Reports

Recent Biogenic Phosphorite: Concretions in Mollusk Kidneys

Abstract. *Phosphorite concretions have been detected in the kidneys of two widespread species of mollusks,* Mercenaria mercenaria *and* Argopecten irradians, *which have relatively high population densities. These concretions are the first documentation of the direct biogenic formation of phosphorite grains. The concretions are principally amorphous calcium phosphate, which upon being heated yields an x-ray diffraction pattern which is essentially that of chlorapatite. These concretions appear to be a normal formation of the excretory process of mollusks under reproductive, environmental, or pollutant-induced stress. Biogenic production of phosphorite concretions over long periods of time and diagenetic change from amorphous to crystalline structure, coupled with secondary enrichment, may account for the formation of some marine phosphorite desposits which are not easily explained by the chemical precipitation-replacement hypothesis.*

The genesis and age of marine phosphorite (rocks composed mostly of carbonate apatites) have been controversial for years. Many investigators favor a process of chemical formation in which apatite is precipitated when strong upwelling brings deep cold water laden with phosphates and CO_2 near the surface where warming and increasing pH cause the requisite decrease in apatite solubility (*1–3*). Alternatively, phosphatization of carbonates may take place under generally similar oceanographic conditions with the additional requirements that there be a low oxygen content at the replacement site, little detrital deposition, and limited deposition of carbonate detritus (*4, 5*). Most marine phosphorites have been thought to be ancient (*6, 7*), but recently Baturin *et al.* (*8*), Veeh *et al.* (*2*), Manheim *et al.* (*3*), Burnett (*5*), and Burnett and Veeh (*9*) have shown that contemporary phosphorite is forming by precipitation or replacement off southwestern Africa and Peru.

However, widespread deposits of phosphorites were formed on ancient open continental shelves unlikely to be subjected to the requisite rather restrictive oceanographic conditions necessary for precipitation or replacement. Other hypotheses of phosphorite formation that have been advanced with less force of evidence (*6, 10*) include deposition as a consequence of vulcanism, mass mortality, and biogenic activity. Vertebrate skeletons and renal stones, many polychaete annelid worm tubes, some arthropod carapaces, and inarticulate brachiopod shells such as those of the genera *Lingula* and *Discimisca* are composed of calcium phosphate and may contribute to phosphorite formation when dissolved and reprecipitated (*11*).

We report here the first documented occurrence of biogenic phosphorite grains forming at present in the kidneys of two common species of Pelecypoda, *Mercenaria mercenaria* and *Argopecten irradians*, taken from widely disparate sediments and from widely separated locations. *Mercenaria mercenaria* were collected from a muddy sand, which smelled strongly of H_2S (indicating reducing conditions) in approximately 6 m of water at two stations off Sabin's Point in a heavily polluted part of Narragansett Bay, Rhode Island. Specimens of *A. irradians* were collected from a clean quartz sand with up to about 20 percent $CaCO_3$, mostly in the form of shell fragments, in about 2 m of water from Boca Ciega Bay on the west coast of Florida.

Concretions which proved to be phosphorite were first detected in the kidneys of both groups of animals by light microscopy of tissues undergoing histopathologic analysis (Fig. 1). The kidneys of eulamellibranch pelecypods (*M. mercenaria*) are located along the adductor muscle and consist of folds of connective tissue covered with a clear columnar epithelium. The apical portions of the epithelial cells usually contain vacuoles with concretions which vary in color. In the kidneys of filibranch pelecypods (*A. irradians*) the kidneys are separate, distinct bodies lying on the adductor muscle. They are tubular and consist of clear columnar epithelial cells which may contain concretions. In some individuals of both species, the concretions choke the entire organ. The size of the concretions varies considerably, with those in *A. irradians* ranging up to 30 μm and those in *M. mercenaria* ranging up to a maximum of about 250 μm.

Argopecten concretions were analyzed in tissue sections; *Mercenaria* concretions were removed from approximately 400 animals from each station. About 2.8 g of concretions were recovered from each group of 400 *Mercenaria*. We examined the concretions, using light microscopy and a scanning electron microscope; we analyzed for elemental and mineralogical content with a scanning electron microscope (SEM) and an attached energy-nondispersive element analyzer, an argon plasma emission spectrometer-spectrograph, and an x-ray diffraction system.

Figure 2, a and b, shows SEM photographs of some of the *Mercenaria* concretions. Most are well rounded and are concentrically layered. The layers within the grains themselves have a coarse to fine microbotryoidal texture (Fig. 2c). Coarse-textured grains have a sugary appearance under a light microscope, whereas those that are fine-textured have a highly polished appearance. Shapes, textures, and colors, predominantly browns and black but also off-white through gray, yellow, orange, beige, and ochre, are reminiscent of

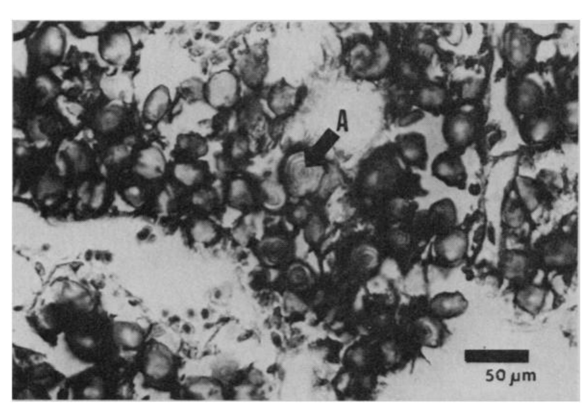

Fig. 1. A tissue section (6 μm thick) of an *Argopecten irradians* kidney choked with phosphorite concretions. Note the concentric layering of concretion *A*. The section is stained with hematoxylin-eosin.

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Table 1. Selected trace metals in some *Mercenaria* kidney phosphorite concretions; ppm, parts per million.

Element	Concentration (ppm, by weight)
Ba	75
Cu	4,000
Zn	59,000 (5.9 %)
Cd	11
Cr	20
Sr	3,174
Ni	50 to 70
Pb	96
Hg	30 to 50

phosphorite grains from deposits such as those of the continental shelf off the southeastern United States.

The concretions are principally amorphous calcium phosphate. Crystalline patterns begin to appear at 400°C and improve upon heating up to 550° to 600°C. The primary mineral phase present is close to the chlorapatite of the Joint Committee for Powder Diffraction Standards [$(CaCl)Ca_4(PO_4)_3$]. In some concretions subjected to heating, aluminum is a major constituent, present as the aluminum phosphate minerals wavellite [$4AlPO_4 \cdot 2Al(OH_3) \cdot 9H_2O$] and childrenite-eosphorite [$AlPO_4 \cdot Fe(OH)_2 \cdot H_2O$].

Figure 3 shows a typical elemental x-ray spectrum of one of the concretions. Calcium phosphates will accept a wide variety of trace and other constituent elements. Zinc comprises up to 5.9 percent of the particles, and iron and manganese are present in minor amounts. Copper, strontium, magnesium, potassium, sodium, and sulfur vary from trace to minor quantities; barium, cadmium, chromium, nickel, lead, and mercury are present in only trace amounts (Table 1). Analyses of a number of concretions show that within one particle the composition of individual layers varies little but considerable variation in composition exists among particles. The concentrations of trace and minor elements are consistent with the wide variety and abundances reported by McConnell (*12*).

The concretions are chemically similar to some marine apatites. Unlike the concretions that are essentially amorphous until heated, most marine phosphorites contain well-crystallized minerals. Therefore, in order to become deposits such as those of the continental shelf off the southeastern United States, crystallinity would have to be diagenetically induced.

Sediments of Boca Ciega Bay contain small amounts of phosphorite, some of which is undoubtedly weathered from known Miocene deposits. Some phosphorite grains from the bay are similar in appearance to those found in the kidneys. Hence, concretions which may be deposited from *Argopecten* at present are not distinguishable by visual means from Miocene grains.

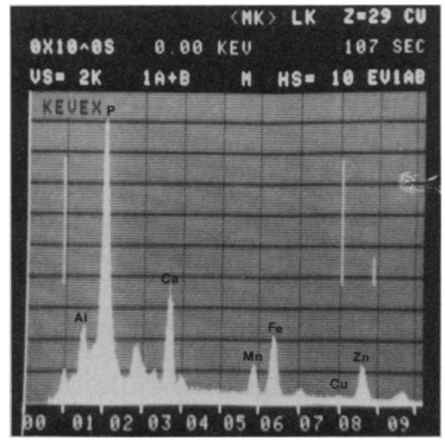

Fig. 3. Typical elemental x-ray spectrum.

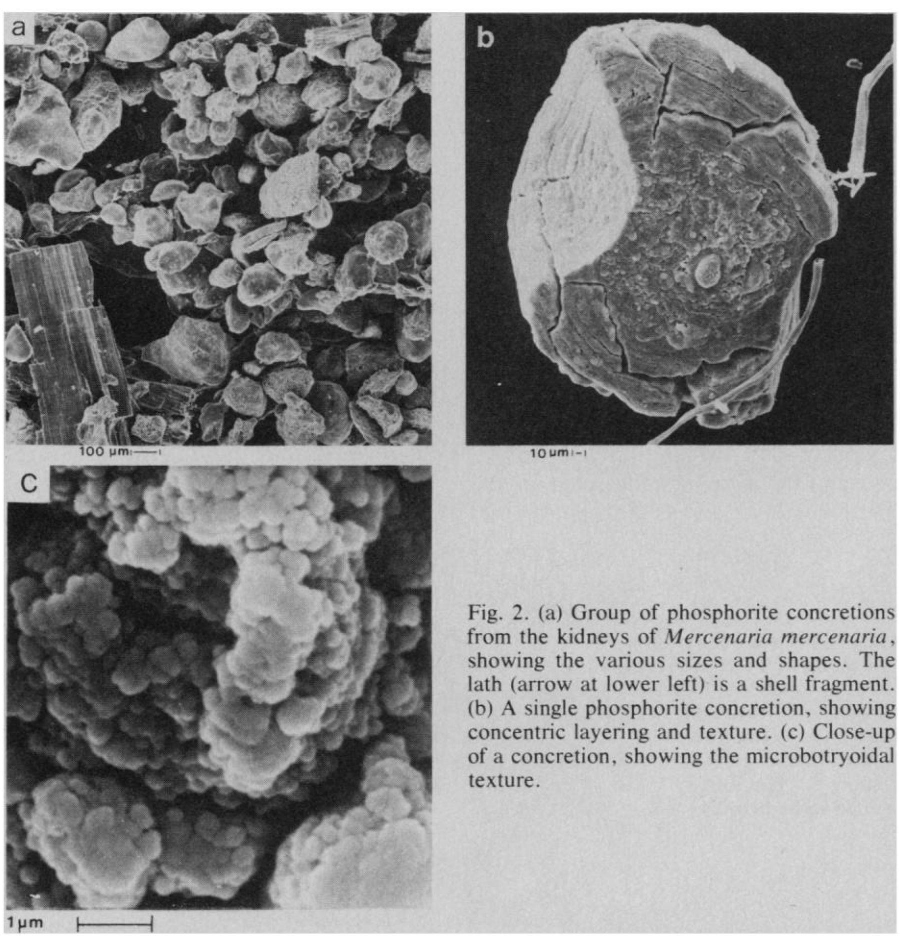

Fig. 2. (a) Group of phosphorite concretions from the kidneys of *Mercenaria mercenaria*, showing the various sizes and shapes. The lath (arrow at lower left) is a shell fragment. (b) A single phosphorite concretion, showing concentric layering and texture. (c) Close-up of a concretion, showing the microbotryoidal texture.

McMaster (*13*) reported apatite derived from a crystalline rock provenance but no phosphorite in the sediments of Narragansett Bay. None would be expected to be contributed by the glacial and continental deposits which act as sources for bay sediments (*14*). Sediments which were subsequently sampled from the Sabin's Point *Mercenaria* collection site contained trace amounts of reddish brown opaque particles similar in appearance to some of the phosphorite concretions found in the *Mercenaria* kidneys and which gave a positive test for phosphorus when subjected to a solution of ammonium molybdate and dilute nitric acid, the standard stain test for phosphorite.

We have observed concretions similar in all visual aspects in many individuals of the two species collected from the west and east coasts of the United States and from the eastern Gulf of Mexico. One of the peculiarities of mollusk kidneys is their ability to excrete solids in the urine in the form of concretions. The exact form and nature of the concretions may vary according to species, cyclic changes, and environmental conditions (*15*). Although all animals from which we have analyzed phosphate concretions to date have come from more or less polluted environments, we have also observed concretions in animals from apparently nonpolluted areas. Thus, pollution may be primarily related to concretion formation in that it serves as a stress on the organism. In animals collected from unpolluted environments, stresses which may lead to concretion formation are abnormal temperature or salinity or proximity in the reproductive cycle to spawning.

Trace metals in the pollutants may also affect the concentrations of elements within the concretions. For example, zinc is known to be concentrated by the kidneys of some mollusks (*16*). High zinc contents in the concretions may be caused by relatively large amounts of zinc in industrial pollutants which are further concentrated by the organism.

Both *A. irradians* and *M. mercenaria* are widespread and common, and range from Nova Scotia to Florida in the Atlantic and from northern Florida to Texas in the Gulf of Mexico. *Argopecten irradians* is usually found in shallow coastal bays containing stands of eelgrass in the northern portions of its range or turtle grass in the southern portions. Populations of scallops fluctuate widely from year to year and location to location, although we have observed densities as great as 22 per square meter. *Mercenaria mercenaria* is found in muddy sediments in coastal waters. Populations of these animals also fluctuate widely, but the densities are often high enough for commercial exploitation. The extensive range and high densities of mollusks suggest that biogenic phosphorite could be deposited in many marine environments. The fact that the same or similar species also extend far back into the geologic past suggests that this process may have been active in earlier times.

Concretions may be incorporated into the sediment when the animal dies either as a result of old age or as a result of renal failure. Some concretions may be excreted from the living animal, since we have observed them in tissue sections in the vicinity of the renal pore. Long periods of time as well as secondary enrichment (suggested by the small weights of phosphorite concretions in 400 animals) and diagenetic change from an amorphous to crystalline structure may be required to form biogenic phosphorite deposits.

Irrefragable evidence of direct biogenic formation of phosphorite has profound consequences. Its deposition is restricted only by range contraints on the organisms involved and does not require the special oceanographic conditions that chemical formation of phosphorite does. Biogenic formation of phosphorite does not rule out chemical or diagenetic formation, either in the past or the present. However, if biogenic phosphorite is preserved in sediments, it may explain deposits that do not seem to fit the chemical precipitation-replacement hypotheses such as those that have been suggested to account for the formation of the continental margin of the Southeast where the phosphorite is distributed throughout the sediments as discrete sand-sized or smaller grains.

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17. We thank D. Bankston who carried out the analyses summarized in Table 1, N. Thayer who collected the sediment samples, and F. T. Manheim who criticized the manuscript. We thank R. Rheinberger who extracted the concretions from *Mercenaria*, D. Johnson who arranged for SEM analyses of tissue sections at the N. C. Brown Laboratory for Ultrastructure Analysis, and J. McLane who provided assistance during SEM analysis of the spherules.

3 June 1977; revised 28 November 1977

Imbrian-Age Highland Volcanism on the Moon: The Gruithuisen and Mairan Domes

Abstract. *The Gruithuisen and Mairan domes on the moon represent morphologically and spectrally distinct nonmare extrusive volcanic features of Imbrian age. The composition, morphology, and age relationships of the domes indicate that nonmare extrusive volcanism in the northern Procellarum region of the moon continued until about 3.3* $\times$ *10^9 to 3.6* $\times$ *10^9 years ago and was partially contemporaneous with the emplacement of the main sequence of mare deposits.*

The lunar maria and highlands show major differences in morphology, petrology, geochemistry, thermal history, and age (*1*). With few exceptions (*2*), these differences are viewed in terms of two distinct periods of lunar history with little or no overlap: an early period of highland crustal formation, volcanic activity, and bombardment, culminating in the formation of the Imbrium and Orientale basins, followed by a period characterized by the extrusion of mare lavas and less intense bombardment. There is some evidence, however, for the continued emplacement of nonmare volcanic geologic units during the period of mare volcanism. We have obtained spectra and vidicon imagery of several such regions and compiled detailed geologic maps in order to (i) characterize these anomalous areas compositionally and compare them to returned samples and to other mare and highland regions, and (ii) establish age relationships and mode of origin. We report here geologic and spectral evidence for the extensive overlap in time of mare volcanism and a distinctive nonmare surface unit apparently of extrusive volcanic origin.

A series of domical features located near the shores of northeastern Oceanus Procellarum adjacent to Iridum crater (Fig. 1) have long attracted attention because of their relatively high albedo and morphological distinctiveness. The domes are very bright (red) in infrared-ultraviolet color-differenced photographs (*3*). Several additional "red spots" occur in a variety of geologic environments in the western portion of the lunar near side (*4, 5*). In this report we concentrate on one of the red spot areas, the Gruithuisen domes, and an adjacent area with similar characteristics (Fig. 1, a through c).

Recently, McCord *et al.* obtained digital images at several wavelengths, using a silicon vidicon imaging system and earth-based telescopes (*6*). The photometric precision of these images is at least 1 percent, and the spatial resolution is about 2 km at the subearth point. We have prepared ratio images for the region of Fig. 1a by dividing images obtained at

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