

Coated phosphate grains: Proxy for physical, chemical, and ecological changes in seawater

Peir K. Pufahl* } Department of Earth and Ocean Sciences, University of British Columbia, 6339 Stores Road, Vancouver,
Kurt A. Grimm } British Columbia V6T 1Z4, Canada

ABSTRACT

Irrespective of geologic age, Phanerozoic coated phosphate grains deposited beneath productive surface waters in organic-rich paleoenvironments are of only two types. Unconformity-bounded grains contain internal discordances and erosional surfaces, attributable to multiple episodes of phosphogenesis and sedimentary reworking during periods of stratigraphic condensation. Redox-aggraded grains consist of concordant concentric phosphate laminae that are intimately interlayered with circumgranular layers containing pyrite, chamosite, or barite, recording in situ diagenetic mineralization driven by changes in pore-water redox potential. Such changes can be attributed to variations in biological oxygen demand within suboxic pore-water environments resulting from fluctuations in sedimentation rate of organic carbon. Redox-aggraded grains are thus sensitive indicators of variations in organic carbon export and record changes in primary productivity and/or ecological dynamics of the surface ocean. This concept of coated-grain formation necessitates a long residence time just below the sediment-water interface. If sedimentation rate is too high, grains are rapidly buried and so removed from the zone of active phosphate precipitation. Coated phosphate grains can therefore be considered the granular equivalents of condensed beds. These concepts are equally applicable to the interpretation of other types of coated grains and concretions that contain Eh-sensitive minerals, such as iron-bearing ooids and polymineralic concretions.

Keywords: phosphorite, coated grains, redox changes, stratigraphic condensation.

INTRODUCTION

Phosphorites commonly contain a variety of grain types that record a wide spectrum of depositional and diagenetic processes and so have long been a subject of intense debate (cf. Riggs et al., 1997). Coated phosphate grains are a unique particle type formed of circumgranular apatite layers. Unlike ooids, which precipitate while the grain is in turbulent suspension (Bathurst, 1975), coated phosphate grains form authigenically just below the sediment-water interface (Garrison and Kastner, 1990; Soudry, 2000). As a result they preserve a record of physical and chemical change in bottom and pore waters and are thus intimately linked to corresponding changes in hydraulic regime and chemistry of overlying seawater. The full spectrum of coated-grain types over geologic history and the conditions under which they formed have until now been unclear.

METHODS

To ascertain the spectrum of coated-grain types and compositions, 35 samples were selected from collections of phosphorite of differing ages and locations (Table 1). Internal grain structure and composition were elucidated by using high-resolution microbeam

techniques (cf. Krajewski, 1983; Glenn et al., 1988). Backscattered-electron micrographs and qualitative analyses were acquired with a Philips XL-30 scanning electron microscope equipped with a Princeton Gamma-Tech energy-dispersive spectrometer. Mineral content was determined from X-ray diffraction photographs taken with a Gandolfi camera using $\text{CoK}\alpha$ radiation and with published X-ray diffraction data. Bulk samples of coated grains intended for carbon stable isotope analysis of the carbonate anionic complex in francolite were prepared using the techniques of Silverman et al. (1952). Stable isotope analyses were performed at the University of Western Ontario following the methods of McCrea (1950).

PHANEROZOIC COATED PHOSPHATE GRAINS

Analyzed coated phosphate grains are associated with depositional hiatuses related to periods of net low and/or negative rates of sedimentation and interpreted to have formed beneath productive surface waters in an array of organic-rich paleoenvironments (Table 1). Examined grain nuclei consist of phosphatic peloids and intraclasts, phosphatized foraminifera tests, carbonate ooids, authigenic glauconite, detrital quartz, feldspar, and dolomite grains. Grain cortices are exquisitely preserved and lack relict carbonate, indicating a nonreplacement, primary origin. In spite of

large differences in geologic age, grain cortices are of only two types (Table 1): unconformity bounded (UB) and redox aggraded (RA).

UB grains are formed of discontinuous and irregular monomineralic phosphatic laminae, 5–100 μm thick, that are erosionally truncated (Table 1; Fig. 1A). In some cases, cortices resemble phosphatized macroonoids (Krajewski, 1983; Soudry and Champetier, 1983; Soudry, 2000) and pedogenic coated phosphate grains (Southgate, 1986). Macroonoids, however, exhibit typical microbial fabrics not present in UB grains, and pedogenic coated phosphate grains always occur with meteoric diagenetic features not associated with grains described here.

RA grains generally consist of concentric, concordant phosphatic layers intimately interlayered with pyrite, chamosite, or barite laminae (Table 1; Figs. 1B, 1C). Laminae are thin (3–50 μm), less well defined than those composing UB grains, and sublaminated on an ultrafine scale; laminae lack unconformable contacts. Pyrite-rich layers are framboidal pyrite disseminated throughout a francolite (sedimentary apatite) matrix. The absence of francolite inclusions within pyrite crystals indicates that pyrite is nonreplacive. Chamosite-rich laminae are mixtures of chamosite and francolite. Barite layers are pure barite. Monomineralic RA grains composed entirely of francolite have textural attributes identical to those of polymineralic grains. Hybrid grains contain characteristics of both UB and RA grains. The range of $\delta^{13}\text{C}$ (CO_3 -francolite) values (–1.35‰ to –15.88‰; Table 1) are consistent with phosphogenesis (francolite precipitation) driven primarily by production of pore-water phosphate derived from the suboxic to anoxic bacterial degradation of sedimentary organic matter (Jahnke et al., 1983; McArthur et al., 1986; Froelich et al., 1988; Glenn et al., 1988).

ORIGIN OF THE GRAINS

UB grains, because of the numerous cortex unconformities, are interpreted to have formed through multiple episodes of phosphatization, exhumation, and erosion, followed by reburial into the zone of phosphogenesis (ZOP) (Fig. 2A). UB grains thus contain a record of substrate reworking and/or winnowing and indicate breaks in quiet-water deposition caused

*Present address: Department of Geological Sciences and Geological Engineering, Queen's University, Kingston, Ontario K7L 3N6, Canada. E-mail: pufahl@geol.queensu.ca.

TABLE 1. CHARACTERISTICS OF SAMPLES INVESTIGATED

Location	Age (no. samples)	Host lithology and sedimentology	Environment	Grain type and description	$\delta^{13}\text{C}$ (‰, PDB)	Reference
Peru	Quaternary (3) Pliocene (2)	Diotom-rich mud; numerous omission surfaces and reworked phosphatic hardgrounds; coated grains from laminae and graded beds (≤ 1 m thick) marking hiatuses	Upwelling-related sediments on outer shelf or upper slope. Well-developed OMZ	UB : mg-cg; well sorted; nuclei = phosphate peloids, quartz silt, rare framboidal pyrite; cortices = irregular, erosionally truncated, phosphatic laminae (10–20 μm thick)	–8.71 to –4.08	[1]
	Quaternary (1)	Bioturbated and laminated organic-rich silty mud; fish bones common; numerous depositional hiatuses; coated grains are from a granular layer just beneath the seafloor	Upwelling-related sediments on outer shelf or upper slope. Well-developed OMZ	RA-py : vfg-fg; well-sorted black grains; nuclei = quartz sand and feldspar; cortices = interlayered, concentric francolite and pyrite-rich laminae (5–10 μm thick); layers are sublaminated	–1.35*	[2]
Spitsbergen	Cambrian Tokammane Formation (1)	Organic-rich shale and siltstone; layers of reworked phosphatic pebbles common; coated grains occur within thin, bioturbated sandstone beds and sandy lenses	Upwelling-related sediments on passive margin	RA-py : fg-mg; well sorted; nuclei = quartz sand; cortices = concentric francolite and rare pyrite-rich laminae (3–10 μm thick); pyrite laminae are thinner than francolite layers and discontinuous		[3,4]
Jordan	Campanian Alhisa Phosphorite Formation (12)	Interbedded phosphatic grainstones and organic-rich chalks; common firmgrounds and reworked concretionary horizons; coated grains are within thickly bedded, graded, and massive grainstones	Upwelling-related sediments deposited on storm-dominated epeiric platform during marine transgression	UB : vcg-granular; moderately well sorted; nuclei = phosphate peloids-intraclasts, phosphatized foraminifera tests; cortices = irregular, erosionally truncated francolite laminae (45–100 μm thick)	–8.40 to –5.51	[5]
USA	Pliocene Glenns Ferry Formation (1)	Interbedded sand and oolite; inferred to have been organic-rich; numerous omission surfaces; reworked phosphatic pebbles common; coated grains occur in thin beds marking hiatuses	Nearshore sediments in highly productive lake. Hiatal surfaces formed during transgression	RA-py : cg-vcg; moderately well sorted; nuclei = detrital sand, ooids, phosphatic intraclasts; cortices = concentric francolite and rare pyrite-rich laminae (8–30 μm thick); layers are sublaminated	–2.76	[6]
South Africa	Miocene (3)	Organic rich, glauconite- and siderite-bearing, Pleistocene shelly sand; highly condensed section; Miocene coated grains occur disseminated throughout shelly sand	Upwelling-related inner-shelf sediments reworked during Quaternary lowstands	RA-py : small black pebbles containing quartz silt; moderately well sorted; nuclei identical in composition to francolite laminae; cortices = concentric francolite and pyrite-rich layers (5–30 μm thick)	–15.88	[7]
Canada	Triassic Doig Formation (2)	Interbedded sandstones and organic-rich mudstone-siltstone; condensed section; coated grains are reworked and occur within fine-grained sandstone bodies	Regressive shoreface sands prograding over organic-rich midshelf sediments	UB : vfg; well sorted; compose $\leq 20\%$ of grains; nuclei = vfg quartz sand, rare detrital dolomite; cortices = a single or multiple irregular, discontinuous, erosionally truncated francolite laminae (5–15 μm)		[8]
Sweden	Ordovician Gullhög Formation (2)	Organic-rich lime mudstone; numerous hardgrounds and discontinuity surfaces; coated grains occur in thin beds marking hiatuses; ash horizons common	Sediments deposited on productive shelf with intermittent volcanism	RA-ch, ba : mg-vcg; poorly sorted; nuclei = quartz silt, carbonate/chamosite grains; cortices = concentric chamosite and rare francolite laminae or francolite and barite laminae (5–50 μm thick); layers are sublaminated	–5.55 to –8.35	[9]
	Ordovician Kunda units (1)	Glauconite-bearing micritic calcarenite; inferred to have been organic-rich; phosphatic hardgrounds; coated grains occur below major disconformity	Nutrient-rich inner shelf environment	RA-ch : cg-vcg; well sorted; nuclei = chamosite/phosphate peloids; cortices = interlayered francolite and chamosite-rich laminae (5–30 μm thick); layers are sublaminated	–3.16	[10]
	Cambrian Oelandicus Shale (1)	Organic-rich, fine-grained, glauconitic sandstones; condensed section; coated grains occur within sandstone beds	Deposition in inner shelf and midshelf settings during marine transgression	RA-ch : cf; well sorted; nuclei = detrital grains, phosphate-glauconite peloids; cortices = interlayered francolite and chamosite-rich laminae (5–15 μm thick); layers are sublaminated	–8.35	[11]
Mexico	Oligocene-Miocene Timbabichi Formation (6)	Interbedded siliceous mudstones, phosphatic grainstones; numerous concretionary horizons, bored hardgrounds; coated grains within massive or graded grainstones	Upwelling-related sediments deposited in an active forearc setting during sea-level highstand	UB : mg-cg; poorly sorted; nuclei = detrital grains, phosphate intraclasts; cortices = irregular, erosionally truncated francolite laminae (60–100 μm thick); laminae are endolithically bored		[12]

Note: UB—unconformity-bounded phosphate grain; RA—redox-graded phosphate grain (py = pyrite cortex layers, ch = chamosite cortex layers, ba = barite cortex layers); vfg = very fine grained, fg = fine grained, mg = medium grained, cg = coarse grained, vcg = very coarse grained, OMZ = oxygen-minimum zone; PDB is Pee Dee belemnite; 1—Garrison and Kastner (1990); 2—Glenn et al. (1988); 3—Swett and Crowder (1982); 4—Kidder and Swett (1989); 5—Pufahl et al. (2003); 6—Swirydczuk et al. (1981); 7—Compton et al. (2002); 8—Harris (2000); 9—Sturesson (1992); 10—Sturesson (1986); 11—Sturesson (1988); 12—Grimm (2000).
* $\delta^{13}\text{C}$ value from Glenn et al. (1988). Sedimentologic descriptions and environmental interpretations are from literature cited in the last column. No sample material was available from Spitsbergen, Canada, or Mexico for isotopic analysis.

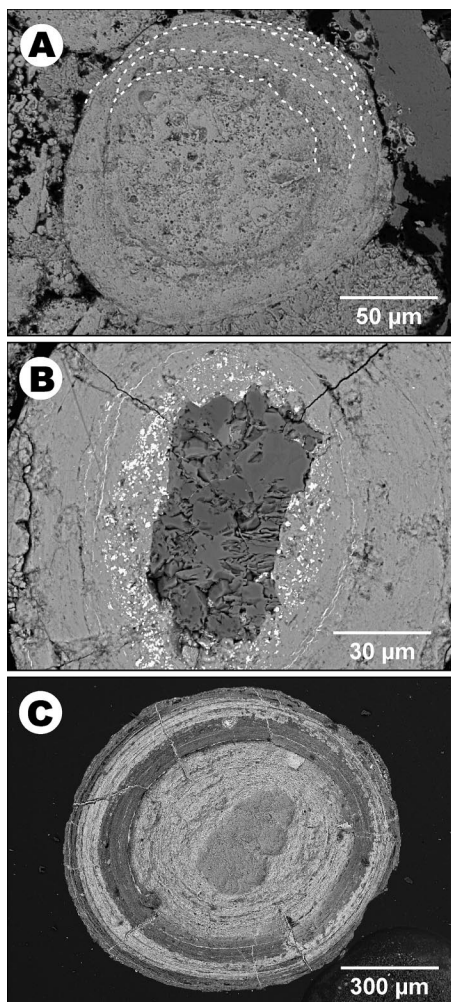


Figure 1. Backscattered-electron micrographs of unconfornity-bounded (UB) and redox-aggraded (RA) grains. **A:** UB grain. Nucleus is phosphatic intracrystalline. Dashed lines highlight irregular, unconfornable contacts between laminae. Campanian Alhisa Phosphorite Formation, Jordan. **B:** RA grain. Silt-sized feldspar nucleus. Compositionally distinct innermost cortex laminae contain abundant framboidal pyrite (white specks). Contacts are marked by thin, discontinuous pyrite laminae. Quaternary, Peru. **C:** RA grain. Silt-sized glauconite nucleus; dark cortex layers are chamosite; light cortex layers are francolite. Cambrian Oelandicus Shale, Sweden.

by storms, episodic undercurrents, and/or shallow-water currents associated with sea-level lowstands. Garrison and Kastner (1990) proposed a similar idea for the formation of coated grains from the Peru continental margin and also emphasized the importance of changing energy levels on coated-grain formation.

RA grains are interpreted to have been produced by francolite precipitation within the ZOP accompanied by changes in pore-water redox potential (Fig. 2B). Such changes are recorded by the intimate interlayering of fran-

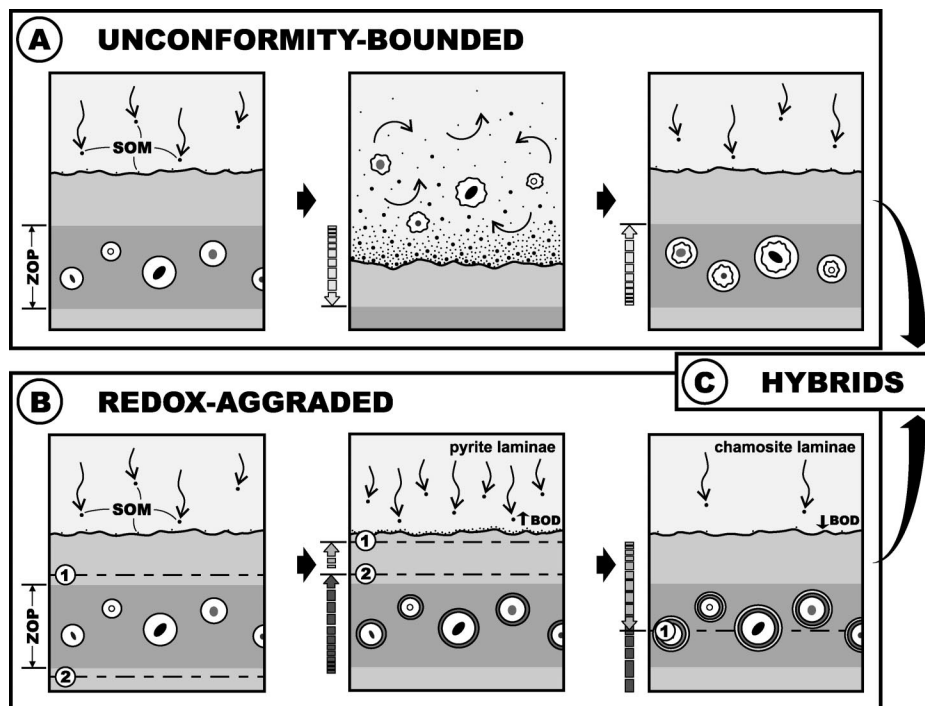


Figure 2. Formation of coated phosphate grains. Zone of active phosphate precipitation (zone of phosphogenesis, ZOP) occurs in upper 5–20 cm of sediment. In high-productivity settings phosphogenesis is stimulated primarily by production of pore-water phosphate derived through suboxic microbial degradation of sedimentary organic matter (SOM). It occurs in association with reduction of NO_3^- , Mn-oxides, Fe-oxides, and SO_4^{2-} and is limited at deeper intervals by lack of seawater-derived F^- (Föllmi et al., 1991) and high alkalinities that develop through cumulative degradation of organic matter (Glenn and Arthur, 1988). **A:** Formation of unconfornity-bounded phosphate grains. Erosion-deposition cycles cause ZOP to migrate up and down within sediment column. **B:** Formation of redox-aggraded phosphate grains. Episodic flux of organic carbon to seafloor causes redox interfaces to shift vertically in sediment through ZOP in response to changes in biological oxygen demand (BOD). Type of cortex laminae depends upon amount of organic matter and bulk composition of sediment; 1 = Fe^{3+} - Fe^{2+} redox interface, 2 = SO_4^{2-} - H_2S redox interface. **C:** Hybrid grains form when both processes act together.

colite, pyrite, chamosite, and/or barite. Chamosite contains Fe^{2+} and Fe^{3+} and so forms close to the Fe-redox boundary (Harder, 1980). Pyrite precipitates within the zone of sulfate reduction (Berner, 1984), whereas authigenic barite forms just above this zone (Torres et al., 1996).

RA Grains and Organic Carbon Export

The variable mineral contents in RA grain cortices are attributed to seasonal fluctuation in the export of sedimentary organic matter to the sediment-water interface (Fig. 2B). Increased flux of organic carbon would cause a concomitant increase in biological oxygen demand at the sediment-water interface, which in turn would cause the redox zones to telescope and move up through the sediment column (Bussmann and Reichardt, 1991; Rasmussen and Jørgensen, 1992; Thamdrup et al., 1994; Gobeil et al., 1997). Once the bulk of organic matter is oxidized, oxygen, nitrate, and sulfate from overlying bottom water can diffuse deeper into the sediment, causing the redox zones to expand and move downward.

Barite laminae form when the SO_4^{2-} - H_2S redox interface shallows in response to the arrival of a pulse of organic matter at the seafloor, bringing this boundary near the ZOP. Pyrite laminae form when the SO_4^{2-} - H_2S redox boundary passes completely through the ZOP. Chamosite laminae precipitate once the majority of organic matter has been respired and the diffusion of oxidants into the sediment column pushes the Fe^{3+} - Fe^{2+} redox boundary into the ZOP. In such a situation, repeated vertical oscillations of these redox interfaces give rise to multiply coated RA grains. Unlike the formation of UB grains, this process does not necessitate exhumation and reburial of grains into the ZOP, but instead only requires a variable flux of organic carbon to the seafloor. The type of laminae is thus governed by the delivery rate of oxidizable organic matter to the seafloor and the bulk composition of the host sediment.

This concept is equally applicable to RA grains formed in low-productivity settings where pore-water phosphate concentration is regulated by small seasonal changes in pro-

ductivity and Fe-redox pumping of P (Heggie et al., 1990). Fe-redox pumping is a cyclic mechanism that enriches phosphate in pore waters by the release of phosphate sorbed onto Fe oxyhydroxides. Phosphate derived from organic-matter degradation is scavenged by Fe oxyhydroxides in the upper few centimeters of sediment and released to pore water during dissolution below the Fe^{3+} - Fe^{2+} redox boundary (Heggie et al., 1990). This mechanism requires either repeated mixing of the sediment to the Fe^{3+} - Fe^{2+} redox boundary (Heggie et al., 1990) or an Fe^{3+} - Fe^{2+} redox boundary that oscillates vertically with time in response to episodic flux of organic matter (Schuffert et al., 1998).

CONCLUSIONS

What links requisites for coated phosphate grain formation regardless of grain type and age is the necessity for long residence times near the sediment-water interface. Sedimentologic evidence indicates that all samples examined in this study are associated with periods of stratigraphic condensation. Net low sedimentation rates and/or repeated reworking of the substrate facilitate phosphogenesis by allowing buildup of pore-water phosphate and fluoride (Föllmi et al., 1991). If the sedimentation rate is too high and/or substrate reworking does not accompany phosphogenesis, multiply coated phosphate grains cannot form because grains are rapidly buried within the sediment column and thus removed from the ZOP. In this context, coated phosphate grains are considered to be the granular equivalent of condensed beds. Their recognition in the geologic record should aid in the interpretation of phosphatic and associated strata by shedding light on the complexity of omission surfaces. For the first time it is possible to pinpoint and separate environments of coated phosphate grain formation. By integrating this information with sedimentologic, ichnologic, and stratigraphic analysis, the sequence stratigraphic significance of any given condensed interval can be resolved with much greater fidelity than previously possible. Such concepts are equally applicable to the interpretation of other types of coated grains and concretions that contain Eh-sensitive minerals, such as iron-bearing ooids and polymineralic concretions.

ACKNOWLEDGMENTS

We thank J.S. Compton, R.E. Garrison, R.G. Harris, A.H. Knoll, U. Sturesson, and B.H. Wilkinson for providing samples. Thoughtful reviews by J.S. Compton, D.E. Fastovsky, K.B. Föllmi, N.P. James, D.L. Kidder, K.G. Taylor, and an anonymous reader are much appreciated. Research was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC), a University of British Columbia Graduate Fellowship, and Killam Predoctoral Fellowships (to Pufahl). This study was completed while Pufahl was in receipt of an NSERC Postdoctoral Fellowship at Queen's University.

REFERENCES CITED

- Bathurst, R.G.C., 1975, Carbonate sediments and their diagenesis (second edition): Amsterdam, Elsevier, 658 p.
- Berner, R.A., 1984, Sedimentary pyrite formation: *Geochimica et Cosmochimica Acta*, v. 48, p. 605–615.
- Bussmann, I., and Reichardt, W., 1991, Sulfate-reducing bacteria in temporarily oxic sediments with bivalves: *Marine Ecology Progress Series*, v. 78, p. 97–102.
- Compton, J.S., Mulabisana, J., and McMillan, I.K., 2002, Origin and age of phosphorite from the last glacial maximum to Holocene transgressive succession off the Orange River, South Africa: *Marine Geology*, v. 186, p. 243–261.
- Föllmi, K.B., Garrison, R.E., and Grimm, K.A., 1991, Stratification in phosphatic sediments: Illustrations from the Neogene of California, in Einsele, G., et al., eds., *Cycles and events in stratigraphy*: Berlin, Springer-Verlag, p. 492–507.
- Froelich, P.N., Arthur, M.A., Burnett, W.C., Deakin, M., Hensley, V., Jahnke, R., Kaul, L., Kim, K.H., Roe, K., Soutar, A., and Vathakanon, C., 1988, Early diagenesis of organic matter in Peru continental margin sediments: Phosphorite precipitation: *Marine Geology*, v. 80, p. 308–343.
- Garrison, R.E., and Kastner, M., 1990, Phosphatic sediments and rocks recovered from the Peru Margin during ODP Leg 112, in Suess, E., et al., *Proceedings of the Ocean Drilling Program, Scientific results, Volume 112*: College Station, Texas, Ocean Drilling Program, p. 111–134.
- Glenn, C.R., and Arthur, M.A., 1988, Petrology and major element geochemistry of Peru Margin phosphorites and associated diagenetic minerals: Authigenesis in modern organic-rich sediments: *Marine Geology*, v. 80, p. 287–307.
- Glenn, C.R., Arthur, M.A., Yeh, Hseuh-wen, and Burnett, W.C., 1988, Carbon isotopic composition of Peru-Chile Margin phosphorites: *Marine Geology*, v. 80, p. 287–307.
- Gobeil, C., MacDonald, R.W., and Sundby, B., 1997, Diagenetic separation of cadmium and manganese in suboxic continental margin sediments: *Geochimica et Cosmochimica Acta*, v. 61, p. 4647–4654.
- Grimm, K.A., 2000, Stratigraphic condensation and the redeposition of economic phosphorite: Allostratigraphy of Oligo-Miocene shelfal sediments, Baja California Sur, Mexico, in Glenn, C.R., et al., eds., *Marine authigenesis: From global to microbial*: SEPM (Society for Sedimentary Geology) Special Publication 66, p. 325–347.
- Harder, H., 1980, Synthesis of glauconite at surface temperatures: *Clays and Clay Minerals*, v. 8, p. 217–222.
- Harris, R.G., 2000, Triassic Doig Formation sand bodies in the Peace River area of western Canada: Depositional and structural models and the impact of diagenesis on reservoir properties [M.S. thesis]: Vancouver, University of British Columbia, 205 p.
- Heggie, D.T., Skyring, G.W., O'Brien, G.W., Reimers, C., Herczeg, A., Moriarty, D.J.W., Burnett, W.C., and Milnes, A.R., 1990, Organic carbon cycling and modern phosphorite formation on the east Australia continental margin: An overview, in Notholt, A.J.G., and Jarvis, I., eds., *Phosphorite research and development*: Geological Society [London] Special Publication 52, p. 87–117.
- Jahnke, R.A., Emerson, S.R., Roe, K.K., and Burnett, W.C., 1983, The present day formation of apatite in Mexican continental margin sediments: *Geochimica et Cosmochimica Acta*, v. 47, p. 259–266.
- Kidder, D.L., and Swett, K., 1989, Basal Cambrian reworked phosphates from Spitsbergen (Norway) and their implications: *Geological Magazine*, v. 126, p. 79–88.
- Krajewski, K.P., 1983, Albian pelagic phosphate-rich macrooncooids from the Tatra Mts (Poland), in Peryt, T., ed., *Coated grains*: Berlin, Springer-Verlag, p. 344–376.
- McArthur, J.M., Benmore, R.A., Coleman, M.L., Soldi, C., Yeh, H.W., and O'Brien, G.W., 1986, Stable isotopes characterisation of francolite formation: *Earth and Planetary Science Letters*, v. 77, p. 20–34.
- McCrea, J.M., 1950, On the isotopic chemistry of carbonates and a paleotemperature scale: *Journal of Chemical Physics*, v. 18, p. 849–857.
- Pufahl, P.K., Grimm, K.A., Abed, A.M., and Sadaqah, R.M.Y., 2003, Upper Cretaceous (Campanian) phosphorites in Jordan: Implications for the formation of a south Tethyan phosphorite giant: *Sedimentary Geology* (in press).
- Rasmussen, H., and Jørgensen, B.B., 1992, Microelectrode studies of seasonal oxygen uptake in a coastal sediment: Role of molecular diffusion: *Marine Ecology Progress Series*, v. 81, p. 289–303.
- Riggs, S.R., Stille, P., and Ames, D., 1997, Sr isotopic age analysis of co-occurring Miocene phosphate grain types on the North Carolina shelf: *Journal of Sedimentary Research*, v. 67, p. 65–73.
- Schuffert, J.D., Kastner, M., and Jahnke, R.A., 1998, Carbon and P burial associated with modern phosphorite formation: *Marine Geology*, v. 146, p. 21–31.
- Silverman, S.R., Fugat, R., and Weiser, J.D., 1952, Quantitative determination of calcite associated with carbonate-bearing apatite: *American Mineralogist*, v. 37, p. 211–222.
- Soudry, D., 2000, Microbial phosphate sediment, in Riding, R.E., and Awramik, S.M., eds., *Microbial sediments*: Berlin, Springer-Verlag, p. 127–136.
- Soudry, D., and Champetier, Y., 1983, Microbial processes in the Negev phosphorites (southern Israel): *Sedimentology*, v. 30, p. 411–423.
- Southgate, P.N., 1986, Cambrian phoscrete profiles, coated grains, and microbial processes in phosphogenesis: Georgina Basin, Australia: *Journal of Sedimentary Petrology*, v. 56, p. 429–441.
- Sturesson, U., 1986, Lower Ordovician ooids from northern Öland, Sweden: *Geologiska Föreningens i Stockholm Förhandlingar*, v. 108, p. 331–348.
- Sturesson, U., 1988, Ooids and oncooids in a Middle Cambrian sandstone from Närke, Sweden: *Geologiska Föreningens i Stockholm Förhandlingar*, v. 110, p. 143–155.
- Sturesson, U., 1992, The Lower–Middle Ordovician transition in south central Sweden: Phosphorite and iron ooid formation induced by volcanic ash: *Geologiska Föreningens i Stockholm Förhandlingar*, v. 114, p. 431–445.
- Swett, K., and Crowder, K., 1982, Primary phosphatic oolites from the Lower Cambrian of Spitsbergen: *Journal of Sedimentary Petrology*, v. 52, p. 587–593.
- Swirydczuk, K., Wilkinson, B.H., and Smith, G.R., 1981, Syngenetic lacustrine phosphorites from the Pliocene Glens Ferry Formation of southwestern Idaho: *Journal of Sedimentary Petrology*, v. 51, p. 1205–1214.
- Thamdrup, B., Fossing, H., and Jørgensen, B.B., 1994, Manganese, iron, and sulfur cycling in a coastal marine sediment, Aarhus Bay, Denmark: *Geochimica et Cosmochimica Acta*, v. 58, p. 5115–5129.
- Torres, M.E., Brumsack, H.J., Bohrmann, G., and Emeis, K.C., 1996, Barite fronts in continental margin sediments: A new look at barium remobilization in the zone of sulfate reduction and formation of heavy barites in diagenetic fronts: *Chemical Geology*, v. 127, p. 125–139.

Manuscript received 9 March 2003

Revised manuscript received 27 May 2003

Manuscript accepted 27 May 2003

Printed in USA

Geology

Coated phosphate grains: Proxy for physical, chemical, and ecological changes in seawater

Peir K. Pufahl and Kurt A. Grimm

Geology 2003;31;801-804
doi: 10.1130/G19658.1

Email alerting services click www.gsapubs.org/cgi/alerts to receive free e-mail alerts when new articles cite this article

Subscribe click www.gsapubs.org/subscriptions/ to subscribe to *Geology*

Permission request click <http://www.geosociety.org/pubs/copyrt.htm#gsa> to contact GSA

Copyright not claimed on content prepared wholly by U.S. government employees within scope of their employment. Individual scientists are hereby granted permission, without fees or further requests to GSA, to use a single figure, a single table, and/or a brief paragraph of text in subsequent works and to make unlimited copies of items in GSA's journals for noncommercial use in classrooms to further education and science. This file may not be posted to any Web site, but authors may post the abstracts only of their articles on their own or their organization's Web site providing the posting includes a reference to the article's full citation. GSA provides this and other forums for the presentation of diverse opinions and positions by scientists worldwide, regardless of their race, citizenship, gender, religion, or political viewpoint. Opinions presented in this publication do not reflect official positions of the Society.

Notes