Marine Cobalt Resources

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Ferromanganese oxides in the open oceans are more enriched in cobalt than any other widely distributed sediments or rocks. Concentrations of cobalt exceed 1 percent in ferromanganese crusts on seamounts, ocean ridges, and other raised areas of the ocean. The cobalt-rich crusts may be the slowest growing of any earth material, accumulating one molecular layer every 1 to 3 months. Attention has been drawn to crusts as potential resources because they contain cobalt, manganese, and platinum, three of the four priority strategic metals for the United States. Moreover, unlike abyssal nodules, whose recovery is complicated by their dominant location in international waters, some of the most cobalt-rich crusts occur within the exclusive economic zone of the United States and other nations. Environmental impact statements for crust exploitation are under current development by the Department of the Interior.

OFTEN OVERSHADOWED BY ITS SISTER ELEMENTS IRON, nickel, and manganese, cobalt suddenly came into prominence in 1978, when Shaba Province of Zaire (formerly Katanga in the Belgian Congo) was invaded by insurgents from Angola and Zambia. The high price peak (Fig. 1) reflects the fact that Zaire (Shaba province) is the world's largest producer of cobalt (1) and that cobalt remains indispensable for "superalloys" used in jet aircraft engines. The Zairian invasion had a particularly tangible effect on the United States, which is the world's largest consumer of cobalt (33.4 percent in 1984) (2). The event also focused attention on the United States' dependence on imports for many mineral raw materials and on the potential uncertainty in supply of the four first-tier "strategic" elements: cobalt, manganese, platinum, and chromium (3). Thus, the influence of the Zairian event remained after cobalt prices returned to normal.

Views differ on national cobalt policy. Some regard the issue as urgent and requiring action (4), and others believe that normal needs can be purchased abroad and that emergency requirements can be met by switching suppliers, recycling cobalt, and releasing it from stockpiles, possibly coupled with diversions from civilian to military use (5). A third view is that our depressed mineral and metallurgical industries would be stimulated by using sea-floor minerals as a basis for a new industry.

Cobalt's relatively small atomic radius (1.24 Å) causes it to form dense and strong alloys with metals and with metalloids such as arsenic. For this reason, in 1910 (6) cobalt began to be used in industry for high-speed cutting tools, wear-resistant rods, armor-piercing projectiles, and hard-facing alloys including carbides. After World War II three important new uses emerged: powerful permanent magnets (ALNICO, an alloy of aluminum, nickel, and cobalt),

desulfurizing catalysts, and, most important, superalloys for jet engine parts (rotors and turbine blades) that must withstand stress and resist corrosion at temperatures in excess of 1000°C. Nutritive additives, paints, coloring glass, ceramics, and reagents fill out the list of main uses of cobalt.

The potential commercial recovery of deep-ocean manganese nodules, first proposed by John Mero in 1959 (7), had important implications for world cobalt supply. "Prime" (high-quality) nodules from the Clarion-Clipperton zone (north equatorial Pacific) contain about 0.24 percent cobalt (by oven-dried weight); this concentration is similar to that in Zairian copper-cobalt ores (Table 1). Interest in nodules peaked in the mid-1970's, with international consortiums preparing for mining (8), commercial operations predicted by the mid-1980's (9), and literally thousands of reports and reviews circulating in scientific, trade, and popular media (10, 11). In June 1980, President Carter signed the Deep Seabed Hard Minerals Act, which authorized licensing of U.S. firms to mine beneath international waters until such time as international covenants were approved. Regulation and environmental monitoring under the act were to be managed by the National Oceanographic and Atmospheric Administration.

In the United Nations, the "group of 77" nations incorporated a United Nations regime or "enterprise," which would regulate and participate in minerals recovery in international waters, into the United Nations Convention on Law of the Sea (UNCLOS III). The assessment that the United Nations draft treaty provided an unfavorable operating climate for U.S. mining activities was a major factor in the U.S. government's decision to refuse to sign the treaty (12). The political uncertainties were compounded by low metal markets in the early 1980's, and nodule mining consortiums reduced operations to skeletal levels or disbanded them altogether.

Just as prospects for commercial development of abyssal manganese nodules receded, another type of marine ferromanganese oxide deposit, "seamount crusts" or "cobalt-rich manganese crusts," emerged in 1981–82. Crusts (13) have a semicontinuous distribution on seamounts, ocean ridges, plateaus, and steep island slopes. They have cobalt concentrations that are from two to five times higher than those in prime (high-quality) manganese nodules in the Clarion-Clipperton zone (Fig. 2, area 39) and Zairian ores. Finally, some of the most promising metal-rich crusts found to date are within 200 nautical miles of the United States and other coasts (Fig. 2) (14). This boundary was proclaimed by President Reagan as an Exclusive Economic Zone (EEZ) on 10 March 1983, adding the United States to the more than 60 coastal nations with similar claims. Cobalt-rich crusts were among resources cited in documentation accompanying the announcement.

Distribution of Cobalt in the Earth's Crust and in Ores

Cobalt's chemical and mineral-forming kinships cause it to be so completely incorporated into minerals dominated by iron and certain other metals (such as magnesium in basalts and granites) that

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separating it from igneous, metamorphic, or sedimentary environments is difficult (15). Even normal iron and manganese ores are generally not enriched significantly in cobalt. Widespread enrichment of cobalt to levels greater than 0.1 percent is confined to a few major land deposits, such as the stratiform "Copperbelt" deposits of Late Precambrian age in central southern Africa, and to deep-ocean nodules and especially ferromanganese crusts.

Only in a few areas of the world, such as the Cobalt and Gowganda mining districts of Ontario and the small and largely mined-out Moroccan deposits of Bou Azzer (Anti-Atlas Mountains), do cobalt minerals such as the cobalt arsenides dominate ore deposits (16). The large deposits in Africa have cobalt as a minor constituent, with concentrations up to 0.4 percent in the Zairian cobalt-rich copper sulfides and oxidized copper ores but values closer to 0.1 percent occur in the Zambian Copperbelt deposits, the Cuban (Moa Bay and Nicaro) and Australian laterites (oxide deposits remaining after tropical weathering of igneous rocks), and the Russian and Canadian iron-nickel sulfides (Petsamo-Karelian, Norilsk, and Sudbury, respectively) (16, 17).

Cobalt in the Ocean Ferromanganese Nodules and Crusts

In the 1960's, the Swedish chemist L. G. Sillén proposed that the oceans be treated as a giant chemical reaction vessel. The open ocean is a natural laboratory of such physical size and long-term stability that unusual separations of metals in great dilution are possible over extended time. Table 1 shows that in the ocean cobalt has been scavenged and accumulated on certain ferromanganese oxides to the highest enrichment levels known in sediments and sedimentary rocks. The remarkably high cobalt concentrations in deep-ocean manganese nodules were first noted by J. Y. Buchanan, chemist on the pioneering H.M.S. *Challenger* expedition of 1873–74 (18). Post–World War II investigators showed that cobalt was preferentially enriched in seamount nodules of the Pacific Ocean (19). Cronan noted the inverse relation between cobalt content of seamount "nodules" and water depth (20). Later, statistical evaluation of large numbers of nodule analyses confirmed the depth relation for all recovered samples in the mid-Pacific mountains area (21). The first expedition specifically focused on cobalt (*Midpac I*) was led by the German marine scientist Peter Halbach in 1981. Although cobalt-rich nodules were already a scientific curiosity and geochemical end-member, the results of this cruise suggested that semicontinuous, cobalt-enriched crusts on hard substrates were distributed over sufficiently wide areas to provide a potential economic resource (22). Confirming data were gathered on expeditions by the U.S. Geological Survey in 1983 and 1984 (23, 24), a second cruise by the R/V *Sonne* in 1984 (*Midpac II*), and University of Hawaii cruises sponsored by the U.S. Mineral Management Service (25). These new data have established that significant portions of the upper slopes of certain seamounts and ridges may be covered with from 2 to more than 4 cm of black oxide dominated by manganese and iron, but containing cobalt, nickel, lead, cerium, molybdenum, vanadium, and many other minor metals.

On most seamounts, the favored "shoulder" region for crust development (region I in Fig. 3) is steep, often step-structured when studied by detailed photography, and generally swept by powerful but incompletely understood "Taylor column" water currents (26). Only seamount substrates exposed for more than about 15 million years (since Miocene time or before) are old enough to accumulate significant cobalt-rich oxide armor. Few original surfaces of a seamount remain intact after emplacement, because as-yet poorly understood tectonic and mass-wasting activities sculpt and alter the
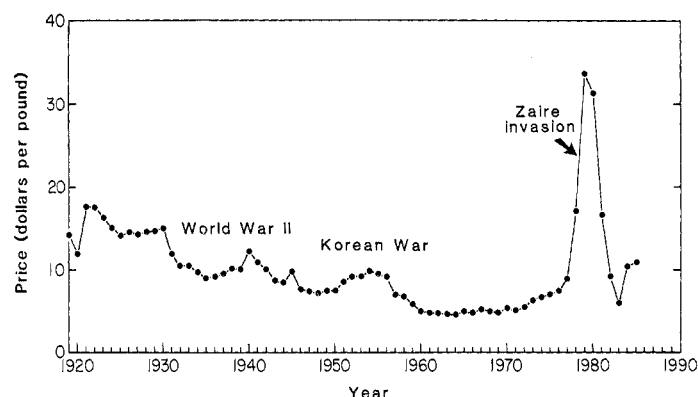

Fig. 1. Average annual cobalt prices, 1919–1985, in constant 1984 dollars [data from (2)].

external faces of seamounts with time. Therefore, on an empirical basis, significant crust coverage occurs mainly on seamounts 60 to 80 million years old or older, where even "newer" surfaces have been exposed long enough to accumulate appreciable crust. Because deeper layers are most affected by downward sediment and talus movement through slumping and sliding, crust occurrence tends to become increasingly irregular and thinner downslope (regions II to IV in Fig. 3).

Among the thickest crusts documented is an 11-cm crust collected from San Pablo Seamount in the New England Seamount chain (27). When crusts reach about 1 cm in thickness, they frequently take on a botryoidal, papillated character, somewhat like the surface of a flattened bunch of grapes. These irregular surfaces are characteristic and often serve to distinguish crusts from basalts in bottom photographs (Fig. 4).

A different kind of ferromanganese crust is found in current-swept plateau areas. One of the most striking of these is the Blake Plateau,

Table 1. Distribution of cobalt, nickel, manganese, and iron in common rocks, sediments, and other phases. Data are reported as grams per ton and include some means or other modifications from data cited in references. World ocean crusts are an average of 537 qualified samples (32).

Co	Ni	Mn	Fe	Co:Fe ($\times 10^4$)	Reference
		Granite			
4	10	460	21,900	1.8	(76)
		Shale			
19	68	850	47,200	4.0	(80)
		Earth's crust			
20	80	950	41,000	4.8	(81)
		Marine hydrothermal Mn-Fe oxides			
23	531	273,000	116,000	2.0	(78)
		Manganese oxide ore, Chiatura, U.S.S.R.			
31	1,110	341,000	8,900	34.8	(82)
		Basalt			
35	150	1,500	56,000	6.2	(76)
		Marine hydrothermal sulfides			
65	8	475	201,000	3.2	(83)
		Pelagic clay			
78	225	6,700	58,000	13.4	(80)
		Oolitic iron ore			
200	200	1,600	310,000	6.5	(84)
		Zaire cobalt ore			
2,000 to 4,000			240,000	125	(2)
		World average, deep ocean nodules			
2,700	5,500	186,000	125,000	216	(85)
		World average, ocean crusts			
6,300	4,500	216,000	165,000	382	This article

off the coast of Florida and North Carolina. Here the Gulf Stream has winnowed out sediments and left a lag gravel of middle Tertiary phosphorite, which has been coated with ferromanganese oxide crusts from a few millimeters to 5 cm thick (28). The deposits include all forms, from round nodules to smooth, scoured pavements (Fig. 4), and they were the first to be raised by airlift methods (29).

Chemical Data Banks

The comprehensive Scripps Institution Sediment Data Bank, currently being updated (30), contains chemical and other information about roughly 10,000 samplings of nodules worldwide, of which about 600 were initially designated as belonging to "crust" categories. These encompass ferromanganese oxides laterally covering hard substrates rather than enclosing discrete nuclei. A U.S. Geological Survey data base limited to crusts was initiated in 1983 to monitor old and new information and to analyze samples on a worldwide basis (Fig. 2) (31). Problems such as variable admixture with rock substrate and depth designation are greater for crusts than for nodules. The older data also provide a less reliable and complete record of crust composition and distribution than data from newer dedicated cruises, but insight can be gained by careful screening and interpretation of data as well as by new analyses.

A world ocean crust average of qualified samples yields about 0.6 percent cobalt (Table 2) (32). Compiling new U.S. Geological Survey and all other qualified data, four large areas from the central
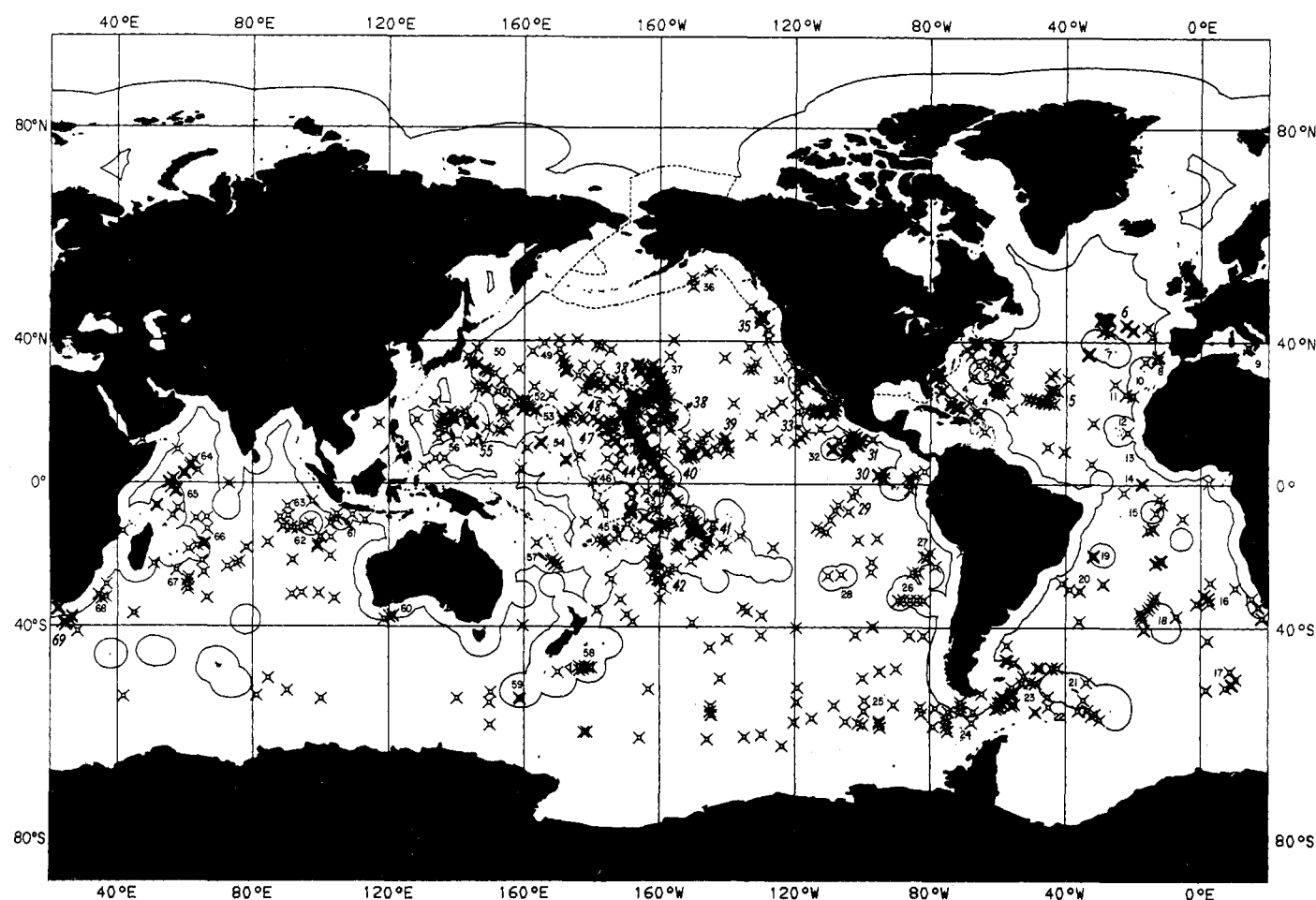

Fig. 2. Distribution of ferromanganese crusts in the world oceans. Contours delineate the 200-mile coastal zone [U.S. government maps 504760 and 541369 (1981) and 5478782 (1982)]. The dashed portion depicts U.S. Exclusive Economic Zone (EEZ), some boundaries of which remain provisional. Numbers refer to geographic locations for areas from which multiple samples exist in the U.S. Geological Survey Ferromanganese Crust Data Base. Larger numbers delineate regions of significant crust development or study. 1, Blake Plateau; 2, Bermuda Island; 3, New England Seamount Chain; 4, Bahama Slope; 5, Mid-Atlantic Ridge hydrothermal field; 6, Mid-Atlantic Ridge "FAMOUS" area; 7, Azores Islands; 8, Gorringe Bank; 9, Tyrrhenian Sea; 10, Saharian Seamounts; 11, Great Meteor Seamount; 12, Cape Verde Island; 13, Sierra Leone Rise; 14, Romanche Trench and fracture zone; 15, Ascension Island (southern Mid-Atlantic Ridge); 16, Walvis Ridge; 17, Bouvet Island; 18, Tristan da Cunha–Gough Island (southern Mid-Atlantic Ridge); 19, Martin Vaz–Trinidad Island; 20, Rio Grande Rise; 21, S. Georgia Island; 22, Scotia Sea; 23, Scotia Ridge; 24, Drake Passage; 25, southeast Pacific Basin Islands; 26, Juan Fernandez Island; 27, Nazca Ridge; 28, Easter Island; 29, East Pacific Rise (Albatross Cordillera); 30, Galápagos Island and EEZ; 31, O'Gorman-Siqueros fracture zone; 32, Clipperton Island; 33, Revilla Gigedo Island–Rivera fault zone; 34, Patton Escarpment; 35, Juan de Fuca fault and hydrothermal discharge zones; 36, Gulf of Alaska Seamounts; 37, Musician Seamounts; 38, Hawaiian Ridge system and EEZ; 39, Clarion-Clipperton fracture zone; 40, Line Islands Seamount chain; 41, Tuamota Archipelago and French Polynesia; 42, Southwest Pacific Basin; 43, Jarvis Island and EEZ; 44, Kingman Reef–Palmyra Island and EEZ; 45, Samoa EEZ; 46, Howland-Baker Islands and EEZ; 47, Johnston Island and EEZ; 48, Mid-Pacific Seamount and Necker Ridge; 49, Emperor Seamount chain; 50, Shatsky Rise; 51, Marcus-Necker Islands; 52, Mapmaker Seamount chain; 53, Wake Island and EEZ; 54, Marshall Islands; 55, Marianas Arc; 56, Palau-Kyushu Ridge; 57, New Caledonia Island; 58, Campbell Plateau; 59, Macquarie Ridge; 60, Diamantina fracture zone; 61, Christmas Island; 62, Keeling Island; 63, 90°E Ridge; 64, Carlsberg Ridge; 65, Seychelles Slope; 66, Seychelles-Mauritius Plateau; 67, Indian Ocean Ridge; 68, Mozambique Plateau; 69, Agulhas Plateau.

Table 2. Concentrations of principal metals (oven-dried weight percent) in nodules and crusts in world oceans at all depths.

| Metal | Nodules | | | | Crusts | | | | | | | |
| | World oceans (85)* | | Clarion-Clipperton (67)† | | World ocean‡ | | Pacific Ocean§ | | Atlantic Ocean‖ | | Indian Ocean¶ | |
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Si	7.69	4.12	7.6	2.9	4.05	1.74	3.71	1.72	3.38	1.70	5.40	1.32
Al	2.7	1.30	2.90	1.04	1.19	0.55	1.06	0.55	1.27	0.64	1.31	0.51
Fe	13.6	5.5	6.9	2.6	16.48	3.86	16.09	3.88	18.56	3.37	16.46	3.61
Mn	17.4	7.0	25.4	4.9	21.62	5.40	23.06	5.35	20.07	5.02	18.04	3.15
Co	0.27	0.19	0.24	0.08	0.63	0.39	0.73	0.38	0.53	0.39	0.38	0.23
Ni	0.55	0.38	1.28	0.30	0.45	0.24	0.47	0.24	0.40	0.25	0.39	0.20
Cu	0.34	0.32	1.02	0.33	0.14	0.18	0.16	0.20	0.11	0.12	0.13	0.12
Ca	2.23	2.54	1.70	0.80	2.44	0.90	2.60	0.88	2.51	0.98	2.02	0.86
Pb	0.093	0.067	0.040	0.019	0.158	0.098	0.163	0.078	0.163	0.076	0.150	0.177
Zn	0.120	0.410	0.140	0.050	0.068	0.043	0.073	0.046	0.080	0.044	0.056	0.017

*n = 509 (Si) to 1979 (Mn and Fe).   †n = 234 (Al) to 2237 (Ni).   ‡n = 279 (Si) to 1005 (Mn).   §n = 251 (Si) to 803 (Mn).   ‖n = 8 (Si) to 75 (Mn, Fe, Co, Ni, and Cu).   ¶n = 20 (Si) to 127 (Mn, Co, and Cu).
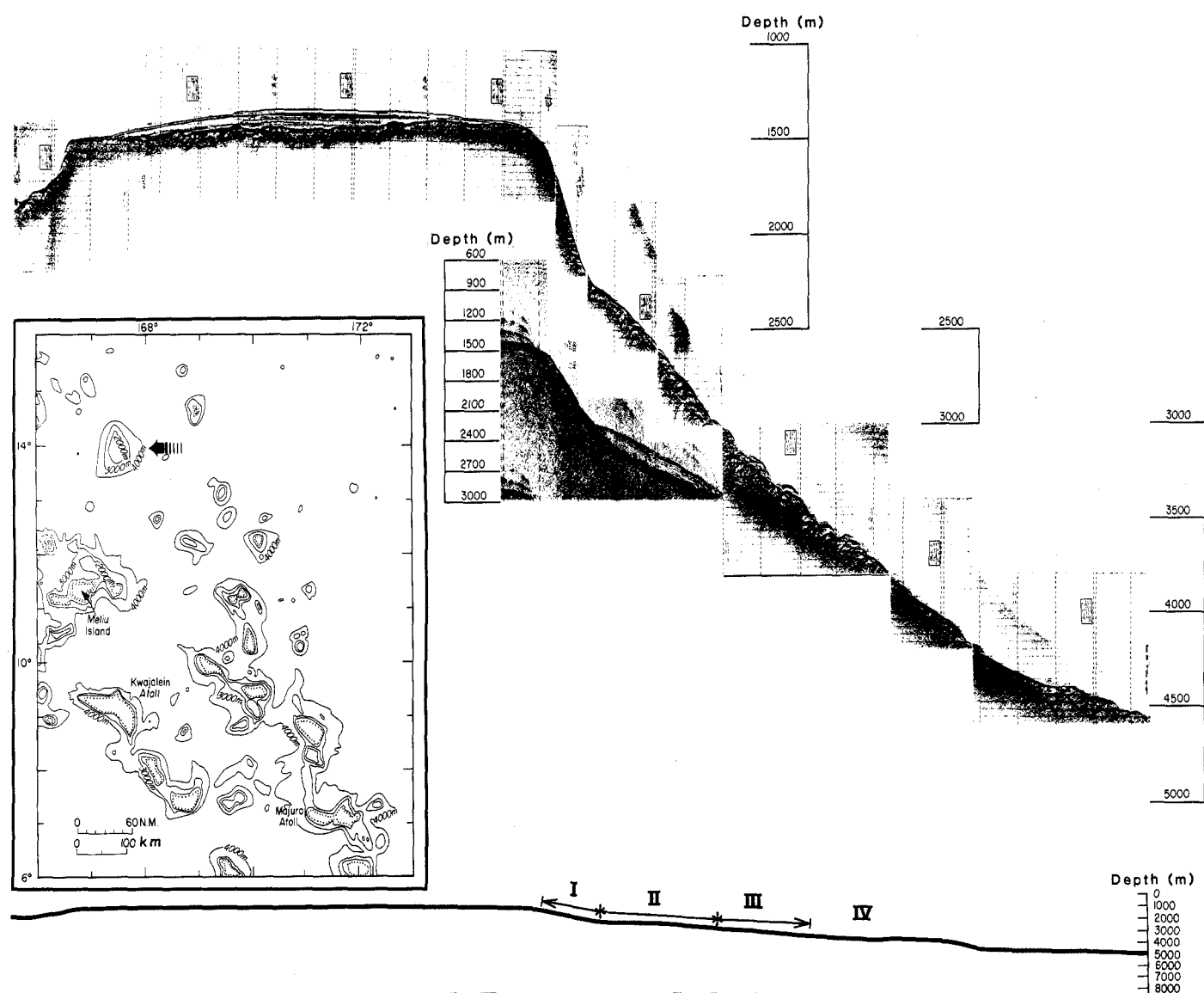

Fig. 3. Single-channel seismic traverse over unnamed seamount (summit, 17 nautical miles in diameter) in the Marshall Islands group [redrawn from Schwab *et al.* (66)]. Zonation on lower, unexaggerated profile: I, upper slope (shoulder area); outcrop with thick and consistent crust development. II, upper-middle slope with slump deposits and talus; medium-irregular crust development. III, lower slope with massive slump and talus aprons; thin, irregular crust development. IV, foot of slope; crust development rare. Shadows are multiple reflections. (Inset) A lower frequency acoustic profile showing sediment onslope. N.M., nautical miles.

Table 3. Depth distribution for cobalt and manganese in crusts. Notation: Pacific A, Hawaiian Ridge–Musicians Seamount area; Pacific B, Marshall Islands–west Mid-Pacific Mountains; Pacific C, Northern Line Islands–Mid-Pacific Mountains; Pacific D, Southern Line Islands–French Polynesia. The number of samples used to calculate the means for each area is shown in parentheses. Concentrations are in weight percent oven-dried matter.

Depth (m)	Pacific A (177)				Pacific B (71)				Pacific C (192)				Pacific D (97)			
	Co		Mn		Co		Mn		Co		Mn		Co		Mn	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
0 to 1000	0.91	0.28	23.85	3.63	1.64		33.38						1.98	0.55	28.09	16.97
1000 to 1500	0.94	0.31	24.24	4.10	0.84	0.33	23.87	7.17	1.05	0.47	27.08	4.50	1.25	0.27	26.97	5.73
1500 to 2000	0.66	0.14	22.02	3.73	0.74	0.27	24.36	5.53	0.93	0.34	26.01	4.56	1.41	0.69	24.87	7.25
2000 to 2500	0.70	0.19	21.68	2.05	0.87	0.34	26.57	7.77	0.59	0.15	21.94	4.61				
All depths	0.76	0.28	22.22	3.67	0.77	0.32	23.80	6.42	0.77	0.38	23.82	5.14	0.78	0.49	20.49	5.76

Pacific yield almost identical mean cobalt values of about 0.77 percent (Table 3). These areas are the Hawaiian Islands–Musicians Seamounts sector, the Marshall Islands–Western Mid-Pacific Mountains area, Mid-Pacific Mountains–Northern Line Islands, and Southern Line Islands–French Polynesia. However, at depths less than 2500 m, significant differences emerge (Table 3), and extraordinarily high values (≥ 2 percent) were obtained from three samples above 1000-m water depth in the Southern Line Islands–French Polynesia area. That these are not wholly due to chance is suggested by a large number of values well over 1.0 percent at water depths between 1000 and 1500 m in the same area.

The data clearly show the preeminence of high cobalt values in the central and south-central Pacific Ocean as well as the very high values in shallow seamount slopes having water depths of about 1000 ± 200 m. The shallow crusts in the open ocean must be distinguished from ferromanganese oxide phases in shallow water near the continents, because nearshore manganese oxide deposits usually have low cobalt content (Fig. 5). Although one cannot yet establish a shallow depth limit on higher cobalt values in the open Pacific Ocean per se, at depths less than 800 m rapidly deposited, biologically produced sediments such as coral debris may limit ferromanganese crust formation.

For other oceans the data are sparser than for the Pacific. There are apparently no results from cruises exclusively dedicated to crust study besides those in the Pacific and at the Blake Plateau. Since elevation of seamounts and other underwater edifices is an obvious and important influence on cobalt content, it will not be possible to establish true regional differences until the influence of depth is removed from comparative studies.

Comparison between prime or Clarion-Clipperton abyssal nodules and mid-Pacific crusts (Fig. 6) shows that, except for manganese, molybdenum, and vanadium, crusts from water shallower than 2500 m in the mid-Pacific area differ substantially from nodules in chemical composition. Iron, calcium, titanium, cobalt, phosphorus, cerium, arsenic, and platinum are all enriched in crusts, whereas silicon, aluminum, nickel, copper, zinc, and cadmium are enriched in prime abyssal (Clarion-Clipperton) nodules. Phosphorus and calcium in crusts can be largely identified as impregnations of carbonate fluorapatite, which frequently occurs as a substrate on central Pacific seamounts (33).

Correlation coefficients on large or widely spaced data sets have less diagnostic power than on small homogeneous subsets, because different relations among subsets tend to cancel each other and produce lowered correlation coefficients. A subset of data from the central Pacific, Horizon, and "S. P. Lee" seamounts (23, 34) yield strong correlation coefficients: Ca-P, 0.99; Mn-Ni, 0.87; Mn-Mo, 0.92; Mn-Co, 0.88; Mn-Cd, 0.75; Si-Al, 0.94; Al-Ti, 0.86; depth-Al, 0.84; depth-Pb, 0.73. The manganese, molybdenum, cobalt, and cadmium are all presumed to represent authigenic or colloidal precipitates from seawater. Silicon, aluminum, and titanium derive mainly from refractory particulate sources, as suggested previously for hydrogenetic oxides characterized mineralogically as vernadite
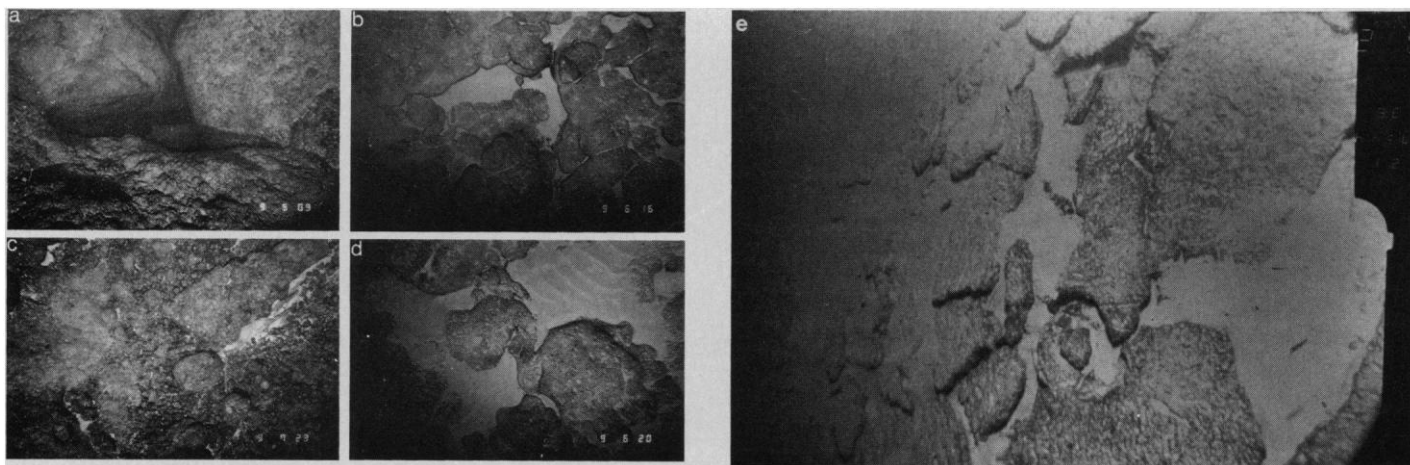

Fig. 4. (a to d) Bottom photographs (width ~2 m) of sea-floor crusts and pavements on Horizon Seamount (19°30'N, 169°W; depth ~1290 m) [photographs by H. Chezar (23)]. (e) Continuous ferromanganese cobbles and pavement on the Blake Plateau, off the Southeast Atlantic margin of the United States (31°N, 78°W; depth, 800 m) [wide-range bottom photograph (8 to 10 m) by Woods Hole Oceanographic Institution's ANGUS team (U.S. Geological Survey Gyre 82/11 cruise)].

| Total Central Pacific (537) | | | | Total Atlantic (77) | | | | Indian (102) | | | | Total world oceans (679) | | | |
| Co | | Mn | | Co | | Mn | | Co | | Mn | | Co | | Mn | |
Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1.31	0.61	26.08	9.05	0.85	0.29	22.28	2.87					0.97	0.53	26.42	9.24
1.00	0.38	25.33	5.24	0.80	0.42	19.87	4.28	0.76	0.24	18.89	3.13	0.83	0.32	22.66	5.71
0.86	0.38	24.57	5.02	0.58	0.26	19.99	3.21	0.39	0.09	18.50	0.93	0.76	0.43	21.87	5.45
0.67	0.22	22.47	4.68	0.55	0.13	17.90	3.05	0.40	0.15	18.98	2.41	0.61	0.28	21.01	5.88
0.76	0.36	22.60	5.28	0.50	0.27	20.15	5.02	0.42	0.24	18.01	3.30	0.63	0.36	21.62	5.23

(δMnO_2) (35). This is a poorly crystalline, hydrous MnO_2 phase that has monovalent, divalent, and trivalent cations substituted in its structure (36).

Notwithstanding the strong interest in Pacific crusts, other oceans and areas also have scientific and possible economic interest. Although low in metal-grade deposits (28), the Blake Plateau deposits (Fig. 2, area 1) cover thousands of square kilometers, are close to the U.S. mainland, and were at one time sought for leases. A possible resource target was use of the oxide pavements and nodules for catalyst purposes, including removal of vanadium and nickel from petroleum feedstocks. Subsequently, the spent oxide, enhanced in nickel and vanadium, may be subjected to metal recovery if markets warrant. Other North Atlantic areas such as seamounts on the Sierra Leone Rise and on the east flank of the Mid-Atlantic Ridge (37) have crusts with cobalt concentrations approaching 1.0 percent. More data are clearly needed because available analyses correspond to little more than the geographic equivalent of one qualified sample per several U.S. states.

Cobalt in Nodules and Crusts

Much progress has been made in understanding the origin of abyssal nodules. Nodules are formed partly from elements supplied by seawater but more abundantly by elements, particularly manganese, nickel, copper, and zinc, that are recycled from local sediments (oxic and suboxic diagenesis). The nickel and copper are derived in large part from the rain of planktonic debris from the surface, and they reach their highest concentrations under the equatorial productivity belt in the central Pacific (38).

In comparison, the origin of 1 percent (and more) cobalt in crusts has been elusive and controversial. Cobalt is perhaps the "purest" representative of elements removed from ambient seawater by oxide precipitation (39). Its enrichment does not follow the pathway of nickel and copper in abyssal nodules. Attribution of cobalt enrichment to vulcanism and volcanic emanations (40) has had appeal because seamounts and ocean ridges on which cobalt-rich nodules were found originated as submarine volcanoes. However, analyses of marine hydrothermal (volcanic) oxides and sulfides (Table 1) and of discharging fluids (41) have shown consistent cobalt depletion with respect to iron and nickel. In fact, high manganese and low cobalt concentrations can be used as an indicator of rapid hydrothermal deposition. Derivation of cobalt from basalt by cold (slow) alteration does not explain why crusts from higher elevations have greater cobalt concentrations than those on basaltic substrates in deep water. The hypothesis that pressure-sensitive minerals affected metal uptake (42) is complicated by the fact that vernadite, the principal manganese mineral in crusts, is now known to be present at all depths (pressures) in the oceans, and it occurs together with todorokite, another manganese mineral, in the same abyssal nodules (43).

Biologic activities have often been used to explain geochemical enrichments. Although microorganisms and macroorganisms probably affect the physical and physiochemical environment of oxide formation (44), analytical and experimental data show that cobalt is less effectively removed by phytoplankton than other transition metals (45), even though manganese and cobalt cycles are related.

In spite of objections on theoretical grounds (46), the concept that cobalt is oxidized to a trivalent state in marine manganese oxides and substitutes for Mn^{4+} (47) has been confirmed experimentally and analytically by x-ray photoelectron spectroscopy (48). Since the oxidation step creates a more insoluble product, more oxidizing conditions (higher redox potentials) on and around seamounts were suggested to account for cobalt enrichment in seamount nodules and crusts (20). However, this concept was countered with the observation that the seamounts actually project into the well-developed oxygen-minimum zone in the Pacific equatorial area, where cobalt enrichments have been most actively studied (22).

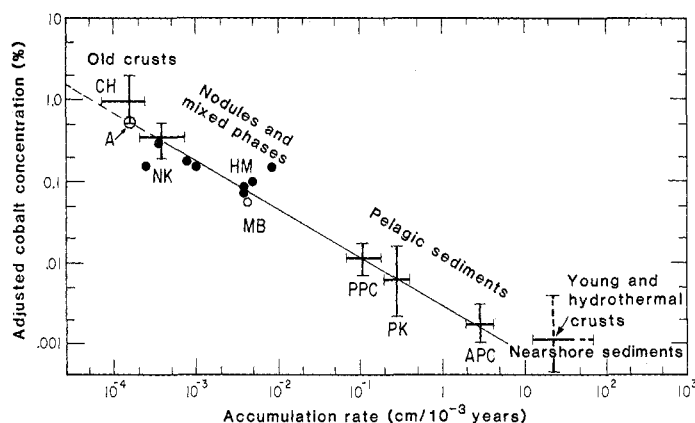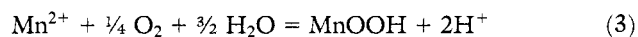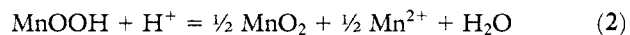Recent experimental and theoretical studies (49) suggest that

Fig. 5. Cobalt concentration (59) in marine deposits plotted against rate of accumulation. Bars indicate a spread of data where individual points are not shown. Abbreviations: CH, high-value crusts from the mid-Pacific area (50); A, average Atlantic crust composition (see text) and accumulation data for nonhydrothermal crusts (67, 68); NK, abyssal manganese nodules (69); HM, manganese nodules of various origin (70); MB, mixed authigenic and hydrothermal crust from Hess Deep, east Pacific (71); PPC, Pacific pelagic clay [composition from various reports (72); rates determined by the stratigraphic method (73)], determined by simultaneous elemental analysis and radiometric growth measurement (69); APC, Atlantic pelagic sediments [elemental analysis from Turekian and Wedepohl (74); rates of accumulation determined by the stratigraphic method (75); for hydrothermal crusts see (76, 77)]

cobalt uptake and crust accretion reactions are the most favored thermodynamically by stepwise disequilibrium processes, resulting in disproportionation of MnOOH to MnO_2 and liberating Mn^{2+} (Eqs. 1 to 3). The Mn^{2+} reacts with oxygen, and an autocatalytic cycle continues at the crust interface.

$$Co^{2+} + MnO_2 + 2H_2O = CoOOH + MnOOH + 2H^+ \quad (1)$$

$$MnOOH + H^+ = \tfrac{1}{2} MnO_2 + \tfrac{1}{2} Mn^{2+} + H_2O \quad (2)$$

$$Mn^{2+} + \tfrac{1}{4} O_2 + \tfrac{3}{2} H_2O = MnOOH + 2H^+ \quad (3)$$

On the basis of the new *Sonne* results, Halbach and collaborators (22, 50) reported a strong inverse relation between cobalt concentration and depth, with a "knick" at 2000 m. There was a relative regional shift to higher cobalt and nickel concentrations from the Mid-Pacific Mountains area to the Line Islands chain (areas 47 and 40 in Fig. 2). Two distinct generations of crust growth were found: a younger cobalt-enriched one, and an older one not radiometrically datable. The greater iron content of crusts from greater water depth was attributed to dissolution of carbonate, which is likewise known to increase with water depth.

U.S. Geological Survey studies found thick crusts but low cobalt, manganese, and nickel concentrations on the large Necker Ridge, which links the Mid-Pacific Mountains and the Hawaiian Archipelago. Intermediate values were obtained on the huge (130 km long) Horizon seamount. Maximum cobalt values of 2.5 percent were found in thin crusts from the S. P. Lee Seamount at 8°N latitude, coincident with the oxygen minimum layer at the shear zone between the equatorial current and countercurrent (34). Cobalt values of about 1.0 percent were obtained from the Marshall Islands area, which is southwest of the Mid-Pacific Mountains (24) (Fig. 2).

Studies from the Line Islands trend (51) confirmed the relation between cobalt values and depth discussed earlier and the distinction between abyssal nodules and hydrogenetic crusts. Mean values of 20 percent manganese and 0.55 percent cobalt in the crusts were reported. The investigators attached significance to recently reported long-distance transport of trace metals from the oxygen-free bottom water zones along the American continental margin to the central Pacific (52). It is tempting to link cobalt enrichments to the equatorial productivity belt and the oxygen-minimum zone, but values for cobalt greater than 1.0 percent have also been found in the Marshall Islands (24, 31), in the western part of the Hawaiian Ridge province (25, 53, 54), and in French Polynesia (Table 3), all of which are areas outside the well-developed oxygen-minimum zone. The possible influence of sea-floor spreading on these phenomena has not been investigated.

Rates of Accumulation

An important study of radiometric accumulation rates and chemical composition of crusts from the Midpac and Line Islands (55) showed crust growth rates from less than 1 to 2.8 mm per million years and indicated that cobalt fluxes (weights per unit area of crust and per unit time) were roughly constant regardless of the water depth from which samples were taken. Thus, the slower the formation of crusts, the higher their cobalt content. Extreme slowness of accumulation is believed to be required to reach cobalt levels as high as 2 percent.

Because studies of rates of accumulation have been important for understanding crust formation, further data are useful in placing Midpac crust data in perspective. Recent studies using radiometric techniques, especially [10]Be measurements (56), have decisively confirmed the magnitudes of "slow" hydrogenetic crust and nodule

Table 4. "Permissive" (favored) areas for ferromanganese crust development (86).

Region	Area (km²)
Northwest Hawaiian Ridge*	5,750
Johnston Island†	13,300
Howland-Baker Islands†	1,200
Marianas Island*†	80,500
Guam	12,700
Marshall Island*†	56,700
Central Seamounts	4,670
Palmyra-Kingman†	21,400
Micronesia†	273,800
Wake Island*	7,500
Blake Plateau pavement and slab areas	14,000

*Maximum inferred age greater than 30×10^6 years. †Maximum inferred age greater than 80×10^6 years.

accumulations determined by a variety of radiometric and other techniques (57). An earlier challenge (58) to the "slow" concept was thus resolved. Cobalt-rich crusts appear to be the slowest forming mineral and rock deposits known, accumulating at the rate of a molecular layer (unit cell thickness of 4.7 Å) (36) per 1 to 3 months (allowing for porosity). A caveat must be observed: crust accumulation rates from dating by uranium daughters must be interpreted with care because they can be applied only to the top millimeter or so of cobalt-rich crusts. They do not yield information about earlier hiatuses and changes in growth rate.

Data on the rate of accumulation and cobalt concentration for a variety of marine phases show a remarkable, inverse log-linear relation over many orders of magnitude of growth rate (Fig. 5). The growth rates include both stratigraphic and radionuclide datings. The relation between cobalt content and accumulation rate holds within the scatter of the data, for pelagic and other clayey sediments (not diluted with biogenic material), nodules of various kinds from all oceans, and "normal" hydrogenetic crusts. The relation can be used to predict cobalt content for a given type of sedimentary deposit, or it can yield an apparent accumulation rate of clayey or ferromanganese phases for a given cobalt content in weight percent (59). It does not necessarily hold for hydrothermal products, and cobalt increments become too small to detect for nearshore (rapidly accumulated) sediments. The data on Midpac crusts (55) show general agreement with the regression line in Fig. 5, but the data lie above the line (area CH in Fig. 5). Thus, the cobalt concentrations
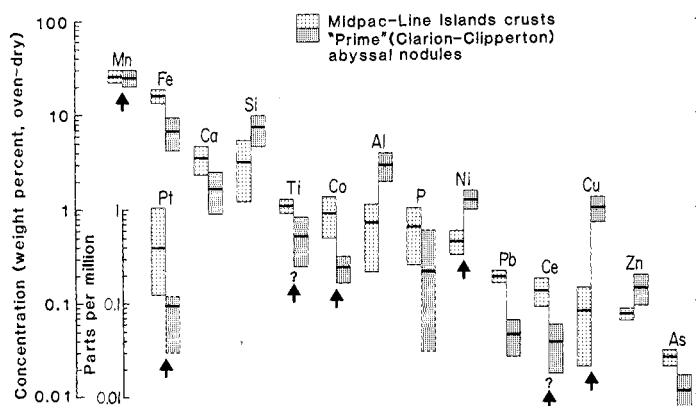

Fig. 6. Comparative chemical composition of mid-Pacific crusts (Necker Ridge excluded) and Clarion-Clipperton abyssal nodules (31, 34, 78, 79). Crust values refer to representative total samples from water depths of 1000 to 2500 m (n = 22 to 75).

Table 5. Rates of production and consumption and supply sources of principal metals.

Metal	Nodules in situ* (tons × 10⁶)	Annual world production† (tons)	Land resources‡ (tons × 10⁶)	Annual crusts production§ (tons × 10³)	Annual U.S. demand (tons × 10³)
Co	6.4 to 24	3.1×10^4	8.5	5.4	5.2
Ni	35 to 131	8.5×10^5	54	2.9	132
Mn	706 to 2600	26×10^6	2000	144	580
Cu	29 to 108	8.2×10^6	460	0.27	1490
Pt	0.4 to 1.5×10^{-3}	184		0.28×10^{-3}	21×10^{-3}

*From the Clarion-Clipperton zone [data from (87)].   †Rates based on data for 1981 (88).   ‡Data from (89).   §Assumed production, 10⁶ wet tons = 700,000 tons of dry crusts; recoveries from 52 to 89 percent (63).

per unit time appear to be higher in this part of the Pacific than in other areas. When more is known about metal incorporation in crusts and their age, they may serve as a monitor of water-mass chemistry and sea-floor activities in the history of the oceans.

Economic and Strategic Background for Cobalt

The United States ceased mining of cobalt in 1961 and ceased domestic production of metal in 1972 (60). Consumption continued to increase from 3 million pounds per year in 1961–65 to 18 million pounds per year in 1976–80. The latter figure was exceeded in 1984 (20 million pounds per year). The United States remains totally dependent on foreign supplies, except for the small proportion recycled from scrap.

The invasion of Zaire provided an opportunity to test the response of cobalt markets to change in cobalt supply or to expectations regarding future supply. Some uses, such as ceramics, declined by up to 38 percent, whereas superalloys in jet engines declined by only 10 percent as a result of abnormally high prices (61). This is attributable partly to the relatively low cost of 900 pounds of cobalt in a $3-million to $4-million jet engine and partly to the lack of approved substitutes. Long-run price elasticity of −0.32 percent for all cobalt uses means that a rise of 1 percent in cobalt price produced a drop of 0.32 percent in use. Elasticity also predicts the expansion of markets as a result of price decreases when new sources of cobalt become available.

Potential of Marine Cobalt Resources

In the 1970's, nodule mining was forecast at 17 million wet tons per year in 1990 (9). Capital and preparatory cost models ranged from about $0.5 billion to about $1.5 billion (62). A 3-million (dry)-ton operation was projected to yield annual production of about 35,000 tons of nickel, 28,000 tons of copper, and 4,000 tons of cobalt. Estimates of profit margins in the 1980's have been considered too low to attract American private investment capital.

In contrast to abyssal manganese nodules, our knowledge of the resource potential of the crusts is in an early stage. The politically and geologically "permissive" (favored) areas are within U.S. EEZ areas in the Pacific at water depths between roughly 800 and 2400 m (Table 4). Assuming that 40 percent of the surface area is covered by accessible crusts, a seamount with a permissive area of 300 km² would yield about 3 million tons of crusts per 2 cm of thickness. Of the hundreds of millions of tons of hypothetical crust thus computed for the Pacific Ocean and for the Blake Plateau in the Atlantic (54, 63), an unknown fraction may have high economic potential. Distribution and thickness of crusts even in the central Pacific is poorly known. Information about crust continuity and local microtopography, which is critical for engineering recovery, is almost

completely absent. Engineers point out that microtopography may be the most important determining factor for "ore" quality since it will affect the amount of substrate rock scraped up with the ore.

Given all the uncertainties, how would crust production compare with U.S. domestic metal demand? The output of an extraction operation with a capacity of 1 million wet tons per year has recently been projected from preliminary processing considerations (63). These and comparative resource data for nodules and land deposits are given in Table 5. The data show that even a crust operation of 1 million wet tons could potentially meet a significant part of U.S. cobalt demand, about one-fourth of the manganese demand, and small fractions of the demand for other metals such as nickel, copper, platinum, vanadium, and molybdenum. Harvey and Amman (63) have pointed out that pure metallic and chemical uses for manganese would be swamped by sea-floor production of either nodules or crusts. It would be necessary to produce ferromanganese, requiring smelting and high-temperature reduction to make full use of manganese in crusts, whereas other metals could be removed with lower energy costs by lower temperature systems.

Environmental effects of nodule recovery systems have been extensively researched, and so far few major hazards have been found (64). Some of the environmental parameters of nodule mining will also apply to mining on seamounts. However, full investigations of hazards are required and are currently in progress in the circum-Hawaii area (26). Potential multiple-use conflicts appear to be greatest concern with regard to processing activity on land, including waste disposal. Some of the economic and environmental aspects of processing-plant siting were evaluated earlier by the state of Hawaii (65).

Documents prepared for the Environmental Impact Statement on Manganese Crust leasing, under sponsorship of the U.S. Minerals Management Service (26), make it clear that possible mining of crusts presents a host of new questions and issues. These problems and uncertainties must be balanced against the substantial potential resources in the political jurisdiction of the United States as well as those of new political entities such as Kiribati. This island confederation exercises sovereignty over vast areas of the Pacific sea floor. France, New Zealand, Japan, Australia, and the United Kingdom also have substantial 200-mile zones around coastal and island territories in the Pacific Ocean. Of course, the greatest uncertainty remains the status of crusts as a resource. However, in response to the mineral potential, at least one new international consortium, International Hard Minerals Company, has begun first-phase feasibility investigations relating to crust mining.

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90. Many persons have assisted in the development of the U.S. Geological Survey data bank, principally C. M. Lane, J. C. Hathaway, J. A. Commeau, T. H. Ling, F. Brown, P. Aruscavage, H. Kirschenbaum, Z. Brown, and C. Moore. I thank C. T. Hillman, W. Kirk, C. J. Johnson, A. Clark, and M. Foose for assistance with data, and P. Halbach, V. Marchig, D. Puteanus, J. R. Hein, and W. C. Schwab for collaboration. Special thanks go to J. D. Bischoff. Supported by the U. S. Minerals Management Service.