ASSOCIATION OF PHOSPHORITES, ORGANIC-RICH SHALES, CHERT AND CARBONATE ROCKS

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ABSTRACT: The single-basin association of sequences of marine phosphorite, organic-rich shale, chert, dolomite and biogenic limestone has been known for a number of well studied deposits for many years. It has long been known that organic matter, silica and phosphorus are supplied to shallow shelf areas by upwelling ocean currents. Recent marine sedimentologic research has shown that phosphorite and dolomite are formed by early diagenesis of organic matter and, in the case of dolomite, by early diagenesis of carbonate sediments.

A literature survey of 135 world-wide phosphatic sequences from Lower Proterozoic to Quaternary age shows that the association of organic-rich sediment, phosphorite, chert and carbonate has been constant over time, but that the type of carbonate rock has shown a temporal variation. Dolomite is the only significant carbonate in Proterozoic and Cambrian sequences, whereas both limestone and dolomite occur in younger sequences. Some of the organic-rich phosphatic sediments are oil shales or petroleum source rocks. It can be concluded that a significant percentage of world petroleum resources were derived from such source rocks.

These phosphatic sequences tend to be cyclic in nature and, in some instances, the regressive sediments include restricted basin evaporites, carbonates and shales. However, these sediments have not been counted in the upwelling marine associations.

INTRODUCTION

Marine phosphorite is a biogenic sediment deposited in shallow-water areas, open to the ocean, where deeper oceanic water wells up to the surface. Other biogenic chemical sediments are closely associated with phosphorites, including biogenic carbonate, siliceous and carbonaceous sediments. Because the source of phosphorus is the deep-ocean geochemical sink, other elements trapped in the sink tend to be associated with phosphorites, including silica, about 25 trace elements and, in rare instances, nitrates. Most phosphorites are formed in reducing environments, at least at one stage of their formation, and tend to be associated with reduced elements including carbon, iron, manganese, sulfur, and uranium. Phosphorites can only be deposited in alkaline environments and are thereby associated with calcium, magnesium and manganese carbonates to varying extents. Phosphorus is derived from marine waters; thus, the conservative marine elements - most importantly calcium, fluorine and magnesium - are available in the environment of phosphorite deposition and can make up apatite and other associated minerals in the sediments. Finally, the temperature of upwelling water is normally low, so that phosphorites are associated with sediments containing cool or cold water biota.

All of these associations are not synchronous; that is, they are not necessarily a mixture with or a facies of phosphorite. Because phosphorites are generally found in cyclic sequences that are the result of changing paleooceanographic conditions, paleoclimates, and sea levels, many of the sediment associations are also the result of these changing conditions within the general upwelling environment.

The continental shelf upwelling environment on its landward side commonly adjoins platform seas, which are indirectly affected by the upwelling environment. Modified deeper-ocean water feeds such platform seas. The areas of coastal upwelling form meteorological high-pressure areas because of the cold water at the surface, while adjacent landward areas form meteorological low-pressure areas because they are warmer than the cold ocean areas. These pressure areas are stable and generate a surface equatorward wind system that enhances oceanic upwelling in the trade wind belt along west coastal areas (Parrish, 1982). Adjacent to continental shelves where phosphorite is being deposited, the normal sediments are evaporites in cratonic basins and eolian sand deposits in terrestrial environments. Trade winds are primarily responsible for this genetic link, because they cause trade-wind deserts, high evaporation in cratonic seas and strong continental shelf upwelling. Desert conditions also result in only minor clastic contributions to the basins of deposition, unless adjacent land areas have high relief.

Thus, a complex but genetically interrelated association exists among chemical and biochemical phosphorites, organic-rich and metal-rich shales, siliceous sediments, sediments rich in magnesium, manganese and iron carbonates, cold-water biota, evaporites, and eolian sands. At the same time, the chemical sediments normally contain only minor clastic components. These associations, which have been reviewed by Cook and McElhinny (1979) and Riggs (1986), are discussed below.

PHOSPHORITES

The sedimentation of phosphorite has been in dispute for many years, and not all questions have yet been settled. However, a consensus among most present workers is that phosphorus is chemically weathered from rocks on land and transported by streams to the ocean, where it is used by phytoplankton as a nutrient. This starts a food chain that results in phosphorus-rich organic matter sinking into deep water where it is trapped in the deeper stratified ocean - the deep ocean sink. Where this deep water is brought back to the surface by upwelling ocean currents, the waters become highly productive of organic matter. If this occurs over deep water, the sinking organic matter - primarily diatoms in the present ocean - is decomposed by bacterial activity and oxidation, and the phosphorus is restored to solution in deep ocean water. Where the upwelling occurs over shallow water, the organic matter accumulates in the bottom sediment. During early diagenesis, sulfate-reducing bacterial decay releases the phosphorus into the interstitial water, where it reacts in an alkaline environment to form carbonate fluorapatite. The fluorine, carbonate and calcium come from the interstitial water; or, in some cases, the carbonate and calcium come from carbonate shell material.

It has been argued that reworking of the sediment is necessary to form apatite pellet concentrate (Cook and Shergold, 1986, p. 369). However, it has been shown that, in Quaternary sediments on the Peru-Chile shelf, apatite pellet concentrate is formed without reworking in water ranging from 100 to 450 meters deep (Froelich and others, 1983; Burnett and Froelich, in press). This gives strong evidence that reworking is not necessary to form the pellet concentrate, although there

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is no argument that, in some cases, reworking does occur. In my opinion, most of the major phoshorites are unreworked, early diagenetic sediments. Except for recent papers, this subject is reviewed by Sheldon (1981).

ORGANIC MATTER

The genetic link between phosphorite and organic matter is shown by a close association between organic-rich black shale and phosphorites in rocks of Proterozoic to Quaternary age. In basin sequences, the two rock types are commonly interstratified. Phosphorites normally grade basinward into black shale. This relationship is well shown in Quaternary phosphorites on the continental shelf of Peru and Chile (Burnett, 1977), and in older phosphorites that have been well studied, as, for example, the Cretaceous Mishash Formation in Israel (Bentor, 1953; Wurzburger, 1968), the Lower Carboniferous Deseret and related formations of the western United States (Roberts, 1979; Sandberg and Gutschick, in press), and the Phosphoria Formation of the western United States (McKelvey *et al.*, 1959; Sheldon, 1984).

Some of the black shales associated with phosphorites are oil shales of potential economic value. In Morocco, in the Timahdit region, a Maastrichtian sequence of interbedded uraniferous phosphorites, phosphatic marls, and bituminous marls occurs in a sequence 150-300 m thick, showing four distinct cycles. The bituminous marls contain 36-120 liters of oil per metric ton and are being evaluated for possible production by the Office National de Recherches et d'Exploitations Pétrolières (ONAREP, 1983; Rahhali, 1983). In Egypt, the Maastrichtian Dahkla Shale, which overlies the upper Campanian to early Maastrichtian phosphorites of the Duwi Formation (Germann *et al.*, 1984), contains oil shale with up to 40 gallons of oil per ton (167 liters per metric ton). This deposit is being studied for its possible economic value, as reported by Darling (1983). These shales may be the source rocks for nearby recent oil discoveries (W.E. Harrison, *in* Darling, 1983). The black shales of the Permian Phosphoria Formation in the western United States contain abundant carbonaceous matter (up to 9 percent organic carbon) and, in some areas of Montana, up to 24 gallons per ton (100 liters per metric ton) of retortable oil (Swanson, *in* McKelvey et al., 1959). However, these beds are not being considered for exploitation at the present time. In Estonia, USSR, Lower and Middle Ordovician rocks in a sequence 150 meters thick include commercial phosphorite (Lower Ordovician) and commerical oil shale (Middle Ordovician). The Estonian oil shale deposit contains about 8 million tons of oil shale resource, which is of major importance to the economy of northwestern USSR (Academy of Sciences, Estonian SSR, 1984).

Some phosphatic sequences contain black shales that are petroleum source beds. The organic-rich shale and diatomite of the Miocene Monterey Formation, which are the source of much of the petroleum of southern California (Graham and Williams, 1985), are interbedded with thin phosphorite beds (Roberts, in press; Garrison, in press). The Upper Cretaceous and Lower Tertiary rocks of northeast Africa and the Middle East contain phosphorite and black shales, and in Libya, Tunisia and Egypt, these black shales are considered to be source beds of petroleum in each country (Peterson, 1983). The petroleum resources of Iran and of a portion of Iraq are derived from Upper Cretaceous to Lower Tertiary source beds (Masters *et al.*, 1982) that also contain phosphorite beds (Samimi and Ghasemipour, 1977). Similarly, in Venezuela, the Upper Cretaceous La Luna Formation, which contains economic phosphate deposits, is regarded as the major source of Venezuelan oil (Bockmeulen *et al.*, 1983). On the North Slope of Alaska, the Triassic Shublik Formation contains beds of both phosphorite and carbonaceous shale. A study of the Prudhoe Bay Field (Magoon and Claypool, 1981) suggested the likelihood that the the crude oil was derived from a phosphatic, calcareous shale, carbonate, or other iron-deficient source rock; and Seifert *et al.* (1979) interpreted, on the basis of biologic marker compounds in the oils and shale extracts, that the major source of Prudhoe Bay Field crude was the Shublik Formation. In the western United States, the basinal black phosphatic shales of the Phosphoria Formation are the source beds for oil fields to the east that contain about 1½ billion barrels of oil (Sheldon, 1967; Maughan, 1980; Peterson, 1984). Other examples of associated petroleum source rocks and phosphorites exist, but are less well established. It can be concluded that a significant percentage of world petroleum resources were derived from black shale associated with phosphorite.

The association of organic matter and phosphorite is obscured by weathering and oxidation of the organic matter. This is particularly evident in semi-arid and arid regions where erosion is slow and exposure long. The phosphate rock at the surface is characteristically light-colored and soft due to weathering and leaching. This is economically important, as the grade and quality of the ore are thereby improved. Fresh samples of the same rock are normally dark-colored due to their organic matter content, a feature that is well shown by comparison of phosphate rock mined underground in Morocco with rock mined at the surface.

Another feature that obscures the organic matter-phosphorite association is the facies relationship between the two. In basinal sequences the association is clear, but in shallow water sequences near the pinchout of phosphorite, organic matter is commonly not present. The phosphorite has either had its original organic matter removed by reworking or it was originally poor in organic matter, as, for example, a coquina of apatite shells of inarticulate brachiopods. Most examples of unweathered phosphorite not associated with organic matter come from such occurrences, and examination of a wider area usually shows that phosphorite and organic matter are associated in deeper water facies.

SILICEOUS SEDIMENTS†

Phosphorus and silica, along with organic carbon as discussed above, are commonly associated in sedimentary rock sequences as organic-rich beds of phosphorite and chert or its equivalents in young rocks, porcellanite or diatomite. However, not all phosphorites are associated with chert, nor are all cherts associated with phosphorites. Both phosphatic and siliceous sediments occur in minor amounts in many different types of rocks in many areas, and in general are not associated. However, when major phosphorite deposits are considered, a distinct association appears. Of 37 major phosphorite deposits, 27 or three quarters show a chert association, and of all phosphorite deposits, both major and minor, half are associated with chert (tables 1 and 2).

McKelvey *et al.* (1953, p. 61) pointed out the close association between chert and phosphorite in the Phosphoria Formation of Permian age, which occurs in the western United States,

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† The association of phosphatic and siliceous marine sedimentary deposits was treated in detail by Sheldon (1987), and the conclusions are summarized in this section.

and extended the association to other geosynclinal phosphorites, apparently for the first time. They pointed out that although both chert and phosphorite occur together in some layers, the most important association is a geographic one. Both chert and phosphorite are most prominent near the margin of the geosynclinal belt. Later work has confirmed the generalization that chert and phosphorite are associated but lack precise coincidence. Petrographically, rocks made up of nearly equal mixtures of apatite and chalcedony or opal are rare. Rather, the association is characterized by interbedding of stratigraphic units of phosphorite with units of chert. The fact that these units do not show facies relationships, that is, time-rock equivalence, agrees with what might be predicted from the lack of mixed rocks.

The differing distributions of chert and phosphorite beds show up on a broad paleogeographic view. Bentor (1979) pointed out that many ancient phosporites were deposited in epicontinental seas adjacent to continental shelves. In North Africa and the Middle East, the epicontinental phosphatic sequences contain little, if any, chert, whereas the adjacent continental shelf deposits contain prominent chert. A strong chert-phosphorite association occurs in the deposits of Turkey, Syria, Israel, and eastern Sahara, all of which were deposited on the outer continental shelf adjacent to the Tethys seaway. The phosphorites of Iraq, Jordan, and Saudi Arabia, which were deposited on the inner continental shelf, contain fewer chert beds, and the Egyptian deposits, which are farthest away from the Tethys seaway, contain the least amount of chert. The phosphorites of Morocco and Tunisia-Algeria were deposited in narrow inlets that opened northward into the Tethys seaway and southward into a broad epicontinental sea in North Africa. Phosphorite extends farther into the open epicontinental sea than does chert, which is concentrated at the mouths of the inlets near the Tethys Sea. Comparable inner shelf phosphorites without a chert association exist in the Permian Phosphoria Formation in the United States, in the Late Cretaceous La Luna Formation in Venezuela and Colombia, and in the Miocene-Pliocene phosphorites of the southeastern United States.

The marine geochemical cycle of silica is similar to that of phosphorus. The supply of both phosphorus and silica to the ocean is predominantly from subaerial chemical weathering of rocks and transport to the ocean by rivers, and is in minor amounts from volcanic activity (Wollast and MacKenzie, 1983; Froelich and others, 1982). In a process similar to that of phosphorus, silica from the frustules and tests of plankton is transferred intact to deeper levels, primarily as diatom-filled fecal pellets, and is released back to the seawater by dissolution. These processes lead to a buildup of silica in the deep ocean below 500-1000 m; there, the concentration of silica reaches 3000-5000 μg/l, whereas at the surface its concentration approaches zero, except at high latitudes in the winter months. The dissolved silica follows phosphorus in its return to the ocean surface by upwelling currents, and supports blooms of phytoplankton. Settling siliceous frustules and tests do not dissolve completely and tend to accumulate on the seafloor.

Silica and phosphate must be separated during sedimentation to give relatively pure siliceous and phosphatic sediments. For the Phanerozoic, before diatoms evolved, the process seems straightforward. Siliceous sediments were made up primarily of sponge spicules. When organic matter accumulation was sufficient for phosphorite formation, the bottom water was probably too oxygen-deficient to allow sponge growth, and when sufficient oxygen was available to allow sponge growth, insufficient organic matter was available to allow phosphosite formation. However, this hypothesis may be too simple, as the possible role of pre-Cretaceous silica-bearing microfauna has not been thoroughly studied. For the time after diatoms evolved, in the Early Cretaceous or, possibly, in the Late Jurassic, the process of separation of silica from phosphate is more uncertain. Of the several hypotheses, variation of diagenetic pH appears most likely to cause separation, with silica fluxed out of the sediment at high pH and phosphorus fluxed out at low pH (Sheldon, 1987); however, the separation of silica and phosphorus clearly needs additional research to be understood.

CARBONATES

Phosphorites from Proterozoic to Quaternary age are dominantly (77%) associated with carbonate rocks (tables 1 and 2). This association occurs as interbedding of phosphorite and carbonate rock in sequences of organic-rich rocks in single basins, and is due to variations of the conditions of sedimentation in time and not to facies. Thus, a continuous petrologic series from phosphorite to carbonate rock does not normally occur, and phosphorite beds do not normally grade into carbonate rock beds. The kind of carbonate rock associated with phosphorite differs with age. All Proterozoic and Cambrian phosphorites are associated with dolomite, with only rare, subordinate limestone; in contrast, most younger phosphorites are associated with limestone or, to a lesser extent, with mixed limestone and dolomite.

Limestone associated with Phanerozoic phosphorite is biogenic in origin. In the Paleozoic and Lower Mesozoic, the limestones were made up mainly of benthonic and nektonic shell debris. In Early Cretaceous time, the evolution of pelagic planktonic globigerinids caused limestone formed from foraminiferal ooze to be added to the phosphorite suite of rocks. The upwelling origin of the phosphorite suite of rocks was accompanied by low temperatures, which inhibited the presence of warm temperature biota. For example, coralline limestone is not directly associated with phosphorites.

Dolomite in the phosphorite suite of rocks of Phanerozoic age is diagenetic in origin. It is forming at present over a large part of the oceans on continental shelves, during early diagenesis of organic-rich sediments (Baker and Burns, 1985). Dissolution of calcium carbonate in the sediments gives calcium and carbon dioxide; oxidation of organic matter gives carbon dioxide; and magnesium is added to pore water by migration from overlying sea water. Dolomite has formed in a comparable manner in Late Tertiary continental margin sediments (various papers in Garrison *et al.*, 1984). Kastner *et al.* (1984) report that dolomite is the stable carbonate in seawater because of its high Mg/Ca ratio - about 5:1, and that calcite is dolomitized experimentally in a solution that has a Mg/Ca ratio of 1:3. Because dolomitization of $CaCO_3$ is inhibited by high concentrations of sulfate in seawater, they suggest that the low sulfate concentration in the sulfate reduction zone of organic-rich sediments enhances the formation of dolomite. Thus, organic matter may be the genetic link between phosphorite and dolomite. Both dolomite and phosphorite require an alkaline environment of sedimention. Phosphorites require organic matter as a source of phosphorus, and dolomite requires organic matter to reduce the sulfate of the pore water. Dolomite formation also requires $CaCO_3$ shell debris to raise the pH to sufficiently high levels. In Proterozoic time, however, no

Table 1. Chert and carbonate rock associations with phosphorites. D=dolomite, DL=dolomite and limestone, L=limestone, N=no carbonate.

Number	Deposit	Country	Chert	Carbonate Rock	Size
Lower Proterozoic					
LP-1	Baraga Group	Michigan, US	+	D	minor
LP-2	Bijawar Series	Central India	+	D	major
LP-3	Aravalli Series	Western India	-	D	major
Upper Proterozoic and Cambrian					
PC-1	Khubsugul Series	Mongolia	+	D	major
PC-2	Tamdy Series	Kazakhstan, USSR	+	D	major
PC-3	Yuhucun Fm.	China	+	D	major
PC-4	Kodjari Fm.	Benin, Niger, Burkina Faso	+	D	major
PC-5	Beetle Creek Fm.	Australia	+	D	major
PC-6	Tal Fm.	Uttar Pradesh	+	D	minor
PC-7	Sturtian Series	Australia	+	D	minor
PC-8	Lao Cai	Vietnam	-	D	major
PC-9	Abbottabad Fm.	Pakistan	+	D	minor
PC-10	Bambui Group	Brazil	-	D	major
PC-11	Fontanarejo Deposit	Spain	-	N	minor
Ordovician					
O-1	Kallavere Fm.	Estonia, USSR	-	N	major
O-2	Maquoketa Fm.	Iowa, US	+	DL	minor
O-3	Stairway Sandstone	Australia	-	L	minor
O-4	Baltic Shield	Sweden	-	L	minor
O-5	Trenton Group	Tennessee, US	-	L	major
O-6	Capinota deposit	Bolivia	-	N	minor
O-7	Labrado and Centinela Fms.	Argentina	-	N	minor
O-8	Swan Peak and Hardin Fms.	Idaho, Utah, US Wyoming, US	-	N	minor
Silurian					
S-1	Los Espejos Fm.	Argentina	-	N	minor
S-2	Red Mountain Fm.	Alabama, US	-	N	minor
Devonian					
D-1	Geirud Fm.	Iran	-	L	minor
D-2	Balong	Guangxi, China	?	L	minor
D-3	Onondaga and Ridgely Fms.	Pennsylvania, US	-	L	minor
D-4		Indiana, US	-	L	minor
D-5	Moscow Fm.	New York, US	-	L	minor
D-6	Sekondi Sandstone	southern Ghana	-	N	minor
D-7	Beacon Subgroup	Antarctica	-	N	minor
Lower Carboniferous (Mississippian)					
LC-1	Chattanooga Shale and Maury Fm.	Tennessee, Alabama, Georgia, US	+	L	minor
LC-2	Deseret and Brazer Fms.	Utah, US	+	L	minor
LC-3	Lisburne Group	Alaska, US	+	DL	minor
LC-4	Tournasian	SW France	+	DL	minor
LC-5	Fayetteville and Pitkin Fms.	Arkansas, US	-	L	minor
LC-6	Exshaw and	Canada; US	+	L	minor
LC-7	St. Ann's deposit	Australia	?	?	minor
LC-8	Talak Fm.	Niger	-	N	minor
LC-9	fore-flysch	Dem. Rep. Germany	?	?	minor
LC-10		Poland	?	?	minor
Upper Carboniferous (Pennsylvanian)					
UC-1	cyclothems	Mid-continent, US	-	N	minor
UC-2	Clare Shales Fm.	Ireland	+	L	minor
UC-3	Alton marine bands	UK	?	L	minor
Permian					
P-1	Phosphoria Fm.	western US	+	DL	major
P-2	Ural Mtns.	USSR	+	DL	minor
P-3	Sonnebit unit	Timor, Indonesia	+	L	minor
Triassic					
T-1	Shublik Fm.	Alaska, US	+	DL	major
T-2	Arctic Islands	USSR	?	?	minor
Jurassic					
J-1	Aramachay Fm.	Peru	+	L	major
J-2	Fernie Fm.	Canada	+	L	minor
J-3	La Caja Fm.	Mexico	+	L	minor
Jurassic-Cretaceous					
JK-1	Vyatka Basin	USSR	-	N	minor
JK-2	Volga Basin	USSR	-	N	minor
Lower Cretaceous					
LK-1	Vaca Muerta Fm.	Argentina	+	DL	minor
LK-2	Pabellon Fm.	Chile	+	L	minor
LK-3	Muerto and Pariatambo Fms.	Peru	+	DL	minor
Upper Cretaceous					
UK-1	Karababa, Kasrik, Karabogaz and Germav Fms.	Turkey	+	L	major
UK-2	Campanian	Syria	+	L	major
UK-3	Digma Fm.	Iraq	+	L	minor
UK-4	Belqa Sereis	Jordan	+	L	major
UK-5	Mishash Fm.	Israel	+	L	major
UK-6	Turayf Fm.	Saudi Arabia	+	DL	major
UK-7	Duwi phosphate	Egypt	+	DL	major
UK-8	La Luna Fm.	Venezuela, Colombia	+	L	major
UK-9	Paris Basin	France	+	L	minor
UK-10	Ciply chalk	Belgium	+	L	minor
UK-11	Aktyubinsk Basin	USSR	-	N	minor
UK-12	Gramame Fm.	Brazil	-	L	minor
UK-13	Napo Fm.	Ecuador	+	L	minor
UK-14	Las Hayas Fm.	Argentina	-	L	minor
Lower Tertiary					
LT-1	Metlaoui	Tunisia-Algeria	+	L	major
LT-2	Um Er Radhuma and Dammam Fms.	Iraq	+	L	major
LT-3	phosphatic series	Morocco	+	DL	major
LT-4	Bu Craa deposit	Western Sahara	+	L	major
LT-5	Eocene	Senegal-Mauritania	+	DL	major
LT-6	Eocene	Syria	+	L	major
LT-7	Eocene	Togo	-	L	major
LT-8	Tilemsi	Mali	-	L	minor
LT-9	Kisil Kum	USSR	-	L	major
LT-10	Pabdeh Fm.	Iran	+	L	minor

Table 1 continued. Chert and carbonate rock associations with phosphorites. D=dolomite, DL=dolomite and limestone, L=limestone, N=no carbonate.

Number	Deposit	Country	Chert	Carbonate Rock	Size
Oligocene					
To-1	Cooper Fm.	S. Carolina, US	-	N	minor
Oligocene-Miocene					
Tom-1	Monterrey Fm.	Mexico	+	N	major
Miocene					
Tm-1	Pungo River Fm.	North Carolina, US	+	DL	major
Tm-2	Hawthorne and Bone Valley Fms.	Florida, US	-	DL	major
Tm-3	Blake Plateau	US Atlantic	-	DL	major
Tm-4	Monterey Fm.	California, US	+	DL	minor
Tm-5	offshore	California, US	+	DL	minor
Tm-6		Cuba	+	DL	minor
Tm-7	Sechura	Peru	+	N	major
Tm-8	Pisco	Peru	+	N	minor
Tm-9	Caleta Herradura Fm.	Chile	-	L	minor
Tm-10	Tongoi	Chile	-	N	minor
Tm-11	offshore	Morocco	+	N	minor
Tm-12	offshore	Gabon-Congo	-	N	minor
Tm-13	Varswater Fm.	South Africa	-	N	minor
Tm-14	offshore	South Africa	-	N	minor
Tm-15	Pietra Leccese Fm., Salentino Pen.	Italy	-	L	minor
Tm-16	Sicily	Italy	-	L	minor
Tm-17	offshore	Spain	?	?	minor
Tm-18	offshore	Portugal	-	DL	minor
Tm-19	Sea of Okhotsk	USSR	?	?	minor
Tm-20	Negros	Philippines	-	L	minor
Tm-21	Java	Indonesia	-	L	minor
Tm-22	Clarenden Hill, Ontago	New Zealand	-	L	minor
Tm-23	Chatham Rise and Campbell Platform offshore	New Zealand	-	L	major
Tm-24	Clifton Fm. Victoria	Australia	-	L	minor
Pliocene					
Tp-1	Monterey and Santa Barbara Counties	California, US	+	N	minor
Tp-2	Yorktown Fm.	North Carolina, US	-	DL	minor
Tp-3	Varswater Fm.	South Africa	-	N	minor
Tp-4	Salentino Peninsula (may be same as Tm-15)	Italy	-	L	minor
Tp-5	eastern Java	Indonesia	-	L	minor
Quaternary					
Q-1	offshore	N. Carolina, US	-	?	minor
Q-2	offshore Baja Calif.	Mexico	+	DL	major
Q-3	offshore	Chile-Peru	+	D	major
Q-4	offshore Mediterranean	France	?	?	minor
Q-5	offshore	Namibia	+	?	minor
Q-6	offshore	Arabian Penin.	-	?	minor
Q-7	offshore Andaman I.	India	-	?	minor
Q-8	offshore, western continental shelf	India	+	?	minor
Q-9	offshore, eastern continental shelf	Australia	-	L	minor

Table 2. Chert and carbonate association with phosphorite over geologic time. Percentage of phosphorites having indicated association. Percentages in parentheses are associations of major phosphorites alone.

age interval	**chert**	**dolomite**	**dolomite + limestone**	**limestone**	**no carbonate**
Lower Proterozoic	67 (50)	100 (100)	-	-	-
Upper Proterozoic + Cambrian	73 (71)	91 (100)	-	-	9
Ordovician	12	-	12	38 (50)	50 (50)
Silurian	-	-	-	-	100
Devonian	-	-	-	72	28
Lower Carboniferous	71	-	29	57	14
Upper Carboniferous	50	-	-	67	33
Permian	100 (100)	-	67 (100)	33	-
Triassic	100 (100)	-	100 (100)	-	-
Jurassic	100 (100)	-	-	100 (100)	-
Jurassic-Cretaceous	-	-	-	-	100
Lower Cretaceous	100	-	67	33	-
Upper Cretaceous	79 (100)	-	14 (25)	79 (75)	7
Paleocene-Eocene	70 (75)	-	20 (25)	80 (75)	-
Oligocene	-	-	-	-	100
Oligocene-Miocene	100 (100)	-	-	-	100 (100)
Miocene	32 (40)	-	32 (60)	36 (20)	32 (20)
Pliocene	20	-	20	40	40
Quaternary	50 (100)	33	33 (50)	33 (50)	-

$CaCO_3$ shells existed, so a different mechanism of dolomite formation was required. Tucker (1982) suggests that dolomite may have precipitated directly from seawater in Precambrian time, as a result of seawater chemistry that was different from that of the Phanerozoic.

Kastner *et al.* (1984) explain the dolomite-phosphorite relationship in the Monterey Formation of California by a decrease in the Mg concentration of pore water as a result of dolomite formation, which resulted in enhanced apatite formation. This cause and effect relationship is plausible, but does not appear to be operating in the modern formation of phosphorite without dolomite on the Peru-Chile continental shelf (Burnett, 1977). Also, many ancient phosphorites are not associated with dolomite (table 2).

In a broader paleogeographic view, the phosphorite suite of rocks, including the carbonate rock discussed above, is deposited on continental shelves and on epicontinental sea floors. Semi-restricted and restricted basins commonly occur adjacent to phosphorite basins on the craton, and are the sites of carbonate rock and evaporite sedimentation not associated with phosphorites. Such carbonate rocks consist of bioclastic, algal or pelletal limestones, which in many cases have been replaced by dolomite. Sabkha-type dolomites associated with evaporites are also found in the restricted evaporite basins. In a broad sense, these carbonates are associated regionally with the phosphorite suite of rocks and are time equivalents. However, such cases are not counted as associated in table 2, which deals with sediments deposited in the same basin. This distinction is sometimes difficult to make. The phosphorite suite of rocks is normally found in cyclic sequences, caused by major eustatic changes of sea level. The sequences are composed of interstratified continental shelf and cratonic sediments, so that transgressive marine sediments can overlie regressive restricted basin sediments. Such relationships are shown in the Permian rocks of the western United States (Sheldon, 1984) and in Tunisia (Sassi, 1980).

The carbonate rock of the phosphorite suite of rocks shows compositional changes through geologic time. Essentially dolomite alone occurs in Proterozoic to Cambrian phosphorite suites. Limestone, on the other hand, is the dominant carbonate rock in younger Phanerozoic phosphorite suites. In phosphorite suites of the Ordovician through Carboniferous and of the Jurassic through Paleogene, 63% contain limestone alone, 15% contain mixed limestone and dolomite, and 22% contain no carbonate rock. In Permian, Triassic, and Neogene phosphorite suites, 35% contain limestone alone, 35% mixed limestone and dolomite, and 29% no carbonate.

The causes of these temporal variations in the type of carbonate rock present in phosphorite rock suites are not known, but speculations can be made. As pointed out above, Tucker (1982) speculated that Precambrian dolomite sedimentation was caused by a seawater composition that was different from that of the Phanerozoic. This may also have been true of the Lower and Middle Cambrian dolomites. Two major phosphogenic episodes occurred in the Phanerozoic during times of polar glaciation, and include the Permian and the Neogene. Both were also times of mixed dolomite and limestone sedimentation in the phosphorite suite. Of the other Phanerozoic phosphorite suites, only the Upper Cretaceous and Lower Tertiary include major phosphorite deposition. These suites are dominantly limestone-only suites, and were not deposited at times of polar glaciation. It can be speculated that water temperature was one control on carbonate sedimentation, with limestone preferentially deposited in warmer water and dolomite in cooler water.

CONCLUSIONS

Phosphorite, chert and dolomite are commonly associated in early diagenetic, organic-rich environments in areas of upwelling ocean currents over shallow water. Biogenic limestone, derived from planktonic and benthonic organisms, and black shale are also found in the rock suite. The association, except for that of black shale with all other rock types and of chert with limestone, is generally one of interbedding and not one of lateral facies gradation. The interbedded sequences generally form lithologic cycles that are probably the result of changes in sea level and upwelling activity.

The association of black shale, chert and phosphorite is constant over Proterozoic to Holocene time, but the associated carbonates show a temporal variation. Dolomite is the only carbonate in Proterozoic and Cambrian sequences, and both limestone and dolomite occur in younger sequences.

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