- The inability to measure accurately the dry deposition of particles; and
- The inability to measure accurately the air/sea exchange of gases.

See also

Chlorinated Hydrocarbons. Metal Pollution. Refractory Metals. Transition Metals and Heavy Metal Speciation.

Further Reading

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AUTHIGENIC DEPOSITS

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Introduction

There are many kinds and forms of authigenic mineral deposits in the deep-sea. Here we concentrate on the more abundant and, in some cases, potentially economic types, namely ferromanganese deposits, phosphorites, marine barite, and the authigenic silicate minerals in deep-sea sediments. Hydrothermal deposits and a class of sedimentary iron and manganese oxides associated with seafloor hydrothermal activity – the metalliferous sediments found as a basal sequence in the deep-sea sedimentary column and in deep basins adjacent to active spreading centers – are described elsewhere in the encyclopedia. Ferromanganese deposits are here divided into nodules and crusts on the basis of morphology and environment of formation. The sources of the major and minor metal enrichments in these deposits are contrasted between continental weathering and submarine volcanism, with important enrichment influences from the marine biosphere. Marine barite has a similar mixed origin with strong biological influence. Knowledge of the origins of submarine phosphorites has been greatly aided by studies of recent seafloor deposits. There are a variety of authigenic silicate minerals in deep-sea sediments. The more abundant zeolites and clays such as smectite form mainly from diagenetic alteration of metastable volcanic glasses, but many other reaction paths are known and suggested.

Ferromanganese Deposits

Marine ferromanganese deposits are complex assemblages of authigenic minerals and detrital components. They are broadly characterized by shape and by environment of formation as deep-sea nodules and crusts. Ferromanganese nodules are commonly found on the abyssal seafloor at and near the top of the underlying pelagic sediment cover. Crusts are usually found on the steep slopes of islands and seamounts but are also found with the pelagic sediment on the deep-sea floor where sedimentation is extremely low. Occasionally, nodules may grow to coalesce into a pavement or crust of ferromanganese deposits. Conversely, crusts can grow around small fragments of the usually lithified sediment or basalt substrate of a seamount or island slope to create ‘pseudo’ or ‘seamount nodules’ that are otherwise indistinguishable from crustal pavements.

Ferromanganese Nodules

Deep-sea ferromanganese nodules are classified as three major types on the basis of their origin: hydrogenetic, early diagenetic, and mixed hydrogenetic–early diagenetic. In this same scheme, crusts are described as primarily hydrogenetic, with comparatively minor diagenetic and hydrothermal occurrences (**Figure 1**). Hydrogenetic nodules obtain their ferromanganese oxides as precipitates from sea water. However, they are rarely if ever pure and also contain a variety of detrital minerals and biogenic debris from the pelagic sediment and fallout from the overlying water column and atmosphere. Early diagenetic nodules obtain their ferromanganese oxides from metals dissolved from the sediment and transported within the pore waters of the upper, peneliquid sediment layer (**Figure 1**). Because manganese and minor metals such as nickel and copper are more readily mobile in pore waters under suboxic seafloor conditions, diagenetic nodules are enriched in these metals relative to concentrations of iron and cobalt. The hybrid or mixed type nodule has both hydrogenetic and diagenetic components. These nodules are usually found at the sediment–water interface where their outer layers record their most recent position. The upper, relatively smooth hydrogenetic top is composed of iron- and cobalt-rich ferromanganese oxides from the bottom water and the lower, relatively bumpy or 'botroyidal' diagenetic bottom is composed of manganese-, nickel-, and copper-rich ferromanganese oxides from the sediment.

Attempts have been made to classify nodules on the basis of morphology and to relate their occurrence to the composition of the underlying sediment. Such field classifications were made to predict metal enrichment and genesis, but reliance upon morphological data for other than abundance information from either seafloor photography or remote acoustic imaging has not yet been widely practiced in exploration. Nodule abundance appears to correlate more strongly with siliceous ooze than with red clays, and both siliceous ooze and red clays have higher nodule abundance than does carbonate ooze.

Ferromanganese nodules and crusts are mainly composed of three types of manganese oxide

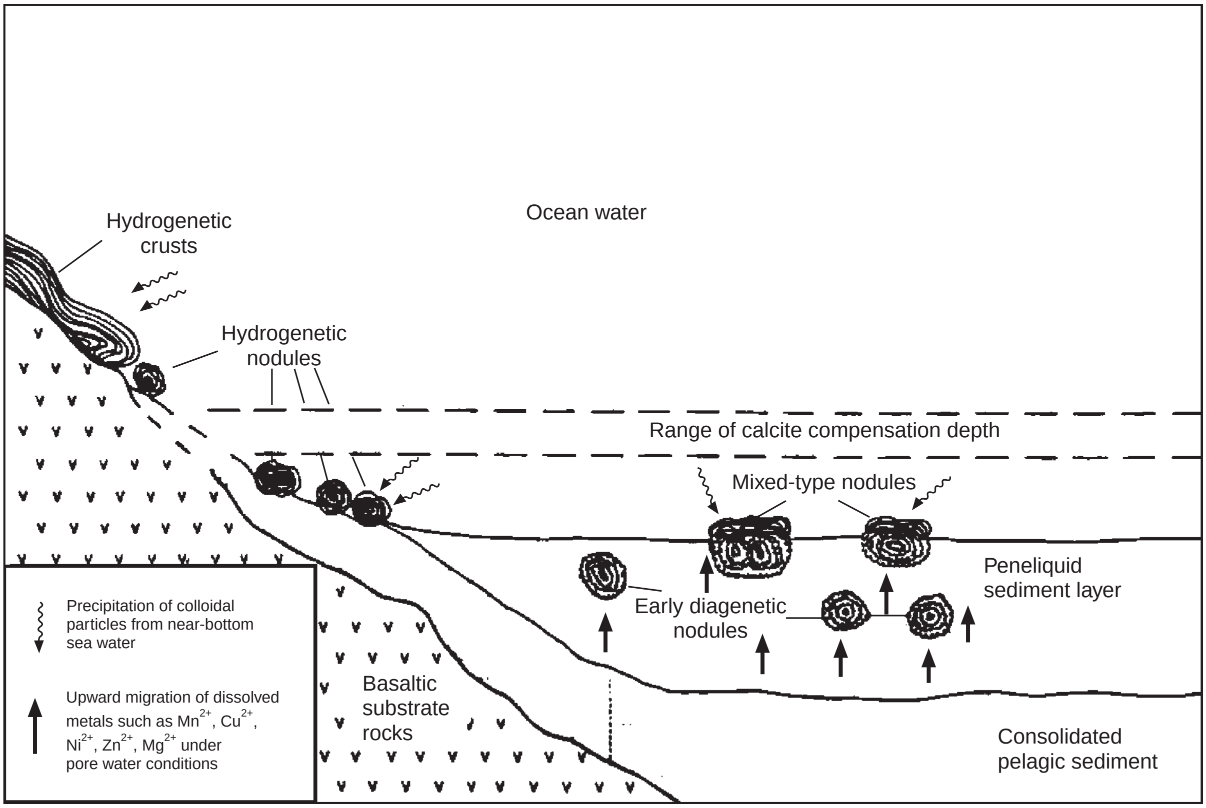


Figure 1 Schematic figure of the principal types of ferromanganese nodules (diameters vary from 1 to 15 cm) and crusts (thicknesses vary from < 1 to 10 cm) distributed in pelagic sediments and on seamounts and island slopes. (After Halbach P (1986) Processes controlling the heavy metal distribution in Pacific ferromanganese nodules and crusts. *Geologische Rundschau* 75: 235–247.)

minerals: vernadite or δ-MnO_2; birnessite; and todorokite. These minerals are listed in order of decreasing E_h or oxidation potential of the formation environment, and increasing crystal order. In vernadite, all manganese occurs as Mn^{4+}, which allows for crystal lattice substitution of metals such as Co^{3+} and Pb^{4+}. Todorokite contains some manganese as Mn^{2+}, which allows for crystal lattice substitution of metals such as Cu^{2+} and Ni^{2+}. Birnessite is an intermediate form. Iron oxides are primarily found as closely intermingled X-ray-amorphous FeOOH and occasionally as goethite or lepidocrocite. Other minerals include detrital quartz, plagioclase feldspar, clay minerals such as smectites, authigenic zeolites, apatite, barite, and calcite.

The global distribution of ferromanganese nodules on the seafloor (**Figure 2**) largely reflects the inverse distribution of thickest sediment cover. Nodules, which accumulate at rates of several millimeters per million years, cannot grow where sediments are accumulating at rates that are greater than 10^3 times faster (several centimeters per thousand years). Otherwise, rapid burial and dissolution would be their fate. Paradoxically, nodules are found to lie atop sediments that are accumulating at rates up to 10^3 times faster; this phenomenon has been explained by bottom current winnowing and gentle bumping or tilting of nodules during the burrowing activities of benthic organisms. Nodules are truly pelagic deposits and are rarely found near the continents or near islands where rapid hemipelagic sedimentation occurs. Exceptions are found on the Blake Plateau off eastern Florida, within the Drake Passage off South America, and near the Cape of Good Hope off Southern Africa, where bottom currents are strong and sweep sediments from these areas (**Figure 2**). Highly concentrated nodule fields occur between the Clarion and Clipperton fracture zones just north of the equatorial high productivity zone in the Eastern Pacific, just south of this zone in the Indian Ocean, and near the Antarctic Convergence in the Southeast Pacific.

Source of major metals The sources of the major metals in ferromanganese nodules and crusts – iron and manganese – are commonly described as products of the weathering of the continents, seafloor hydrothermal activity, and sediment diagenesis. Other than a small but distinct cosmogenic component (see Ferromanganese Crusts below), the iron and manganese must ultimately come from the Earth's crust and mantle. The fraction coming from the continents is more geologically recycled than that from the ocean crust, and diagenesis in this regard is clearly not an ultimate source but a process of further recycling of these metals within the sediment column. The relative importance of continental weathering versus seafloor hydrothermal activity as a source of iron and manganese to pelagic sediments and marine ferromanganese deposits has been debated since the 1890s. Early work by able geochemists on both sides of this issue was hampered by a lack of convincing evidence. For example, on the basis of early distribution maps of manganese and other trace metals in surface Atlantic sediments and

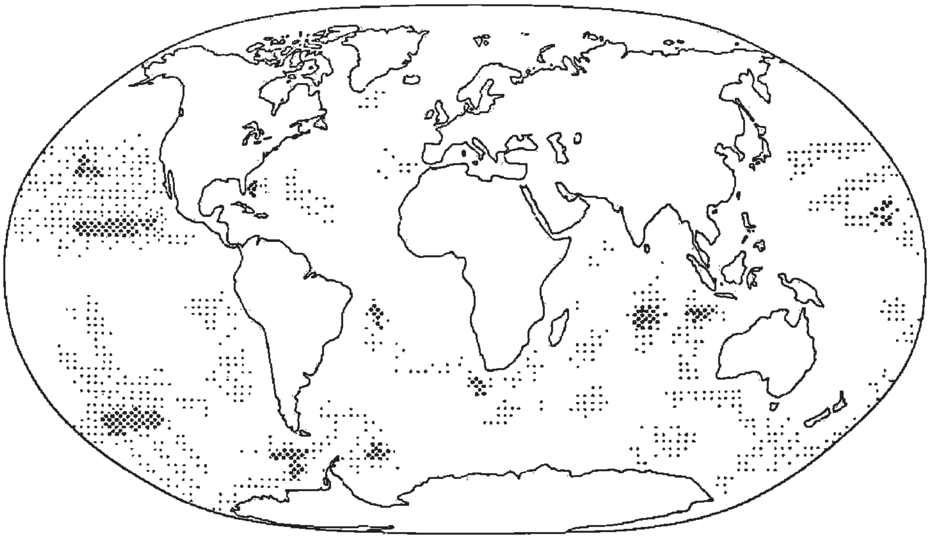


Figure 2 Distribution of ferromanganese nodule abundance on the world ocean floor. (After Cronan, 1980.)

evidence for iron and manganese enrichments in atmospheric dust, it was suggested that continental weathering and atmospheric transport was an important pathway of these metals to the ocean. However, the manganese distribution in Atlantic sediments can more readily be explained by hydrothermal enrichments from hot springs along the Mid-Atlantic Ridge, unknown at that time but well-known today. Likewise, early arguments for extensive hydrothermal iron and manganese enrichments from volcanic hot springs located along the mid-ocean ridges were compelling, but were not confirmed until the discovery of hot springs there in 1977. Water column trace-metal analytical techniques have improved to the point that a very convincing argument can be made for continental weathering and atmospheric transport as a path for at least some fraction of the iron and manganese in marine ferromanganese deposits. Another approach, which additionally answers the old question of the relative contributions of these two sources to ferromanganese deposits at any given location of the seafloor, was made for the Pacific (**Figure 3**) using a 'Co-chronometer'. This dating method is based upon the inverse relationship to growth rate of some minor metals' concentrations in hydrogenetic ferromanganese crust deposits, more painstakingly measured by radiometric techniques such as U-series (excess ^{230}Th) or ^{10}Be dating. Using the relatively easy Co-chronometer, hundreds of ferromanganese deposits were measured to construct the detailed map of ferromanganese crust growth rates for the Pacific in **Figure 3**. The highest growth rates are associated with active spreading along the East Pacific Rise, Juan de Fuca Ridge, and Galapagos Rift, and with submarine arc volcanism in the Mariana Island arc. The deposits in these areas therefore receive most of their iron and manganese from hydrothermal sources. The slowest crust growth rates and highest cobalt enrichments are located near the Mid-Pacific Mountains seamount province west of Hawaii, far from active hot springs and the continents.

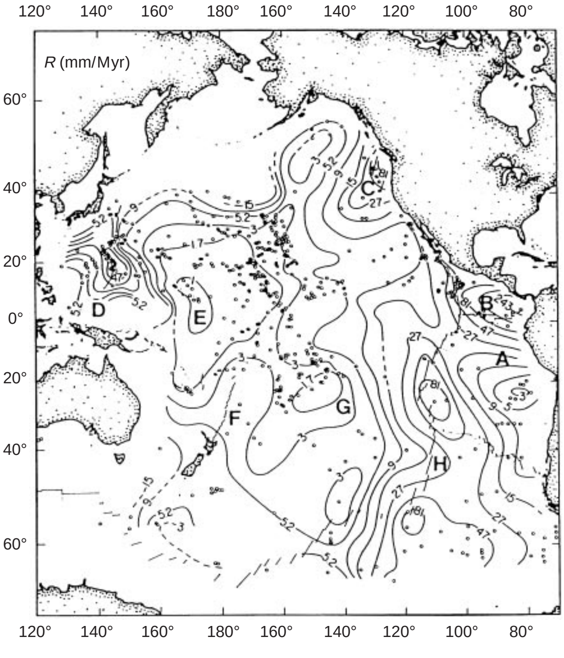


Figure 3 Distribution of ferromanganese crust accumulation rates in the Pacific Ocean. (After Manheim FT and Lane-Bostwick CM (1988) Cobalt in ferromanganese crusts as a monitor of hydrothermal discharge on the Pacific sea floor. *Nature* 335, 59–62.)

Source of minor metals Relative to sea water and the Earth's crust, ferromanganese nodules are enriched in nickel, copper, cobalt, and a host of other minor metals such as the platinum-group elements (PGE) and the rare-earth elements (REE). Concentrations of nickel and copper reach up to 2 wt% in 'high-grade' nodules from fields between the Clarion and Clipperton fracture zones, with cobalt concentrations approaching 0.5 wt%. Broadly, nodules from the Pacific appear to be more enriched in these metals than those from the Indian and Atlantic Oceans, but metal concentrations can vary widely within basins and nodule fields. For at least the better-studied Pacific, concentrations of nickel and copper show good correlation to the nodule Mn/Fe ratio, suggesting that manganese-rich, todorokite-containing diagenetic nodules are the major depositories of these metals (**Figure 4A, B**). There is also a regional trend of nickel and copper enrichments and Mn/Fe ratios in the Pacific that is highest in the equatorial NE Pacific, the Peru Basin, and the SE Pacific near the Antarctic Convergence. The distribution of nodule cobalt concentrations shows little correlation to the Mn/Fe ratio, however, being enriched instead near the Mid-Pacific Mountains and in the South Central Pacific (**Figure 4C**).

The ultimate source for the minor metals in ferromanganese nodules is again the Earth's crust and mantle, but with minor metals the case for continental weathering versus seafloor hydrothermal activity is stronger. First, hydrothermal ferromanganese crusts, like many rapidly accumulating diagenetic crusts, are known to have very low concentrations of minor metals. Second, studies of copper and nickel distributions in pelagic surface sediments suggest that the highest concentrations are nearest to regions of high surface productivity, implying that plankton are involved in the enrichment process.

There is an inverse relationship of depth of copper and nickel concentration in Pacific nodules with the sedimentary concentration of calcium carbonate tests from planktonic organisms, with deeper sediment deposits containing lesser $CaCO_3$ because of increased dissolution. Comparative studies of copper, nickel, and cobalt in plankton and the labile or easily mobilized fraction of pelagic sediment and associated deep-sea nodules has also suggested that diagenesis of organic matter in the sediments leads to an enrichment of these metals in the nodules. All told, scavenging by organisms in the surface waters enriches the particle rain in minor metals that originally enter the world's oceans by winds and rivers, and further concentration of these metals occurs within the surface sediments during suboxic diagenesis, with ferromanganese nodules as the final metals depository.

Ferromanganese Crusts

Crust deposits differ from nodules in form, occurrence, and composition. Hydrogenetic crusts are

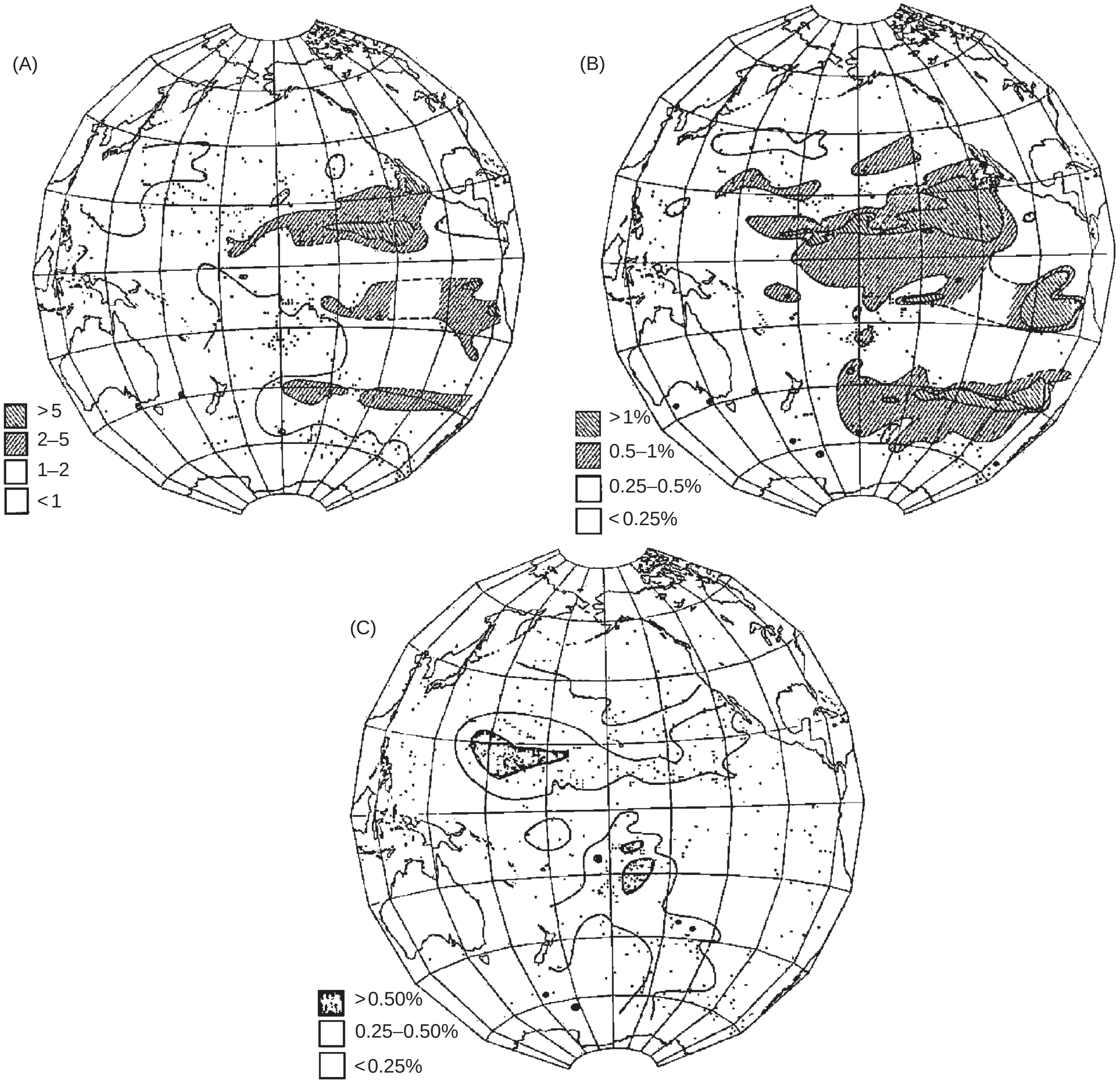


Figure 4 (A) Distribution of Mn/Fe ratios in ferromanganese nodules from the Pacific. (B) Distribution of nickel concentrations in ferromanganese nodules from the Pacific. Copper shows a similar distribution. (C) Distribution of cobalt concentrations in ferromanganese nodules from the Pacific. (After Calvert SE (1978) In: *Sea Floor Development: Moving into Deeper Water*. London: The Royal Society.)

principally composed of vernadite with iron oxides and minor detrital mineral and carbonate fluorapatite (CFA) contaminates. They grow at extremely slow rates from less than 1 mm to tens of millimeters per million years. Because the cobalt flux is for the most part invariant throughout the world's oceans, cobalt concentrations approach 2 wt% on comparatively shallow seamount slopes between 800 and 2000 m water depth within the Western Equatorial Pacific (**Figure 3** – compare with **Figure 4C**) where crust growth rates are slowest. Above approximately 800 m dilution and coverage of crustal pavements by principally carbonate-rich sediments limits their growth, and below 2000 m incorporation of increasing fluxes of seamount and wind-blown detritus and ferromanganese oxides causes crust growth rates to increase, effectively decreasing the cobalt concentration. The oxygen minimum zone (OMZ) presently intersects seamounts and island slopes in the Central Pacific at between 500 and 1500 m water depth. Although not presently anoxic enough to inhibit manganese oxide precipitation in this area, the OMZ was probably more intense in the past, thereby providing a mechanism for both transport of dissolved Mn^{2+} and inhibition of crust growth. Cobalt concentrations also show a general trend of decreasing values within older crustal layers, suggesting that past seafloor conditions favored increased manganese fluxes and growth.

Relative to nodules, crusts are on average enriched in Fe, Ca, P, Ti, Pb, Ce, As, and Pt, as well as cobalt, and are depleted in Si, Al, Ni, Cu, and Zn. Manganese concentrations are similar. The relative enrichments of calcium and phosphorus in crusts reflect the more widespread incorporation of CFA in seamount crusts (see Phosphorites below), whereas the higher silicon and aluminum contents of nodules reflect their origin within loose, aluminosilicate-rich sediments of the abyssal seafloor. The mechanism for cobalt enrichment is oxidative scavenging, whereby dissolved Co^{2+} is oxidized to Co^{3+} on the manganese oxide surface. This mechanism also explains the relative enrichments of cerium, and possibly some of the lead and titanium enrichments in crusts. Lower concentrations of iron (and arsenic, an oxyanion in sea water scavenged by positively charged FeOOH; MnO_2 surfaces are negatively charged at sea water pH) in nodules reflect a greater diagenetic component that favors mobilization of manganese over iron. Because of their extremely slow growth in areas relatively free of detrital input, crusts also accumulate large amounts of cosmogenic debris. Enrichments of platinum and PGE metals can be partially explained by this source, but several lines of geochemical evidence indicate that the majority of platinum and the other PGE (Ir, Os, Pd, Rh, Ru) are scavenged from sea water. Oxidation and reduction mechanisms have been proposed for both incorporation and postdepositional remobilization of the PGE in crusts and nodules.

Phosphorites

Submarine phosphorites are principally composed of CFA or francolite with usually large admixtures of detrital impurities from the sediments in which they form or replace during authigenesis. Concentrations of P_2O_5 commonly range from 5 to 28 wt%, reaching values of 35 wt%, with minor element enrichments of strontium, yttrium, and the REE. There are three principal types of phosphorite deposits in the world's oceans: offshore or continental shelf-slope nodules and concretions; massive insular deposits originating from sea bird guano; and 'seamount' phosphorites that often associate with ferromanganese crusts as layers, veins, impregnations, and substrate material (**Figure 5**). Submarine phosphorites were originally thought to be fossil deposits no younger than Miocene age, like those marine phosphorites mined on land, but were subsequently found to be actively forming in shelf-slope areas off Western South America, Southwest Africa, and Australia. Studies of the deposits off Peru and Chile have demonstrated their contemporaneous origin near anoxic sediments where the OMZ impacts the continental shelf-slope there at between 200 and

Figure 5 Photograph of a ferromanganese crust on a phosphorite substrate recovered from the summit of Schumann seamount, north of Kauai, Hawaii. Note the inclusions of altered basalt clasts from the seamount within the phosphorite, which has likely replaced limestone. (From G. McMurtry and D. L. VonderHaar, unpublished data.)

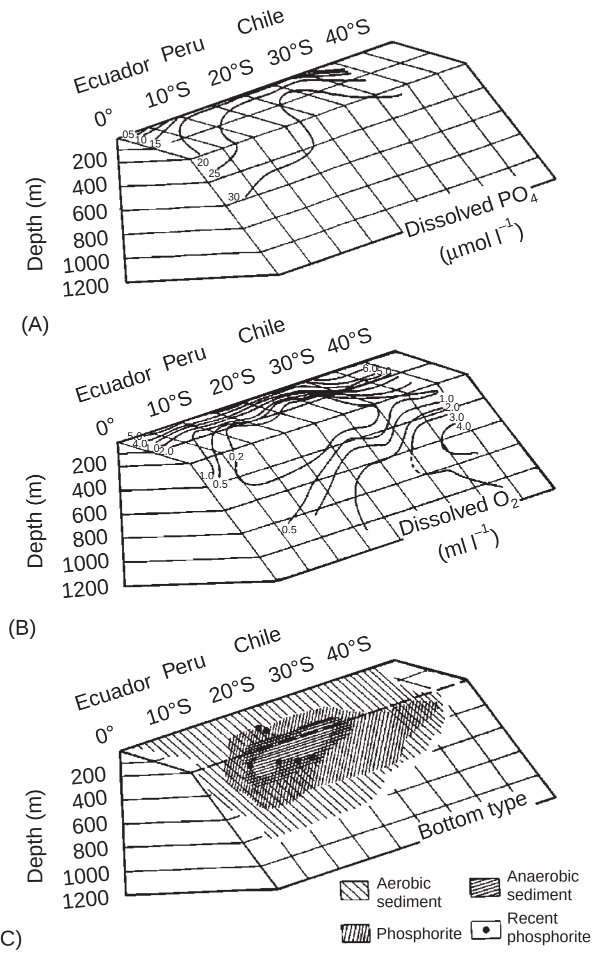


Figure 6 Schematic figure of the western South American shelf and slope, showing contours of dissolved phosphate and oxygen in the bottom waters and the locations of aerobic and anaerobic sediments, phosphorite and Recent phosphorite deposits. (After Burnett WC, Veeh HH and Soutar A (1980) U-series, oceanographic and sedimentary evidence in support of recent formation of phosphate nodules off Peru. In: *Marine Phosphorites*, SEPM Special Publ. no. 29, pp. 61–72.)

400 m (**Figure 6**). Upwelling currents bring waters rich in dissolved PO_4 onto the continental slope and shelf, increasing surface productivity and enhancing the reduction potential in sediments underlying the OMZ. Bacterial consumption of organic matter within the sediment releases $HPO_4{}^{2-}$ that can combine with dissolved Ca^{2+}, F^- and $CO_3{}^{2-}$ in pore waters to form authigenic precipitates of CFA. This process is thought to occur in sediments near the boundaries of the OMZ where the hydrogen ion concentrations (low pH) produced during bacterial consumption and in CFA precipitation are diluted by relatively alkaline (high pH) sea waters. Associated sediment diagenetic reactions involving dolomite formation and Mg^{2+} exchange in clays reduce the concentration of apatite precipitation inhibiting Mg^{2+} in pore waters, aiding CFA formation.

The distribution of phosphorites throughout the Phanerozoic rock record is highly irregular, correlating broadly with periods of warm climate and higher sea level. Off South America and Southwest Africa, U-series dating of the deposits has demonstrated their correlation with warm, interglacial periods back to 150 000 years before present. Increased chemical weathering of the continents during warm periods may provide enhanced PO_4 fixation into hemipelagic sediments. Concurrent encroachment of the OMZ onto the continental shelf-slope during marine transgressions increases the extent of organic matter preservation. When combined, these effects are thought to promote initial phosphorite formation. Subsequent marine regressions may enhance the initial enrichment by winnowing detritus from older phosphatic sediments, producing deposits of economic value.

Insular phosphorites are relatively easily understood deposits from guano in the nesting areas of ancient sea birds that created the ore deposit by transporting and further biologically concentrating scarce dissolved phosphate in surface sea waters within the flight radius of the island. The island of Nauru in the central Equatorial Pacific is a prime example. Although some are presently submerged, these deposits have all formed subaerially and are no older than Tertiary.

Comparatively less is known about the formation of seamount phosphorites. Substrate samples show cryptocrystalline CFA matrix replacement of preexisting limestones that often contain altered basalt breccia and other evidence of high-energy deposition upon the summits and upper slopes of Cretaceous seamounts in the Pacific (**Figure 5**). Within ferromanganese crusts, these deposits show the effects of lowered redox conditions (e.g., platinum remobilization) with impregnation and replacement of older ferromanganese oxides. Strontium and oxygen isotope-derived ages of CFA formation appear to center on the Eocene–Oligocene (36 Ma) and Oligocene–Miocene (24 Ma) boundaries, with some evidence for a minor Middle Miocene event at about 15 Ma. Paleotracking of the Pacific Cretaceous seamounts shows that many were close to the equatorial high productivity belt during the late Cretaceous and Paleocene–Eocene periods, where their then-shallower summits and slopes could have intersected the OMZ in a region of equatorial upwelling. Later depositional episodes would require a greatly expanded and more intense OMZ than the present one.

Marine Barite and Authigenic Silicates

Marine Barite

Barite ($BaSO_4$) is a widespread mineral in deep-sea sediments, varying between 1 and 10 wt% on a carbonate-free basis. It is the predominant barium phase in the ocean. $BaSO_4$ is known to compose a solid solution series with $SrSO_4$ as celestobarite in the skeletal portions of some marine organisms (i.e., the *Xenophyophoria*) and is often found in association with marine organic matter, such as in suspended particles and fecal pellets. Barite is also a well-known gangue mineral in hydrothermal deposits on land and has more recently been found as a principal component of moderate-temperature hydrothermal chimneys on mid-ocean ridges and volcanically active seamounts. Early work on the distribution of marine barite in deep-sea sediments had difficulty distinguishing the relative importance of hydrothermal sources from continental weathering as cycled through the marine biosphere. Distribution maps of marine barite in Pacific deep-sea sediments and the more quantitative barium accumulation rate (**Figure 7**) show both an association with the equatorial high productivity zone and the East Pacific Rise–Bauer Basin areas that are heavily influenced by metalliferous hydrothermal deposition. The key question is how much of the relatively dispersed, fine-grained (usually < 2 μm) marine barite particles in deep-sea sediments result from hydrothermal plume fallout and bottom current redistribution of ridge-crest metalliferous sediments versus those carried to the seafloor in the particle rain from surface productivity.

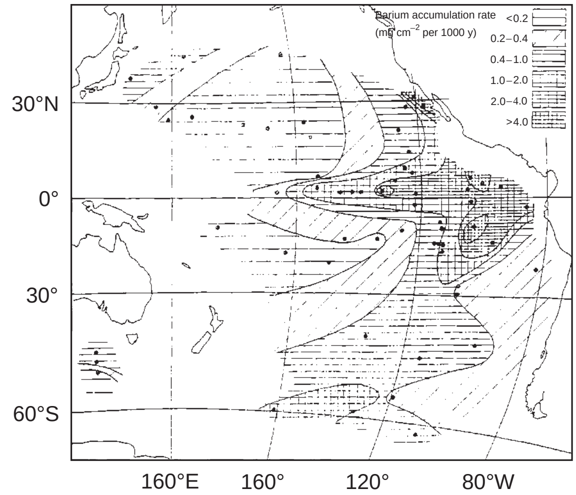


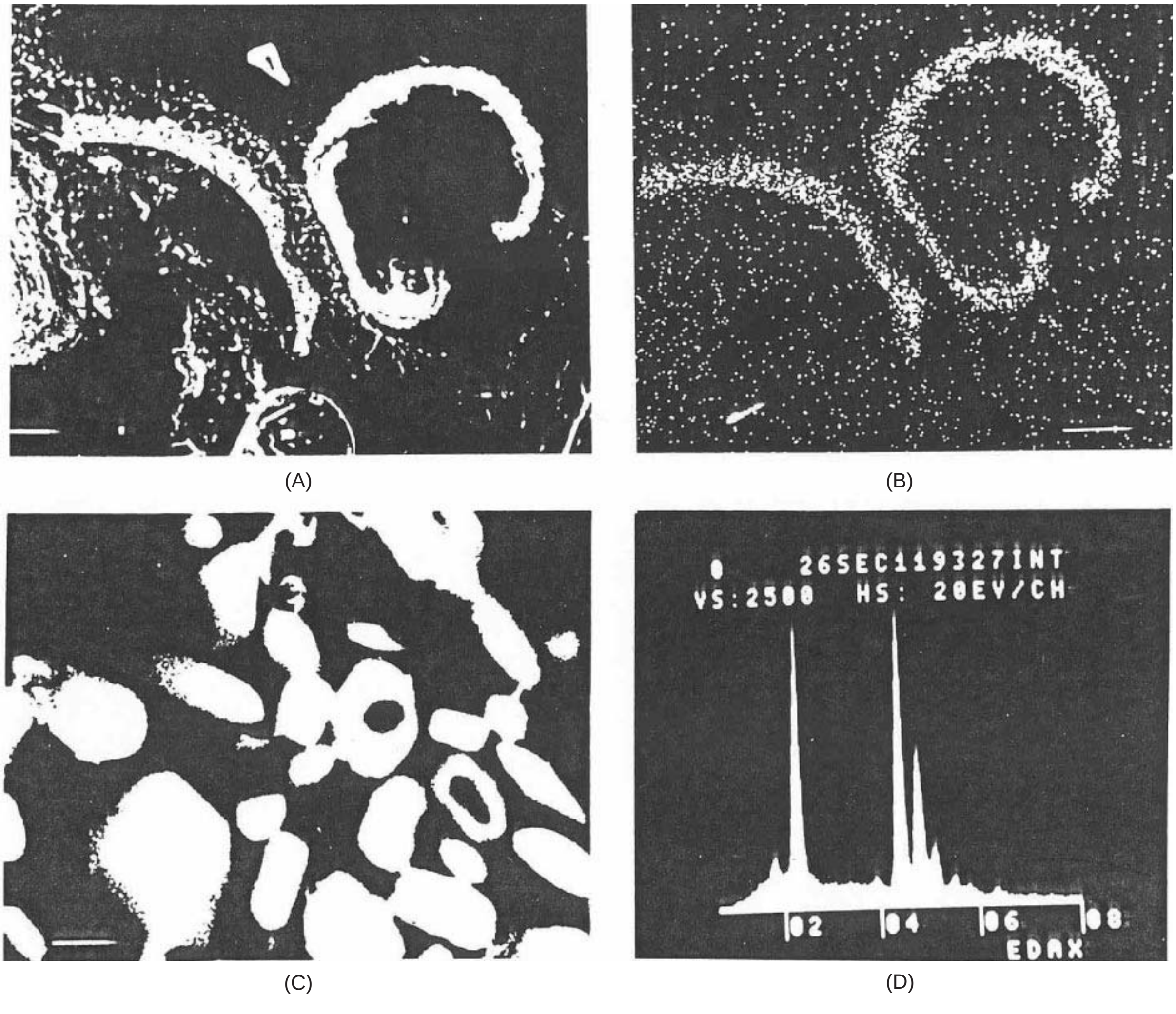
Figure 7 Distribution of barium accumulation rates (units of mg cm^{-2} per 1000 years) in the Pacific sediments. (After Boström K, Joensuu O, Moore C *et al.* (1973), Geochemistry of barium in pelagic sediments. *Lithos 6*: 159–174.)

The association of marine barite with organic matter complicates the interpretation of occurrence of increased barite deposition found along midocean ridges because greater preservation of organic matter also occurs with increased carbonate sedimentation above the calcite compensation depth. Additionally, basin-scale dispersal of hydrothermal particles appears limited, especially for the relatively dense barite. Studies of marine barite saturation show that barite is below saturation in the water column but rapidly approaches saturation in the pore waters of deep-sea sediments. Discrete barite particles are nevertheless found in the microenvironments of suspended biogenic matter and in fecal pellets that rapidly fall to the seafloor; their dissolution on the seafloor and in transit is likely the dominant control on the barium concentration in the deep ocean. Within the sediment and in ferromanganese deposits, barite can form authigenically as discrete particles and diagenetically as replacement of biogenic skeletal remains (**Figure 8**).

Authigenic Silicates

Zeolites Low-temperature alteration of basalt and metastable volcanic glasses on pillow rims, in layers, and dispersed throughout deep-sea sediments can produce a variety of diagenetic alteration phases. (Low temperature is defined as ranging from modern ambient seafloor conditions, or near 0°C to up to 150°C, the low-temperature metamorphism limit.) These include X-ray-amorphous palagonite, the zeolites phillipsite, clinoptilolite, analcite (plus several others of rarer occurrence), smectites, and authigenic K-feldspar (**Table 1**). Phillipsite is a hydrated potassium- and sodium-rich aluminosilicate that forms elongated and sometimes twinned crystals from 8 to 250 μm length with numerous inclusions that indicate rapid growth. Oxygen isotope values of 34‰ for phillipsite indicate formation in the marine environment at modern seafloor temperatures. Phillipsite appears metastable on geological timescales, becoming rarer beyond Cenozoic age. The mineral is found globally at the sediment–sea water interface and continues to grow within the sediment column until it dissolves and disappears in the deepest drill holes (usually below 500 m depth). Marine clinoptilolite forms finer grained (<45 μm), platy crystals of relatively silicon-rich hydrated potassium- and sodium-rich aluminosilicate (high Si/Al ratio). Clinoptilolite is more frequently encountered at depths > 100 m in the sediment column and persists to great depths and geological age, suggesting that it is thermodynamically stable in the deep-sea. Analcite is a rarer, sodium-rich zeolite in deep-sea sediments that displays a general trend of increasing abundance with geological age which parallels that of clinoptilolite. Both clinoptilolite and analcite can form directly from alteration of more siliceous volcanic glass (andesite, rhyolite, from active island arcs and explosive continental volcanism), by diagenetic reaction of phillipsite and dissolved silica (clinoptilolite) or Na/K exchange with clinoptilolite (analcite).

Palygorskite and sepiolite Authigenic clay minerals ($< 2\,\mu m$ particle size) in the deep-sea include the fibrous minerals palygorskite and sepiolite and the smectite family of expandable phyllosilicates. Both palygorskite and sepiolite are rare in recent marine sediments, occuring more often in Eocene and older sediments. Palygorskite is a hydrous silicate containing Mg, Al and Fe^{3+}, whereas sepiolite is almost a pure hydrous magnesium silicate. Pore water solutions of alkaline pH with high concentrations of dissolved silica and magnesium favor the formation of both minerals. Fine fibrous textures and overgrowths of siliceous tests and opal-CT attest to their authigenesis. Reactions range from the diagenetic alteration of (mainly silicic and intermediate) volcanic ash, either directly or indirectly via smectite with biogenic silica, formation upon magnesium



(A) (B) (C) (D)

Figure 8 Photograph of barite crystals inside a ferromanganese nodule. (A) Scanning electron micrograph of foraminifera shell walls that have been replaced by barite. (B) Barium elemental X-ray map produced by EMP. (C) Magnification of (A) showing individual barite crystals. (D) Elemental spectrum of the barite crystals: S Kα at 2300 eV; Ba Lα, β, γ at 4460 eV. (After Lalou C, Brichet E, Poupeau G, Romany P and Jehanno C (1979) Growth rates and possible age of a North Pacific manganese nodule. In Bischoff JL and Piper DZ (eds) *Marine Geology and Oceanography of the Central Pacific Manganese Nodule Province,* pp. 815–834. New York and London: Plenum Press.

Table 1 Summary of observed and suggested diagenetic reactions in deep-sea sediments

Opal-A → opal-CT → quartz
Opal-A → quartz
Basaltic glass → palagonite
Volcanic glass → smectite minerals
Volcanic glass → zeolites
Basalt → smectite minerals
Basalt + H_4SiO_4 → smectite minerals
Basaltic glass + H_4SiO_4 → phillipsite
Poorly cyrstalline smectite → phillipsite
Andesitic and rhyolitic glass + H_4SiO_4 → clinoptilolite
Andesitic and rhyolitic glass → smectite minerals
Phillipsite + H_4SiO_4 → clinoptilolite
Phillipsite + smectite + H_4SiO_4 → clinoptilolite + palygorskite
Opal-A + $Al(OH)_4^-$ + K^+ → clinoptilolite
Opal-A + $Al(OH)_4^-$ + K^+ → opal-CT + clinoptilolite
Plagioclase + K^+ + H_4SiO_4 → K-feldspar + Na^+ + Ca^{2+}
? → K-feldspar
? → albite
Clinoptilolite + Na^+ → analcite + K^+ + quartz
Clinoptilolite → K-feldspar + quartz
Clinoptilolite + Na^+ → analcite + K-feldspar + quartz
H_4SiO_4 + Mg^{2+} + $Al(OH)_4^-$ → palygorskite
H_4SiO_4 + Mg^{2+} → sepiolite
Volcanic glass + Mg^{2+} + H_4SiO_4 → palygorskite
Smectite + Mg^{2+} + H_4SiO_4 → palygorskite
Clinoptilolite + palygorskite + calcite → K-feldspar + dolomite + quartz
Clinoptilolite + sepiolite + calcite → K-feldspar + dolomite + quartz
Amorphous hydroxides (mainly Fe) + H_4SiO_4 + Mg^{2+} → Fe-montmorillonite
Nontronite + Mg^{2+} + reduced sulfur → saponite + FeS_2
Dissolved silica adsorption by clay minerals
Amorphous aluminosilicate reconstitution?
Smectite → mixed-layer illite–smectite?

After Kastnev (1981).

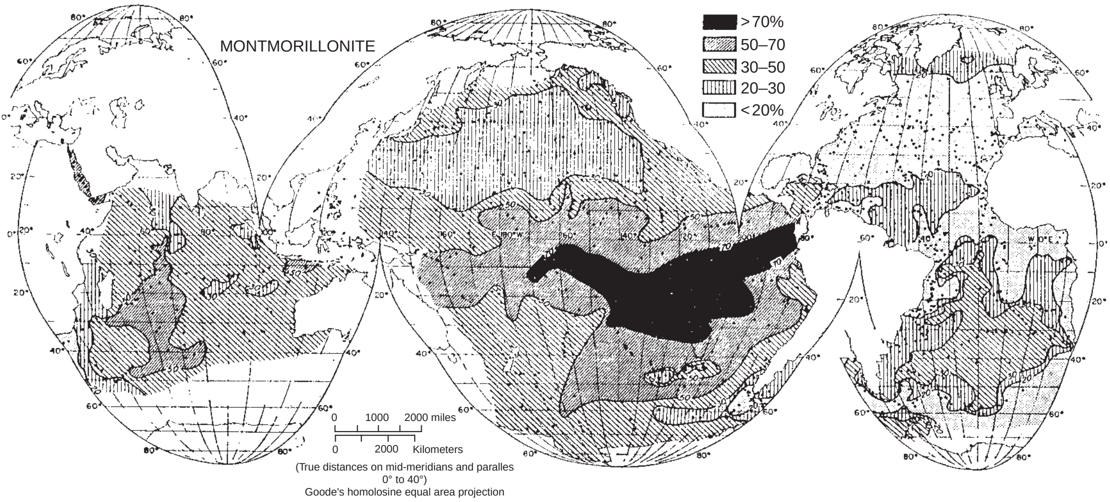


Figure 9 Distribution of montmorillonite (smectite) abundance in the < 2 μm fraction of sediments in the world ocean, carbonate-free basis. (After Griffin JJ, Windom H and Goldberg ED (1968) The distribution of clay minerals in the world ocean. *Deep-Sea Research* 15: 433–459.)

release after conversion of biogenic opal-A to opal-CT, and reaction of biogenic silica tests with marine pore waters, including hypersaline brines enriched in magnesium (**Table 1**).

Smectites Most clay minerals in deep-sea sediments are detrital phases from continental weathering. These minerals compose the bulk of the nonbiogenic sediments in the < 2 μm fraction and

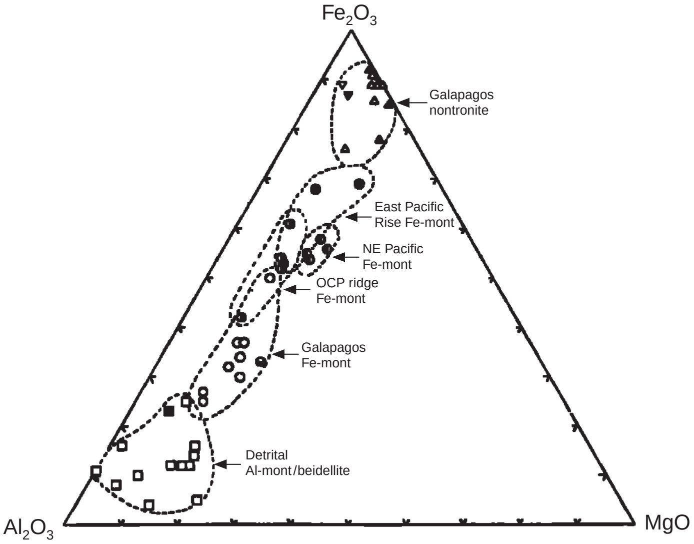


Figure 10 Triangle plot of octahedral Mg–Al–Fe composition for marine smectites. (After McMurtry GM, Wang CH and Yeh HW (1983) Chemical and isotopic investigations into the origin of clay minerals from the Galapagos hydrothermal mounds field. *Geochimica et Cosmochimica Acta* 47: 475–489.)

include clay-sized quartz and the phyllosilicates kaolinite, illite, chlorite, and smectite. The smectite group of expandable clay minerals includes these common end-members: magnesium-rich saponite, found mostly as a diagenetic or low-temperature metamorphic product of basalt; iron-rich nontronite, often found as a low-temperature ($<100°C$) hydrothermal deposit; and aluminum-rich beidellite predominantly derived from volcanic ash alteration on land. The surface distribution of marine smectite in the world's oceans shows broad areas, such as in the south-eastern Pacific where $>70\%$ of the mineral's abundance is far from land and blankets the active East Pacific Rise spreading center (**Figure 9**). Most of this smectite is iron-rich montmorillonite. Up to 50% of this mineral has been described as authigenically formed from the seafloor temperature alteration of volcanic glass, with the remaining 50% from detrital sources. Early oxygen isotope studies of deep-sea montmorillonite suggested that much of it formed pedogenically on land, but iron-rich montmorillonite is not typically found in wind-blown dust. More recent oxygen isotope work has suggested either a low-temperature submarine hydrothermal origin for the iron-montmorillonite or formation from low-temperature submarine hydrothermal alteration of ash within subaerial volcanoes that is periodically deposited in the ocean by explosive volcanism. Nontronite and iron-montmorillinite have also been suggested to form at seafloor temperatures by reaction of hydrothermally derived iron oxides with biogenic silica. One of the difficulties in assigning a precise origin to this mineral class is the possibility of physical admixtures of truly authigenic iron-rich smectites with more aluminum-rich smectites derived from the continents (**Figure 10**).

Glossary

Aluminosilicate A silicate containing aluminum in coordination with oxyhydroxides and/or in substitution for silicon in SiO_4 tetrahedra.

Authigenesis New origin. Process of formation of new minerals in place.

Detrital Formed from detritus, usually from rocks, minerals, or sediments from elsewhere than the depositional site.

Diagenesis Changed origin. Recombination or rearrangement of a mineral that results in a new mineral, usually postdepositionally.

Hemipelagic Deep-sea sediment that accumulates near the continental margin, so that the sediment contains abundant continentally derived material and rates of sedimentation are high.

Hypersaline Excessive salinity, much greater than the normal salinity of sea water.

Metalliferous Metal bearing, usually enriched toward economic extraction of the metals.

Metastable State of a phase that is stable toward small disturbance, but is capable of reaction if sufficiently disturbed.

Pedogenesis Soil origin. Mineral formation within the soil.

Pelagic Open ocean environment. A marine sediment with that fraction derived from the continents indicating deposition from a dilute suspension distributed throughout deep-sea water.

Phyllosilicate Layered or sheet silicate mineral, formed by sharing three of the four oxygens in neighboring silicon tetrahedra.

Plankton Aquatic organisms that drift, or swim weakly. Can be either plants (phytoplankton) or animals (zooplankton).

Redox Abbreviation for reduction–oxidation, usually expressed as a potential.

Seamount Underwater mountain, 1000 m or higher elevation from seafloor base. Morphology may be peaked or flat-topped, with the latter called guyot.

Suboxic Condition lacking free oxygen, but not extremely reducing.

Zeolite Any of the minerals of the zeolite group. Aluminosilicate minerals with an open framework structure that allows for easily reversible hydration, gas adsorption, and either cation or anion exchange.

See also

Aeolian Inputs. Clay Mineralogy. Hydrothermal Vent Deposits. Manganese Nodules. Mineral Extraction, Authigenic Minerals. Platinum Group Elements and their Isotopes in the Ocean. Pore Water Chemistry. Rare Earth Elements and their Isotopes in the Ocean. River Inputs. Sediment Chronologies. Sedimentary Record, Reconstruction of Productivity from the. Tracers of Ocean Productivity. Transition Metals and Heavy Metal Speciation. Uranium–Thorium Decay Series in the Oceans Overview.

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AUTONOMOUS UNDERWATER VEHICLES (AUVs)

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An autonomous underwater vehicle (AUV) is an uncrewed, untethered, underwater vehicle capable of self-propulsion. Such vehicles are mobile instrumentation platforms that have actuators, sensors, and on-board intelligence to successfully complete survey and sampling type tasks with little or no human supervision. A large number of AUVs have been developed, ranging in dry weights from less than 50 kg to nearly 9000 kg, with the majority of vehicles at the small end of the scale. In the last several years, acceptance of AUVs for oceanographic, commercial, and military missions has risen dramatically, leading to a sharp rise in AUV operations.

By far the most common AUV configuration is as a torpedo-like vehicle, consisting of a streamlined body with propeller and control surfaces at the stern (**Figure 1**). Operational speeds for such vehicles range from 0.5 to 5 $\mathrm{m\,s^{-1}}$, with most vehicles operating at a cruising speed of about 1.5 $\mathrm{m\,s^{-1}}$. In order to remain controllable, torpedo-like AUVs must move forward at some minimum speed in order to maintain flow over control surfaces, and therefore are not capable of station keeping. When a higher