

Geochemistry of the Phosphoria Formation
at Montpelier Canyon, Idaho:
Environment of Deposition

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Chapter B

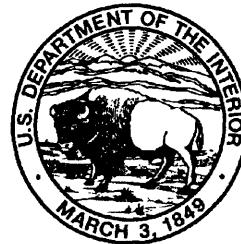
Geochemistry of the Phosphoria Formation at Montpelier Canyon, Idaho: Environment of Deposition

By D.Z. PIPER and M.D. MEDRANO

U.S. GEOLOGICAL SURVEY BULLETIN 2023

THE PHOSPHORIA FORMATION:
ITS GEOCHEMICAL AND BIOLOGICAL ENVIRONMENT OF DEPOSITION

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary



U.S. GEOLOGICAL SURVEY
Gordon P. Eaton, Director

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Geochemistry of the Phosphoria Formation at Montpelier Canyon, Idaho: Environment of Deposition

By D.Z. Piper and M.D. Medrano

Abstract

The Permian Phosphoria Formation of southeastern Idaho, western Wyoming, southwestern Montana, and north-eastern Utah was deposited in a broad ocean-margin basin, which was tectonically quite stable but underwent several transgressive-regressive events, owing possibly to glacial advances and retreats. Throughout most of its depositional history, intense upwelling supported exceptionally high primary productivity in the photic zone of the water column, resulting in a high flux of organic debris to the sea floor. In contrast, the flux of detrital material was low. Thus, the lithology of the rocks is dominated by marine phases—carbonate fluorapatite, biogenic silica, calcite, dolomite, and organic matter. The rocks also contain high concentrations of minor elements—Cd, Cr, Cu, Mo, Ni, rare-earth elements (REE's), V, and Zn. Partitioning of the minor elements into these host phases is largely a function of diagenesis.

The geochemistry of the water column at the time of deposition, however, is more likely to be understood by examining the partitioning of minor elements among the following source fractions: a detrital fraction, a marine biogenic fraction, and a marine hydrogenous fraction. Interelement relations of several major-element oxides and minor elements show that the detrital fraction has a composition closely approaching that of shale standards, requiring that this fraction had a terrigenous origin. Interelement relations of Cu, Mo, Zn, and, possibly, Cd and Ni within the marine fraction resemble those in modern marine plankton. Rates of accumulation for these minor elements furthermore required accumulation rates for organic debris on the sea floor similar to that at present on the Peru and Namibian Continental Shelves, areas of high primary productivity. Our interpretation of these relations is that these minor elements accumulated as biogenic debris, derived from the photic zone of the Phosphoria Sea.

The contents of Cr, REE's, and V in the marine fraction cannot be attributed solely to a biogenic source. Instead, these elements accumulated from seawater by inorganic precipitation and (or) adsorption onto other particulate phases.

Their marine chemical properties and distributions in the ocean today require their precipitation and (or) adsorption onto settling particulate matter, under bottom-water conditions of denitrification. Their accumulation rates can be used to estimate the residence time of bottom water on the shelf versus the rate of bacterial respiration, which is determined by the rate of settling organic matter from the photic zone—again, a function of primary productivity. The distributions of these and the biologically derived minor elements indicate that the composition of seawater during the Permian was virtually identical to its composition today.

Of the major-element oxides and minor elements, only Cr, V, and REE's—that is, the minor elements with a hydrogenous source—show a difference in their distribution in rocks deposited during the proposed glacial and interglacial episodes. Their distributions suggest that the bottom water was more reducing, albeit still denitrifying, during glacial than interglacial times. Because bottom-water respiration is governed by the balance between the rates of settling of organic matter and advection of bottom water, the distribution of these minor elements suggests greater photic-zone productivity or lower bottom-water advection during glacial episodes; we favor enhanced productivity.

INTRODUCTION

The Phosphoria Formation, in the Northwestern United States (fig. 1), was first examined in detail by Mansfield (1927). The formation was later carefully described and measured by McKelvey and others (1959). Samples were analyzed for their minor-element contents (Gulbrandsen, 1966), particularly uranium (Gulbrandsen, 1960; Swanson, 1961). Thousands of samples were collected from natural outcrops and tens of freshly dug trenches. Although the formation failed to yield the sought-for uranium, it continues to be a major producer of phosphate and vanadium. Since 1911, it has yielded some 140 million t of phosphate rock as of 1980 (Cathcart, 1991), with approximately 524 billion t of resource remaining (Sheldon, 1989). In addition to reserves of phosphate and vanadium, the Phosphoria Formation is also a major source rock for oil in Permian and younger rocks of

the Northwestern United States (Claypool and others, 1977; Maughan, 1984; Thornburg, 1990).

The environment of deposition of the Phosphoria Formation has been interpreted as one of exceptionally high ocean upwelling and biologic productivity (McKelvey, 1967), a hypothesis first proposed by Kazakov (1937) to explain the high content of seawater-derived phases—organic matter, carbonate fluorapatite, biogenic silica, and carbonates (Calvert and Price, 1983; Froelich and others, 1988; Glenn and Arthur, 1988)—in this type of deposit. The modern continental shelves of Namibia and Peru, where primary productivity of organic matter averages as much as 200 mg/cm² per year (Chavez and Barber, 1987; Berger and others, 1988), are commonly cited as modern analogs of the Phosphoria and other seas within which large amounts of sedimentary phosphate accumulated. The high rate of primary productivity is driven by upwelling of cold, nutrient (principally NO₃⁻ and PO₄³⁻)-rich water into the photic zone from approximately 80- to 200-m depth (Sverdrup and others, 1942; Wyrski, 1963; Calvert and Price, 1971; Codis-

poti, 1980). The resulting sediment is strongly enriched in organic matter, carbonate fluorapatite, biogenic silica, and carbonates (Glenn and Arthur, 1988; Froelich and others, 1988). These same marine fractions dominate the bulk composition of the Phosphoria Formation (McKelvey and others, 1953, 1959). Conodont and brachiopod assemblages of the Phosphoria Formation furthermore indicate a cold-water depositional environment (Wardlaw and Collinson, 1986).

The dissimilarities between modern shelf environments and the Phosphoria Sea, however, must also be considered. The Peru Shelf is approximately 10 km wide, bordered by the Peru-Chile Trench to the west and the Andes Mountains to the east. It is an extremely active tectonic area. This narrow shelf is swept by one of the strongest surface currents in the ocean, the Peru Current. As a result, the sea floor is eroded in some areas but shows high sediment-accumulation rates in other areas. Although the shelf off Namibia is much wider (Hart and Currie, 1960), it, too, is swept by one of the ocean's great currents, the Benguela Current. The sea floor exhibits a sedimentation regime as complex as that on the Peru Shelf, of erosion, sediment reworking, and primary deposition (Calvert and Price, 1983). On both the Peru and Namibia Shelves, nodular phosphate seems to represent a major proportion of the phosphatic fraction (Baturin and others, 1972; Burnett and others, 1980). Hardgrounds are also abundant (W.E. Dean, oral commun., 1993), and pelletal phosphate is much less common (Burnett and others, 1988).

In contrast, the shelf of the Phosphoria Sea was several hundred kilometers wide and gently sloping. Surrounding landmasses to the east were low lying (Paull and Paull, 1986), providing minimal detritus (Cook, 1968) to this broad shelf. The outer west boundary of this ocean-margin sea was characterized by a remnant of the Antler Uplift and, farther to the west, by an island arc (Stevens, 1991), which would have shielded the Phosphoria Sea from such great ocean current as those that sweep the modern phosphogenic provinces of the open shelves of Peru and Namibia. The sea-floor bathymetry and oceanographic setting resulted in a minimal, but relatively uniform, average accumulation rate of the detrital fraction of 0.5 mg/cm² per year, comparable to its accumulation rate in the pelagic environment of the ocean today. The phosphatic fraction, which is virtually totally pelletal, accumulated at a comparable rate. Sediment thickness increased rather continuously from east to west and southwest (McKelvey and others, 1959). To the east, primarily in western Wyoming and northern Utah, coeval carbonates of the Park City Formation intertongue with the Phosphoria Formation. These rocks are interpreted as having been deposited on a shallow shelf area. Somewhat farther to the east, evaporites and continental red beds of the Goose Egg Formation accumulated (fig. 1). Thus, the Phosphoria Sea was a gently sloping, broad foreland (or sag) basin,

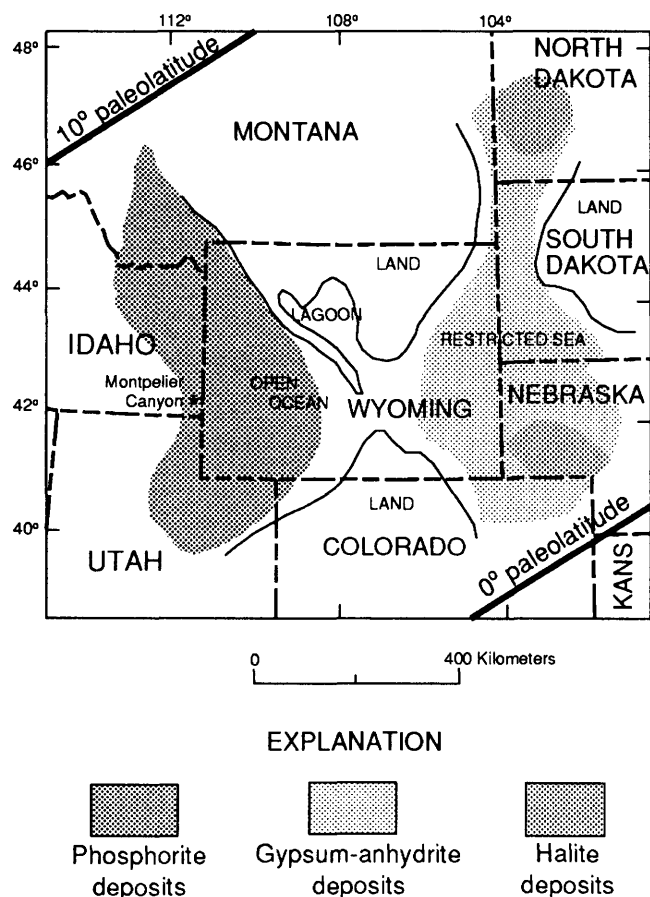


Figure 1. Northwest-Central United States, showing extents of phosphorite deposition and of correlative facies during the middle Permian (Wordian), along with paleolatitudes from Sheldon (1964). More recent work by Scotese and McKerrow (1990) gives 10° N. latitude line as 25° N.

behind an outer island arc, basin, and highland (Antler Uplift).

We have analyzed samples from Montpelier Canyon (McKelvey and others, 1953), southeastern Idaho (fig. 2), for their major-element-oxide and minor-element composition (Medrano and Piper, 1992). The aim of this study is to establish the marine geochemistry of the environment of deposition. The great abundance of marine mineral phases (for example, biogenic silica, organic matter, and apatite) in the Phosphoria Formation suggests that the marine minor-element content was only slightly diluted by the detrital fraction and, possibly, not erased by postdepositional alteration. Thus, the marine fraction of minor elements might address such aspects of the depositional environment as (1) primary productivity in the photic zone and (2) redox conditions of the bottom water of the Phosphoria Sea. We show that the Permian Ocean must have had a composition virtually identical to that of the modern ocean, whose composition is maintained by the addition of minor elements through both hydrothermal activity (Von Damm and others, 1985a, b) and continental denudation (Martin and Maybeck, 1979). Such an ocean was the source for the marine constituents of this deposit and, quite likely, nearly all similar sedimentary deposits (Holland, 1979; Piper, 1994). It is unnecessary to invoke an unusual or exotic seawater chemistry to account for the composition of this deposit.

Determination of the seawater chemistry of deposition of ancient deposits, on the basis of their current minor-element contents, is complicated by the hydrodynamics of O_2 -depleted waters and the coarseness of most sampling schemes. The chemical properties of bottom water can change quite drastically over a period of seasons to years (Sholkovitz and Gieskes, 1971; Anderson and Devol, 1973; Codispoti, 1980), as well as over longer time periods, largely in response to changes in seawater advection. Probably, no sampling of sedimentary rocks can identify such short-term changes as surely occurred in the past. Sampling schemes of ancient sedimentary deposits unavoidably average ocean conditions at the time of deposition over hundreds to thousands of years. For a sedimentary rock that accumulated at a rate of 2 mg/cm^2 per year, a sample that is only 1 cm thick represents several hundred years of deposition. The integration imposed by this aspect of most investigations limits our ability to sort the ancient record. We might see in a single sample the geochemical signal of several different conditions, the sum of hundreds of years, rather than the details of season-to-season and year-to-year events. As a result, an individual sample might contain a record of contrasting bottom-water conditions. For example, it might have both high Mo and high rare-earth-element (REE) contents, whereas such a cooccurrence would seem to be excluded by the geochemistry of these minor elements in modern marine environments (Piper and Isaacs, in press).

A final complexity is introduced by the changes that sedimentary deposits undergo during diagenesis (Shaw and others, 1990) and, later, during burial and uplift (Isaacs, 1980). Indeed, in some rocks, the record of deposition can be erased beyond our ability to decipher it from the current rock composition. The abundance, mineralogy, and composition of the host phases for minor elements that survive these changes—or, more accurately, that are formed as a result of these changes (for example, apatite, glauconite, pyrite, bauxite, palygorskite, opal-CT, and so on)—largely record these postdepositional environments within which alteration occurred. Such minerals can indicate the extent to which alteration proceeded (Vieillard and others, 1979). This aspect of the history of a formation is interesting from a scientific, as well as economic, point of view because it can either add to or subtract from the value of a deposit. Still, its added effect is to create an increasingly dimmer view of the depositional environment. Nonetheless, the marine minor-element signal of the Phosphoria Formation lends strong support to our interpretation of primary productivity in the photic zone and redox conditions of the bottom water at the time of deposition.

Acknowledgments.—The senior author has had many discussions through the years with the geologists who contributed much to our current understanding of this and similar deposits. Most influential have been two former colleagues at the U.S. Geological Survey, Dick Sheldon and Bob Gulbrandsen. They introduced me to the Phosphoria Formation, pointed me in the direction I first took, and made every effort, sometimes without success, to urged me back on path when I wandered far. Reviews of the manuscript by B. Murchey, J. Herring, G. Breit, and G. Piper greatly improved its organization and clarity.

ANALYTICAL TECHNIQUES

The analytical techniques used in this study, the analytical data, and their precision and accuracy were discussed by Medrano and Piper (1992). Quite briefly, the accuracy of these analyses is established by analyzing a standard rock along with each group of 25 to 40 samples; precision is established by repeatedly analyzing a single sample, or standard (Baedecker, 1987). An alternative approach to accuracy and precision is to analyze groups of samples by more than one technique (fig. 3). Plots of the major-element-oxide analyses measured by X-ray-fluorescence (XRF) and inductively coupled plasma/atomic-emission spectroscopy (ICP-AES), and REE analyses measured by ICP-AES and ICP-mass spectroscopy (ICP-MS), demonstrate this approach. Our reason for showing these plots is to demonstrate that analytical error introduces only a small error in the stoichiometric calculations which we make throughout this report and on which our conclusions are strongly based.

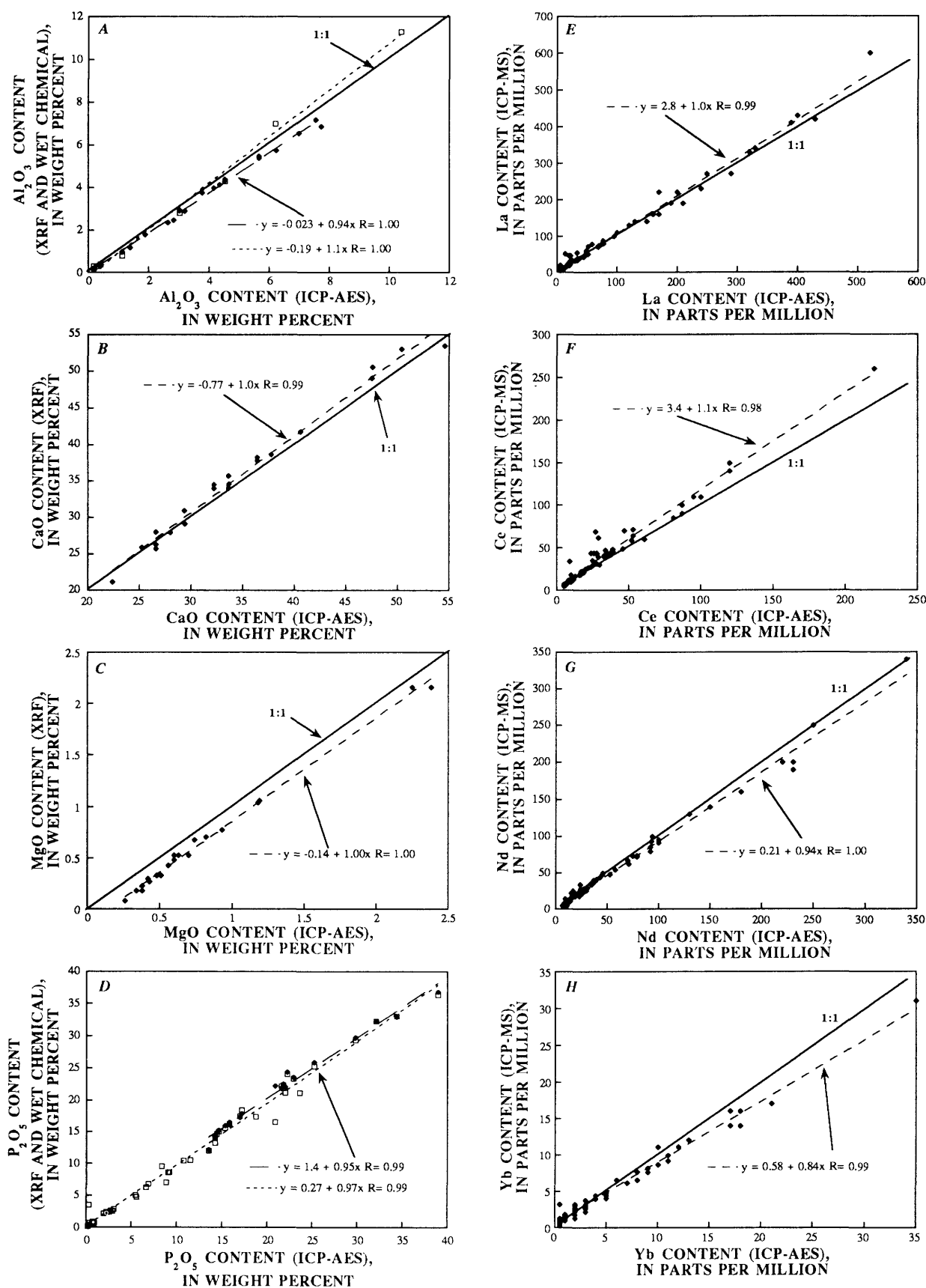


Figure 3. Interelement plots, showing correlations of elements, determined by analysis of samples by more than one technique. Open symbols, wet-chemical data; solid symbols, XRF data.

Plots of individual oxides show an excellent correlation, better than 0.99 in all cases. Clearly, the precision of these analyses approximates the reported values of less than 1 weight percent for XRF (Taggart and others, 1987) and seems to be better than that for ICP-AES (Lichte and others, 1987). The variation from the 1:1 line of about 5 percent (figs. 3A–3C) must somehow reflect the inaccuracy of the analyses. The close agreement of 1.9 percent for the XRF and wet-chemical P_2O_5 data about the 1:1 relation (fig. 3D) suggests that the ICP-AES analyses contribute most to the inaccuracy (the XRF and ICP-AES analyses were made in 1991, and the wet-chemical analyses in about 1952). We should note, however, that both the wet-chemical and XRF data can also have an indeterminate inaccuracy. Because ICP gives both major-element-oxide and minor-element results and all analyses show a high precision, we elect to use the ICP data throughout the following discussion.

The REE analyses by ICP-AES and ICP-MS show a correlation and agreement with the 1:1 line that suggest a precision for the minor-element analyses of better than the approximately 5 percent based on ICP-AES analyses alone (Lichte and others, 1987).

RESULTS AND DISCUSSION

We calculate the mineral composition of the Phosphoria Formation at Montpelier Canyon from its major-element-oxide composition by a normative scheme (Isaacs, 1980; Medrano and Piper, 1992). Appropriate stoichiometric values and major-element-oxide contents are substituted into the following formulas: $Al_2O_3 \times 6.4$, SiO_2 —detrital SiO_2 , $(P_2O_5$ —detrital $P_2O_5)/0.406$, $(MgO$ —detrital $MgO)/0.219$, $[CaO$ —(detrital CaO +apatite CaO +dolomite CaO)]/0.56, and organic carbon $\times 1.7$, to give the amounts of detritus, biogenic silica, carbonate fluorapatite, dolomite, calcite, and organic matter, respectively, in each sample (see Medrano and Piper, 1992, table 4). The accuracy of our calculations depends on the assumption of a constant composition for each fraction and the validity of the stoichiometric values assigned to each fraction. The sum of these fractions in the Phosphoria Formation at Montpelier Canyon is 100 ± 2 percent for 35 of 41 samples and ± 4 percent for all 41 samples (Medrano and Piper, 1992). The close approach to 100 percent and the random scatter about 100 percent support our choices of the above stoichiometric values.

Detrital Fraction

The partitioning of minor elements in the detrital host phase can be critical to the discussion of the geochemical properties of the depositional environment. We attach such importance to the detrital fraction because the seawater—

that is, the marine contribution of minor elements—is calculated as the difference between the bulk minor-element composition of each sample and the minor-element contribution of the detrital fraction. Because the abundance of the detrital fraction is based solely on the Al_2O_3 content, the uncertainty in calculating the abundance of detritus in each sample is the sum of the uncertainties in the determination of Al_2O_3 contents, approximately 5 percent (fig. 3A), and the uncertainty of the stoichiometric determination of detrital Al_2O_3 contents. The sum of all host fractions is 100 percent, however, supporting our selection of the Al_2O_3 content of the detrital fraction. Also, strong correlations exist between the abundance of the detrital fraction and TiO_2 and K_2O contents (Medrano and Piper, 1992), and lines of best fit extrapolate to zero (fig. 4). Furthermore, $Al_2O_3:TiO_2$ and $Al_2O_3:K_2O$ ratios are similar to those of the World Shale Average (WSA) and the North American Shale Composite (NASC), all of which supports our interpretation of a uniform composition for detritus. Thus, our conclusion is that the uncertainty in our calculation of the detrital fraction is less than 10 percent.

Minor elements, which are hosted predominantly by the detrital fraction of many, though certainly not all, sedimentary rocks, include Sc, Ga, Li, and, possibly, Th and Co. The strong correlations between the abundance of the detrital fraction and Ba, Co, Ga, Sc, and Li contents (table 1) supports the results for major-element oxides, of a uniform composition between samples. Their convergence toward standard shale values (figs. 5A–5D) further supports a terrigenous origin for the detrital fraction. Implicit in this interpretation is that the detrital fraction has remained nonreactive: It is both source phase and current host phase.

It would be a mistake, however, to assume that the detrital contribution of those minor elements which do not correlate with Al_2O_3 can be determined merely from the composition of WSA or NASC. The variations in the composition of the rocks analyzed in many different laboratories to obtain the averages of these two standards (Wedepohl, 1969–78; Gromet and others, 1984) demonstrate variations in the composition of sedimentary rocks, even of similar lithology, and require that any comparison with other rocks is merely a first step in determining the detrital contribution of minor elements to the total inventory in any single deposit. In this study, the detrital contribution of this group of minor elements is determined from the minimums of the detritus-element plots (figs. 5E–5H). In every case, this procedure gives a value that is similar to the minor-element content of WSA (table 1).

Although the error in our estimate of the minor-element contribution from detritus is large for some minor elements, it introduces little uncertainty to the minor-element contents of the marine fraction. The detrital contribution of Cr, Cu, Ni, Mo, REE's, V, and Zn is small relative to the contributions from the marine frac-

tions. For example, the abundance of the detrital fraction averages approximately 35 percent. The uncertainty in

estimating the marine fraction of La from its bulk content minus its detrital content is, on average, approximately $\pm\{(0.05 \times 32 \text{ ppm} \times 0.35) + [0.02 \times \text{bulk content (in parts per million)}]\}$, where detritus is considered to contain 32 ppm La (table 1). The uncertainty clearly is dominated by the 2-percent uncertainty in the ICP-AES measurement of bulk La content (fig. 3E).

There is nothing surprising about the result that the detrital fraction in the Phosphoria Formation had a terrigenous origin of uniform composition. The lithology and stratigraphy suggest that the Phosphoria Formation accumulated on a stable ocean margin (McKelvey and others, 1959; Swanson, 1973). However, the conclusion that the detrital fraction had the same approximate composition (figs. 2, 4, 5) during previously proposed glacial and interglacial times (Sheldon, 1984; Piper and Kolodny, 1988) is somewhat unexpected. Nonetheless, these results allow us to dismiss any significant error in the minor-element contents of the marine fraction, introduced by possible major variations in the composition of the detrital fraction of the Phosphoria Formation. Also, these results diminish the possibilities of a major local hydrothermal input to the Phosphoria Sea or of severe alteration during weathering.

Marine Fraction

The marine fractions of Cu, Cr, and, less so, several other minor elements correlate with the organic-matter content (fig. 6; table 2). Partitioning of minor elements into organic matter was reported by Leventhal (1989), Odermatt and Curiale (1991), and Piper and Isaacs (in press) for the Monterey Formation; by Swanson (1961) for several Paleozoic organic-matter-enriched shales; and by Nissenbaum and Swaine (1976) for modern marine sediment. Lewan (1984), Moldowan and others (1986), and Odermatt and Curiale (1991) further examined the fractionation of metals between the various phases of organic matter. For example, Lewan (1984) interpreted the $V/(Ni+V)$ ratio in crude oils to reflect the Eh, pH, and sulfide activity of the depositional environment.

The REE's are partitioned into apatite (fig. 7), similar to their partitioning in other phosphate deposits (Wright and others, 1987; Piper, 1991). Additional host phases include glauconite and metal sulfides (Glenn and Arthur, 1988; Piper and others, 1988), predominantly iron sulfides. They form various minerals, but pyrite is the stable end product (Goldhaber and Kaplan, 1974). Pyrite is present in many sections of the Phosphoria Formation (Sheldon, 1963), but only in trace amounts in Montpelier Canyon rocks (McKelvey and others, 1953). We have also detected trace amounts of sphalerite by microprobe.

Partitioning of minor elements into these host phases and, particularly, into organic matter must occur during diagenesis and, possibly, during later alteration of the

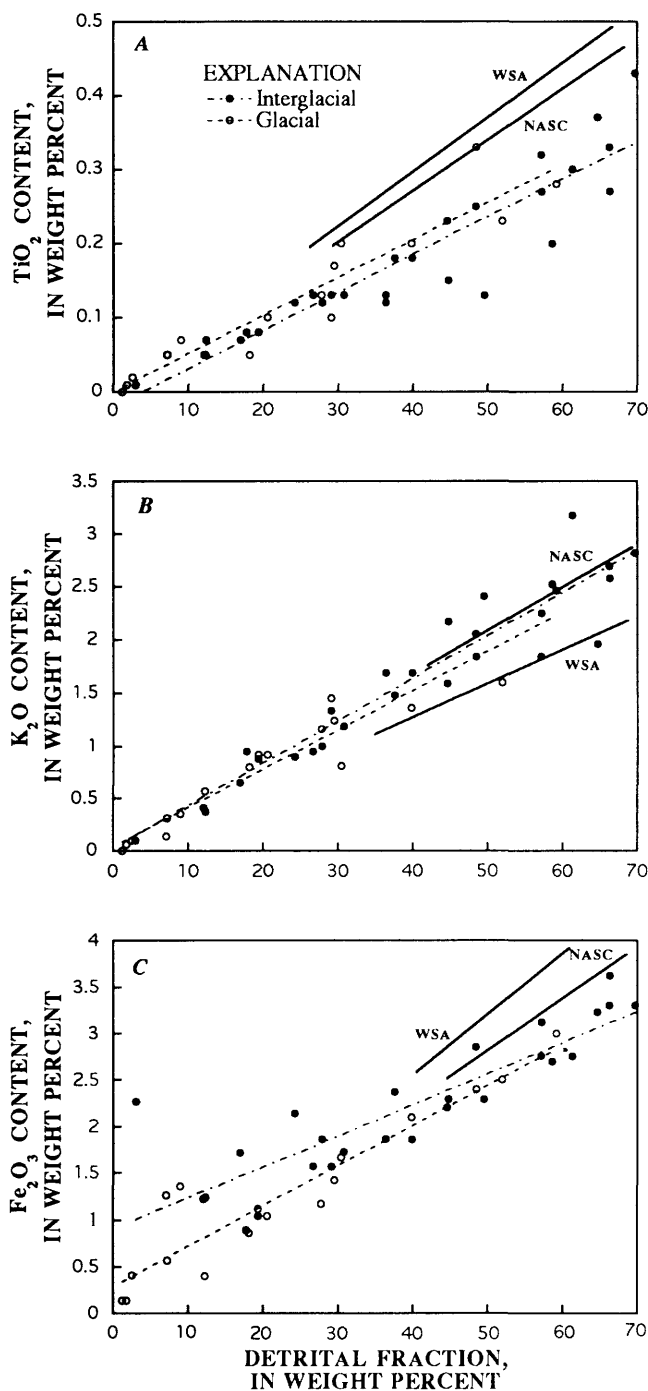


Figure 4. Detrital fraction ($Al_2O_3 \times 6.4$) versus major-element-oxide contents in Permian rocks of the Phosphoria Formation. Dashed curves, least-squares lines of best fit; solid curves, World Shale Average (WSA; Wedepohl, 1969–78) and North American Shale Composite (NASC; Gromet and others, 1984). Glacial-interglacial episodes determined from lithology (Sheldon, 1984) and supported by $\delta^{18}O$ values of PO_4^{3-} (Piper and Kolodny, 1988). See figure 2 for identification of glacial and interglacial events.

Table 1. End-member major-element-oxide and minor-element contents in sedimentary fractions of the Phosphoria Formation

[Major-element-oxide contents in weight percent; minor-element contents in parts per million. Values for the detrital fraction of the Phosphoria Formation represent minimums, or single trends, obtained from plots of element or element-oxide versus detritus contents (see figs. 4, 5); values for the detrital fraction in parentheses are for the World Shale Average (WSA) or North American Shale Composite (NASC). Dashes, no data available. Other minor-element contents for the detrital fraction of the Phosphoria Formation and WSA, in parentheses, are as follows: As, 10 (10); Ba, 360 (640); Ga, 18 (21); Li, 45 (60); Sc, 16 (13); Sr, 210 (125); Y, 35 (26). Data sources: WSA, Wedepohl (1969–78); NASC, Gromet and others (1984); biogenic SiO_2 , Elderfield and others (1981); calcite, Palmer (1985); organic matter, Sverdrup and others (1942), Elderfield and others (1981), and Brumsack (1986)].

	Detrital fraction	Marine biogenic fractions			Authigenic fraction
	Phosphoria Formation (WSA or NASC)	Biogenic SiO_2	Calcite	Organic matter	Apatite
Major-element oxides					
P_2O_5 -----	.16 (0.16)	--	--	1.74	40.7
TiO_2 -----	.77 (0.48)	--	--	--	--
K_2O -----	3.98 (3.2)	--	--	--	--
CaO -----	3.9 (3.09)	--	56.0	--	55.5
Fe_2O_3 -----	6.75 (4.81)	--	--	.050	--
Al_2O_3 -----	15.6 (15.5)	--	--	--	--
SiO_2 -----	58.5 (58.4)	100	--	--	--
Minor elements					
La -----	33 (31.2)	5.80	0.128	0.14	--
Ce -----	66 (66.7)	8.21	.105	.23	--
Pr -----	--	--	--	--	--
Nd -----	28 (27.4)	6.71	.106	.30	--
Sm -----	5.59	1.56	.019	--	--
Eu -----	1.18	.40	.004	--	--
Gd -----	--	1.78	.022	--	--
Tb -----	.85	--	--	--	--
Dy -----	--	1.69	.024	.01	--
Ho -----	--	--	--	--	--
Er -----	--	--	--	--	--
Tm -----	--	--	--	--	--
Yb -----	2.85 (3.06)	.86	.015	--	--
Lu -----	.456	--	--	--	--
Cu -----	36 (35.0)	--	.700	11.0	--
Cd -----	.2 (0.2)	--	--	12.0	--
Co -----	11 (19)	--	--	1.0	--
Cr -----	83 (83)	--	--	2.0	--
Mo -----	2.6	--	--	2.0	--
Ni -----	44	--	--	7.4	--
Se -----	1.0	--	--	3.0	--
U -----	3.0	--	--	--	--
V -----	110 (110)	--	--	3.0	--
Zn -----	110 (110)	--	--	110.0	--

originally deposited marine phases. Minor elements commonly are enriched by a factor of more than 10 in the

residual organic fraction over their concentrations in modern planktonic debris. For example, the slopes of the

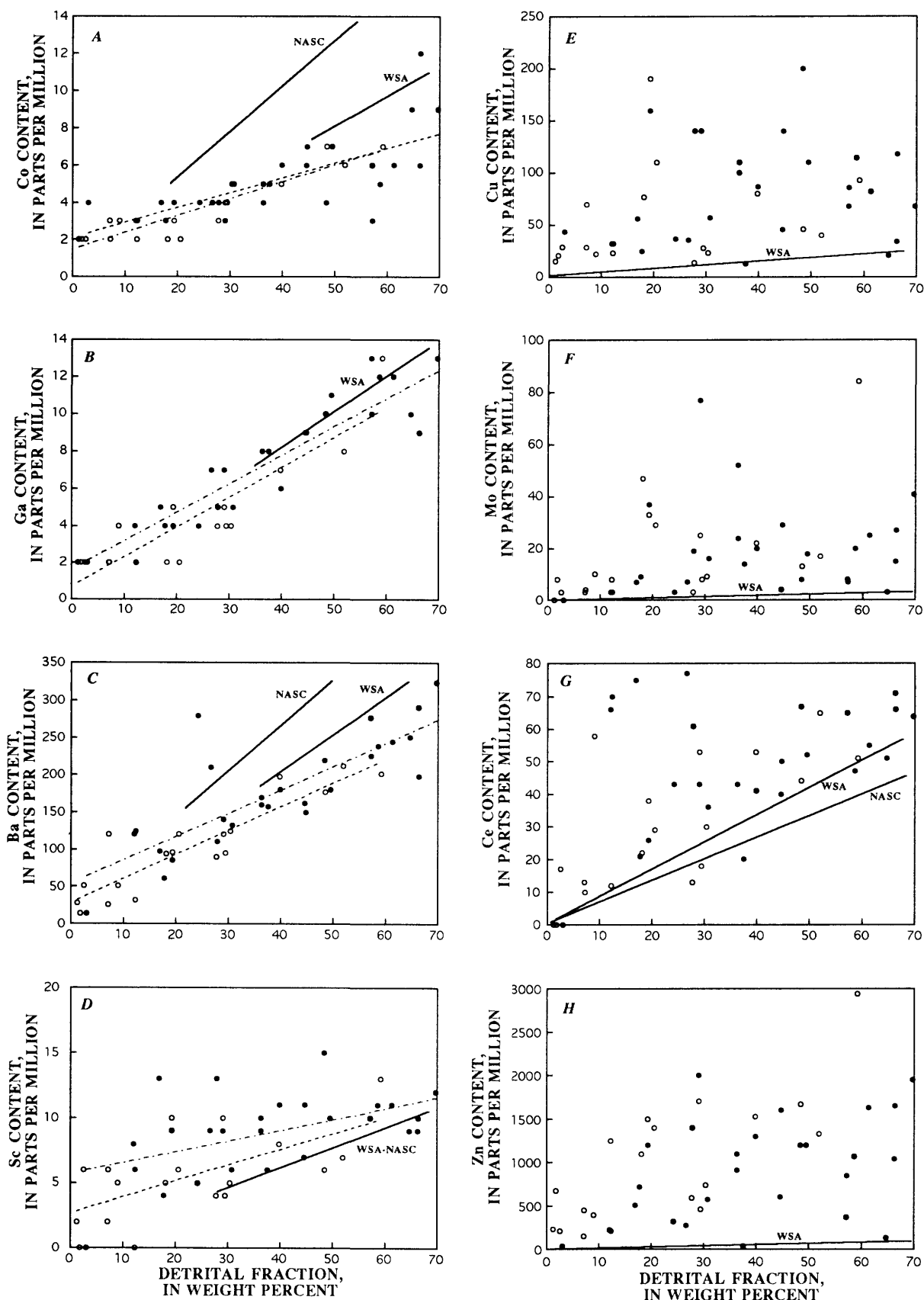


Figure 5. Detrital fraction versus minor-element contents in the Phosphoria Formation at Montpelier Canyon. Same symbols as in figure 4. See table 2 for correlation coefficients.

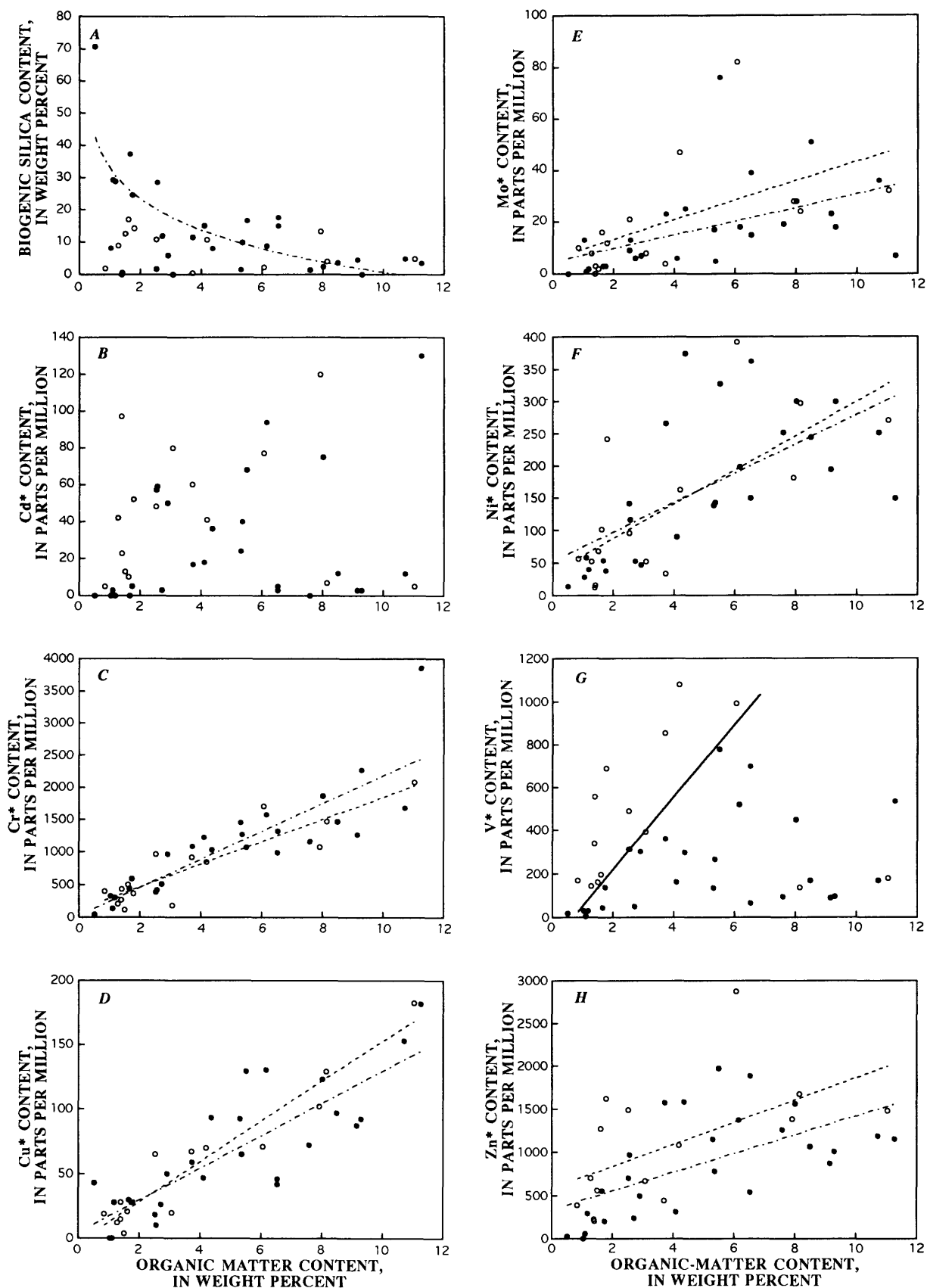


Figure 6. Organic-matter versus minor-element contents in the Phosphoria Formation at Montpelier Canyon. Same symbols as in figure 4, except for figure 6G, where solid line separates glacial from interglacial group of samples. See table 2 for correlation coefficients.

Table 2. Correlation coefficients (A) between major sedimentary fractions and bulk minor-element contents and (B) between major marine fractions and minor-element contents in the Phosphoria Formation at Montpelier Canyon, Idaho

[Values ≥ 0.393 are significant at the 1-percent level]

A	Dolomite	Calcite	Apatite	Organic matter	Detritus	Biogenic SiO ₂	Ag	As	Ba	Cd	Ce	Co	Cr	Cu	Ga	La	Li	Mo	Nd	Ni	Pb	Sc	Sr	V	Y	Yb	Zn
Dolomite	1																										
Calcite	.17	1																									
Apatite	.36	.34	1																								
Organic matter	.25	.18	.18	1																							
Detritus	.18	.39	.51	.19	1																						
Biogenic SiO ₂	.10	.10	.41	.41	.03	1																					
Ag	.24	.36	.25	.65	.26	.33	1																				
As	.28	.38	.12	.58	.49	.37	.71	1																			
Ba	.29	.47	.32	.13	.87	.10	.16	.31	1																		
Cd	.02	.19	.13	.16	.10	.29	.48	.24	.18	1																	
Ce	.41	.60	.08	.17	.62	.04	.30	.52	.67	.08	1																
Co	.19	.25	.48	.02	.80	.14	.12	.34	.62	.23	.48	1															
Cr	.31	.33	.21	.87	.33	.40	.77	.64	.28	.29	.38	.10	1														
Cu	.35	.31	.26	.89	.20	.29	.83	.67	.11	.27	.26	.07	.88	1													
Ga	.22	.34	.41	.28	.91	.05	.25	.43	.77	.09	.58	.70	.45	.28	1												
La	.33	.43	.56	.43	.05	.25	.43	.39	.06	.10	.63	.13	.58	.52	.08	1											
Li	.17	.35	.30	.36	.67	.03	.34	.29	.64	.05	.40	.44	.56	.41	.74	.15	1										
Mo	.16	.16	.04	.49	.25	.23	.51	.44	.14	.15	.12	.16	.39	.51	.31	.11	.22	1									
Nd	.31	.41	.51	.32	.03	.21	.34	.34	.06	.06	.67	.07	.47	.40	.09	.97	.11	.08	1								
Ni	.18	.26	.13	.66	.56	.28	.61	.71	.36	.07	.33	.49	.58	.66	.56	.17	.40	.76	.13	1							
Pb	.24	.59	.05	.26	.64	.18	.59	.59	.52	.23	.64	.43	.43	.38	.57	.30	.38	.33	.29	.48	1						
Sc	.38	.60	.17	.60	.61	.31	.60	.68	.58	.08	.76	.42	.76	.64	.67	.65	.56	.39	.63	.60	.64	1					
Sr	.32	.18	.68	.67	.22	.57	.46	.39	.21	.13	.16	.20	.60	.62	.08	.64	.06	.20	.58	.27	.06	.49	1				
V	.12	.12	.24	.20	.04	.14	.41	.15	.03	.64	.10	.18	.15	.22	.08	.03	.00	.38	.07	.24	.39	.03	.03	1			
Y	.32	.40	.63	.29	.18	.21	.31	.25	.02	.04	.57	.21	.41	.39	.05	.97	.01	.06	.96	.05	.22	.53	.59	.03	1		
Yb	.33	.42	.58	.28	.10	.18	.32	.26	.05	.04	.61	.16	.41	.39	.02	.95	.06	.08	.95	.08	.27	.56	.53	.02	.99	1	
Zn	.21	.20	.05	.53	.47	.29	.66	.70	.29	.31	.31	.36	.52	.61	.47	.15	.35	.79	.11	.88	.49	.53	.23	.42	.04	.07	1

B	Dolomite	Calcite	Apatite	Organic matter	Biogenic SiO ₂	Marine Ag	Marine Ba	Marine Cd	Marine Ce	Marine Co	Marine Cr	Marine Cu	Marine Ga	Marine La	Marine Li	Marine Mo	Marine Nd	Marine Ni	Marine Pb	Marine Sc	Marine Sr	Marine V	Marine Y	Marine Yb	Marine Zn	
Dolomite	1																									
Calcite	.17	1																								
Apatite	.36	.34	1																							
Organic matter	.25	.18	.18	1																						
Biogenic SiO ₂	.10	.10	.41	.41	1																					
Marine Ag	.24	.36	.25	.65	.33	1																				
Marine As	.27	.34	.21	.58	.40	.72	1																			
Marine Ba	.29	.31	.18	.06	.14	.09	.20	1																		
Marine Cd	.02	.19	.13	.16	.29	.48	.27	.18	1																	
Marine Ce	.37	.43	.53	.06	.08	.17	.27	.34	.01	1																
Marine Co	.07	.41	.39	.29	.06	.31	.35	.16	.03	.06	1															
Marine Cr	.31	.33	.22	.87	.40	.77	.63	.01	.30	.20	.42	1														
Marine Cu	.33	.26	.34	.87	.30	.80	.63	.11	.29	.18	.13	.85	1													
Marine Ga	.02	.28	.34	.10	.18	.10	.24	.11	.04	.06	.44	.10	.17	1												
Marine La	.32	.40	.60	.42	.26	.41	.39	.19	.11	.84	.05	.56	.53	.28	1											
Marine Li	.06	.16	.36	.12	.01	.02	.27	.06	.09	.02	.44	.16	.26	.64	.26	1										
Marine Mo	.15	.15	.05	.48	.23	.51	.43	.14	.15	.06	.25	.38	.48	.08	.10	.08	1									
Marine Nd	.29	.36	.55	.29	.21	.31	.32	.16	.07	.87	.09	.44	.41	.26	.97	.21	.06	1								
Marine Ni	.17	.24	.09	.68	.30	.61	.67	.19	.08	.05	.41	.57	.61	.15	.14	.28	.76	.08	1							
Marine Pb	.12	.33	.60	.11	.25	.45	.27	.11	.41	.39	.10	.19	.29	.08	.42	.07	.15	.39	.02	1						
Marine Se	.28	.34	.72	.51	.41	.48	.42	.08	.20	.60	.17	.58	.62	.39	.85	.36	.24	.80	.20	.42	1					
Marine Sr	.30	.15	.70	.64	.56	.44	.43	.05	.13	.40	.24	.58	.65	.40	.65	.27	.20	.60	.27	.31	.83	1				
Marine V	.12	.10	.26	.19	.14	.40	.15	.01	.64	.08	.04	.14	.22	.06	.09	.37	.05	.23	.56	.09	.05	1				
Marine Y	.31	.39	.65	.28	.21	.30	.28	.25	.05	.87	.15	.40	.42	.31	.97	.26	.06	.97	.05	.45	.81	.60	.40	1		
Marine Yb	.31	.38	.62	.25	.17	.28	.25	.25	.04	.85	.13	.37	.39	.29	.94	.25	.05	.95	.04	.44	.77	.54	.02	.99	1	
Marine Zn	.20	.19	.04	.53	.30	.67	.67	.20	.31	.01	.41	.51	.55	.14	.12	.23	.79	.07	.87	.12	.19	.21	.40	.03	.02	1

minor-element/organic-matter curves (fig. 6) are unrelated to the composition of modern marine planktonic organic matter, a relation similar to that observed for other depos-

its (Calvert and Price, 1983; Piper, 1991; Piper and Isaacs, in press).

The minor-element/organic-matter relations probably do not change drastically during settling through the water column. Fisher and Wentz (1993, p. 671) concluded that Am, Ag, and Sn are “* * * retained sufficiently long, even by decomposing cells, to suggest that phytoplankton sinking as aggregates at rates of 100 m day⁻¹ would effectively transport these metals hundreds of meters out of oceanic surface waters.” We might conclude from this finding that the current high minor-element content of sedimentary organic matter reflects uptake of minor elements by the residual organic phase within the sediment. This interpretation parallels that advanced to explain the relation between C and S in organic matter of modern sediment (Mossman and others, 1991). Also, apatite, which precipitates not from seawater but within the upper few centimeters of the sediment (Kolodny, 1981; Burnett and others, 1988), must acquire its minor-element signal and, particularly, its REE signal from sediment pore water. Thus, the partitioning of minor elements among the different marine host phases of sediment (residual organic matter, apatite, and so on) reflects pore-water conditions, that is, diagenetic conditions. The original source phases (planktonic organic matter, opal-A, CaCO₃, and hydrogenous minor-element precipitates and adsorbed phases) must be evaluated to decipher the seawater environment of deposition.

Biogenic Fraction

The marine source phases are (1) planktonic debris and (2) hydrogenous precipitates and adsorbed phases. The biogenic contribution of minor elements is determined, first, by assuming a stoichiometry for plankton; then, the residual minor-element content is assigned to the hydrogenous source. Minor-element contents in plankton vary considerably (Martin and Knauer, 1973; Eisler, 1981; Collier and Edmond, 1984), owing to inconsistencies introduced during sample collection and analysis, but also to such natural factors as variations among species, geography, growth rates, and seawater pH (Eisler, 1981). The care with which the samples were collected and analyzed (Martin and Knauer, 1973; Collier and Edmond, 1984; Sherrell, 1989) requires that the reported variations in the composition of plankton (fig. 8) are real, rather than artifacts of sampling and analysis. The results indicate that we can never expect to obtain a single value for any minor-element content in individual samples of plankton but must settle for an average value, or best estimate. We might add that significant variations also are reported for the NO₃⁻ and PO₄³⁻ contents in plankton (Sverdrup and others, 1942; Collier and Edmond, 1984); these ions constitute the major nutrients (Redfield and others, 1963), whose functions in plankton growth are well established. Given these variations, we chose to use the estimates of

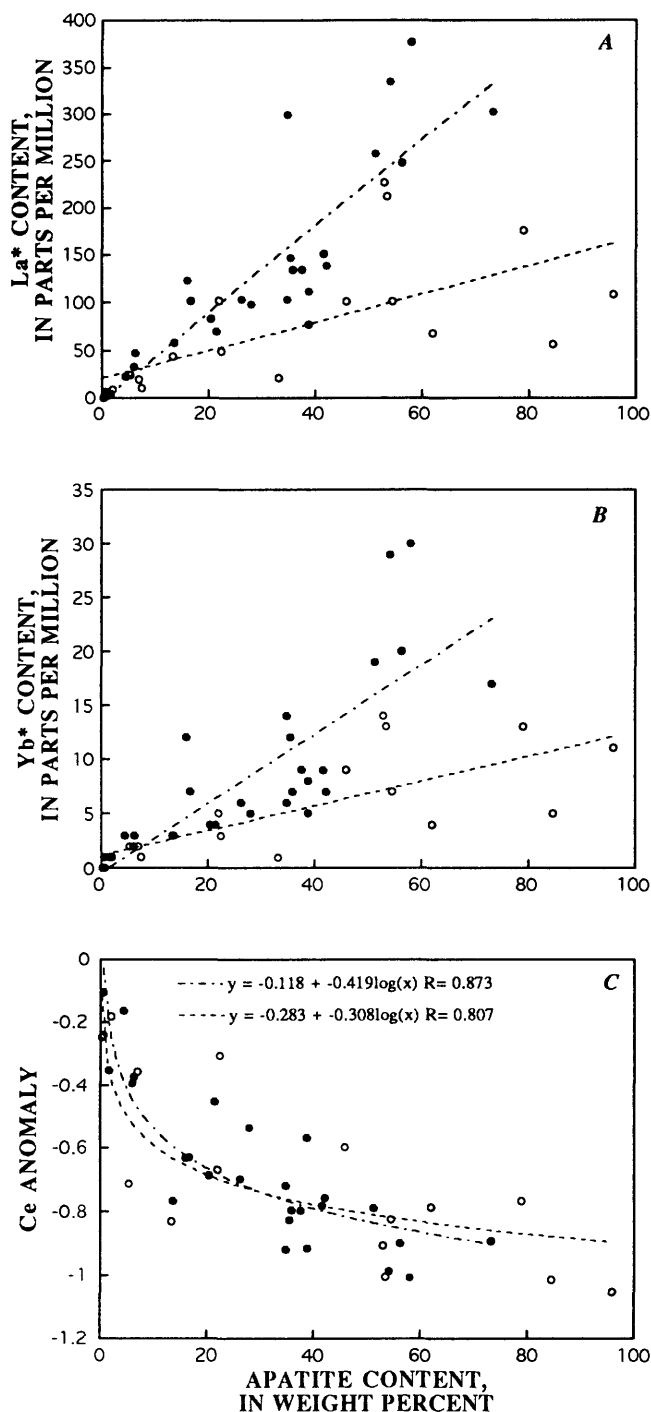


Figure 7. Apatite versus rare-earth-element (REE) contents and Ce anomaly in the Phosphoria Formation at Montpelier Canyon. Ce anomaly is defined as $\log \{ (3 \times \text{Ce}/83) / [(2 \times \text{La}/41) + (\text{Nd}/38)] \}$, where each REE is normalized on an element-by-element basis to World Shale Average (WSA; Piper, 1974). Same symbols as in figure 4.

Brumsack (1986) rather than introduce a new set of values (table 1).

The magnitude of minor-element variations in plankton (fig. 8) can easily discourage further consideration of the data and their application to geochemical investigations of sedimentary rocks. However, two important aspects of the marine environment require that the contribution of organic debris to the accumulation of minor elements be examined. First, rates of primary productivity throughout the ocean margin are high (Berger and others,

1988), resulting in a large flux of organic matter to the sea floor (Calvert, 1990; Pedersen and Calvert, 1990; Calvert and others, 1991). Second, a significant amount of the organic matter produced in the photic zone accumulates on the sea floor of ocean margins, owing to shallow water depths (Reimers and Suess, 1983). Thus, this fraction of sediment on ocean margins should represent a major sink for many minor elements in the oceans today (Collier and Edmond, 1984) and in ancient oceans as well.

The distributions of Cd, Cu, Cr, Ni, V, and Zn in the water column (fig. 9A), relative to those of PO_4^{3-} , NO_3^- , and Si(OH)_4 (fig. 9B), reflect the importance, if not predominance, of plankton (that is, organic detritus) as a carrier of many metals from the photic zone to the sea floor. More importantly, the distributions of these elements provide a critical evaluation of the minor-element stoichiometry of plankton. NO_3^- and PO_4^{3-} are the *limiting* nutrients to phytoplankton productivity in the photic zone of the ocean today (Sverdrup and others, 1942; Broecker and Peng, 1982; Codispoti, 1989), and Si(OH)_4 may be a limiting nutrient in some ocean-margin areas (Dugdale and Goering, 1970; Nelson and others, 1981). NO_3^- and PO_4^{3-} (and Si(OH)_4) are extracted from seawater in the photic zone during photosynthesis and returned to the ocean at depth by bacterial respiration, and only a small portion of the initial particulate form survives to the deep-ocean sea floor. As a result of their cycling through the water column, the NO_3^- and PO_4^{3-} concentrations in surface water are relatively low and can even approach zero; their concentrations increase sharply below the photic zone to the thermocline and then remain relatively constant below approximately 500-m depth.

Many minor elements show a similar depth profile. The variation in Cd content with depth parallels that of PO_4^{3-} concentration (Boyle and others, 1976), more so than those of the other minor elements. Zn and Ni depth profiles resemble that of Si(OH)_4 (Sclater and others, 1976; Bruland, 1983). For Zn, the Zn- Si(OH)_4 relation in seawater (Broecker and Peng, 1982) corresponds to a Zn content in opal of approximately 60 ppm. The measured Zn content of opal averages only 5 to 10 ppm (Martin and Knauer, 1973), much less than its bulk content in plankton of 110 ppm (table 1). Thus, the high Zn content in plankton (Collier and Edmond, 1984) and its much lower measured content in the siliceous fraction of

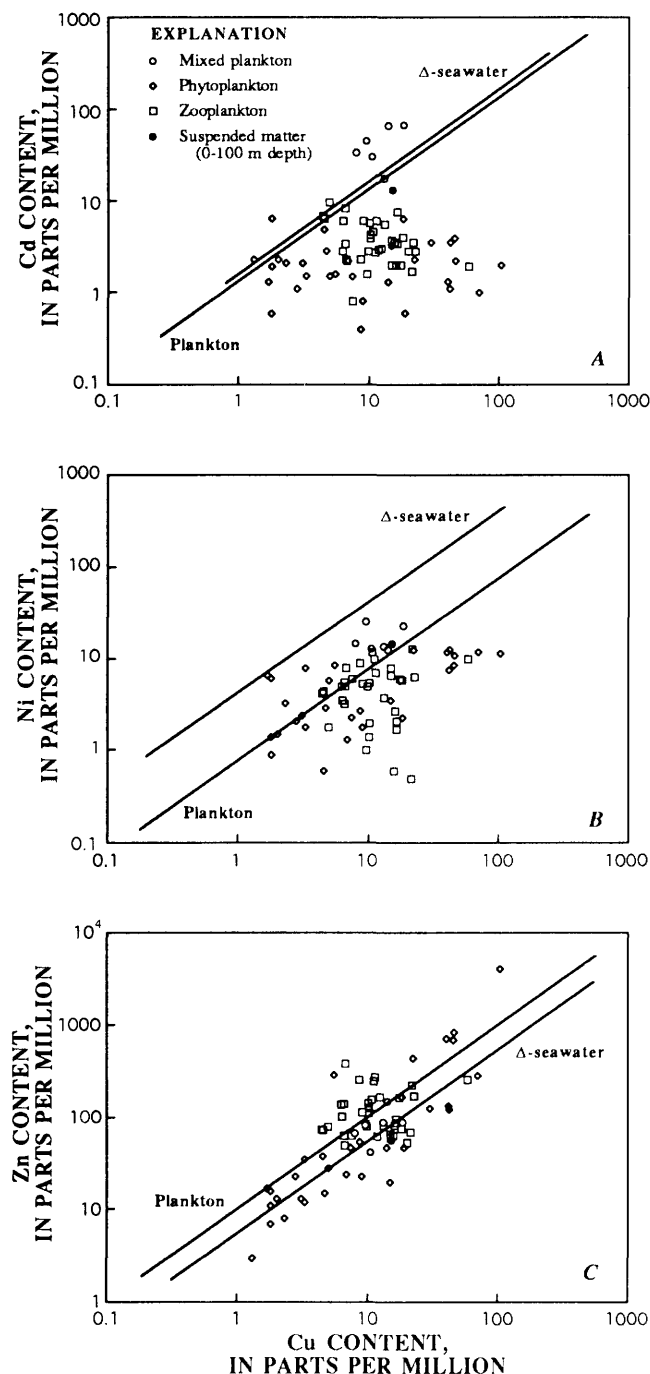


Figure 8. Minor-element versus Cu contents in modern plankton. Phytoplankton and zooplankton values are for Monterey Bay, Calif., and the North Pacific Ocean (Martin and Knauer, 1973); mixed plankton values are for the North Pacific Ocean (Collier and Edmond, 1984); and suspended-matter values are for two samples from photic zone of the California Current (Sherrell, 1989). Curve labeled "plankton" represents a best estimate of element:Cu ratio of plankton (Brumsack, 1986); Δ -seawater values are ratios of δ -seawater values listed in table 3.

plankton (Martin and Knauer, 1973) indicate that Zn and, probably, Ni are associated predominantly with the soft parts of organisms, similar to Cd.

The distribution of these minor elements in seawater, relative to that of PO_4^{3-} , can be used to evaluate their measured contents in plankton (table 3). The $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio,

$$\delta\text{-seawater}[\text{NO}_3^-] =$$

$$\frac{\text{NO}_3^- (\text{deep ocean}) - \text{NO}_3^- (\text{photic zone})}{\text{PO}_4^{3-} (\text{deep ocean}) - \text{PO}_4^{3-} (\text{photic zone})}, \quad (1)$$

based on the chemical profiles of these two ions in seawater (fig. 9), equals the average N:P atomic ratio of plankton of 15:1. This agreement indicates that metabolic and advective processes dominate their distributions in the deep ocean. If this conclusion is true for the minor elements as well, $\delta\text{-seawater}$ values for minor elements also should equal the metal:P ratios in plankton. Although the

two values for Cd closely approach each other, the $\delta\text{-seawater}$ values for Cr, Ni, Se, and V are higher, and for Zn lower, than the mean element:P ratios in plankton. The $\delta\text{-seawater}$ value for Cu also resembles the Cu:P ratio in plankton, although it is 2.5 times higher than the ratio in plankton when the Cu concentration in bottom water (fig. 9A) is used in the calculation, rather than the Cu concentration at 2,000-m depth (table 3).

Boyle and others (1977) explained the distribution of Cu in the deep ocean by a combination of biologic and nonbiologic processes; the nonbiologic processes involve scavenging of Cu throughout the water column by settling particles and recycling of Cu into bottom water from oxic pelagic sediment. These and other nonmetabolic processes might also explain the high $\delta\text{-seawater}$ values for Cr, Ni, Se, and V, but their marine chemistry has not been examined as thoroughly as that of Cu. Nonetheless, the similarities of the seawater depth profiles of many metals to those of NO_3^- , PO_4^{3-} , and $\text{Si}(\text{OH})_4$, and the fact that their $\delta\text{-seawater}$ values are within a factor of 2 to 3 of the average compositional ratios in plankton (fig. 8; table 3), suggest

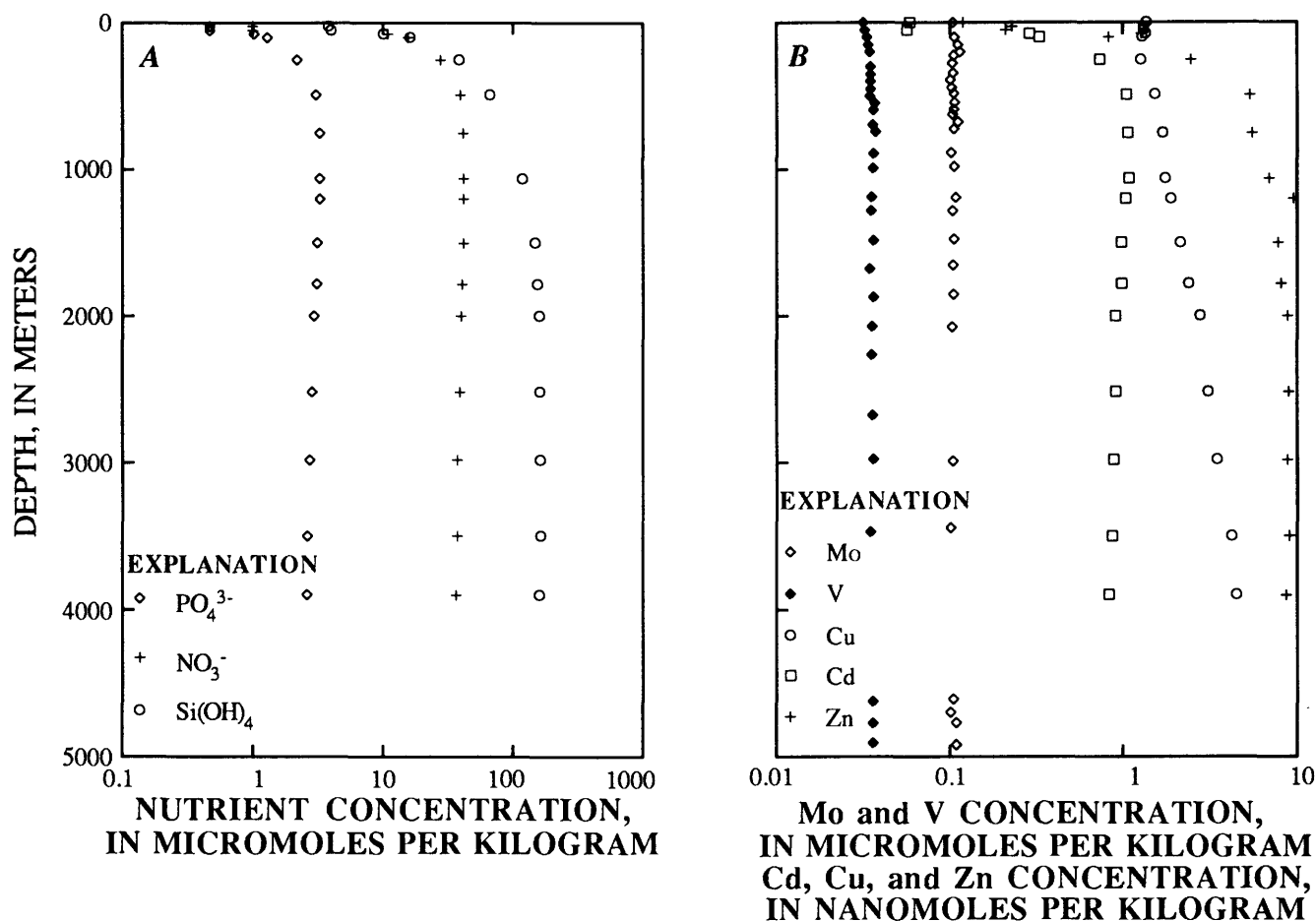


Figure 9. Nutrient (A) and metallic-ion (B) concentrations versus depth in the Pacific Ocean (from Bruland, 1983, and Collier, 1984, 1985).

Table 3. Minor-element contents in organic matter and seawater

[Seawater content is the approximate elemental concentration for the Pacific Ocean at 2,000-m depth. Data sources for minor-element contents in organic matter are listed in table 1, and in seawater in table 4]

Element	Organic matter content (ppm)	Element:P ratio (organic matter)	δ -seawater (weight ratio)	Seawater content (ppb)
Cd-----	12	$.6 \times 10^{-3}$	1.3×10^{-3}	0.10
Co-----	<1	--	--	.0012
Cr-----	2.0	$.26 \times 10^{-3}$	$.95 \times 10^{-3}$.22
Cu-----	11	1.4×10^{-3}	1.1×10^{-3}	.18
Mo-----	2	$.26 \times 10^{-3}$	--	10.60
Ni-----	7.5	1.0×10^{-3}	5.3×10^{-3}	.59
Se-----	3.0	$.40 \times 10^{-3}$	1.5×10^{-3}	.13
U-----	<1	--	--	3.00
V-----	3.0	$.40 \times 10^{-3}$	1.1×10^{-3}	1.80
Zn-----	110	14.00×10^{-3}	6.1×10^{-3}	.52
REE's (La)-----	<1	--	--	.0052

that the elemental composition of plankton approximates the average composition of marine organic detritus settling into the deep ocean. Ni is a major exception; it has a δ -seawater value 5 times larger than the Ni:P ratio in plankton (table 3). Owing to the coarseness of our sampling, as discussed above, only the average δ -seawater value is germane to our study, and this should be the value given by seawater profiles.

Nonbiologic processes, which likely influence the distributions of many metals in the deep ocean, might contribute much less to metal distributions in the shallower continental shelf and slope environments. This reduced influence is suggested by the Cu distribution. Its δ -seawater value, based only on the uppermost 2,000 m of seawater (1.1×10^{-3}), is very close to the Cu:P ratio in plankton (1.4×10^{-3}). If we consider its concentration in bottom water, then its δ -seawater value is 3.5×10^{-3} .

The distributions of Mo, U, and REE's in seawater are little influenced by the biologic cycle. Mo and U concentrations are constant with depth (Broecker and Peng, 1982; Collier, 1985; Emerson and Husted, 1991). Mo is mildly bioreactive (table 3), but its uptake by plankton in the photic zone and the remineralization of planktonic debris at depth by bacteria are simply insufficient to measurably affect the vertical distribution of Mo in the water column (fig. 9A). The content of Mo in plankton is only $\frac{1}{6}$ that of Cd, but the Mo concentration in seawater is approximately 100 times greater (table 3). Thus, oxidation of organic matter at depth increases the Mo concentration above its surface-water value by less than 2 percent, somewhat less than the precision of the analyses (Collier, 1985). This result is analogous to our inability to detect

the change in Ca^{2+} concentration (Broecker and Peng, 1982), forced by phytoplankton precipitation of CaCO_3 in the photic zone—for example, by coccolithophorids—and dissolution at depth.

U and REE's apparently are even less bioreactive. U, similar to Mo, is conservative in seawater. Although REE concentrations in seawater increase with depth and are relatively high in handpicked diatom tests (Elderfield and others, 1981), their seawater profiles are explainable largely in terms of nonbiologic processes (de Baar and others, 1985). Such an explanation suggests that the REE contents are very low in silica, possibly similar to their contents in biogenic calcite (Palmer, 1985), despite the elevated values of single analyses.

We present the minor-element contents of plankton below as single, well-defined values that we consider to be the best averages, as suggested by Brumsack (1986). However, they certainly are not well defined and unlikely to be single values. Nonetheless, the successful application of this approach to ancient rocks (Piper, 1991; Piper and Isaacs, in press) lends support to the values recommended by Brumsack (1986).

Before considering the minor elements, we calculate the accumulation rate of PO_4^{3-} in the Phosphoria Formation, relative to the current extraction of PO_4^{3-} from the photic zone of the ocean by photosynthesis. The duration of deposition for the Meade Peak Phosphatic Shale Member of the Phosphoria Formation (fig. 2), based on the conodont and brachiopod zones of Wardlaw and Collinson (1986) and the time scale of Harland and others (1990), was approximately 7.2 m.y. The amount of P_2O_5 in the Meade Peak Member, at Montpelier Canyon, is 7.65 kg-m P_2O_5

per kilogram of sediment (McKelvey and others, 1953), giving a mean accumulation rate for P_2O_5 of 0.23 mg/cm^2 per year. Assuming a composition for settling organic matter which equaled that of modern plankton, the rate of accumulation of organic matter necessary to deliver P_2O_5 to the Phosphoria Sea floor would have been 14 mg/cm^2 per year.

We can compare this accumulation rate with that for organic matter on the Peru Shelf, an area of high primary productivity with a sediment composition (Burnett and Froelich, 1988) similar to that of the Meade Peak Phosphatic Shale Member (McKelvey and others, 1953). Primary productivity of organic matter on this shelf is approximately 200 mg/cm^2 per year (Chavez and Barber, 1987), as high as that of any region in the oceans (Berger and others, 1988). Of this amount, approximately 15 to 45 percent settles out of the photic zone (Dugdale and Goering, 1970; Von Bockel, 1981; Baines and others, 1994). A widely varying amount, as much as 8 percent or approximately 16 mg/cm^2 per year, escapes oxidation in the water column altogether and accumulates on the sea floor (Reimers and Suess, 1983). This amount corresponds closely to the required value for the Phosphoria Formation of 14 mg/cm^2 per year and to the amount predicted for a water depth of 500 m (Suess, 1980).

It may not be entirely surprising that primary productivity in these two environments, separated in time by about 260 m.y., is similar. Could the rate of primary productivity of 200 mg/cm^2 per year represent an approximate upper limit for the photic zone, both past and present? The depth of the photic zone on the Peru Shelf today is only approximately 30 m (Von Bockel, 1981; L.A. Codispoti, oral commun., 1992), limited by the high content of particulate organic matter in the water. Higher productivity would yield more organic matter within any volume of water in the photic zone but also limit even more the depth to the base of the photic zone. As this depth decreases relative to that of the mixed layer, phytoplankton growth per area of sea surface must decrease, owing largely to mixing below the photic zone. At some photic-zone versus mixed-layer depth, mixing will carry phytoplankton into the aphotic zone at a rate that must limit total productivity and the flux of organic matter to the sea floor. The boundary conditions are a photic zone of 0-m depth and a photic zone of a depth equal to the mixing depth, or to the depth of the sea floor. Both the Phosphoria Sea and the Peru Shelf might have achieved a self-limiting maximum productivity of organic matter, approaching 200 mg/cm^2 per year. We note that the average productivity of the Phosphoria Sea remained near this inferred maximum, if indeed it is a maximum, for about 7.2 m.y.

The ratio of the depth of the photic zone to that of the mixed layer must surely influence other aspects of the flux of organic matter to the sea floor. For example, the loss of organic matter as the fecal debris of grazing zooplankton, relative to the loss of phytoplankton from the

aphotic zone through mortality, might decrease with a decrease in the above ratio. We can only speculate how the loss of phytoplankton by mortality versus that by grazing might influence the overall flux and composition of accumulating organic matter. Our assumption is that the two different loss terms will not change the composition of organic matter.

The minor-element contribution from settling organic matter (plankton) can be evaluated in the same way as for P_2O_5 . Consider Cu: If the average marine Cu content in the Phosphoria Formation is 95 ppm (fig. 6) and the stoichiometry of accumulating organic matter was the same as that of modern plankton (table 3), then the accumulation rate of organic matter required to deliver Cu to the sea floor was 14 mg/cm^2 per year. Calculations based on the marine Mo and Zn contents (fig. 6)—that is, in excess of the terrigenous contribution (WSA, fig. 5) and their contents in plankton (table 1)—give rates of 16 and 17 mg/cm^2 per year, respectively. Cd requires a slightly lower rate.

The accumulation rate of organic matter required to deliver Ni to the sea floor is approximately 40 mg/cm^2 per year, or 3 times higher than that based on the contents of P_2O_5 and other trace elements. Although a similar result was obtained for the Monterey Formation, a phosphatic formation of Miocene age (Piper and Isaacs, in press), no simple explanation seems adequate to account for such a high rate. The $\delta\text{-seawater}[\text{Ni}]$ value suggests that Ni content of organic matter is 5 times higher than our stoichiometric model allows (table 3). It seems unlikely that the mean Ni content of plankton could be 35 to 40 ppm without such high contents being observed (Martin and Knauer, 1973; Collier and Edmond, 1984). Although only 25 ppm is required to bring the Ni content of plankton into agreement with the relation between Ni and the above minor elements and P_2O_5 , this value still seems high to us. Its disagreement with the accumulation rates of P_2O_5 , Cu, Mo, and Zn is unfortunate because Ni should provide the best estimate of primary productivity (see discussion below).

An alternative approach to examining the contribution of minor elements from organic matter is provided by ratios of the minor elements (fig. 10). The major reason for this approach is the similarity in the marine geochemistry of several of the minor elements. They precipitate as sulfides (Jacobs and others, 1985, 1987; Landing and Lewis, 1991) and should be retained in the sediment as metal sulfides during and after early diagenesis. Phosphate, in contrast, is retained as carbonate fluorapatite (Burnett and others, 1988; Froelich and others, 1988). This difference could result in fractionation between PO_4^{3-} and the minor elements during diagenesis and weathering, and explain the absence of correlation between apatite and the bioreactive minor elements (table 2). The minor elements, in contrast, should be less fractionated from each other, possibly allowing for a comparison between the interelement ratios in rocks, plankton, and seawater through simple x - y plots.

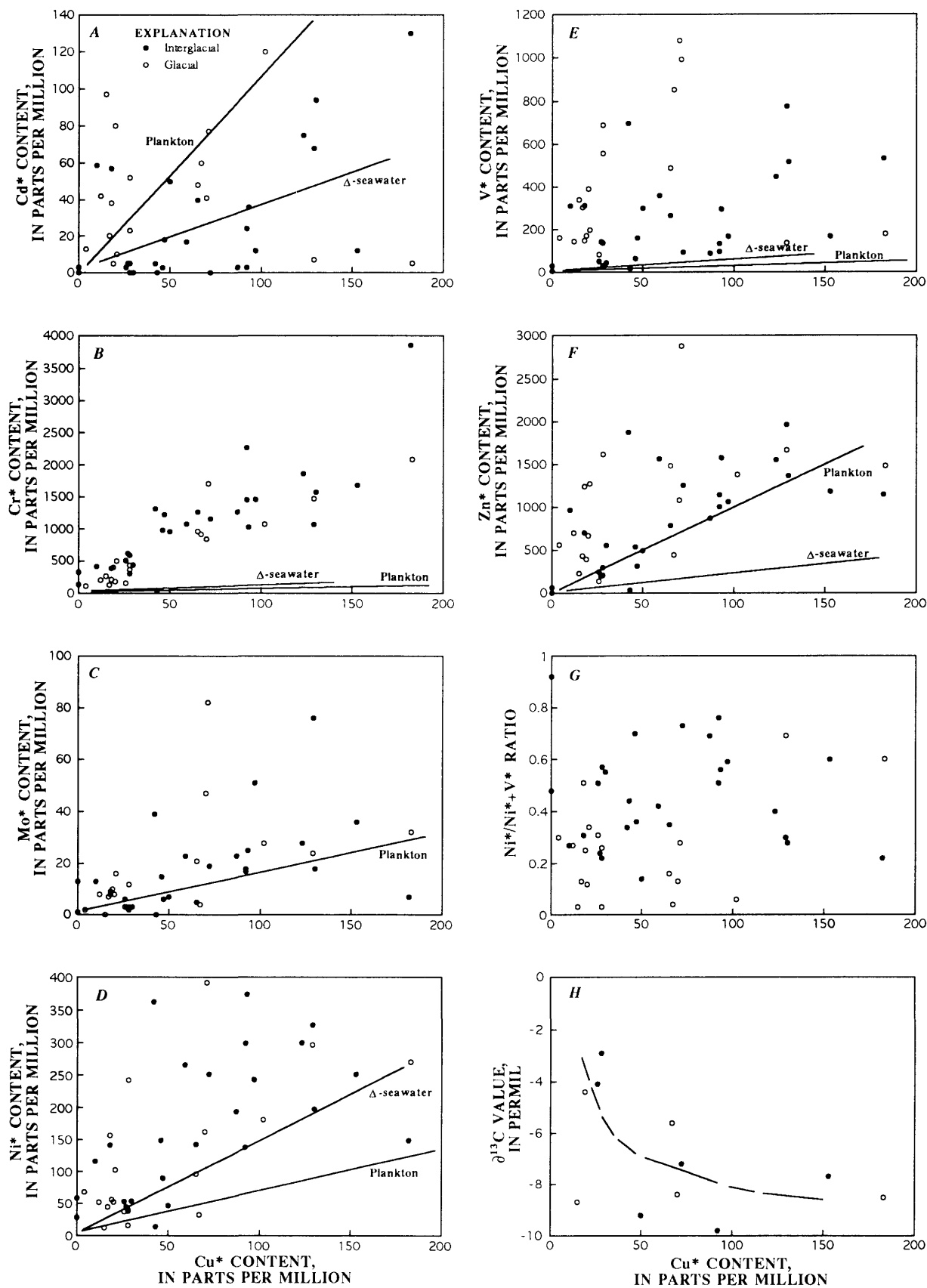


Figure 10. Minor-element versus Cu contents in marine fraction of the Phosphoria Formation at Montpelier Canyon during glacial and interglacial episodes. See figure 8 for definition of curves, except for figure 10H, in which curve was fitted visually to data.

A second reason to consider minor-element ratios is that sediment-accumulation rates are seldom or poorly known. It might be argued that they are too poorly known even for the Phosphoria Formation to permit an evaluation of rates of primary productivity, as we did above. The agreement between the different calculations, however, suggests otherwise. The x - y plots should permit an even more precise estimate of elemental contributions from the biogenic fraction and identify any possible hydrogenous fractions. This procedure is aided when the minor elements exhibit strong interelement correlations. Simple x - y plots of minor elements will clearly show those elements that are enriched above a biogenic contribution.

This procedure points up the desirability of a single master element that defines the marine organic source, as Al_2O_3 defines the detrital source. In this discussion, we use Cu as the master element for the marine biogenic (planktonic) fraction. Several aspects of its chemistry recommend it.

1. The content of Cu in plankton (table 3) exceeds that of most other minor elements (Martin and Knauer, 1973; Broecker and Peng, 1982; Bruland, 1983; Collier and Edmond, 1984; Brumsack, 1986), and so its biogenic signal might be strongly imprinted in rocks that initially had a high content of organic matter.
2. Cu accumulates in oxic sediment in strong association with Mn (Piper, 1988), but it precipitates virtually completely from seawater under seawater sulfate-reducing conditions as a sulfide (Jacobs and others, 1985). Its absolute concentration in seawater should make the biogenic input, however, greater than or, at worst, approximately equal to the hydrogenous input of many sedimentary deposits. If we assume redox and advection conditions similar to those in the Cariaco Trench (Jacobs and others, 1987) and a Cu concentration in seawater advecting into the basin equal to that in seawater at 2,000-m depth (table 3), then the accumulation rate for Cu that would precipitate as a sulfide is approximately $0.1 \mu\text{g}/\text{cm}^2$ per year, slightly less than its accumulation rate in the biogenic fraction of $0.22 \mu\text{g}/\text{cm}^2$ per year.
3. Cu should be retained in organic-matter-enriched sediment. The current organic-matter content of the Phosphoria Formation (Medrano and Piper, 1992) is high in terms of sedimentary rocks, even though it represents only approximately 1 percent of the rain rate of $14 \text{ mg}/\text{cm}^2$ per year. It is considerably less than the organic-matter content of surface and near-surface sediment accumulating currently on the Peru Shelf, but it likely exceeded Peru Shelf values at the time of deposition. Such a high accumulation rate for organic matter allows sulfate reduction in the pore water to extend to or near the surface (Froelich and others, 1988). One result of such pore water chemistry is strongly negative $\delta^{13}\text{C}$ values, measured in Peru Shelf

pore water (Glenn and Arthur, 1988) and in the CO_3^{2-} of carbonate fluorapatite in these samples (fig. 10H) and in other samples from the Phosphoria Formation (Piper and Kolodny, 1988). Cu is quickly recycled into the overlying water under oxic pore-water conditions (Boyle and others, 1977; Fischer and others, 1986), but it should be retained under sulfate-reducing conditions. This interpretation is based on the low solubility of Cu_2S or CuS , as reflected by its precipitation under natural seawater sulfate-reducing conditions (Jacobs and others, 1985).

4. The marine fraction of Cu correlates with those of several other minor elements in the Phosphoria Formation (fig. 10; table 2), allowing a precise comparison of minor-element ratios in the Phosphoria Formation with those in different modern marine fractions through the use of simple x - y plots. The absence of such correlations does not preclude the use of this approach, inasmuch as the strength of present correlations should depend more on the composition of host, authigenic phases than on that of source phases. For elements that fail to correlate with Cu or some other master element, many samples may have to be analyzed to document an average minor-element ratio. As we demonstrated above, the marine fractions of Cu and P_2O_5 give similar accumulation rates for organic matter, yet the two do not correlate (table 3).

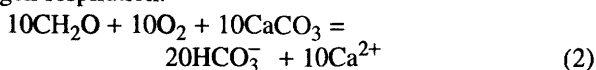
Plots of the contents of minor elements versus Cu (fig. 10) reinforce the calculations of their accumulation rates. We should have expected this result because both schemes are based on the assumption that the composition of deposited organic matter was the same as that of modern plankton. Nonetheless, our conclusion from this exercise is that primary productivity in the photic zone provided the dominant marine fractions of Cu, Cd, Mo, and Zn to the floor of the Phosphoria Sea. Identification of the Ni source will require further work on both modern and ancient deposits.

Hydrogenous Fraction

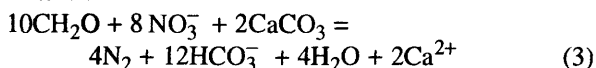
The low REE, Cr, and V contents in organic matter (table 1) and their relatively high contents in Montpelier Canyon rocks require that these elements had a hydrogenous marine source, in addition to their detrital and biogenic sources. Before accounting for these high values, we examine the geochemical properties of seawater under which these and all minor elements in the modern ocean accumulate through inorganic processes. Their behaviors have been thoroughly examined under redox conditions of oxygen respiration to sulfate reduction. Their precipitation-dissolution under varying redox conditions is driven by the bacterial oxidation of organic matter, for which the three major electron acceptors are O_2 , NO_3^- , and SO_4^{2-} . The major seawater redox reactions that drive the precipi-

tation-dissolution reactions of individual minor compounds can be written as follows:

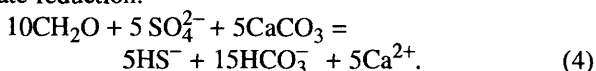
Oxygen respiration:



Denitrification:



Sulfate reduction:



The formula for organic matter is better represented by



Its minor-element contents are listed in table 1. The hierarchy of these three reactions is determined by the reaction yielding the greatest free energy (Froelich and others, 1979). Thus, reaction 2 proceeds until O_2 decreases to a concentration such that denitrification yields equal free energy, and so on.

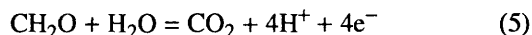
Within several ocean-margin basins, advection is weak enough and the flux of settling organic matter great enough to allow depletion of successive electron acceptors with depth in the water column (Richards, 1965; Emerson and others, 1979). These basins include the Golfo Dulce (Costa Rica), Baltic Sea, Black Sea, Cariaco Trench (Venezuela Shelf), and several fiords at high latitudes. Concentration profiles of O_2 , NO_3^- , and H_2S show that O_2 is abundant in the surface mixed layer, owing to mixing with atmospheric O_2 and to photosynthesis, but decreases in the water column below the mixed layer, in response to oxygen respiration, predominantly by bacteria. O_2 concentration is low at intermediate depth (Emerson and others, 1979), the depth interval over which NO_3^- concentration decreases in response to denitrification. O_2 and NO_3^- are virtually absent in bottom water, that is, in the presence of H_2S under conditions of sulfate reduction (eq. 4). Sulfate reduction continues into the sediment until SO_4^{2-} is depleted in the pore water, at which depth the residual labile organic matter is broken down through methanogenesis and fermentation reactions (equations not shown). In the Santa Barbara Basin (California Continental Borderland) and Darwin Bay (Galápagos Islands), bacterial respiration in the bottom water does not proceed beyond denitrification (Richards and Broenkow, 1971; Sholkovitz and Gieskes, 1971).

By contrast, the deep ocean exhibits oxygen respiration throughout. Denitrification occurs at intermediate depth, in the oxygen-minimum zone (OMZ), but only along the Peru and Mexico Shelves in the eastern Pacific

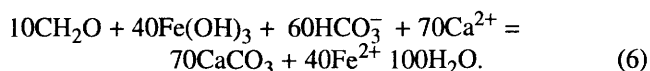
Ocean (Codispoti, 1980) and at a few other localities of limited areal extent in the Atlantic Ocean (Calvert and Price, 1971) and the Indian Ocean. Although the OMZ is present at intermediate depth throughout most of the oceans, only in these relatively small areas is the balance between advection in the OMZ and organic-matter productivity in the photic zone such that bacterial oxidation of settling organic matter drives down the O_2 content within the OMZ of the water column to a value that promotes and maintains denitrification.

On a single cruise to the Peru Shelf in 1976, low H_2S concentrations were measured in the OMZ (Dugdale and others, 1977), indicating that sulfate-reducing conditions occur in the OMZ of the open ocean, at least briefly. The existence of such conditions is easily understood because the maximum O_2 , NO_3^- , and SO_4^{2-} concentrations in seawater are approximately 0.36, 0.04, and 28 mM, respectively. From equations 2 through 4, NO_3^- has only about 15 percent the oxidizing potential of O_2 and only 0.1 percent that of SO_4^{2-} . The NO_3^- should be relatively quickly utilized once O_2 is depleted, pushing bacterial respiration into the field of sulfate reduction. It is somewhat surprising that H_2S has not been detected in the water column more often than on this single occasion.

Minor elements that act as electron acceptors include Cu^{2+} , CrO_4^{2-} , $\text{Fe}(\text{OH})_3$, MnO_2 , MoO_4^{2-} , SeO_4^{2-} , $\text{UO}_2(\text{CO}_3)_2^{2-}$ (or, possibly, $\text{UO}_2(\text{CO}_3)_3^{4-}$), and VO_4^{3-} . Their reduction can be calculated from Nernst equations and ordered according to Eh (table 4), where we merely omit the half-cell reaction representing the oxidation of organic matter:



If this half-cell is included, as was done in equations 2 through 4, Fe(III) reduction can be written in the following form:



Its reduction occurs before sulfate reduction (table 4) and toward the end of denitrification (Berner, 1980; Bender and others, 1989); CrO_4^{2-} also is reduced under conditions of denitrification (table 4; Murray and others, 1983). For completeness, table 4 includes the reduction of other redox reactions (for example, the reduction of Re and I), although they are not discussed further here.

The minor-element contents of inorganic particulate phases in seawater reflect these redox conditions. Under conditions of oxygen respiration, inorganic precipitates consist mostly of Fe and Mn oxyhydroxides (Landing and Bruland, 1987). Other minor elements are undersaturated in oxic seawater, but high concentrations of several minor elements in deep-ocean ferromanganese nodules indicate that a small

Table 4. Half-cell reactions, assuming standard-state conditions

[Activity coefficients calculated by using the Debye-Hückel equation (Wagman and others, 1982); \bar{a} , effective ionic diameter used in the Debye-Hückel equation (from Nordstrom and Munoz, 1985, or estimated from their table 7-4). Seawater concentrations of dissolved species (in moles per kilogram) are those at approximately 2,000-m depth. The pH was taken to be 7, although it is closer to 8 under conditions of oxygen respiration and 7.5 under denitrification. Data sources for thermodynamic constants and species concentrations in seawater: 1, Bruland (1983); 2, Latimer (1953); 3, Wagman and others (1982); 4, Landing and Bruland (1987); 5, Broecker and Peng (1982); 6, Murray and others (1983); 7, Elderfield (1970); 8, de Baar and others (1985); 9, Langmuir (1978); 10, Jacobs and others (1985); 11, Collier (1984); 12, Boyle and others (1976); 13, Collier (1985); 14, Emerson and Husted (1991); 15, Anbar and others (1992); 16, Koide and others (1986)]

Eh	Half-cell reaction	\bar{a}	Seawater concentration in moles per kilogram or partial pressure	Reference
1.099	$3\text{Co}_{(\text{aq})}^{2+} + 4\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Co}_3\text{O}_{4(\text{s})} + 2\text{e}^- + 8\text{H}_{(\text{aq})}^+$	6	$\text{Co}^{2+} = 2.04 \times 10^{-11}$	1, 2
.805	$2\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{O}_{2(\text{g})} + 4\text{e}^- + 4\text{H}_{(\text{aq})}^+$		$\text{O}_2 = 0.2 \text{ atm}$	3
.704	$\text{Mn}_{(\text{aq})}^{2+} + 2\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{MnO}_{2(\text{s})} + 2\text{e}^- + 4\text{H}_{(\text{aq})}^+$	6	$\text{Mn}^{2+} = 2.5 \times 10^{-10}$	3, 4
.702	$\text{I}_{(\text{aq})}^- + 3\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{IO}_3^-_{(\text{aq})} + 6\text{e}^- + 6\text{H}_{(\text{aq})}^+$	3	$\Gamma^- = 5.0 \times 10^{-9}$	1, 3
		4	$\text{IO}_3^- = 4.5 \times 10^{-7}$	
.698	$\text{N}_{2(\text{g})} + 6\text{H}_2\text{O}_{(\text{l})} \rightarrow 2\text{NO}_3^-_{(\text{aq})} + 10\text{e}^- + 12\text{H}_{(\text{aq})}^+$	3	$\text{NO}_3^- = 3.9 \times 10^{-5}$, $\text{N}_{2(\text{g})} = 0.8 \text{ atm}$	3, 5
.545	$\text{Cr}(\text{OH})_{3(\text{s})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{CrO}_4^{2-}_{(\text{aq})} + 3\text{e}^- + 5\text{H}_{(\text{aq})}^+$	4	$\text{CrO}_4^{2-} = 4.04 \times 10^{-9}$	2, 6, 7
.320	$\text{Ce}_{(\text{aq})}^{3+} + 2\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{CeO}_{2(\text{s})} + \text{e}^- + 4\text{H}_{(\text{aq})}^+$	9	$\text{Ce}^{3+} = 1.0 \times 10^{-11}$	3, 8
.296	$\text{Fe}_{(\text{aq})}^{2+} + 3\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Fe}(\text{OH})_{3(\text{s})} + \text{e}^- + 3\text{H}_{(\text{aq})}^+$	6	$\text{Fe}^{2+} = 1.20 \times 10^{-9}$	3, 4
.153	$\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{e}^-$		$\Sigma\text{Cu} = 3.59 \times 10^{-9}$, $\text{Cu}^+ = 1.80 \times 10^{-9}$	1, 3
.013	$\text{UO}_{2(\text{s})} + 2\text{HCO}_3^-_{(\text{aq})} \rightarrow \text{UO}_2(\text{CO}_3)_2^{2-}_{(\text{aq})} + 2\text{e}^- + 2\text{H}_{(\text{aq})}^+$	4.0	$\text{HCO}_3^- = 2.47 \times 10^{-3}$	3, 5,
		4.5	$\text{UO}_2(\text{CO}_3)_2^{2-} = 1.26 \times 10^{-8}$	9
-.018	$2\text{Fe}_{(\text{aq})}^{2+} + 3\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Fe}_2\text{O}_{3(\text{s})} + 2\text{e}^- + 6\text{H}_{(\text{aq})}^+$	6	See above	
-.040	$\text{V}_2\text{O}_{4(\text{s})} + 4\text{H}_2\text{O}_{(\text{l})} \rightarrow 2\text{H}_2\text{VO}_4^-_{(\text{aq})} + 2\text{e}^- + 4\text{H}_{(\text{aq})}^+$	5.6	$\text{H}_2\text{VO}_4^- = 4.0 \times 10^{-8}$	2, 11
-.055	$\text{HS}_{(\text{aq})}^- + 4\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{SO}_4^{2-}_{(\text{aq})} + 8\text{e}^- + 9\text{H}_{(\text{aq})}^+$	3.5	$\text{HS}^- = 7.75 \times 10^{-25}$	3, 5
		4	$\text{SO}_4^{2-} = 2.8 \times 10^{-2}$	
-.055	$\text{Cu}_2\text{S}_{(\text{s})} + 4\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{SO}_4^{2-}_{(\text{aq})} + 2\text{Cu}_{(\text{aq})}^+ + 8\text{e}^- + 8\text{H}_{(\text{aq})}^+$	4	$\text{SO}_4^{2-} = 2.8 \times 10^{-2}$	1, 3,
		2.5	$\text{Cu}^+ = 3.59 \times 10^{-9}$	10
-.137	$\text{CdS}_{(\text{s})} + 4\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{SO}_4^{2-}_{(\text{aq})} + \text{Cd}_{(\text{aq})}^{2+} + 8\text{e}^- + 8\text{H}_{(\text{aq})}^+$	4	$\text{SO}_4^{2-} = 2.8 \times 10^{-2}$	1, 3,
		6	$\text{Cd}^{2+} = 6.94 \times 10^{-10}$	5, 12
-.162	$\text{ZnS}_{(\text{s})} + 4\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{SO}_4^{2-}_{(\text{aq})} + \text{Zn}_{(\text{aq})}^{2+} + 8\text{e}^- + 8\text{H}_{(\text{aq})}^+$	4	$\text{SO}_4^{2-} = 2.8 \times 10^{-2}$	1, 3, 5
		6	$\text{Zn}^{2+} = 5.97 \times 10^{-9}$	
-.170	$\text{MoO}_{2(\text{s})} + 2\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{MoO}_4^{2-}_{(\text{aq})} + 2\text{e}^- + 4\text{H}_{(\text{aq})}^+$	4.5	$\text{MoO}_4^{2-} = 1.1 \times 10^{-7}$	3, 13
-.175	$\text{MoS}_{2(\text{s})} + 12\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{MoO}_4^{2-}_{(\text{aq})} + 18\text{e}^- + 2\text{SO}_4^{2-}_{(\text{aq})} + 24\text{H}_{(\text{aq})}^+$	4.5	$\text{SO}_4^{2-} = 2.8 \times 10^{-2}$	3, 13, 14
		5	$\text{MoO}_4^{2-} = 1.1 \times 10^{-7}$	
-.188	$\text{NiS}_{(\text{s})} + 4\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{SO}_4^{2-}_{(\text{aq})} + \text{Ni}_{(\text{aq})}^{2+} + 8\text{e}^- + 8\text{H}_{(\text{aq})}^+$	4	$\text{SO}_4^{2-} = 2.8 \times 10^{-2}$	1, 3,
		6	$\text{Ni}^{2+} = 8.01 \times 10^{-9}$	5, 10
-.209	$\text{FeS}_{(\text{s})} + 4\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{SO}_4^{2-}_{(\text{aq})} + \text{Fe}_{(\text{aq})}^{2+} + 8\text{e}^- + 8\text{H}_{(\text{aq})}^+$	4	$\text{SO}_4^{2-} = 2.8 \times 10^{-2}$	1, 3, 4
		6	$\text{Fe}^{2+} = 1.20 \times 10^{-9}$	
-.210	$\text{UO}_{2(\text{s})} + 3\text{CO}_3^{2-}_{(\text{aq})} \rightarrow \text{UO}_2(\text{CO}_3)_3^{4-}_{(\text{aq})} + 2\text{e}^-$	4.5	$\text{CO}_3^{2-} = 1 \times 10^{-4}$	3, 5,
		5.5	$\text{UO}_2(\text{CO}_3)_3^{4-} = 1.26 \times 10^{-8}$	9
-.250	$\text{ReO}_{2(\text{s})} + 2\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{ReO}_4^-_{(\text{aq})} + 3\text{e}^- + 4\text{H}_{(\text{aq})}^+$	4.5	$\text{ReO}_4^- = 4.5 \times 10^{-11}$	3, 15, 16
-.250	$\text{HS}_{(\text{aq})}^- + 4\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{SO}_4^{2-}_{(\text{aq})} + 8\text{e}^- + 9\text{H}_{(\text{aq})}^+$	3.5	$\text{HS}^- = 2.8 \times 10^{-25}$	3, 5
		4	$\text{SO}_4^{2-} = 4.3 \times 10^{-6}$	

fraction coprecipitates with the Fe and Mn oxide phases (Goldberg, 1961) or is scavenged by these oxides (Goldberg, 1954; Balistrieri and others, 1981; Li, 1981; Clegg and Sarmiento, 1989). Pelagic sediment, however, remains a minor sink for most metals, except Mn (Lyle and others,

1984). Their high metal contents reflect very low bulk-sediment-accumulation rates rather than high metal-accumulation rates.

Within basins that exhibit sulfate reduction in bottom water, Fe^{2+} , Cu^+ , Cd^{2+} , and Zn^{2+} precipitate as sulfides,

CrO_4^{2-} is reduced and precipitates as $\text{Cr}(\text{OH})_3$ (Brewer and Spencer, 1974; Emerson and others, 1979; Jacobs and others, 1985, 1987), and VO_4^{3-} may be reduced to V_2O_3 or, more likely, some form of $\text{V}(\text{OH})_3$ (Wanty and Goldhaber, 1992). Mo and U also are removed from the bottom water (Bruland, 1983; Anderson and others, 1989; Emerson and Husted, 1991), possibly according to the reactions listed in table 4. Although this environment is limited in areal extent, it represents an important sink for several elements in the ocean today (Kolodny and Kaplan, 1970; Bertine and Turekian, 1973; Cutter, 1982; Jacobs and others, 1987; Haraldsson and Westerlund, 1988; Emerson and Husted, 1991; Klinkhammer and Palmer, 1991). The much higher concentration of Mo in open-ocean seawater relative to the other minor elements (tables 1, 3) and its low content in detrital phases and organic matter (table 1) make it possibly the most important minor element for identifying rocks that accumulated in a sulfate-reducing environment. Its distribution in modern sediment of the Cariaco Trench supports this contention (Jacobs and others, 1987).

Of the elements that precipitate under the intermediate redox conditions of denitrification, U, V, and Cr should have the highest concentrations in sediment, although there are possible problems with V and U. The absence of a clear signal of U reduction and precipitation in the water column under denitrifying conditions (Anderson and others, 1989) makes its distribution in sedimentary deposits possibly less diagnostic of bottom-water conditions than that of other minor elements. Its possible occurrence as $\text{UO}_2(\text{CO}_3)_3^{4-}$ (Goldberg, 1963; Anderson and others, 1989), instead of $\text{UO}_2(\text{CO}_3)_2^{2-}$, an equally thermodynamically stable species (Langmuir, 1978), may account for this; $\text{UO}_2(\text{CO}_3)_3^{4-}$ should be reduced well into the zone of sulfate reduction ($E_h = -0.21$), rather than in the zone of denitrification. The precipitation of V occurs near the $\text{NO}_3^-/\text{SO}_4^{2-}$ -reduction boundary, which we define rather arbitrarily by the precipitation of the least soluble minor-element sulfide (Cu_2S) under consideration. A slight error in either the V or Cu half-cell reactions could push the precipitation of V into the zone of sulfate reduction, although the close association of V with Cr in some phosphate deposits (Piper, 1991; Piper and Isaacs, in press) indicates initial precipitation in the less reducing environment.

REE's have a unique distribution in O_2 -depleted seawater environments. They maintain their 3+ valence state throughout the marine environment except for Ce, which is oxidized to the 4+ valence state under oxic conditions (table 4). Within the zone of denitrification in the Cariaco Trench and the Black Sea, immediately above the zone of sulfate reduction (Hashimoto and others, 1983; Codispoti and others, 1991), the concentrations of the 3+-valence-state light REE's (La, Pr, Nd, and Sm) show minimums (de Baar and others, 1988; German and others, 1991; Schijf and others, 1991). In both basins, their concentrations increase sharply at greater

depth, toward the $\text{NO}_3^-/\text{SO}_4^{2-}$ -reduction interface and into the sulfate-reducing water. Within the zone of denitrification in the OMZ in the eastern Pacific Ocean, the concentrations of the 3+-valence-state REE's also show minimums. They are scavenged by particulate phases, most likely oxyhydroxides of Mn (German and others, 1993) or Fe (Sholkovitz, 1993), under mildly denitrifying conditions and released to solution under sulfate-reducing conditions. The carrier phase in the zone of denitrification in the OMZ of the eastern Pacific Ocean is unlikely an Mn phase. The concentration of dissolved Mn shows a maximum, whereas those of the REE's show minimums (Klinkhammer and Bender, 1980; de Baar and others, 1985; German and others, 1991). Thus, the mechanism whereby the 3+-valence-state REE's are transferred to the sea floor within the hydrogenous fraction remains problematic, although the redox conditions under which their removal to the sediment occurs are well established.

Ce is somewhat more complex than the other REE's. Its occurrence as insoluble $\text{Ce}(\text{OH})_4$ under oxic conditions (table 4) accounts for the negative Ce anomaly (see fig. 7) of seawater. Its reduction to the 3+ valence state under denitrifying conditions has been proposed to account for the increase in Ce concentration and the more positive Ce anomaly in the OMZ of the eastern Pacific Ocean and the Cariaco Trench (de Baar and others, 1988).

In the Black Sea, however, the trend of the Ce anomaly is different (German and others, 1991; Schijf and others, 1991): the dissolved-Ce concentration in the zone of denitrification decreases to a minimum, but so does the anomaly. This trend parallels those of the 3+-valence-state REE's, which mirror the maximum concentration of particulate Mn. All the REE's are scavenged in the upper part of the zone of denitrification, Ce more so than the other REE's. This distribution should be expected if Mn is the dominant carrier, because Ce^{4+} reduction occurs at a lower E_h than MnO_2 reduction. The difference in the distribution of the Ce anomaly between the Black Sea and the Cariaco Trench places an unfortunate constraint, at present, on the uniqueness of the Ce anomaly in unraveling the geochemistry of ancient sediment (Wright and others, 1987).

The low concentrations of Ce and other minor elements in seawater severely limit their contributions to the actual oxidation of organic matter but contribute significantly to the sensitivity with which their contents in the marine fraction of sediment might record redox conditions in the water column. Let us consider Mo. Its concentration in seawater is approximately 10^{-7} M, or $1/400$ that of NO_3^- . Clearly, it will contribute insignificantly to the oxidation of organic matter; and of the minor elements considered here, it is the most abundant in seawater. Assuming that the bottom-water of the Phosphoria Sea was sulfate reducing, and neglecting for the moment the conditions necessary to bring about the depletion of O_2 and NO_3^- , then for the Phosphoria Formation, which had an average bulk-sediment-accumulation rate of about 1.7 mg/cm^2 per year, 35 percent of which was a terrigenous

fraction (Medrano and Piper, 1992), the detrital Mo-accumulation rate would be $0.0016 \mu\text{g}/\text{cm}^2$ per year. If primary productivity was similar to that on the Peru Shelf, as we demonstrated above, the Mo-accumulation rate within organic matter (that is, within planktonic debris) was $0.04 \mu\text{g}/\text{cm}^2$ per year. Allowing that the hydrodynamics of the Black Sea represents that of the Phosphoria Shelf, the hydrogenous Mo-accumulation rate would have been $2 \mu\text{g}/\text{cm}^2$ per year, or about 850 to 2,000 ppm. This value is based on a bottom-water residence time ranging from 350 to 1,000 yr (Östlund, 1974; Murray and others, 1991) and an Mo content in seawater of 10 ppb, to which we must add the amount of Mo added to the bottom water by the oxidation of organic matter, or approximately $0.1 \mu\text{g}/\text{cm}^2$ per year. (The adjustment is small for Mo, but it is significant for Zn and the other minor elements.) Such an accumulation rate requires the Mo content of the Phosphoria Formation to be 40 to 100 times higher than that observed, if Mo accumulation occurred under sulfate-reducing conditions. We could change several factors to reduce this value. The thickness of the bottom water could be reduced, but doing so would change other factors, for example, the residence time of bottom water, which, in turn, would increase the flux of Mo to the sediment. Indeed, observations of O_2 -depleted environments of the open ocean (Sholkovitz and Gieskes, 1971; Codispoti, 1980) suggest that the residence time of bottom water is likely to have been a few years, rather than tens or even hundreds of years. Even though this calculation is extremely simplistic, it suggests to us that the bottom water of the Phosphoria Sea could not possibly have been sulfate reducing for any significant period of time. The five samples with high Mo contents (fig. 10C) suggest that bottom-water Eh might have slipped into the field of sulfate reduction, but only very briefly.

Assuming that primary productivity in the Phosphoria Sea equaled that on the Peru Shelf today, as seems plausible from our earlier calculation, we can expect the bottom water to have been denitrifying. The high contents of Cr, V (fig. 6), and REE's (fig. 7), in excess of a detrital and marine biogenic source, strongly support the interpretation of a bottom-water chemistry similar to that on the Peru Shelf. The concentration of marine Cr can be used to calculate the residence time of the bottom water, the reverse of the calculation for Mo-accumulation rate. The average Cr content in the Phosphoria Formation is 1,200 ppm, giving an accumulation rate of $2.9 \mu\text{g}/\text{cm}^2$ per year. If the denitrifying layer was 500 m thick (its approximate thickness on the Peru Shelf) and the initial Cr content of seawater was 0.21 ppb (table 3), the residence time of bottom water was 3.6 yr. A similar calculation based on La content gives a shorter residence time of 0.62 yr. The agreement, which is certainly within reason, can be improved by a greater efficiency in the removal of La than of Cr, as clearly suggested by their distributions in NO_3^- -reducing seawater (Murray and others, 1983; German and others,

1993). However, a residence time of much less than 1 to 3 yr seems unlikely to us.

This calculation of the accumulation of marine fractions on the sea floor demonstrates the balance between primary productivity in the photic zone of the ocean and advection of the bottom water. The relation is further represented by the following calculation. Primary productivity of organic matter in the photic zone produces $200 \text{ mg}/\text{cm}^2$ per year, approximately 25 percent of which must be oxidized in the bottom water. Assuming an initial NO_3^- concentration in the bottom water of $40 \mu\text{M}$, the maximum residence time for the bottom water that precludes sulfate reduction is 2 to 3 yr. The greatest uncertainty in this estimate stems from the absence of information on the initial O_2 content of seawater, because an unknown amount of the O_2 present in the water when it left the surface ocean (approx 8 mL/L) was surely reduced before it reached the sea floor at the Montpelier Canyon site. We have made other rather gross assumptions, some stated and some unstated, but the overall agreement of these calculations suggests that they give a reasonable first approximation of the bottom-water residence time versus surface-water productivity.

The distribution of V clearly cannot be treated in the same way as we treated those of Cr and La. The content of V is much lower in the Phosphoria Formation than that of Cr (fig. 6), but, in seawater, its concentration is much higher than that of Cr (table 3). There is far too little V relative to Cr (fig. 11) for the bottom water to have been strongly denitrifying. The reduction of V at a lower Eh (table 4) offers one possible explanation. Throughout the deposition of much of the Meade Peak Phosphatic Shale Member, the OMZ was denitrifying enough to precipitate Cr; only for relatively brief periods of time was it reducing to the point that V also precipitated. The high Mo contents in five samples (fig. 10C) suggest, albeit weakly, that

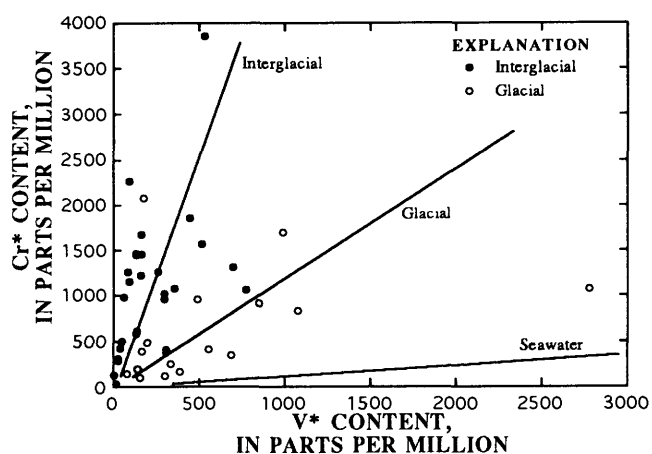


Figure 11. Cr versus V content in marine fraction of the Phosphoria Formation at Montpelier Canyon during glacial and interglacial episodes. Seawater curve shows extrapolated values at approximately 2,000-m depth (table 3).

the OMZ might have exhibited sulfate reduction for even briefer periods of time. Examination of other sections of the formation, such as the Vanadiferous Zone (a discrete section within the Meade Peak Phosphatic Shale Member with unusually high V content; Love, 1961; McKelvey and others, 1986), might show higher Mo contents and, thus, evidence of sulfate reduction. In such sediment, the V:Cr ratio should increase toward its seawater value of 8.6.

The V-Cr relation (fig. 11) shows that, on average, the bottom water was more reducing during glacial than during interglacial episodes; the sediment deposited during glacial episodes has higher V:Cr ratios. The lower La content in these same rocks (fig. 7A) supports this interpretation. These trends raise the question whether primary productivity was higher in the photic zone (greater flux of settling organic matter) or advection lower in the bottom water (longer residence time) during the glacial episodes. Glaciation would have lowered sea level, possibly by 75 m (Piper and Kolodny, 1988). Primary productivity might have been higher during these episodes, although we have no supporting evidence to offer for this interpretation. A probable change in the rate of input of terrigenous debris further complicates any interpretation of the distribution of any single minor element. Although we are unable to identify the exact change in the environment that led to a change in the V:Cr ratio and La content between these two populations, the separation of the two populations lends support to earlier interpretations of the lithology (Sheldon, 1984) and stable-isotope data (Piper and Kolodny, 1988) that the Phosphoria Formation was deposited during a time of glacial events.

CONCLUSION

The high precision of the major-element-oxide and minor-element analyses of this study allows us to identify, for the Phosphoria Formation, the current host fractions for minor elements (detrital material, organic matter, apatite, biogenic silica, dolomite, calcite, and trace-metal sulfides) and their source phases at the time of deposition (detrital debris, marine biogenic matter, and marine hydrogenous phases). The interelement relations between Al_2O_3 and K_2O , TiO_2 , Co, Ga, Li, Sc, and Ba approach those of the standard WSA and NASC. These relations indicate that the detrital fraction is the sole host for these elements and that it had a terrigenous source. The strength of these relations allows us to determine the detrital contribution of the other minor elements (Cd, Cr, Cu, Mo, Ni, U, Zn, and REE's) from the Al_2O_3 content of each individual sample.

The difference between the bulk content and the detrital contribution of minor elements to each sample represents the marine contribution. The interelement relations

between Cu, Mo, and Zn in this marine fraction of the rocks approximate those in modern plankton, suggesting that these minor elements and, possibly, Cd and Ni had a predominantly biogenic source. During Phosphoria time, the rate of accumulation of organic matter on the sea floor at Montpelier Canyon necessary to provide these elements to the sediment was approximately equal to the rate of accumulation of organic matter on the present-day Peru Continental Shelf, an area of exceptionally intense coastal upwelling and high primary productivity in the photic zone. Thus, primary productivity must have been similarly high in the Phosphoria Sea.

The enrichments of Cr, V, and REE's required accumulation directly from seawater, a hydrogenous input. On the basis of their chemical properties and distributions in O_2 -depleted environments of the ocean today, their accumulation from seawater would have been enhanced by conditions of denitrification in the bottom water. The rate of accumulation of Cr and La in this fraction gives a residence time for bottom water in the basin of approximately 1 to 3 yr. The relation between these two elements and REE's furthermore suggests that the bottom water was more strongly denitrifying during earlier-proposed glacial episodes than during interglacial episodes of the Permian Period.

Sulfate reduction was not established in the bottom water for any significant period of time. This interpretation is based on the preservation of a strong, seawater-derived REE enrichment throughout the Phosphoria Formation and the absence of an enrichment of Cu, Cd, Zn, and, particularly, Mo above a biogenic input. Otherwise, this group would have accumulated as inorganic sulfides, in addition to accumulating in an organic fraction (a slight enrichment of Mo was detected, but in only five samples), and REE's would not have accumulated from seawater at all but would have had solely a terrigenous source. A hydrogenous input of Mo, which could have been 100 times more abundant than Cd, would have been easily detected. Sulfate reduction was restricted to the sediment pore water; it likely closely approached the benthic boundary layer but did not extend into the water column.

No single environment in the ocean today represents a perfect analog of the Phosphoria Formation. Chemical and biologic processes were similar to those on the Peru and Namibia Shelves, both of which exhibit intense upwelling, resulting in high primary productivity in the photic zone apparently across much of the shelf, and denitrification in an OMZ at intermediate depth (Calvert and Price, 1971; Codispoti, 1980). In the section above entitled "Introduction," however, we noted possibly strong differences between the Phosphoria Sea and these shelf environments with regard to sea-floor bathymetry, tectonism, and proximity to major ocean currents. We still offer no example of a shelf that receives detritus at a rate less than 1 mg/cm^2 per year. The overall bathymetry and isolation

from major currents, however, might be represented by the East China Sea, although the differences, again, are noteworthy. The Phosphoria Shelf was situated on the west coast of the United States, not an east coast of Asia. It was at much lower latitude (Sheldon, 1964), within the belt of the easterly trade winds. Low rainfall limited the influx of terrigenous debris, and the continuous intense winds drove upwelling and maintained high primary productivity in the photic zone. The low elevation of the landmass to the east and the vastness of the shelf further reduced the flux of otherwise-diluting terrigenous debris, allowing the accumulation of marine-dominated deposits throughout the basin—evaporites along the coast and biogenic sediment within the basin. The Antler Uplift or a more westerly island arc, analogous to the Ryukyu Islands in the East China Sea, shielded the shelf from strong coastal currents, such as the Peru, Benguela, and Kuroshio Currents, thus providing a relatively undisturbed depositional regime for the dominantly marine debris that did settle out of the water column. The basin floor, itself, was rather featureless and, as Yochelson (1968) concluded from faunal evidence, likely had a maximum depth of approximately 200 m. A trough oceanward of the shelf, analogous to the Okinawa Trough in the East China Sea, limited the flux of detritus from the west into the shallower phosphogenic area of the basin. Weak tectonic activity and strong easterlies further limited the input of volcanic debris. Because few formations compositionally equivalent to the Phosphoria Formation are present in the geologic record, these conditions of sea-floor morphology, seawater chemistry, climate, provenance, and tectonism likely have seldom coexisted in the past.

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