and reported that the apatite in most marine phosphorites, including nodules, is carbonate fluorapatite.

Nodules in pebble beds have been concentrated there mechanically, the nodules having been formed elsewhere. Consequently, the conditions under which the pebble beds were accumulated have no relation to the conditions under which the nodules had their primary origin. These conditions of primary origin can be studied best only where there is reason to think that the nodules have not be disturbed. Petrographic studies of nodules in pebble beds, however, can provide a basis for reasonable inferences concerning conditions of formation of some phosphate nodules and that is the purpose of this study.

NODULES AT BASE OF NIOBRARA FORMATION

REGIONAL SETTING

The position of the outcrops in the Black Hills region where phosphate nodules occur at the base of the Niobrara Formation is shown in relation to the paleogeography of the formation in figure 1. The sea in which



1. Cody Shale
2. Pierre Shale
3. Frontier Formation
4. Niobrara Formation
5. Precambrian rocks in the Nemaha ridge
6. Carlile Shale

FIGURE 1.—Regional setting of area of known phosphate nodules at base of Niobrara Formation in the Black Hills region. From unpublished data of J. R. Gill and W. A. Cobban.

the Carlile Shale and Niobrara Formation were deposited extended from western Montana to points in Minnesota, Wisconsin, and Iowa. Just prior to the deposition of the Niobrara Formation and for part of earliest Niobrara time, the western source area supplied sand to the sea on the east. This sand makes up the Frontier Formation that is an eastward-extending tongue underlain and overlain by shale. Relatively coarse-grained clastics continued to accumulate along the western source area during Niobrara time. To the east of this sand deposition lay fine noncalcareous muds which were deposited in the lower part of the Cody Shale and the Carlile Shale. The mud zone was bordered on the east by a large area of fine-grained shelf carbonates that make up the Niobrara Formation. (See p. L2).

The area of carbonate deposition extended as far east as the Niobrara Formation is preserved. The formation lapped onto the Nemaha Ridge of Precambrian rocks and extended beyond the ridge over a generally smooth surface of rocks of Paleozoic and Precambrian ages to the east. Some detritus undoubtedly was shed from the Nemaha Ridge into Niobrara sediments. The eastern source area in general, however, seems to have supplied little material to the Niobrara sea.

The phosphate nodules thus were formed within an area of carbonate deposition far from shore. There is no evidence that the contemporaneous shales to the west were deposited in water significantly deeper than the water in which the carbonates were formed. The position of the western sandstones with respect to shore suggests that they, too, were deposited in relatively shallow water.

Phosphate nodules at the base of the Niobrara Formation have been reported from Colorado by Gilbert (1897) and Johnson (1930). Fish teeth and bones are abundant, as well as some pebbles of quartz. Hattin (1962, p. 90) mentioned polished pebbles of phosphate at the base of the Niobrara Formation in Kansas. Neither occurrence is described in sufficient detail for comparisons to be made with the phosphate nodules in South Dakota. Such occurrences, however, indicate that the nodules in South Dakota are not unique.

OCCURRENCE OF NODULES NEAR FAIRBURN

The phosphate nodules at the base of the Niobrara Formation occur at many places in the Black Hills region (p. L2). Figure 2 shows the outcrop at which the identifiable fossils preserved as internal casts in phosphate were found. The white band is weathered marlstone of the Niobrara Formation resting on weathered dark shale of the Sage Breaks Member of the Carlile Shale. The nodules are strewn on the surface

FIGURE 2.—Contact between light-colored marlstone of the Niobrara Formation (above) and dark shale of the Carlile Shale (below). The locality is USGS Mesozoic loc. D3757, 8 miles south of Fairburn, Custer County, S. Dak. (NE¼NW¼SW¼ sec. 36, T. 5 S., R. 7 E., Fairburn SW 7½-minute quadrangle). Phosphate nodules preserving identifiable fossils and other nodules showing only vague traces of fossils or none at all are strewn along contact. All nodules showing well-preserved fossils had been collected previously. Nodules visible just below hammer and the bush on the left. White objects on shale are platy limestone flakes washed down from the Niobrara Formation.

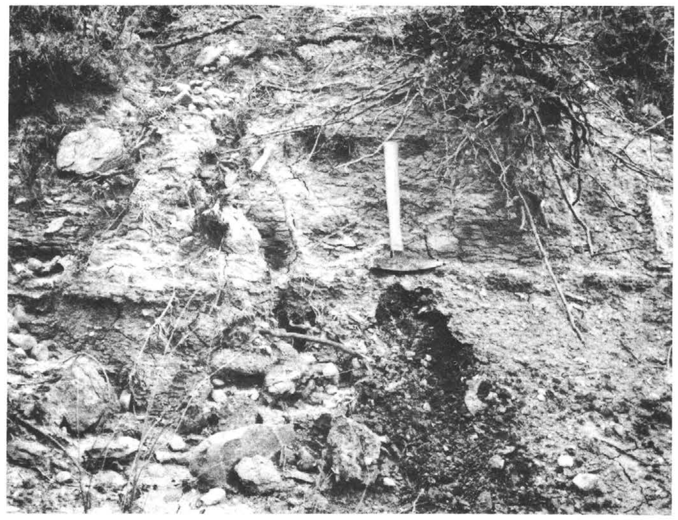


FIGURE 3.—Contact between Niobrara Formation (above) and Carlile Shale (below) at a locality about 4 miles south of Fairburn in the NW¼SE¼ sec. 13, T. 5 S., R. 7 E., Custer County, S. Dak. The phosphate nodules are in the bed at the head of the hammer. The matrix of the bed consists of pyrite, mostly oxidized to yield iron oxides and gypsum.

of the Carlile Shale and are particularly evident just below the hammer and the bush shown at the left center of the photograph. Hard platy limestone flakes can be seen on the marlstone surface, and several flakes have drifted onto the shale surface in the foreground. The light-colored marlstone has been washed over the shale particularly along the vaguely defined border of the light surface, and a few nodules are found on this washed marlstone. The bulk of the nodules, however, are found on the shale. Nodules were not found in place at this locality, and the nature of the contact cannot be demonstrated here.

At another locality, about 4 miles to the north, in the NW¼SE¼ sec. 13, T. 5 S., R. 7 E., Custer County, S. Dak., the boundary is well exposed (fig. 3). The hammer shown in figure 3 rests on a bed ½–1 inch thick of pyrite, iron oxide, and gypsum that contains phosphate nodules. The iron oxide and gypsum are secondary minerals formed by the oxidation of pyrite.

A specimen of the upper surface of this cemented bed of nodules is shown in figure 4. The bluish-gray to black and brown nodules are not much more than 1 cm in maximum dimension as revealed on the slab and most of them project above the general surface of the slab. The nodules are irregular in shape and have an irregular surface that is marked by lighter colored iron oxides filling small depressions. No pattern of distribution of larger and smaller nodules is evident. Part of the cross section along *A–A′* in figure 4 is magnified in figure 5. The bed is made up of many small phosphate nodules and incorporates erratic larger ones without any noticeable sedimentation pattern. Most of the nodules are 0.5 cm or less in maximum dimension. Included among them, although not visible in the photograph, are fragments of fish bones and teeth. The matrix along the bottom of the bed is mostly iron oxides and gypsum and is not photographically distinguishable from the rest of the bed that contains much pyrite. Very sparse grains of quartz as large as 0.4 mm and averaging about 0.1 mm in maximum dimension are scattered through the lower part of the bed. A few flakes of biotite also are present. The white flecks in some of the nodules are oolitelike bodies filled with gypsum.

MORPHOLOGY OF NODULES

All the nodules from the base of the Niobrara Formation in the Black Hills area are dark brown to brownish black with variable and irregular stains of brown and red iron oxide. A few nodules show irregular borings (pl. 1, lower part figs. 32 and 33) that may have been made after the nodules were formed, but this interpretation is by no means certain. None of the nodules show encrusting epifauna, such as oysters, that would indicate that the nodules had lain exposed for a very long time on the sea floor under conditions in which sessile organisms could live.

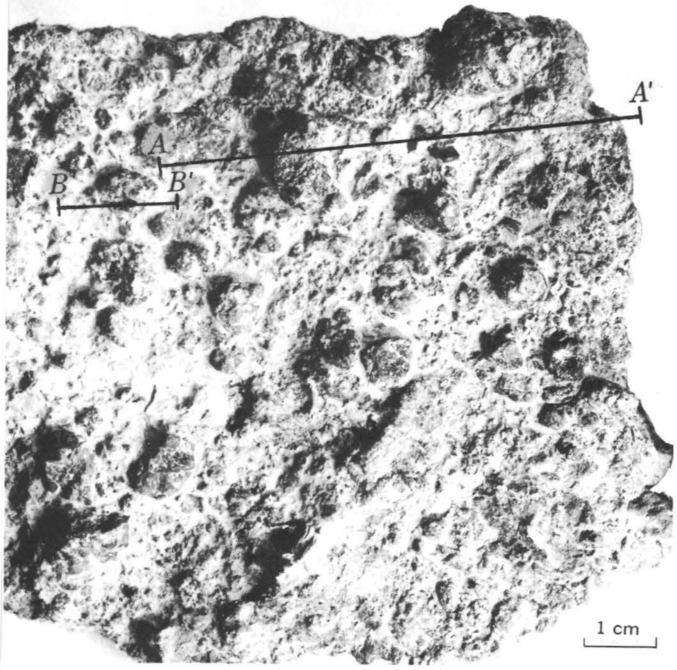


FIGURE 4.—A rock specimen of the upper surface of the nodule bed at locality pictured in figure 3. The upper surface of the matrix in which the nodules are embedded is made up of iron oxides resulting from the oxidation of underlying pyrite. Section *A–A'* shown in figure 5; *B–B'*, figure 7.

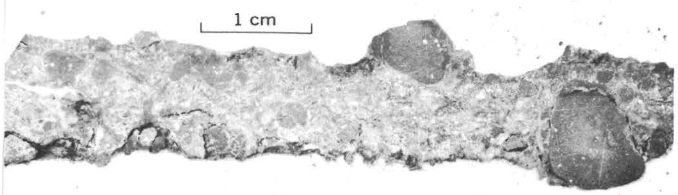


FIGURE 5.—Part of cross section of nodule-bed specimen cut along line *A–A'* (fig. 4); specimen from locality pictured in figure 3. Many small nodules and fragments of fish teeth and bones make up groundmass of the larger nodules. The matrix is cemented with pyrite, much of which has altered to iron oxides and gypsum along bottom and top of bed. The light-colored streak at the left is ferruginous gypsum.

The nodules are of three kinds believed to be of the same general origin: (1) relatively complete, identifiable internal molds of segments of baculites and scaphites (pl. 1, all figs. except 18–20), gastropods, inocerams, and a single specimen of another pelecypod (*Veniella*) with both valves represented; (2) irregular lumpy masses, not more than 50 mm in maximum dimension, on either the original or a broken surface of which is a mold of the interior of a cephalopod (fig. 6, specimen 16; pl. 1, figs. 24–25), a pelecypod, or an obscure trace of a fossile (fig. 6, specimens 10, 20, 23, 24, pl. 2, figs. 8, 9) some of which may be identifiable; and (3) similar irregular masses that do not show any positive traces of a fossil.

The relatively complete molds which are known only from the Fairburn locality, preserve the original internal sculpture of the fossil shell in sharp detail (pl. 1, figs. 10–12, 21, 22, 24–26, 27, 28). It does not seem reasonably that such specimens could have been transported very far by currents of velocities capable of moving fragments an inch or so in diameter. For the rounding that is evident at the tops of figures 3–5 (pl. 1) to be caused by physical abrasion seems incompatable with the preservation of shell sculpture on the rest of the specimen. Rounded surfaces such as these could originate either by incomplete phosphatization or by post-nodule solution. The absence of the surface of the fossil shown on plate 1 in figures 21–23 and in the lower parts of the fossil in figures 32 and 33 (jl. 1) suggests incomplete phosphatization. The appearance of these specimens is very similar to that of many specimens preserved along the edges of limestone concretions or individually in shale where postfossilization solution obviously was not involved.

Some of the nodules have numerous boringlike tubes along the surfaces that are the casts of the ammonite or pelecypod shells (pl. 1, figs. 9 and 32. See pl. 2, fig. 3 for appearance in thin section). Similar borings penetrate the interior of these nodules but are conspicuously less abundant than on the surface. One poorly preserved fossil (fig. 6, specimen 24) bears the mold of the shell of a worm similar to a serpulid. This indicates that the worm grew on an empty shell. The concentration of borings along the surface of a cast suggests that these boring animals were most active along the contact between a shell and the matrix filling it. Even though the boring pattern is not similar to known encrusting bryozoa or worms that secrete a tubular shell, it is believed that these borings are the trails of a boring worm that followed the contact. Such borings are thus of prephosphatization origin. They seem to be more common in the better preserved phosphatic fossils.

Additional phosphate was added to some internal casts after the internal cast was completed and the shell dissolved, such as the specimen of *Allocrioceras* in figure 25 of plate 1. Worm trails show that the cast of this specimen is of the interior of the shell but phosphate around the cast is deposited directly against its surface without any indication of shell material. The lower part of the specimen shown in figure 25 is a mold of the internal cast.

The nodules from the Fairburn locality with casts or parts of casts on their surface, chiefly *Inoceramus*, may represent the outer limit of formation of the nodule, or they may represent broken surfaces similar to that which revealed the *Allocrioceras* already mentioned. Most of the fossils in such nodules are small inocerams or pieces of large inocerams.

A very few nodules show more than one fossil. One of these (pl. 2, fig. 9) is a piece of a cast of the aragonitic internal layer of a large inoceram. Lying above this cast surface is the cast of the calcitic external surface of a similar inoceram. A crevice above this external cast, now filled with gypsum, represents the shell before its original minerals, calcite and aragonite, were dissolved. On top of this crevice rests a nearly complete internal cast of a small inoceram. Another specimen shows the internal cast of an inoceram on one side (pl. 2, figs. 1 and 8) and the internal cast of a piece of a small baculite on the other. A crevice representing the original aragonitic shell of the baculite borders one side of the cast. No trace of the opposite side of the baculite can be seen in the phosphate between the baculite and the inoceram. One broken nodule shows a small part of the external surface of a large pelecypod. Another contains the hollow molds of the external surfaces of several small gastropods arranged in such a way as to indicate that a sediment volume of almost a cubic inch had been phosphatized.

It is thus evident that the matrix around the fossils was replaced with phosphate to some extent as well as the matrix material within the fossils. Credner (1895) illustrated nodules in which phosphate wholly surrounds complete shells, the aragonite of which was dissolved after formation of the nodule.

Nodules with obscure traces of fossils are found at most localities where the base of the Niobrara Formation is exposed. A nodule may clearly involve a baculite (fig. 6, specimen 16) or a pelecypod (fig. 6, specimen 20) without the fossil being further identifiable. Or the nodule may present a smooth surface (fig. 6, specimen 24) that can only represent some kind of shell.

The nodules that show no traces of fossils on their exterior surfaces are irregular in shape (fig. 6). They are generally rounded, however, without signs of abrasion or of fractures that might indicate they are broken fragments of some larger platelike mass. Nor have any specimens been found that indicate the cementing together of nodules that were first formed as independent objects. The size and general shape of the nodules are compatible with nodules that show traces of fossils, and the impression is created that both types of nodules formed in the same way. That the internal structure and mineralogy of both kinds of nodules are the same seems to confirm this impression.

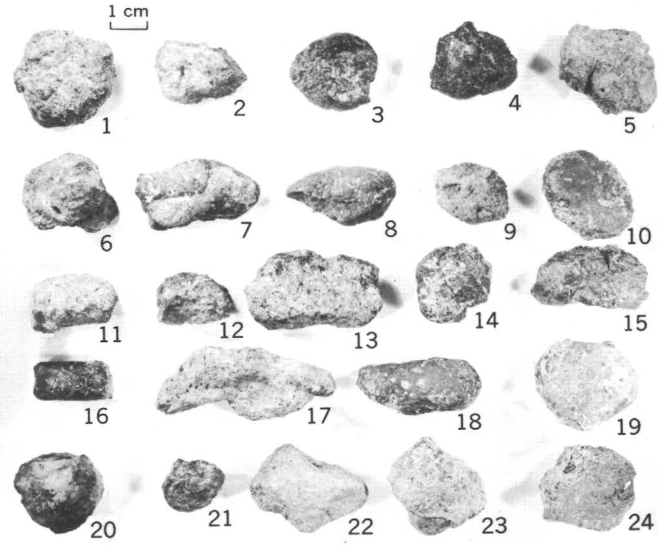


FIGURE 6.—Nodules from USGS Mesozoic loc. D3757 that show recognizable but not identifiable traces of fossils and irregular lumpy nodules that do not reveal traces of fossils. Specimen 16 is a fragment of a baculite, and specimens 20–24 are pelecypods.

The nodules that show no traces of fossils are by far the most abundant kind of nodule at the locality south of Fairburn (p. L2), where identifiable fossils occur, and at the other localities in the Black Hills area (p. L2). Therefore, because they are the most abundant, the nodules that show no traces of fossils would be a logical basis for any interpretation of the origin of all the nodules. The nodules themselves, however, are not particularly instructive. All that can be deduced from them is that phosphate deposition was somehow initiated, presumably at a pH less than 7.5 (Krumbein and Garrels, 1952, p. 9) if the general principles of phosphate precipitation were followed.

The nodules without traces of fossils and those with traces of fossils are related by their common occurrence together and their structure and mineralogy. The preservation of traces of fossils is regarded as a continuum. At one end of the continuum are the fossils sufficiently well preserved to be identifiable; these are known only from the Fairburn locality. In the middle are nodules with unidentifiable traces of fossils ranging from positive to obscure; these are known from nearly all localities including Fairburn. At the other end are nodules without any recognizable traces of fossils; these are known from all localities. It thus seems reasonable to think that the nodules preserving identifiable fossils represent the most complete record of the processes by which all the nodules were formed. This implies that the presence of a mollusk in the original sediments may have had a role in the initiation of phosphate deposition.

PETROGRAPHY AND MINERALOGY

The nodules are composed of carbonate fluorapatite according to X-ray analysis. This basic groundmass incorporates preexisting material, such as detrital minerals and foraminifers, and some secondary minerals inferred to be of diagenetic origin and other minerals that have formed at or near the outcrop. These constituents are arranged in the interpreted order of formation in the following listing:

1. Preexisting material—quartz, clay, biotite, foraminifers, radiolarians, *Inoceramus* prisms.
2. Nodules—carbonate fluorapatite in groundmass and ooids.
3. Secondary minerals in nodules:
   - Inferred diagenetic origin—pyrite, barite, calcite.
   - Inferred weathering origin—gypsum, iron oxides.

PREEXISTING MATERIAL

Sharply angular grains of detrital quartz amount to less than 5 percent of the piece of a nodule that was X-rayed. In thin section (pl. 2, fig. 2), the grains are so sparse that bedding cannot be discerned. Clay minerals are not detectable by X-ray analysis and are inferred to amount to less than 10 percent. A few grains of biotite were seen in thin section.

Tests of pelagic foraminifers and radiolaria (pl. 2, fig. 7) are present in nearly all thin sections. The calcareous tests of the foraminifers have been invariably replaced by barite. Definitely recognizable radiolarian tests have been converted to a very fine grained weakly birefringent mineral that may be a zeolite. These tests seem to be filled with a mixture of zeolite and apatite. Scattered *Inoceramus* prisms have been replaced by barite but are recognizable by their elongate shape and polygonal cross section.

NODULES

Carbonate fluorapatite makes up the groundmass of the nodules and is so fine grained that it is essentially isotropic. Scattered randomly throughout the groundmass are round bodies with concentric layers of more coarsely crystalline apatite having weak birefringence. The bodies are a conspicuous feature of the nodules (fig. 4; pl. 2, fig. 1) ; although only a few of them are in what is inferred to be their original condition. Most of these bodies have been replaced by pyrite or barite or complex mixtures of pyrite and barite or by other secondary minerals.

The term "ooid" is used to denote those bodies resembling small fish eggs because it has no genetic implications. Both oolith and oolite, although sometimes used as general terms, seem inextricably involved with the connotation that such bodies are formed by accretion around a nucleus while the bodies are in suspension in an agitating medium. (Howell, 1957, p. 204.) The origin of the ooids in the phosphate nodules seems to be quite different and it is not possible to think of these ooids as ordinary ooliths or oolites.

The ooids have a maximum diameter of about 0.7 mm and nearly all are spherical, although a few (pl. 2, fig. 2) are ovoid. The layering is marked in plane light by slight differences in color. Under crossed nicols, the lighter bands are seen to be made up of a patite crystallites large enough to show a faint birefringence. The crystallites have no preferred orientation and no recognizable radial structure; they thus differ from the light-colored bands in generally similar ooids illustrated by Lowell (1953, p. 16).

The boundaries between unaltered phosphatic ooids and unaltered phosphatic groundmass (pl. 2, fig. 2) are not conspicuously sharp. The random distribution of the ooids, which is independent of the original shells that would be expected to influence the distribution of detrital particles, indicates that the ooids originated in place rather than elsewhere and could not have been brought as detrital material to the site of nodule formation.

No nucleating grain can be seen in any of the ooids except one. In this ooid, a frayed but still pleochroic biotite flake occupies the center of the ooid and is surrounded by barite that has replaced all the original material of the ooid. The function of the biotite as a nucleus can be inferred only from its position. The nearly total replacement of the ooids by both pyrite and barite has destroyed most of the chances of observing nuclei if they exist. The ooids, however, do not incorporate recognizable foreign grains such as quartz in positions within the ooid other than nuclear.

SECONDARY MINERALS

Pyrite

Pyrite forms the matrix of the nodule bed (fig. 7), fills veins in some of the nodules (figs. 7 and 8), and replaces ooids and parts of ooids (fig. 7; pl. 2, fig. 1). Pyrite also occurs as grains scattered in the phosphate of ooids and in barite (pl. 2, fig. 5) and is disseminated in the groundmass of the nodules (pl. 2, fig. 2). The pyrite in the groundmass is so fine grained that individual crystals can barely be made out in reflected light on the surface of a thin section. In transmitted light, however, portions of the groundmass are almost opaque as the result of such fine-grained pyrite scattered

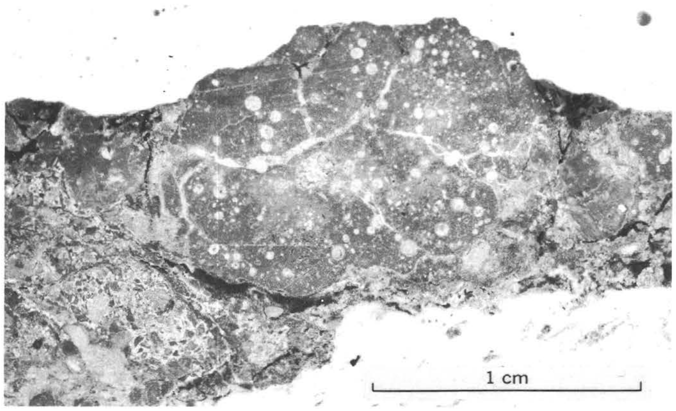


FIGURE 7.—Part of cross section of nodule-bed specimen cut along line *B–B'* in figure 4; specimen from locality pictured in figure 3. Most of the ooids are replaced with pyrite. The veins in the nodules are filled mostly with pyrite that extends into the matrix. Calcite incorporates pyrite in some parts of the veins, and some of the pyrite has altered to gypsum. The light-gray mineral surrounding fragments at the lower left of the nodule is pyrite.

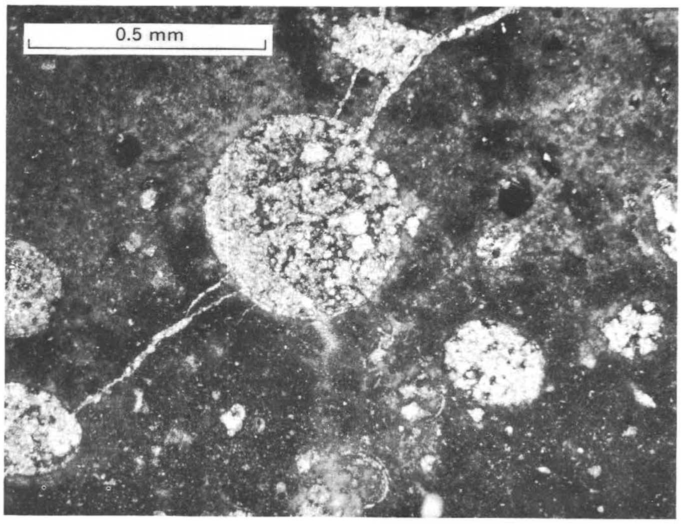


FIGURE 8.—Ooids largely replaced by pyrite. Note that pyrite in vein is not distinguishable from pyrite in the ooids that the vein cuts. Enlargement 80 ×. Thin section photographed in reflected green light.

through the thickness of the thin section. Elsewhere, the pyrite is in individual cubes several microns in maximum dimension and in closely packed aggregates of such cubes. Pyrite was nowhere observed in a coarsely crystalline mass. It is estimated that pyrite amounts to several percent in the nodules and perhaps 50 percent of the bed matrix.

Pyrite fills voids between nodules and tooth and bone fragments in the matrix of the bed (fig. 9). The nodules and fragments are so loosely packed that the pyrite

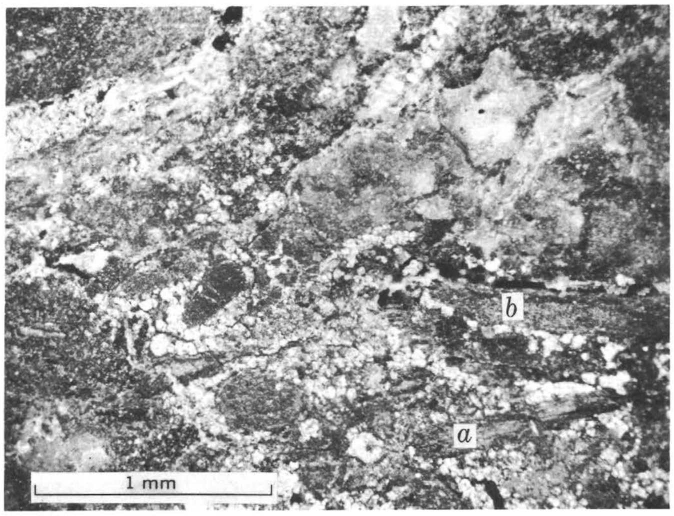


FIGURE 9.—Pyrite in matrix of nodule bed. At upper left is the border of relatively large nodule in bed. At lower left is an area clouded with iron oxides. Note small nodules in lower center. Objects at *a* and *b* are fragments of fish bone in matrix. Enlargement 40 ×. Smoothed surface photographed in green light.

probably replaced some preexisting material that is no longer recognizable. Because the edges of some phosphate particles in the bed have been partly replaced by pyrite, the particles have a corroded appearance. Some of the quartz grains have similar corroded edges against pyrite.

The veins in some nodules from the pyritic bed are filled with pyrite (fig. 7) that merges with the pyrite in the bed matrix and is not distinguishable from the pyrite that replaces some ooids (fig. 8). The pyrite in ooids replaces some, much, or all of the ooids. It may follow closely one or more concentric bands within the ooids. Commonly, however, the pyrite is concentrated in the outer parts of ooids, and it ranges in amount from scattered to closely packed grains (pl. 2, fig. 5).

Plate 2, figure 5 provides evidence that there are two generations of pyrite. In this ooid, and others not illustrated, pyrite was formed in the phosphate of the ooid. The phosphate was later replaced by barite that encloses some of the pyrite. The pyrite was thus formed early in the history of the nodule before the episode in which the barite was deposited. It is inferred that the very fine grained pyrite in the groundmass of the nodules is essentially contemporary with the pyrite in the ooids, but the inference has no necessary bearing on the sequence of events indicated by the relation of pyrite to barite in the ooids. Barite has not been found in the matrix of the nodule bed, and barite thus is inferred to have formed before the nodules were accumulated into a bed. The pyrite in the bed matrix, however, clearly formed after the accumulation of the nodules into a bed. Some ooids may have been replaced by pyrite during the deposition of the pyrite in the bed matrix, as shown by the pyrite-filled ooids cut by pyrite veins (fig. 8). No criteria have been found, however, to distinguish between such ooids filled with late pyrite and those filled with early pyrite.

Barite

Barite occurs in the nodules as replacement of part or all of individual ooids and as minute crystals in the phosphate groundmass. In replacing ooids, barite may be influenced by the concentric structure of the ooid (pl. 2, fig. 2, upper right) or it may crystallize independently of the ooid structure (pl. 2, fig. 2, lower right). In most ooids, the barite forms a coarse mosaic of individual crystals. In some, however, the barite is a single crystal that tends toward a euhedral shape (pl. 2, fig. 5). In a few ooids noted, the barite also replaced some of the groundmass surrounding the ooid. Although the barite generally replaces the phosphate of the ooid, in a few (pl. 2, fig. 4), fragments of the concentric rings seem to have fallen into open spaces and been surrounded by barite. The barite, however, does not have comb structure characteristic of open space growth. Bladed crystals of barite are uncommon. They were found only in ooids that do not now have any marked concentric structure and in which the phosphate is heavily iron stained (pl. 2, fig. 6).

The barite crystals are clear and do not contain ghosts of the structures they replace. Barite presumably was deposited after some pyrite was formed inasmuch as pyrite is included in barite (pl. 2, fig. 5). The pyrite in barite is not oxidized.

Calcite

The nodules contain only very small amounts of calcite. Barite has completely replaced originally calcitic material such as foraminifers and *Inoceramus* prisms. A few small areas of recrystallized clear calcite were noted. These evidently represent originally larger masses of calcite but are so recrystallized or replaced by barite that nothing can be inferred about the origin of the calcite.

Some calcite occupies parts of veins that mostly are filled with pyrite. It is not clear whether this represents essentially contemporaneous deposition of calcite and pyrite in different parts of the same vein or whether the calcite replaces pyrite. Particles of pyrite are isolated in the calcite where principal masses of the two minerals join.

Gypsum

Gypsum occurs as a secondary mineral in the outer parts of the nodules and in the matrix of the nodule bed. It also occurs within the nodules as a complete replacement of some of the ooids. Locally, both the calcite and pyrite in the veins mentioned under "Calcite" are partly replaced by gypsum. Gypsum fills some cavities (pl. 2, fig. 9) and may replace pyrite and barite in highly weathered nodules. The derivation of the gypsum from the oxidation of pyrite seems obvious.

Iron oxides

The nodules are variably weathered and iron oxides occur in an erratic pattern within them. A few ooids, inferred to have been completely replaced with pyrite, are now composed of iron oxides (pl. 2, fig. 1, upper left). In other ooids (pl. 2, figs. 1 and 2), iron oxides take the place of pyrite where pyrite, phosphate, and barite were intermixed prior to oxidation.

The iron oxides range from brown to red. Both hematite and geothite were identified from X-ray diffraction traces of similar-appearing but different parts of oxideoe rich areas of nodules and matrix.

NODULES FROM OTHER LOCALITIES

Nodules from the base of the Niobrara Formation at other localities in the Black Hills region, as seen in thin section, show remarkable similarities to the nodules from the two localities near Fairburn (p. L7) that are the basis for this paper. All the nodules contain ooids that have concentric banded structure, but the ooids are not as abundant as in the Fairburn. Pyrite is abundant, but the nodules are more weathered than those from near Fairburn and hence contain more iron oxide and gypsum. Foraminifers and radiolarians are present, but radiolarians are more abundant in some nodules than in those from near Fairburn. Some nodules also contain pellets, now phosphatized, that are identical with pellets of probable fecal origin which are found in many beds of marlstone and shale in the Pierre Shale.

Barite has not been identified in the nodules from other localities. Some of the ooids have been partly replaced by gypsum. It is not clear if this is actually replacement of phosphate by gypsum or alteration of preexisting pyrite to gypsum.

The nodules from localities other than from near Fairburn obviously have an origin similar to those near Fairburn except that fossils are not well preserved in them.

ORIGIN

PHOSPHATE IN NODULES

In considering the origin of the nodules and the paragenesis of the minerals in them, the following observations are pertinent:

1. The best preserved fossils are molds of the living chambers of cephalopods or molds of pelecypod shells where the concavities of the shells are opposed.

2. Nearly all specimens are internal molds. One of the few external molds noted is incidentally included between two opposing internal molds.
3. Phosphatization began before the aragonitic shell of cephalopods and the aragonitic inner layer of inoceramid shells were dissolved and was able to continue after the solution of the aragonite (pl. 1, fig. 25).
4. Calcite endured longer than aragonite and is still sparsely present in a few nodules. Calcite in foraminifers and *Inoceramus* prisms persisted until after the nodules were formed, but most of it was later replaced by barite.
5. The spatial arrangement of preexisting materials, such as quartz grains and Foraminifera, indicates that a volume of rock was phosphatized by a replacement process rather than by accretion of phosphate that was chemically precipitated.

These observations imply that a semiclosed environment was the most favorable for phosphatization in these rocks and that the process took place early in the diagenesis of the strata enclosing the shells.

The fossiliferous phosphate nodules lie in a thin bed at the base of the Niobrara Formation. The bed consists of calcareous shale and marlstone; the nodules are surrounded by marlstone. The underlying Carlile Shale consists of noncalcareous shale, although at many places the shale contains limestone concretions. It is inferred that the phosphate concretions at the base of the Niobrara Formation were formed by the phosphatization of marlstone similar to the marlstone in the rest of the Niobrara Formation. This inference is based chiefly on the pelagic foraminifers in the nodules. The marlstone of the Niobrara Formation contains abundant foraminifers, but they are scarce or absent in black shales like the Carlile.

Phosphate nodules, as well as several other kinds of phosphate deposits, have long been recognized to form by replacement of preexisting rock, usually limestone. Kazakov (1937, p. 95–96) reviewed the development of thought on the subject. Cayeux (1941) emphasized the importance of the role of replacement and presented his concept of its involvement in the formation of phosphates in general. Altschuler (1965) described several sequences of replacement processes in material from Florida. Bushinsky (1964, p. 68) accounted for concretions and nodules by diagenetic formation in bottom muds. Dietz, Emery, and Shepard (1942) and Kramer (1964), among others, have shown that sea water is supersaturated with respect to apatite; and data cited by Bushinsky (1964, p. 67) indicates that pore water in modern bottom sediments may contain more than 30 times as much phosphate as sea water. Evidently, special conditions other than saturation are necessary for the formation of phosphate nodules.

Experiments on the replacement of calcium carbonate date at least from 1891, according to Ames (1959, p. 830). Ames' experimental work seems to clarify the conditions under which calcium carbonate can be replaced by phosphate—conditions that are similar to those inferable for many geologic situations.

Calcium carbonate is readily replaced by solutions containing low concentrations of phosphorus to give a carbonate apatite, as shown by Ames (1959, p. 839), who listed the following conditions for apatite replacement of calcium carbonate:

1. A nondepositional environment.
2. Limy sediments or limestone available for replacement.
3. Sea water Ca-saturated, or nearly so, in order that the limestone present be in near-equilibrium with the sea water.
4. pH 7.0 or greater.
5. PO_4^{-3} concentration of 0.1 ppm or greater.

All these conditions except the first are well matched by the geologic setting inferred for these nodules at the base of the Niobrara Formation.

Ames' experiments did not involve fluoride ions, so the phosphatic replacement product probably was a carbonate-hydroxy apatite. This would not seem to invalidate the applicability of his work to marine phosporites, however, because hydroxy-apatites, and other kinds, acquire fluorine after their deposition (Altschuler and others, 1958, p. 49, 75). Ames' experiment was repeated using sodium phosphate solutions with and without fluoride ions provided by sodium fluoride. No difference between the replacement products within reaction times of about 3 months can be detected by X-ray diffraction.

Phosphate deposition generally is assumed to be in otherwise nondepositional environments, and the concept requires discussion. This concept was emphasized, in the North American geologic literature at least, by Goldman (1922), who traced its development from Tawney (1874, p. 173–174). (See Goldman, 1922, p. 172). Dietz, Emery, and Shepard (1942, p. 845; see also Emery and Dietz, 1950, p. 14) were greatly influenced by this concept in considering the origin of the phosphate nodules off southern California, although Emery (1948, p. 803) expressed a somewhat different view for similar nodules off Mexico. Some phosphate nodules may well have formed in part by accretion on sea floors receiving little or no sedimentation, but the data on nodular phosphate deposits indicate to me that this process is not the only way that phosphate nodules can form and that perhaps it was not even the predominant process for the nodules in the geologic column. Goldman (1922, p. 173) made it clear that accumulations of phosphate nodules can be of diverse origin; in his summary (p. 173), however, he did not deal with either a residual or a detrital mechanism for the concentration of nodules, but he clearly considered them to have formed in the absence of other sedimentation.

Teall (1900, p. 383), like Goldman, emphasized the importance of conditions of slow sedimentation for formation of phosphates, but he also recognized a replacement origin. Replacement-type processes are preeminent among the processes that Teall (1900, p. 385) summarized. Earlier, Fisher (1873, p. 53) had recognized that nodule beds contained many fossils derived from rocks other than those enclosing the nodules and that the geologic conditions inferable from the present situation of the nodules are not necessarily those under which the nodules formed. He also commented on the fact that the nodules showed only interior casts of fossils and that the shells of only certain kinds of calcitic fossils remained as calcite (Fisher, 1873, p. 53–54).

Phosphatic fossils often occur in condensed deposits in which a single fossil zone is represented by pebbles (Casey, 1961, p. 526; Jefferies, 1963, p. 22) or several zones may be represented in stratigraphic order in a single bed (Tawney, 1874, p. 173–174). Such occurrences are sometimes referred to as remanié (Teall, 1900, p. 383; Casey, 1961, p. 500). Although the word generally means only reworked, the special implication of remanié with respect to fossils is that the fossils represent a time span and rock unit that is not otherwise present. This contrasts with derived fossils, which can be reworked from any older rock unit. Some occurrences of remanié fossils of Cretaceous age in England have been interpreted as representing slow sedimentation with the implication that the fossils were phosphatized on the sea floor (Casey, 1963, p. 3; Jefferies, 1961, p. 617). Miller and Swineford (1957) gave a similar interpretation for nodules of Pennsylvanian age.

Some characteristics of phosphatic nodules and fossils interpreted to have been phosphatized on the sea floor in the absence of sedimentation clearly indicate that the phosphatized fossils were exposed for some time on the sea floor. These characteristics include the presence of epifauna on the nodules, such as encrusting oysters, calcareous tubes of worms, bryozoa, corals, and borings that penetrate the nodules. The borings may be filled either with another generation of phosphate or with the same kind of sediment as that in which the nodules are found. These characteristics are not, however, necessarily related to the conditions of formation of the nodules or the phosphatized fossils. The characteristics may represent only the last events in the history of the nodules.

Each occurrence must be studied separately, and it is not yet possible to arrive at conclusions that are applicable to all occurrences. It may be pointed out, however, that the nodules from the Agulhas Banks were generally interpreted as having formed in situ until Cayeux's study (1934) showed that the nodules were derived from several sources. Restudy of other occurrences could lead to different conclusions about the origin of the nodules as well.

The stipulation by Ames (1959, p. 839) of a nondepositional environment thus is an extension of the overemphasis by others on the apparent nondepositional characteristics of the geologic environments in which nodules are concentrated but not necessarily formed.

The relation between Ames' other conditions and those that would obtain in marlstone such as in the Niobrara Formation are evident enough. The experimental work showed that the most important factors controlling the rate of apatite replacement of calcium carbonate are the grain size (Ames, 1959, p. 834) and the pH (p. 836). Marlstone such as that in the Niobrara Formation is extremely fine grained because it was largely derived from coccolithophorids (p. L2); it is estimated that almost 50 percent of a typical sample would be finer than 2 microns. The greater speed and effectiveness of replacement of fine-grained carbonate probably explains why so few shells, whether of calcite or aragonite, are replaced by apatite, as noted by Fisher (1873, p. 54).

The pH of the semiclosed spaces that seemed to favor the formation of these nodules is difficult to assess. The gross pH regimen of marlstones must be close to 7.8, which marks the limestone fence pointed out by Krumbein and Garrels (1952, p. 26). Apatite replacement of calcium carbonate is effective at a pH as low as 7, but the process operates at a rate nearly 8 times as fast at a pH of 11 (Ames, 1959, p. 836). The anaerobic decay of proteinaceous matter can be expected to yield ammonia as pointed out by Murray and Irvine (1889, p. 86). This could raise the microenvironmental pH considerably above 7.8 and would be an important factor in initiating the replacement process.

The phosphate concentration of 0.1 ppm specified by Ames (1959, p. 839) represents the maximum average amount of total phosphorus reported for modern sea water (Mason, 1958, p. 187); and the largest expectable amounts of phosphates in sea water are on the order of 3 micromoles per liter (2.7 ppm), according to Goldberg and Parker (1960, p. 63). Dissolved phosphate in pore solutions of some modern sediments may be as much as 7 ppm (Bushinsky, 1964, p. 67). It does not seem necessary to speculate on the phosphate content of Cretaceous water because it is evident that there was sufficient phosphate for the replacement process to operate. The proteinaceous matter of the animals themselves could be a local source of phosphate since many modern mollusks contain more than 0.1 percent elemental phosphorus in their living matter (Vinogradov, 1953, p. 287–293). Ames (1959, p. 839) found little difference in effectiveness of the replacement process at different concentrations of phosphate and pointed out that replacement can take place at concentrations of both phosphate and calcium far below those required for apatite precipitation.

The ooids in the nodules are interpreted as the original nucleating sites for the replacement process as a whole. As mentioned, actual nuclei of the ooids have not been observed, and thus no data are available on any substance that caused the ooids to begin to grow. In spite of this defect, this interpretation seems the most reasonable in light of what is known now. It does not seem reasonable to consider them as segregations formed after the formation of the nodules, analogous to the formation of spherulites in a precipitate. The precipitate would require a gel-like state of the nodule that is inconsistent with the formation of the nodules within the sediment. Such segregations probably would have a radial structure rather than a concentric one. The possibility that the ooids originated elsewhere and are mechanical constituents (detrital, in a sense) of the marlstone, deposited before the replacement that formed the nodules, seems to be eliminated by the random distribution of the ooids in the nodules.

The replacement of marlstone by phosphate is not necessarily a slow process, as evinced by the coprolites described by Buckland (1835). Fisher (1873, p. 62) also pointed out the geologically short period of time likely to be involved in replacements such as this one at the base of the Niobrara Formation. An example of extreme rapidity of a phosphate replacement, although of a slightly different kind, is the phosphatic preservation of the intestines of a gastropod described by Casey (1960). The shells of ammonites and other gastropods associated with this remarkable specimen are replaced by phosphate (Casey, 1960, p. 273) and are surrounded by phosphate cementing the sandy matrix. The shell substance of the ammonites and gastropods was the only calcium carbonate in the environment and hence was the only available base for the replacement process, although additional phosphate was deposited around the shells.

Shark and ray teeth occur with the fossiliferous nodules (p. L2). Shallow concavities at the bases of some of the teeth in which root structures were not preserved were filled with phosphate like that in the nodules. Foraminifers were seen in thin sections of the teeth indicating that the teeth were originally deposited in marlstone that subsequently was phosphatized. There are no accretionary deposits of apatite on the tooth or lying between the tooth and the phosphatized marlstone; therefore the phosphatic material itself of the teeth did not serve as a nucleus for the precipitation of apatite. The teeth may, however, have stimulated the replacement of marlstone by phosphate, or they have been chemically passive objects in a volume of rock in which some other condition had initiated phosphate replacement.

OTHER MINERALS IN NODULES

Pyrite

Pyrite is an expectable constituent in material, such as phosphate nodules, that was formed in a reducing microenvironment rich in organic material. Bacterial reduction of sulfate in conjunction with anaerobic decay of organic matter provides a sufficient source of sulfide. The occurrence of pyrite in the ooids, in the groundmass of the nodules, and in the matrix of the nodule bed indicates that the pyrite formed both penecontemporaneously with the replacement of marlstone by phosphate and also subsequently to the accumulation of nodules in a bed.

Barite

The barite was formed in the groundmass and replaced ooids and parts of ooids after the formation of pyrite in the ooids. Simultaneous deposition of the two minerals is inconsistent with the different oxidation states of their forms of sulfur.

Reports of other occurrences of barite in phosphatic material are rare. Buckland (1835, p. 224) mentioned barite on the outer surface of coprolites. Emery (1948, p. 802) found barite replacing diatoms in nodules dredged off the coast of Mexico. Altschuler (1953, p. 33) found barite in the heavy mineral fraction of several samples of Idaho phosphate.

Seemingly, the abundant barite in the nodules at the base of the Niobrara Formation required relatively large amounts of barium and of sulfate to be present. Although no explanation is clearly evident, the data presented by Gates and Caraway (1965) on the formation of barium sulfate scale in water-flooding operations in the Wilmington oil field, California, suggest a mechanism that may be applicable. Barium sulfate scale forms in producing wells when the injected sea water that is used for flooding mixes with formation water and the mixture breaks through to enter the wells. The injection water contains less than 1 ppm (part per million) barium and about 2,000 ppm sulfate. The formation water contains from 16 to about 150 ppm barium and less than 15 ppm sulfate. The mixture of these two waters, however, is supersaturated with barium sulfate (Gates and Caraway, 1965, p. 12), and barium sulfate is precipitated.

The pore water in the marlstone surrounding the phosphate nodules after they were formed and any water within the nodules would be deficient in sulfate because of the extensive reduction of sulfate to sulfide and the resultant deposition of pyrite. The barium content of the pore water is not determinable, but any amount larger than a few parts per million would be sufficient to exceed saturation concentration when the pore water was mixed with a normal marine water, such as the Cretaceous sea water is assumed to be. During the submarine erosion of the beds in which the nodules were formed, pore water and normal marine water would be mixed; the saturation point for barium sulfate would be exceeded, and barite would be deposited. The pyrite was not oxidized during this process. The manner in which the waters were mixed, the volume of pore water involved, and the way these two factors interacted to result in the relatively large amounts of barite now present in these nodules cannot be determined. Other hypothetical origins are possible but seem less satisfactory.

If the sulfate in the barite is considered to be the result of oxidation of pyrite on or near the present outcrop surface, it would seem that only gypsum, not barite, would be formed inasmuch as marlstone surrounds the nodules. No barite has been found in any of the abundant secondary gypsum. The problem of the amount of barium present in the environment to give such large amounts of barite still remains. The presence of epigenetic solutions from which barite could have been deposited also is unlikely, both with respect to a plausible source and the paragenesis of pyrite and barite as well as to the concentration of the barite in the nodules and the absence of determinable barite in the associated rocks.

Calcite

Patches of calcite in the nodules probably were of organic origin. Calcite mixed with pyrite in veins in the nodules was derived from the marlstone that covers the nodule bed.

Gypsum and iron oxides

Gypsum and iron oxides are normal products of weathering of marlstone and pyrite in the nodules.

ABSENCE OF PHOSPHATE NODULES IN MAIN PART OF NIOBRARA FORMATION

Before discussing the relation of other minerals in the nodules to the geologic history of the nodules, consideration should be given to the significance of the apparent absence of such nodules in the remainder of the Niobrara Formation. Seemingly, if nodules could form in a marlstone unit that was the precursor of the Niobrara Formation, the nodules could form in the Niobrara Formation itself, and their presence there would be good evidence for the process of replacement advanced here for the origin of the nodules and for their later concentration.

Several factors need to be considered. First, the nodules at the base of the Niobrara Formation, although noted at many localities (Cobban, 1952; Robinson and others, 1964; and Connor, 1963), nowhere constitute an accumulation of much bulk. As described by Cobban (p. L2 of this report), and observed by others (J. J. Connor and W. J. Mapel, oral commun., Apr. 5, 1966), the nodules are scattered on the upper surface of the Carlile Shale. In an outcrop, they may occur in a thin bed largely cemented by pyrite along the contact. Second, phosphate nodules are not necessarily absent from the Niobrara Formation in the Black Hills region. The Niobrara commonly weathers to an orange clayey residuum in which nodules would not be conspicuous, and they would be unlikely to be noted unless they were particularly sought. It is possible that more phosphate nodules occur in the main part of the Niobrara Formation than has been recorded. This question has importance, really, only for its implications with respect to a third factor, namely, the assumption that conditions of deposition for the main part of the Niobrara Formation were the same as for the postulated precursor unit. It is indicative of the moot nature of questions of this kind that the presence of phosphate nodules in the precursor marlstone and their apparent absence in the main part of the Niobrara Formation can be interpreted to mean that the conditions of deposition for the two units were not the same.

The instability of aragonite compared to calcite in mollusk shells is well known (Sorby, 1863, 1879, p. 65–66; Bøggild, 1930, p. 244–245). Most calcitic chalk units, such as the Niobrara Formation, contain only calcitic shells, such as oysters, and the outer prismatic calcite layer of *Inoceramus*, and other forms (see also Fisher, 1873, p. 53–54). Shells of ammonites are almost completely lacking in the main part of the Niobrara Formation, yet they are abundant in contemporaneous shale units in Montana and elsewhere where the shells are preserved in limestone concretions. There is no reason to believe that ammonites did not live in the waters beneath which the Niobrara was deposited; the absence of such forms in the Niobrara seems entirely a matter of preservation. In contrast, the phosphatic nodules at the base of the Niobrara Formation record the aragonitic shells of ammonites and the inner aragonitic layer of shells of *Inoceramus*. The conditions of deposition in the precursor marlstone unit thus must have been different from those in the main part of the Niobrara Formation, because aragonitic shells in the marlstone unit were preserved in the marlstone long enough for them to be phosphatized.

The chief factor in the preservation of aragonitic shells in limestone concretions in shale seems to be the relatively rapid sealing off of the shell in the concretions that formed nearly at the sediment-water interface (Tourtelot, 1966). By analogy, then, aragonitic shells in the precursor marlstone unit were buried sufficiently rapidly to be preserved for long enough for the marlstone matrix inside the shells to be replaced by phosphate. Sedimentation of the main part of the Niobrara Formation can thus be inferred to have been sufficiently slow that aragonitic shells were dissolved before phosphatization or any other process of preservation could be effective. "Slow" and "rapid" obviously are only comparative terms in this context. Considering, however, that organic matter in the shell cavities seem to be an important material for the initiation of phosphate replacement, the rate of deposition of the precursor marlstone unit might have been rapid in an absolute sense as well.

Neither the characteristics of the fossiliferous nodules nor their depositional setting suggests any reasons why the depositional rate should have been more rapid for the precursor marlstone unit than for the remainder of the Niobrara Formation.

SUMMARY

The origin and history of the phosphate nodules are interpreted as follows. Benthonic and nektonic fossils were buried in marlstone during deposition in a normal marine environment. This marlstone was a precursor to the Niobrara Formation as it exists today. Living chambers of ammonites, accidentally opposed separate valves of pelecypods, and pelecypods buried with the valves in opposition provided semiclosed systems, or microenvironments, that favored the replacement of the contained finely divided calcium carbonate with calcium phosphate. Nodules were thus formed that are internal molds of the fossils. The depth of burial of the microenvironments when the phosphate replacement began is not determinable, but probably was not great. The decay products of proteinaceous organic matter and the pore water expressed from the marlstone by compaction provided a supply of phosphate ions. The concentration of phosphate in the source solutions did not need to be large. The replacement process began with nucleation which formed ooids. In some nodules, phosphatization extended into the marlstone matrix beyond the shell. Pyrite was deposited in, and perhaps with the replacing phosphate. The replacement process was ended by diminution of phosphate supply. This could have been caused by decrease in movement of pore water as compaction reached an optimum state, or by exhaustion of the organic matter that controlled the conditions of the microenvironment. Solution of the aragonite shells that bounded the original microenvironment could also be a factor. The aragonite shells probably began dissolving shortly after burial.

At some later time, after a very short interval, geologically, deposition of marlstone ceased, perhaps because of a local shift in currents, and the marlstone previously laid down was eroded. The thickness of sediment eroded could have been great or small and the density of distribution of nodules likewise was variable. In any event, erosion concentrated the nodules along the surface at which erosion stopped. Some of the underlying shale unit could have been eroded, also. As erosion went on, barite was deposited in the nodules, perhaps because of the mixing of sulfate-bearing sea water and barium-containing pore water in the nodules and in the surrounding marlstone. The nodules accumulated as a lag gravel (Udden, 1898, p. 7) of remanié fossils. Marlstone deposition was resumed, probably at a slower rate from that of the precursor unit, and the Niobrara Formation was deposited. As bacterial reduction of sulfate proceeded, pyrite either replaced the existing matrix of the nodule bed or was deposited in voids.

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[Italic page numbers indicate either major references or fossil descriptions]

PLATES 1–2

PLATE 1

[All figures natural size except as noted on plate]

FIGURES 1, 2. *Scaphites* cf. *S. frontierensis* Cobban (p. L3).
Rear and lateral views (× 2) of the older part of a body chamber showing constrictions. From base of Niobrara Formation at USGS loc. D3757, 8 miles south of Fairburn, S. Dak. USNM 153056.

3–9. *Scaphites frontierensis* Cobban (p. L3).
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3–5. Two lateral views and rear view of most of a body chamber. USNM 153057.
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Lateral view of a fragment of the older part of a body chamber from the same locality as figures 1, 2. USNM 153063.

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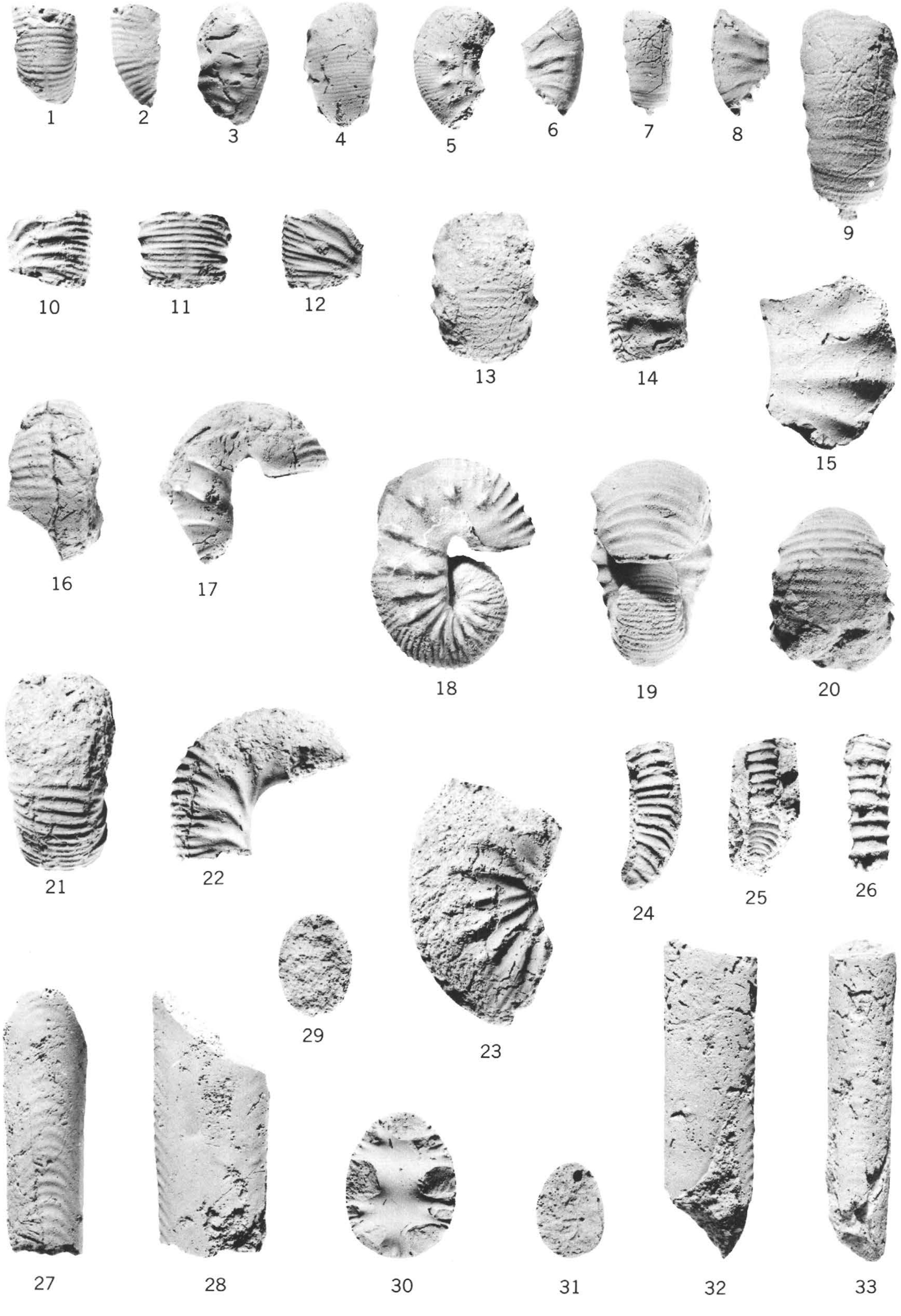


AMMONITES CHIEFLY FROM BASE OF NIOBRARA FORMATION

PLATE 2

[Abbreviations for minerals: A, apatite; B, barite; X, iron oxide; P, pyrite; Q, quartz. All photomicrographs in plane light]

FIGURE 1. Thin section of area outlined in figure 8 (below); *a* and *c* are same as in figure 8. Note that there is no trace of baculite shell in continuation of the shell mold at *c*. The darker mottled parts represent disseminated fine-grained pyrite. Most of the clear ooids are filled or partly filled with barite. The dark ooids and the dark rings and masses in them are pyrite or iron oxide. See figure 2 for detail in outlined area. (× 12).

2. Detail of figure 1. Light-colored area is pyrite-free phosphate. The light-colored ooids are pale-brown nearly isotropic apatite. Dark spots in ooids are pyrite or iron oxide; clear areas in ooids are barite, and in groundmass are both barite and quartz. (× 40).

3. Thin section showing mold of interior of inoceramid shell (emphasized by dashed line) and borings made along the contact between mud and shell before phosphatization. See also plate 1, figures 9 and 32. (× 40).

4. Ooid filled with barite showing disruption of annular phosphate rings during barite deposition. Main part of apatite is highly ferruginous. (× 40).

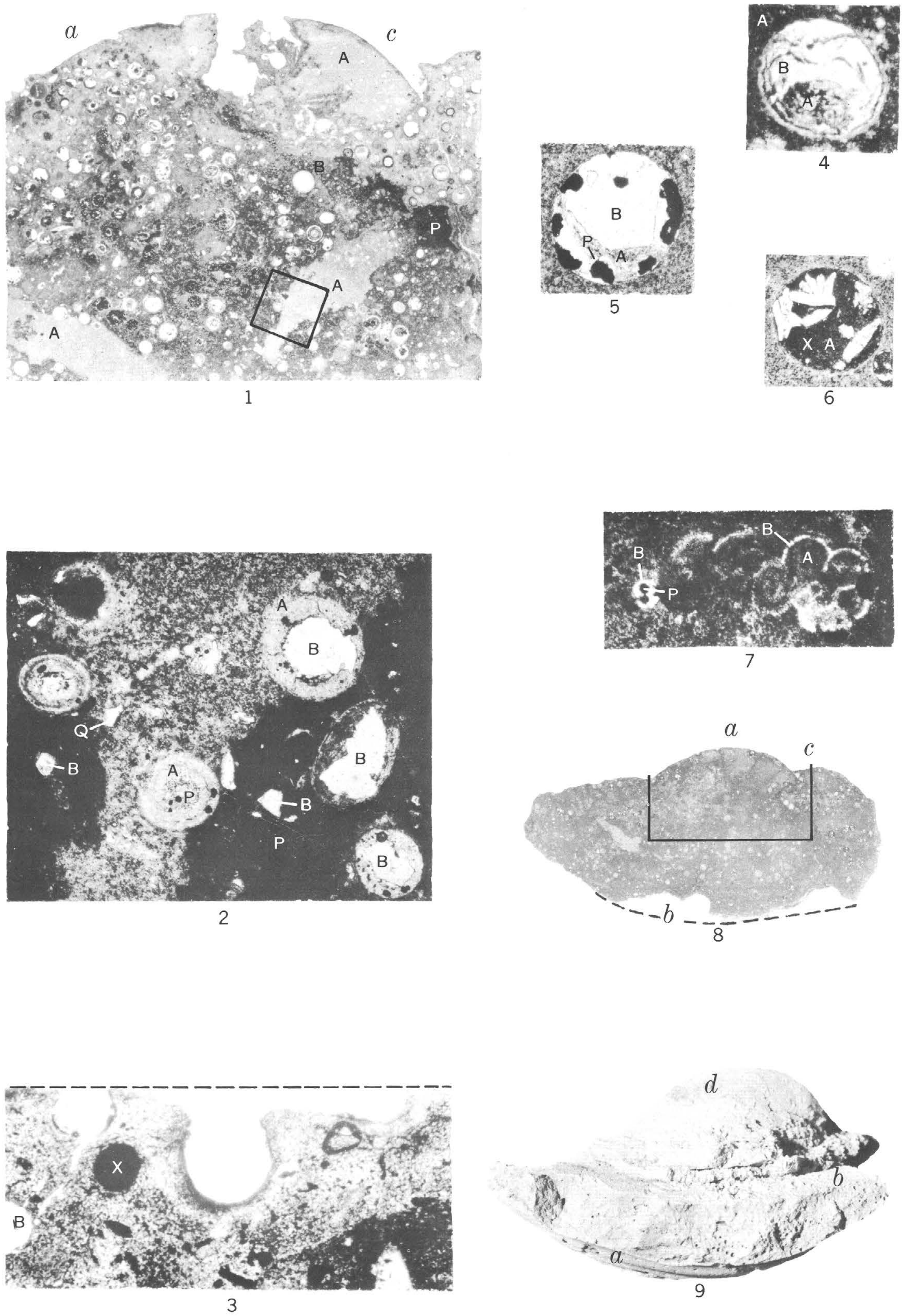
5. Ooid consisting of original pale-brown apatite containing pyrite, both partly engulfed by a euhedral crystal of barite. Note annular phosphate ring at lower left, terminating against face of barite crystal, and absence of ghosts in barite. Pyrite in barite is not oxidized. (× 40).

6. Bladed crystals of barite in a matrix of iron oxide and apatite. (× 40).

7. Pelagic foraminifer replaced by barite and filled with apatite and pyrite. Fragments of other foraminifer tests also are visible. Globular body at left is a section of either a foraminifer chamber or a radiolarian filled with barite and containing two pyrite crystals. (× 100).

8. Cross section of a phosphate nodule showing casts of a baculite (*a*) and an inoceram (*b*). The dashed line shows the continuity of the inoceramid shell surface. Groundmass is microcrystalline apatite. Note mottled nature of apatite and the randomly distributed lightcolored ooids; dark ooids also are present. Crevice (*c*) is mold of baculite shell. See figure 1 (above) for detail in outlined area. (× 2).

9. Phosphatic nodule containing three fossils: *a*, concave upwards internal cast of an inoceram; *b*, cast of outer surface of an inoceram also concave upward; *c*, crevice that is a mold of the inoceramid shell; now filled with gypsum; *d*, internal cast of a small inoceram concave downward. The beak is at the right. (× 2).



PETROLOGY AND MINERALOGY OF PHOSPHATE NODULES

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