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By D.Z. Piper and C.M. Isaacs

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ABSTRACT

We have analyzed samples of the Monterey Formation of southern California, collected at one site in the Santa Barbara-Ventura Basin and at another in the Santa Maria Basin, for major-element oxides and minor elements. Agreement between the analyses by three different laboratories, using three different methods, is excellent. These analyses allow identification of the following host phases for minor elements: terrigenous quartz, clay minerals, and other Al silicate minerals (detrital fraction), and biogenic silica, calcite, dolomite, organic matter, and apatite (marine fraction). Part of the marine fraction of minor elements also might be present as sulfides, but we have no evidence for the presence of this phase, except for pyrite.

The current minor-element contents in the marine fraction alone required, at the time of deposition of the sediment in these two basins, a moderate level of primary productivity in the photic zone (Cd, Cu, Fe, Mo, Se, Zn) and denitrifying bacterial respiration in the bottom water (Cr, V, and rare-earth elements). We interpret the absence of any enrichment in Cu, Cd, Se, Mo, and Zn above that provided by accumulating organic matter to preclude the establishment of sulfate reduction in the water column.

INTRODUCTION

The geochemistry of sedimentary formations composed of the four units organic-carbon-enriched mudstone, limestone and dolomite, chert and porcellanite, and phosphorite have been widely studied because of (1) their oil-source and reservoir potential (Waples, 1983), (2) their source of phosphate for fertilizers, and (3) the information that their geochemistry might shed on paleoceanography. For example, Cook and Shergold (1986) and Donnelley and others (1988) suggested that this suite of rocks accumulates during times of oceanic anoxia (seawater sulfate reduction), a seawater chemistry that may contribute to the preservation of organic matter in marine sediment and, ultimately, to the formation

of major oil deposits (Demaison and Moore, 1980; Jenkyns, 1980; Schlanger and others, 1987).

The Miocene Monterey Formation in southern California, which is both a source rock and a reservoir rock for oil, consists of these four units (Bramlette, 1946; Pisciotto and Garrison, 1981; Isaacs and others, 1983) and has been interpreted as accumulating in an environment of intermittently high primary productivity in the photic zone of the water column (Blueford and Isaacs, 1989) and under anoxic conditions in the bottom water (Bramlette, 1946; Govean and Garrison, 1981). This interpretation was based largely on the occurrence of finely laminated porcellanite and diatomite units in both the lower and upper parts of the formation and on the exceptionally high organic-matter contents.

In this study, we examine the chemical composition (major-element oxides, organic carbon, and minor elements) of the Monterey Formation. The aim of our research is to establish criteria, based on minor-element contents, for (1) defining the approximate primary productivity in the seawater photic zone and (2) identifying the redox conditions of the bottom water at the time of deposition, as opposed to the redox conditions of the sediment pore water during early diagenesis. Basically, we attempt to determine the source phases of minor elements at the time of their deposition, as opposed to their current host phases in the rocks. These criteria may be applicable to other sedimentary formations. The success of determining the seawater chemistry of deposition from the current minor-element contents of a formation, however, depends largely on the degree to which the marine fraction of minor elements is diluted by the detrital fraction and on the extent to which this marine fraction was retained in the sediment during early diagenesis, lithification, and deep burial, at one extreme, and subaerial weathering, at the other extreme. In the Monterey Formation, the rocks consist of a large fraction of marine mineral components, suggesting that the marine minor-element signal may not be masked by terrigenous debris or erased by postdepositional events. That is, the minor-element contents of this formation might be interpretable in terms of the environment of deposition, specifically the seawater chemistry.

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ANALYTICAL PROCEDURES

A total of 22 samples were analyzed, representing splits of rock samples distributed for the Cooperative Monterey Organic Geochemistry Study. Of these samples, 13 (KG-1 through KG-13, tables 1, 2) are from the Naples Beach section of the Miocene Santa Barbara-Ventura Basin, including 9 samples from the Monterey Formation and 2 samples from each of the overlying Sisquoc Formation and the underlying Rincon Shale; the other samples are from stratigraphically equivalent strata of the Lions Head section in the Santa Maria Basin (fig. 1). Although we refer to these samples collectively, we note that they come from two separate basins. Detailed descriptions of individual samples and of the regional geologic setting of the two basins were given by Isaacs and others (1992).

Analyses of major elements, reported as oxides (table 1) and referred to subsequently as such, and of minor elements (table 2) were performed by three separate laboratories: the U.S. Geological Survey laboratories in Menlo Park, Calif., and Denver, Colo., and the X-Ray Assay Laboratory in Don Mills, Ontario, Canada (M, D, and X, respectively, tables 1-3). The methods used were X-ray-fluorescence (XRF) spectroscopy, inductively coupled plasma (ICP) spectroscopy, and instrumental neutron-activation analysis (NAA). Although details of these methods vary between the laboratories, the basic techniques are quite similar in all three laboratories, and all use internationally accepted rock standards for calibration. Complete descriptions of the procedures used at laboratories D and M were given by Baedeker (1987).

Agreement between the different techniques used at the three laboratories for major-element-oxide analyses is excellent (table 3); for example, for Fe, the agreement is within 3 percent (fig. 2A), and correlation coefficients are greater than 0.985. Correlation coefficients for 93 of the 101 pairs of analyses exceed 0.98. We elected to use the XRF analyses for major-element oxides (tables 1-3) from laboratory D (analyses D-XRF, fig. 2A).

Rather than discuss the precision and accuracy for each minor element, we use the data for Cr (fig. 2B) and Ba (fig. 2C) to establish the confidence level of the minor-element analyses and to identify possible analytical problems. Our reasons for selecting Cr are that we have four analyses of each sample and Cr is an element that we discuss below in some detail. The X-NAA and X-ICP analyses agree closely about the 1-to-1 line. The D-ICP analyses are uniformly higher than the X-NAA and X-ICP analyses, but they otherwise correlate strongly with both sets of analyses; that is, they have a high precision (table 4). This variation

likely results from a systematic bias, rather than from a failure of the analytical methods in either laboratory, given the excellent agreement between the X-NAA and X-ICP analyses. Still, the disagreement is not insignificant and needs to be resolved. The deviation of the X-XRF analyses from both the X-ICP and X-NAA analyses cannot be explained in this way because all three analyses are from the same laboratory. The agreement between the ICP and NAA analyses suggests that both methods give superior results for Cr. The XRF analyses for other minor elements may be equally reliable, or even superior, to the NAA and ICP analyses; we simply have not examined the XRF technique thoroughly.

Incomplete dissolution of minor minerals, such as rutile and sphene, can introduce serious analytical errors into the ICP analyses (Gromet and others, 1984; Sholkovitz, 1990). These minerals are extremely difficult to dissolve with the acids used in conjunction with the ICP procedure. This condition may have greatly affected the ICP analyses for Ba in this study (fig. 2C). In sample KG-24 (table 2), the Ba content is 2,500 ppm by NAA and only 61 ppm by ICP analysis; the difference corresponds to a possible barite content of about 0.40 weight percent, a mineral that also is highly insoluble.

This problem might have biased the rare-earth-element (REE) analyses, as well as the Ba analyses. Marine barite is known to have exceptionally high REE contents (Guichard and others, 1979). For example, in sample KG-24, the La content by ICP analysis is 7.2 ppm (31 percent) lower than by NAA analysis (table 2). If this discrepancy is a result of incomplete dissolution of barite in the ICP procedure, then the barite in this sample also has extremely high REE contents. As discussed below, the REE pattern of sample KG-24 lends some support to this interpretation. The Ba contents of other samples are much less than that of sample KG-24, and although there is a disagreement between the NAA and ICP analyses for Ba, for La the two procedures show no consistent differences (table 2).

Therefore, we elected to use the X-NAA analyses because this technique measures the bulk concentration of an element without resorting to chemical pretreatment, similar to the XRF technique. For those minor elements not measured by NAA, we used the X-ICP analyses. Agreement between the X-ICP and D-ICP analyses for these minor elements, an agreement not seen in the Ba analyses (fig. 2C), supports the interpretation that the data are not biased by incomplete dissolution of barite or other weakly soluble minerals.

REVIEW: ELEMENTAL SOURCES— THE MODERN OCEAN

Marine sediment is a complex mixture of detrital debris and seawater-derived material (Goldberg, 1963a). The

Table 1. Major-element-oxide contents in the Monterey Formation.

[All values in weight percent. LOI, loss on ignition; TOC, total organic carbon; dashes, not analyzed. Laboratories: D, U.S. Geological Survey, Denver, Colo.; M, U.S. Geological Survey, Menlo Park, Calif.; X, X-Ray Assay Laboratory, Don Mills, Ontario, Canada. TOC and sulfur were determined in laboratories identified only by number (#). Methods: ICP, inductively coupled plasma spectroscopy; NAA, instrumental neutron-activation analysis; XRF, X-ray-fluorescence spectroscopy]

Sample (fig. 1)	KG-1	KG-2	KG-3	KG-4	KG-5	KG-6	KG-7	KG-8	KG-9	KG-10	KG-11	KG-12	KG-13	KG-14	KG-15	KG-16	KG-17	KG-18	KG-19	KG-20	KG-22	KG-24
SiO ₂ —X-XRF	29.4	45.7	40.2	60.8	50.5	67.5	51.9	47.2	39.9	57.6	64.6	66.4	56.2	58.1	33.5	43.2	24.2	3.69	58.2	38.2	40.5	54.5
SiO ₂ —D-XRF	28.4	45.1	39.9	57.6	50.3	66.9	51.0	46.9	39.5	57.3	64.0	64.5	55.5	57.1	32.6	42.5	23.8	3.61	57.8	39.6	54.0	54.0
SiO ₂ —M-XRF	28.2	45.7	40.3	57.7	50.4	67.8	50.9	47.0	39.8	57.7	65.1	65.4	55.9	57.6	32.7	43.0	23.0	3.13	58.5	40.1	54.5	54.5
Al ₂ O ₃ —X-ICP	6.44	6.75	12.30	6.88	11.64	8.62	9.81	12.45	5.56	3.44	10.15	8.94	11.30	7.27	4.69	3.85	3.67	3.57	12.66	4.70	7.99	7.99
Al ₂ O ₃ —X-XRF	6.81	11.9	10.6	7.08	12.0	9.23	11.6	12.45	5.80	3.51	10.16	9.65	11.1	7.37	4.63	3.75	3.75	4.0	12.5	4.67	8.22	8.22
Al ₂ O ₃ —D-XRF	5.70	6.26	11.5	9.94	6.50	11.6	8.81	11.0	5.44	3.28	10.2	9.14	10.7	6.98	4.41	3.52	3.51	3.7	12.1	4.33	4.76	4.76
Al ₂ O ₃ —M-XRF	6.0	6.5	11.8	10.0	6.7	11.7	8.9	11.2	5.7	3.4	10.2	9.2	10.7	7.2	4.6	3.5	3.5	4.1	12.3	4.6	4.9	4.9
Fe ₂ O ₃ —D-ICP	6.24	6.44	11.49	9.64	6.78	11.39	8.67	10.73	12.64	5.93	10.17	9.01	10.73	7.37	4.81	3.70	3.93	4.2	11.75	4.69	7.37	7.37
Fe ₂ O ₃ —D-XRF	2.33	2.33	3.35	2.53	4.17	2.73	4.13	5.39	2.27	1.30	3.76	3.12	3.95	2.56	1.74	1.66	2.93	1.6	6.13	2.00	3.46	3.46
Fe ₂ O ₃ —M-XRF	2.12	2.17	4.72	3.07	2.26	3.89	2.53	4.02	5.26	2.27	1.30	3.99	3.27	3.85	2.50	2.44	1.3	6.02	1.66	3.39	3.39	
Fe ₂ O ₃ —X-ICP	2.14	2.23	5.36	3.33	2.37	4.10	2.57	3.87	5.02	1.96	1.17	1.64	1.41	2.45	2.20	2.12	9.53	53	12.20	20.90	2.64	2.64
Fe ₂ O ₃ —X-XRF	1.47	2.89	1.46	1.74	1.69	1.09	1.75	3.56	2.00	1.17	1.65	1.44	2.45	2.20	2.12	9.53	53	12.20	20.90	2.64	2.64	
MgO—D-XRF	9.4	1.32	2.80	1.40	1.11	1.64	1.07	1.70	3.52	1.87	1.07	1.64	1.41	2.43	2.12	9.53	53	12.20	20.90	2.64	2.64	
MgO—M-XRF	8.5	1.2	2.8	1.4	1.0	1.6	1.1	1.7	3.5	1.8	1.0	1.6	1.4	2.3	2.0	9.4	0.45	11.4	2.5	1.8	6.5	6.5
MgO—X-XRF	9.6	1.28	2.72	1.33	1.14	1.59	1.04	1.62	3.38	1.91	1.11	1.62	1.38	2.34	2.16	9.02	5.5	11.26	17.08	2.47	1.89	6.6
Na ₂ O—D-ICP	1.62	1.48	1.35	1.75	1.62	2.16	2.02	2.16	1.62	1.27	9.3	2.02	1.75	2.89	1.35	4.2	4.7	6.3	2.23	2.25	5.1	9.4
Na ₂ O—M-XRF	1.62	1.48	1.35	1.75	1.62	2.16	2.02	2.16	1.62	1.27	9.3	2.02	1.75	2.89	1.35	4.2	4.7	6.3	2.23	2.25	5.1	9.4
Na ₂ O—X-XRF	2.00	1.82	1.62	1.97	1.98	2.51	2.08	2.36	1.85	1.48	1.12	2.22	1.86	2.00	1.48	6.7	5.0	8.2	2.3	2.25	7.7	9.8
NiO—X-XRF	1.30	1.57	1.86	1.54	2.28	2.21	2.42	1.75	1.16	1.05	2.37	1.93	1.96	1.51	1.46	5.0	5.0	8.2	10	2.23	5.7	10.5
NiO—D-XRF	1.45	1.45	1.81	1.73	2.14	1.89	2.18	1.65	1.17	0.86	2.06	1.75	1.80	1.35	1.42	4.0	5.8	<15	1.97	4.7	9.2	9.2
NiO—M-XRF	1.6	1.5	1.4	1.9	2.3	2.1	2.3	1.8	1.5	1.0	2.2	1.9	1.9	1.9	1.5	2	2.1	5	2	2.1	5	1.0
NiO—X-XRF	1.94	1.75	1.63	1.94	2.06	2.33	2.08	2.36	1.87	1.51	1.13	2.28	1.90	2.00	1.62	5.3	5.7	8.0	0.8	2.08	6.2	9.7
K ₂ O—D-ICP	1.46	1.18	2.53	1.75	1.24	2.05	1.78	2.00	2.72	1.35	1.63	1.39	2.41	1.34	1.19	9.9	7.6	1.2	2.29	9.3	2.17	2.17
K ₂ O—M-XRF	1.08	2.49	1.93	1.32	2.18	1.89	2.20	2.83	1.32	0.77	1.75	1.53	2.43	1.40	1.29	1.02	6.4	0.7	2.35	9.8	2.30	2.30
K ₂ O—X-XRF	1.07	0.96	2.33	1.66	1.14	1.98	1.75	1.97	2.63	1.23	1.59	1.37	2.28	1.29	1.13	9.1	6.5	0.5	2.19	8.6	2.09	2.09
P ₂ O ₅ —D-ICP	1.24	1.08	2.38	1.74	1.14	2.02	1.76	1.98	2.68	1.28	1.58	1.38	2.30	1.30	1.18	9.2	7.6	0.4	2.18	8.8	2.12	2.12
P ₂ O ₅ —M-XRF	1.55	1.20	2.46	1.71	1.30	2.06	1.81	2.02	2.81	1.51	1.66	1.42	2.41	1.45	1.35	1.01	8.7	0.8	2.18	9.8	2.04	2.04
P ₂ O ₅ —X-XRF	2.29	3.55	3.02	9.2	7.6	7.3	3.0	9.9	1.70	4.4	2.1	4.1	2.7	4.4	4.4	9.2	3.60	1.8	2.5	5.7	1.81	1.70
P ₂ O ₅ —D-XRF	3.22	2.47	8.1	6.2	6.0	7.2	3.2	8.2	1.37	3.7	1.8	3.3	2.5	3.3	4.2	9.1	3.12	1.9	2.6	4.8	1.67	1.41
P ₂ O ₅ —M-XRF	2.37	3.70	3.04	9.7	7.8	7.2	3.2	10.0	1.71	4.3	2.2	4.1	2.8	4.1	5.1	10.6	3.76	2.1	2.8	6.0	1.98	1.74
P ₂ O ₅ —X-XRF	3.24	4.36	3.84	9.8	7.0	6.8	2.8	9.6	2.60	3.6	1.8	3.8	2.6	3.6	4.4	9.6	4.72	1.6	2.2	5.6	2.96	1.72
P ₂ O ₅ —D-ICP	2.61	3.87	3.09	9.9	8.5	7.3	3.2	10.1	1.74	4.6	2.3	4.4	3.0	4.1	5.5	11.7	4.03	2.5	3.2	6.2	2.18	1.76
P ₂ O ₅ —M-XRF	2.8	3.3	6.3	5.3	3.7	6.0	4.5	5.8	7.0	2.8	1.7	5.2	4.7	5.5	3.3	2.3	2.3	1.7	0.2	5.7	2.7	4.7
P ₂ O ₅ —X-XRF	3.4	6.1	4.6	6.1	4.6	6.0	7.0	2.9	1.5	1.5	5.2	5.2	5.2	5.5	3.4	2.4	2.5	1.9	0.3	6.5	2.7	5.1
TiO ₂ —D-XRF	2.5	3.1	5.9	5.0	3.2	5.8	4.3	5.7	7.0	2.7	1.8	4.8	4.4	5.3	3.2	2.1	1.6	<0.2	6.3	2.4	4.6	4.6
TiO ₂ —M-XRF	2.6	3.4	6.2	5.4	3.4	6.2	4.8	6.0	7.2	2.8	1.8	5.2	4.8	5.4	3.4	2.4	2.2	1.8	0.2	6.6	2.6	5.0
TiO ₂ —D-ICP	2.5	2.8	5.5	4.3	3.2	5.2	3.8	5.0	6.3	2.7	1.5	4.5	4.0	4.5	2.5	2.2	2.0	1.5	0.1	4.8	2.2	4.0
MnO—X-XRF	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
MnO—D-XRF	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
MnO—M-XRF	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
LOI	39.1	20.5	35.9	13.8	21.7	13.2	21.4	17.4	25.6	18.5	12.2	14.5	13.4	15.1	28.9	23.0	30.5	43.8	12.7	25.3	25.1	25.1
LOI	34.3	39.1	20.6	36.3	20.1	22.4	14.1	22.4	17.3	26.2	19.0	13.2	16.1	13.5	15.6	28.6	23.1	31.2	44.7	12.7	23.7	25.2
LOI	33.8	38.4	20.0	35.9	22.2	19.0	13.9	22.4	16.7	25.9	18.3	12.7	15.7	11.6	14.6	28.9	21.0	30.9	46.6	12.3	23.2	24.8
Total—X-XRF	99.88	100.20	100.46	98.20	99.92	99.55	100.12	100.28	99.29	100.25	99.44	100.83	99.51	99.79	98.69	98.96	98.05	99.12	100.52	99.70	100.27	100.27
TOC—#26	10.02	15.90	6.51	16.40	3.33	3.97	5.79	4.12	4.15	2.57	8.9	8.9	2.35	3.92	5.60	6.85	9.0	9.3	4.29	6.56	14.80	14.80
TOC—#15	9.61	15.71	6.16	16.25	3.04	5.31	3.72	5.82	3.94	3.88	2.40	8.7	8.6	2.22	3.71	5.12	6.63	7.2	2.17	3.99	6.44	14.77
TOC—#36	10.26	16.81	6.65	17.28	3.30	4.90	4.03	5.81	4.19	4.15	2.57	—	9.1	2.30	3.78	5.67	8.0	7.3	4.12	6.57	14.82	14.82
S—#15	2.47	3.05	1.86	3.06	1.23	1.76	1.31	1.30	0.98	0.59	4.1	5.6	3.61	1.29	2.35	3.01	1.17	1.15	3.54	3.54	7.32	7.32

Table 2. Minor-element contents in the Monterey Formation.

[All values in parts per million. Dash, not analyzed. Laboratories: D, U.S. Geological Survey, Denver, Colo.; X, X-Ray Assay Laboratory, Don Mills, Ontario, Canada. Methods: ICP, inductively coupled plasma spectroscopy; NAA, instrumental neutron-activation analysis; XRF, X-ray-fluorescence spectroscopy]

Sample (fig. 1)	KG-1	KG-2	KG-3	KG-4	KG-5	KG-6	KG-7	KG-8	KG-9	KG-10	KG-11	KG-12	KG-13	KG-14	KG-15	KG-16	KG-17	KG-18	KG-19	KG-20	KG-22	KG-24
Ag	1.4	2.4	1.0	0.9	0.4	0.6	1.1	0.5	1.0	0.6	0.4	0.6	0.7	1.1	1.3	1.5	0.3	0.4	1.0	1.4	4.2	
As	12	12	22	5	9	7	8	13	10	6	7	6	6	7	10	12	2	<2	20	9	24	
Ba	1,000	1,100	500	400	500	500	700	500	400	200	400	400	500	400	500	400	400	100	400	400	2,500	
Ba	654	246	383	401	326	326	504	369	356	168	422	320	404	304	301	280	275	103	329	253	61	
Ba	80	52	86	42	358	109	309	66	441	199	297	323	49	343	270	132	369	143	88	119	22	
Be	4.7	4.7	5.4	3.9	5.2	3.6	4.7	5.4	4.5	3.1	4.1	2.9	4.2	3.2	3.8	4.1	3.3	2.8	4.1	2.9	4.1	
Be	73	100	13	78	54	55	41	15	28	19	26	25	7	7	6	8	6	6	7	7	5	
Cd	8	8	32	3	3	5	8	1	11	7	2	1	3	8	16	6	<1	<1	1	3	22	
Cd	8	8	28	3	3	4	8	<2	12	8	<2	<2	3	8	16	6	<1	<2	1	4	19	
Ce	18	19	37	28	44	35	40	42	18	10	33	28	32	19	20	11	13	<4	32	15	21	
Ce	20	22	39	29	49	39	50	43	18	11	38	27	37	21	25	16	12	<3	16	16	27	
Co	7	9	12	11	7	8	12	14	8	5	7	7	11	7	6	5	4	1	14	5	11	
Co	5	5	11	7	5	6	8	13	5	3	5	7	8	6	4	4	3	<1	12	3	9	
Co	7	7	13	9	10	7	11	15	9	6	8	7	11	8	6	6	5	1	14	6	12	
Cr	320	200	200	90	140	77	170	250	130	77	99	83	140	160	130	140	47	21	240	130	440	
Cr	209	315	215	292	89	137	104	145	232	102	65	74	69	115	128	117	144	38	16	208	116	
Cr	369	231	398	112	174	143	203	282	111	68	122	171	143	205	176	132	26	<10	271	117	519	
Cr	309	428	264	410	120	173	138	196	333	155	112	104	143	178	177	195	57	24	268	173	570	
Cs	3	6	4	4	5	5	4	8	3	3	3	3	4	3	2	1	2	<1	5	1	3	
Cs	85.4	91.1	47.0	31.5	52.9	35.9	55.3	39.0	33.6	21.7	17.3	16.3	32.8	38.3	46.4	58.8	14.4	13.6	48.9	53.7	176.0	
Cu	93	98	47	116	33	37	56	40	35	21	18	16	32	40	53	60	13	10	47	57	177	
Cu	4	4	5	7	8	6	7	8	8	2	8	4	8	7	5	5	3	<2	1.1	6	11	
Ga	8	8	16	13	9	11	14	17	8	5	12	11	14	9	8	5	5	6	4	6	11	
Hf	1.5	1.5	2.5	1.3	3.1	2.6	2.9	2.6	1.6	9	3.3	2.3	3.4	2.1	1.3	1.5	1.3	<5	2.9	1.8	2.2	
Hf	13.9	15.8	23.6	16.5	27.8	23.3	25.9	28.0	12.0	7.2	18.6	15.4	2.6	12.9	14.9	12.0	7.8	1.5	19.9	17.0	23.2	
La	16	17	25	18	27	22	24	31	14	9	19	16	20	14	16	14	9	<2	20	18	16	
La	16	20	52	34	19	39	22	40	9	6	31	29	14	16	8	9	5	2	31	13	19	
Li	17	21	22	20	38	22	34	48	14	7	31	29	10	20	12	9	7	<2	25	10	19	
Lu	14	22	25	17	29	27	30	36	23	12	20	17	30	20	20	19	24	12	<0.5	3.6	33	
Lu	40	17	33	26	8	15	12	19	8	13	5	5	8	24	21	17	17	<5	5	7	78	
Mo	47	26	49	13	20	18	20	7	16	10	4	3	10	28	27	22	5	4	6	8	88	
Mo	58	31	55	41	16	25	20	27	11	22	17	6	5	11	32	33	26	9	5	6	14	
Mo	9	11	18	13	20	17	21	20	9	5	15	12	17	11	12	12	5	<5	16	14	16	
Nd	11	12	20	13	23	19	20	24	9	5	18	14	18	11	12	10	5	5	18	12	12	
Nd	156	240	114	261	94	80	129	116	91	56	38	40	74	89	87	135	18	116	106	331	331	
Ni	197	283	127	271	105	97	152	132	121	78	49	49	92	123	125	178	37	19	143	148	373	
Ni	50	50	80	50	80	70	60	100	40	<20	40	50	80	40	30	20	20	20	70	20	60	
Rb	3.0	8.0	1.4	3.6	3.9	2.7	5.3	1.5	2.3	1.3	1.0	0.8	2.2	3.1	5.1	8.2	8	6	4.3	3.4	12.0	
Rb	4.5	6.4	12.2	9.1	6.3	9.5	7.8	10.5	15.6	8.1	4.7	9.5	8.9	12.1	7.5	4.9	5.1	4.2	4	15.3	5.7	
Rb	4.3	6.1	12.6	8.9	6.2	9.0	9.3	13.8	7.0	4.2	9.1	8.5	10.8	6.7	3.8	4.8	3.3	<5	12.8	4.7	9.4	
Sc	5	7	13	9	7	10	8	11	16	5	10	9	12	8	5	5	4	<2	14	6	10	
Sc	24	35	13	45	6	9	13	5	6	3	<3	<3	5	13	17	20	<3	<3	16	18	56	
Sm	2.0	2.3	3.5	2.2	3.9	3.2	3.8	4.0	1.9	1.1	2.8	2.3	3.5	2.1	2.2	2.0	1.1	1.1	3.4	2.6	3.6	
Sm	772	605	385	231	333	245	128	209	311	451	157	120	194	251	154	512	248	176	118	421	161	
Sm	947	708	423	257	388	277	149	246	367	572	181	137	214	301	203	594	338	245	129	519	172	
Th	4.1	4.4	6.7	4.7	8.8	6.9	8.9	7.8	3.3	2.1	5.9	4.7	5.8	3.7	4.2	1.9	2	<5	6.2	2.3	4.3	
Th	12.3	15.6	22.5	22.4	8.4	12.3	13.7	16.9	14.3	7.1	3.9	3.4	4.5	4.9	14.1	13.5	4.1	1.8	5.3	9.2	23	
U	204	357	180	417	156	253	213	260	130	113	95	90	161	262	290	278	56	40	278	93	563	
U	212	370	172	407	157	248	214	264	138	199	126	95	91	159	274	340	290	70	49	280	109	
V	15.9	22.5	25.6	27.9	12.8	19.7	16.3	30.9	13.7	7.9	12.6	10.3	18.6	13.4	13.0	20.1	6.3	1.8	22.0	27.3	35.6	
Y	19	26	28	14	22	19	21	37	17	9	14	11	20	15	16	23	7	<2	25	34	42	
Y	1.0	1.5	1.8	2.1	1.9	1.6	1.9	2.2	1.6	7	1.2	1.0	2.0	1.2	1.2	1.6	0.6	<2	2.3	2.1	2.9	
Zr	40.7	39.1	50.0	28.7	75.9	29.0	47.0	53.5	59.9	78.9	41.4	38.5	44.7	25.7	78.6	19.4	51.3	12.0	45.2	81.0	39.2	
Zr	170	240	190	280	90	100	130	160	130	70	60	40	100	90	190	180	60	<40	170	230	460	
Zr	181	267	237	313	85.3	157	101	152	173	117	70	77.1	112	116	161	163	38.9	26.3	164	181	451	
Zr	196	281	222	304	144	103	153	175	135	78	71	65	108	134	191	186	30	14	156	218	434	

Laboratory-
method

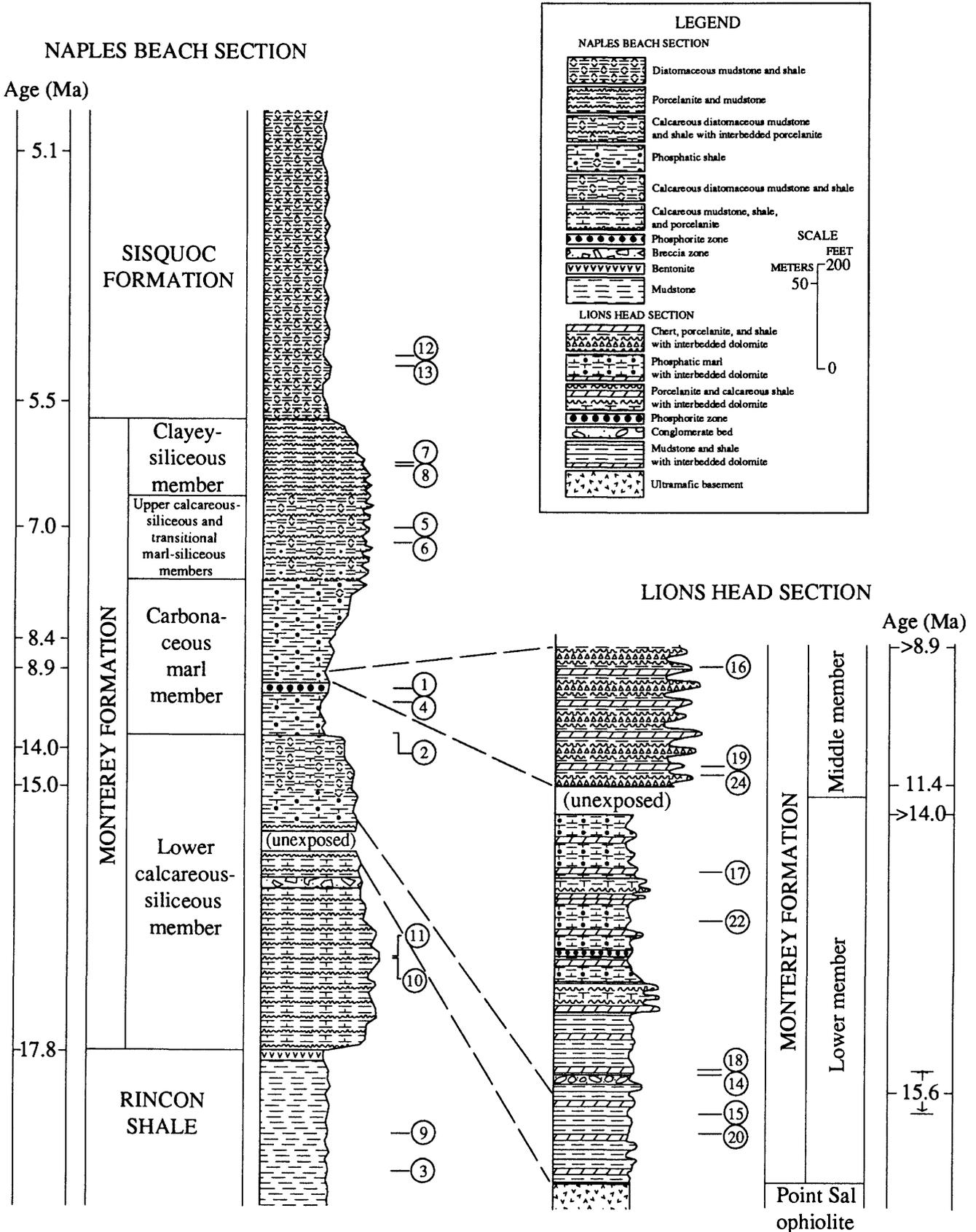


Figure 1. Stratigraphic sections of the Monterey Formation at Naples Beach (Santa Barbara-Ventura Basin) and Lions Head (Santa Maria Basin), Calif., showing locations of samples. Ages compiled from Arends and Blake (1986), Barron (1986), and DePaolo and Finger (1991). Stratigraphic positions revised from Isaacs and others (1992); Point Sal ophiolite from Hopson and Frano (1977).

detrital fraction consists mostly of terrigenous Al silicates and quartz, introduced into the oceans by way of riverine and eolian transport, and marine volcanoclastic debris. The seawater-derived marine fraction is predominantly inorganic

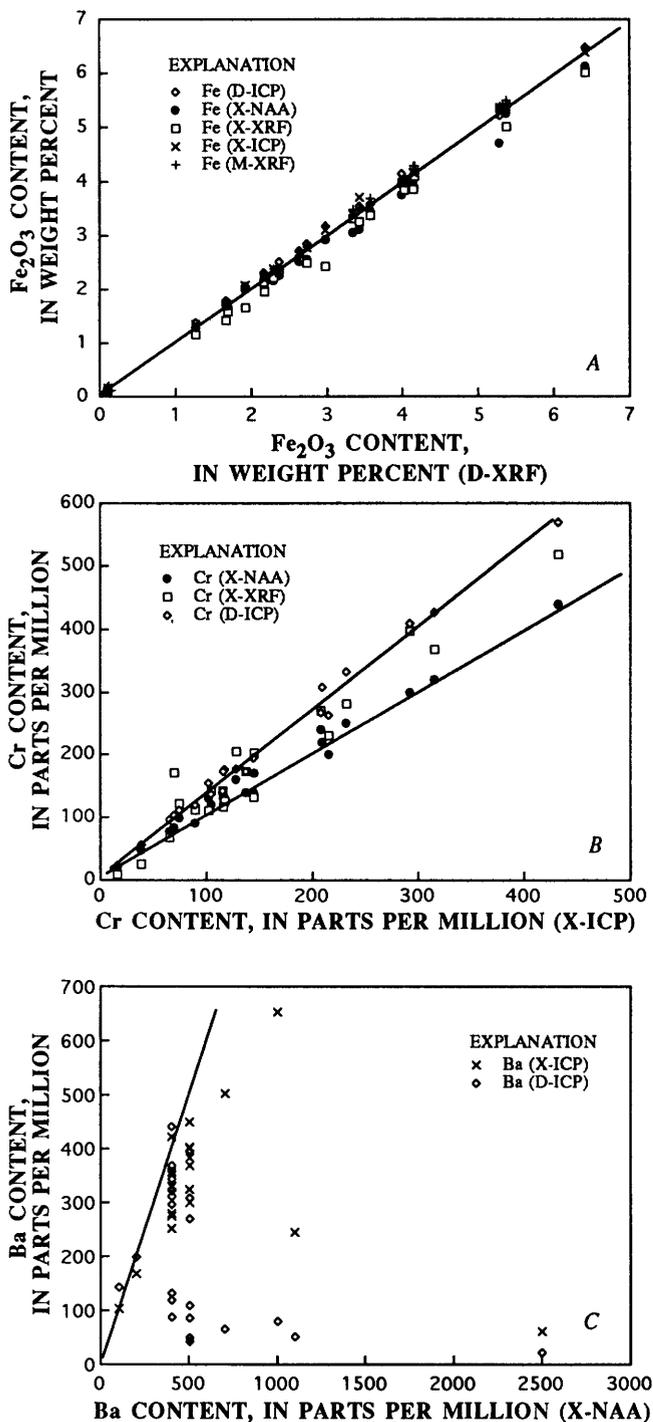


Figure 2. Intraelement ratios for Fe₂O₃ (A), Cr (B), and Ba (C). Analyses are identified by laboratory (D, U.S. Geological Survey, Denver, Colo.; M, U.S. Geological Survey, Menlo Park Calif.; X, X-Ray Assay Laboratory, Don Mills, Ontario, Canada) and method (ICP, inductively coupled plasma spectroscopy; NAA, instrumental neutron-activation analysis; XRF, X-ray-fluorescence spectroscopy).

precipitates and adsorbates (hydrogenous fraction) and CaCO₃, opal, and organic debris (biogenic fraction). The distribution and abundance of the detrital and marine fractions, their composition and rates of accumulation, and their alteration products vary widely within the oceans. Geochemists have used the complex distributions and major-element-oxide and minor-element compositions of these fractions to identify the past record of such phenomena as eolian transport of terrigenous material, biologic productivity in the photic zone, hydrothermal activity along midoceanic ridges, and sediment diagenesis as it might relate to metallogenesis.

An evaluation of the geochemistry of ancient depositional environments for marine sedimentary rocks must be based on the major-element-oxide and minor-element compositions of their marine fractions alone. For major-element oxides, the marine signal is commonly masked by the detrital fraction, even in sediment for which the accumulation rate of detrital debris is low. In modern sediment from the central Pacific Ocean, where the accumulation rate is as low as 0.1 mg/cm² per year, the ratio of the marine to detrital fraction of Fe is approximately 0.05 to 0.10 (Piper, 1988), ferromanganese nodules aside. By contrast, this ratio is as high as 2 to 10 for many minor elements in pelagic sediment (Chester and Hughes, 1967; Fischer and others, 1986; Piper, 1988). In sediment from ocean-margin areas, however, where accumulation rates are as much as 10⁵ times higher, the marine fraction of minor elements also can be masked by the detrital fraction, making identification of the marine fraction uncertain, if not impossible.

Two procedures are commonly used to partition minor elements among the different sedimentary fractions. One procedure uses a chemical leaching procedure (Chester and Hughes, 1967; Bruland and others, 1974; Bowser and others, 1979; Lyle and others, 1984; Tessier and others, 1984; Boust and others, 1988); the other involves modeling the sediment on the basis of end-member compositions of the major fractions (Leinen, 1977; Isaacs, 1980; Dymond, 1981; Calvert and Price, 1983; Isaacs and others, 1983; Medrano and Piper, 1992)—a stoichiometric approach—or on the basis of factor analysis or other similar statistical approaches.

Both the leaching and modeling procedures are not without problems. For the leaching procedure, sample treatment can introduce a bias (Belzile and others, 1989; Sholkovitz, 1990; Tessier and Campbell, 1991; Piper and Wandless, 1992). Among the problems are incomplete isolation of a fraction at any single step of the procedure, which then imposes an operational rather than genetic interpretation on the origin of the varyingly soluble fractions. For the modeling procedure, a major uncertainty can be introduced by selecting a single end-member composition for each of the different fractions (Leinen and Piasias, 1984). Multiple and varying detrital sources (Böstrom and others, 1969; Calvert, 1990), as well as marine sources, can impart a complex chemistry to both the detrital and marine fractions.

Despite these and other problems, both procedures have been used with some success (Chester and Hughes, 1967; Bruland and others, 1974; Dymond, 1981; Isaacs and others, 1983; Leinen and Piasias, 1984; Tessier and others, 1984; Piper, 1988; Belzile and others, 1989; Calvert, 1990). We use a modeling procedure in this study, although the leaching procedure might be the only way to collect information about the marine fraction of the several minor elements whose bulk contents are strongly dominated by the detrital contribution.

DETRITAL SOURCE

Studies using a stoichiometric, or normative, scheme to evaluate the detrital input of elements to the marine environment typically use Al_2O_3 to estimate the abundance of the detrital fraction (Isaacs, 1980; Dymond, 1981; Leinen and Piasias, 1984; Medrano and Piper, 1992). Implicit in the calculations is the assumption that the sum of the components of the detrital fraction (quartz, feldspar, clay minerals, and other Al silicate minerals) has a constant major-element-oxide and minor-element content (table 5), that is, that the interelemental ratios with Al_2O_3 are constant between samples, which is clearly a more reasonable assumption for any single formation than it is for formations separated both temporally and areally.

The detrital contribution of SiO_2 , P_2O_5 , MgO , and CaO to each sample is calculated on the basis of their ratios to Al_2O_3 in a standard. The standard most often referenced is the World Shale Average (WSA; Wedepohl, 1969–78). The major-element-oxide contents in excess of the detrital contribution then give the amounts of biogenic silica, apatite, dolomite, and calcite (also adjusted for CaO content in apatite and dolomite) by using appropriate stoichiometric factors. The determination of organic-carbon content gives the abundance of organic matter present (table 6). The $\text{K}_2\text{O}:\text{Al}_2\text{O}_3$ and $\text{TiO}_2:\text{Al}_2\text{O}_3$ ratios can evaluate the degree to which the selected composition of WSA is representative of the detrital fraction because K_2O and TiO_2 , along with Al_2O_3 , occur virtually totally in the detrital fraction of many, though certainly not all, sedimentary rocks.

The same procedure determines the contribution of minor elements by the detrital fraction. That is, minor-element:detritus ratios are assumed to be constant and similar to those in the WSA, or another, standard. In this study, we used the REE contents of the North American Shale Composite (NASC; Gromet and others, 1984), except for Ce. The contents of other minor elements in detritus (table 5) are from Wedepohl (1969–78). Previous studies have shown that $\text{Co}:\text{Al}_2\text{O}_3$, $\text{Ga}:\text{Al}_2\text{O}_3$, $\text{Li}:\text{Al}_2\text{O}_3$, $\text{Sc}:\text{Al}_2\text{O}_3$, and $\text{Th}:\text{Al}_2\text{O}_3$ ratios may be used to evaluate this procedure for the minor elements (Piper, 1991; Dean and Arthur, 1992) because they, like K_2O and TiO_2 , are present predominantly in this fraction.

MARINE SOURCE

Within the modern open ocean, the bulk of the marine fraction of Cu, Cd, Se, Zn, and, possibly, Cr, Mo, and V accumulating in the sediment may be transported to the sea floor by organic debris, whose minor-element stoichiometry (table 5) has been estimated from field studies (Martin and Knauer, 1973; Bruland, 1983; Collier and Edmond, 1984; Brumsack, 1986). Organic matter is most important to minor-element budgets in shelf-slope environments (Collier and Edmond, 1984), which have high rates of accumulation of organic matter.

In addition to organic matter, biogenic silica and calcite contribute to the marine flux of minor elements to the sea floor. Silica may be an important carrier of Ni (Sclater and others, 1976) and Zn (Bruland, 1983), and its content of Cu, on the basis of the analyses by Martin and Knauer (1973), is slightly higher than that of Zn. Conversely, biogenic carbonate contributes little to the minor-element contents of sediment other than Sr (Palmer, 1985). If the biochemical pathways of minor elements in ancient oceans were similar to those in the modern ocean, organic debris would have provided a major flux of several minor elements to ancient marine sediment.

Many minor elements in sediment have a marine hydrogenous source, as well as a biogenic source. Under oxic seawater conditions, such elements as Fe and Mn and, less so, REE's, Co, Cu, Ni, and Zn are transported to the sea floor as hydroxides and oxides or as adsorbates on other particulates. Under sulfate-reducing conditions, Fe, Cd, Cu, and Zn precipitate as sulfides. Cr, Mo, and Se precipitate, or are adsorbed onto other particulate matter, owing to their reduction to less soluble valence states. Under intermediate redox conditions of denitrification, Cr and REE's are extracted from sea-water, either by precipitation or adsorption. The accumulation of U and V requires some special attention because their distributions in the natural environment seem to conflict with their behavior as predicted by their thermodynamic properties.

Thus, the accumulation of minor elements within the marine fraction of sediment may reflect the level of primary productivity in the photic zone, assuming a stoichiometry for the biogenic fraction of minor elements preserved in the sediment. The suite of minor elements that show an enrichment in excess of that due solely to the rain rate of organic matter onto the sea floor defines the redox conditions of bottom water under which the sediment accumulates.

BIOGENIC SOURCE

The minor-element contents of modern plankton have been measured by several researchers. Measurements vary considerably (Martin and Knauer, 1973; Collier and Edmond, 1984), owing to inconsistencies introduced during sample

Table 3. Correlation coefficients for major-element oxides in the Monterey Formation—Continued.

Laboratory-method	N ₂ O X-ICP	N ₂ O X-RRF	N ₂ O D-RRF	N ₂ O M-RRF	N ₂ O D-ICP	K ₂ O X-ICP	K ₂ O X-RRF	K ₂ O D-RRF	K ₂ O M-RRF	K ₂ O D-ICP	P ₂ O ₅ X-ICP	P ₂ O ₅ X-RRF	P ₂ O ₅ D-RRF	P ₂ O ₅ M-RRF	P ₂ O ₅ D-ICP	TiO ₂ X-ICP	TiO ₂ X-RRF	TiO ₂ D-RRF	TiO ₂ M-RRF	TiO ₂ D-ICP	LOI X-	LOI D-	LOI M-	TOC #26	TOC #15	TOC #36	
N ₂ O X-ICP	1																										
N ₂ O X-RRF	.97	1																									
N ₂ O D-RRF	.98	.98	1																								
N ₂ O M-RRF	.99	.99	.99	1																							
N ₂ O D-ICP	.67	.73	.70	.68	.67	1																					
K ₂ O X-ICP	.69	.75	.71	.68	.67	.99	1																				
K ₂ O X-RRF	.68	.74	.71	.68	.67	.99	.99	1																			
K ₂ O D-RRF	.67	.73	.71	.68	.67	.99	.99	.99	1																		
K ₂ O M-RRF	.67	.73	.71	.68	.67	.99	.99	.99	.99	1																	
K ₂ O D-ICP	.67	.72	.70	.68	.68	.99	.99	.99	.99	.99	1																
P ₂ O ₅ X-ICP	.05	-.04	.02	-.05	.03	.29	.24	.24	.27	.27	.1																
P ₂ O ₅ X-RRF	.01	-.08	-.02	-.09	-.01	.23	.18	.18	.20	.21	.1																
P ₂ O ₅ D-RRF	.02	-.06	-.01	-.08	.01	.26	.22	.21	.24	.24	.1																
P ₂ O ₅ M-RRF	.00	-.08	-.03	-.10	-.02	.26	.21	.21	.24	.25	.98	.98	1														
P ₂ O ₅ D-ICP	.00	-.09	-.03	-.10	-.02	.23	.19	.18	.21	.21	.1	.99	.99	1													
TiO ₂ X-ICP	.80	.83	.83	.79	.79	.95	.96	.95	.94	.94	.29	.23	.26	.27	.23	1											
TiO ₂ X-RRF	.81	.85	.84	.81	.80	.94	.95	.95	.94	.93	.24	.19	.22	.22	.22	.99	1										
TiO ₂ D-RRF	.79	.84	.82	.79	.78	.96	.96	.96	.96	.94	.26	.20	.23	.24	.20	.99	.99	1									
TiO ₂ M-RRF	.80	.84	.82	.80	.78	.95	.96	.96	.96	.96	.26	.20	.23	.24	.20	.99	.99	.99	1								
TiO ₂ D-ICP	.78	.81	.81	.77	.77	.95	.96	.96	.96	.95	.30	.24	.27	.28	.24	.1	.99	.99	.99	.99	1						
LOI X-	.53	.62	.56	.58	.57	.53	.55	.55	.56	.53	.28	.32	.29	.25	.31	.51	.51	.51	.51	.50	1						
LOI D-	.51	.60	.53	.54	.54	.57	.59	.60	.57	.60	.22	.28	.26	.21	.27	.53	.53	.53	.53	.52	.99	1					
LOI M-	.53	.63	.56	.56	.56	.60	.61	.62	.60	.63	.24	.26	.23	.19	.25	.56	.57	.57	.57	.55	.97	.99	1				
TOC #26	.12	.07	.11	.07	.10	.22	.23	.20	.22	.18	.64	.65	.56	.64	.64	.24	.24	.24	.24	.22	.43	.41	.37	1			
TOC #15	.09	.04	.09	.04	.07	.19	.20	.17	.19	.15	.63	.64	.56	.63	.63	.21	.21	.21	.21	.19	.48	.45	.41	1	1		
TOC #36	.11	.06	.11	.07	.10	.21	.22	.18	.21	.17	.64	.66	.57	.64	.64	.23	.22	.21	.21	.21	.44	.41	.38	1	1	1	

collection and analysis, but also to such natural factors as variations among species, geography, and growth rates (Eisler, 1983). Also, waste products (such as molts and fecal material of zooplankton), which constitute a major contribution of organic matter to the sea floor, commonly have minor-element contents significantly greater than those of plankton itself (table 7).

The distributions of Cd, Cu, Cr, Ni, Se, V, and Zn in the water column, relative to those of PO₄³⁻, NO₃⁻, and Si(OH)₄, indicate that organic detritus is the major carrier of many minor elements from seawater to the sea floor. NO₃⁻ and PO₄³⁻ are the limiting nutrients for phytoplankton productivity in 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 (Nelson and others, 1981). These nutrients are extracted from seawater in the photic zone during photosynthesis and returned to the ocean at depth by way of bacterial respiration. As much as 15 to 40 percent of the initial particulate organic matter survives to the sea floor, a function largely of sea-floor depth and primary productivity (Sarnthein and others, 1988; Baines and others, 1994). Thus, concentrations of PO₄³⁻ and NO₃⁻ in surface water are relatively low and even can closely approach zero; they increase sharply below the photic zone to the thermocline and then remain relatively constant below approximately 500-m depth.

Cd, Cu, Cr, Ni, V, and Zn all show a similar depth profile. Cd parallels PO₄³⁻ (Boyle and others, 1976), more so than other minor elements. Zn and Ni profiles resemble that of Si(OH)₄ (Sclater and others, 1976; Bruland, 1983). For Zn, the Zn:Si(OH)₄ ratio in seawater (Broecker and Peng, 1982) corresponds to a Zn content in opal of approximately 60 ppm; however, the measured content averages only 5 to 10 ppm (Martin and Knauer, 1973), much less than its bulk content in plankton of 110 ppm (table 5). Thus, the high measured content of Zn in organic detritus (Collier and Edmond, 1984) and its much lower measured content in the siliceous fraction of plankton (Martin and Knauer, 1973) indicate that it and, probably, Ni are associated dominantly with the soft parts of organisms, similar to Cd.

Se is unique among this group of elements; significant amounts exist in two valence states, with SeO₄²⁻ somewhat more abundant than SeO₃²⁻ (Measures and others, 1980). The distribution of SeO₃²⁻ approaches zero in the photic zone, similar to that of Cd. Although SeO₄²⁻ also shows a nutrient-type profile, it does not approach zero in the photic zone, similar to Si(OH)₄.

The depth profiles of nutrients and minor elements in seawater can be used to evaluate the interpretation that the average measured minor-element composition of plankton (table 8) approximates the composition of organic matter settling through the water column and onto the sea floor. For example, the concentration ratio of NO₃⁻ and PO₄³⁻,

Table 4. Correlation coefficients for selected minor elements in the Monterey Formation.

[All values rounded to nearest hundredth. Laboratories: D, U.S. Geological Survey, Denver, Colo.; X, X-Ray Assay Laboratory, Don Mills, Ontario, Canada. Methods: ICP, inductively coupled plasma spectroscopy; NAA, instrumental neutron-activation analysis; XRF, X-ray-fluorescence spectroscopy]

Laboratory-method	Ba X-NAA	Ba X-ICP	Ba D-ICP	Co X-NAA	Co X-ICP	Co D-ICP	Cr X-NAA	Cr X-ICP	Cr X-XRF	Cr D-ICP	Mo X-NAA	Mo X-ICP	Mo D-ICP	Sc X-NAA	Sc X-ICP	Sc D-ICP	Zn X-NAA	Zn X-ICP	Zn D-ICP
Ba----- X-NAA	1																		
Ba----- X-ICP	-.37	1																	
Ba----- D-ICP	-.39	.08	1																
Co----- X-NAA	.34	.51	-.30	1															
Co----- X-ICP	.29	.42	-.18	.95	1														
Co----- D-ICP	.34	.44	-.19	.96	.96	1													
Cr----- X-NAA	.80	-.08	-.49	.67	.57	.62	1												
Cr----- X-ICP	.80	-.11	-.52	.64	.55	.58	.99	1											
Cr----- X-XRF	.77	-.01	-.47	.68	.60	.61	.98	.97	1										
Cr----- D-ICP	.79	-.10	-.48	.62	.52	.56	.99	1.00	.97	1									
Mo----- X-NAA	.86	-.32	-.40	.31	.28	.34	.75	.77	.72	.75	1								
Mo----- X-ICP	.83	-.28	-.44	.31	.28	.32	.75	.78	.73	.76	.98	1							
Mo----- D-ICP	.84	-.28	-.43	.31	.27	.32	.75	.78	.72	.76	.99	1.00	1						
Sc----- X-NAA	.23	.51	-.14	.94	.96	.97	.52	.48	.54	.46	.18	.16	.15	1					
Sc----- X-ICP	.23	.54	-.16	.93	.96	.96	.53	.50	.56	.47	.21	.20	.19	.99	1				
Sc----- D-ICP	.20	.55	-.10	.93	.95	.96	.50	.46	.52	.44	.17	.15	.14	.99	.99	1			
Zn----- X-NAA	.81	-.23	-.53	.42	.32	.40	.89	.91	.83	.91	.82	.83	.83	.27	.27	.23	1		
Zn----- X-ICP	.81	-.13	-.58	.53	.44	.48	.94	.96	.91	.96	.84	.86	.86	.36	.39	.34	.97	1	
Zn----- D-NAA	.78	-.14	-.55	.48	.37	.44	.92	.94	.88	.94	.82	.84	.84	.31	.33	.29	.98	.99	1

δ -seawater[NO₃⁻] =

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

based on chemical analyses of seawater, should equal the average atomic ratio in plankton of 15:1, if only metabolic and advective processes determine their distributions in the oceans. Although there is considerable scatter in the measurements of the composition of plankton, the average N:P ratio approaches the δ -seawater value. The ratios of minor elements in plankton also should equal their δ -seawater values. This relation seems to be true for Cd, but the δ -seawater values for Cu, Cr, Ni, Se, and V are higher, and for Zn lower, than the mean element:P ratios in plankton. Boyle and others (1977) explained the distribution of Cu in the deep ocean by a combination of biologic and nonbiologic processes, whereby the nonbiologic processes involve scavenging of Cu throughout the water column by settling particles and recycling of Cu into the bottom waters from oxic pelagic sediment. These and other nonbiologic processes also might explain the high δ -seawater values for Cr, Ni, Se, and V, although their marine chemistries have not been examined as thoroughly as that of Cu. Nonetheless, the similarities of the seawater-concentration-versus-depth profiles of many minor elements to those of NO₃⁻ and PO₄³⁻ and the fact that their δ -seawater values are within a factor of 5 of the average compositional ratios of plankton (table 8), suggest that the elemental composition of plankton approximates the average composition of marine organic detritus settling into the deep ocean and, presumably, onto the sea floor.

Nonbiologic processes might influence the distributions of many minor elements in the deep ocean. Their influence can be demonstrated for Cu if we consider the similarity of its δ -seawater value based only on the uppermost 2,000 m of seawater (1.6×10^{-3}) to the Cu:P ratio in plankton (1.4×10^{-3}) and its δ -seawater value based on bottom water (3.5×10^{-3}). Thus, nonbiologic processes might contribute relatively little to the minor-element distributions in shallow-basin and continental-shelf environments along the margins of the oceans.

The distributions of REE's, Mo, and U are little influenced by the biologic cycle. Mo and U concentrations are constant with depth (Broecker and Peng, 1982; Emerson and Husted, 1991). Mo is mildly bioreactive (table 5), but its uptake by plankton in the photic zone and remineralization at depth by bacteria are simply insufficient to affect measurably its vertical distribution in the water column. REE concentrations increase continuously with depth in the ocean, an observation that has been explained in terms of nonbiologic processes (de Baar and others, 1985). Although REE contents are relatively high in handpicked biogenic siliceous tests (Elderfield and others, 1981), indicating that REE's might be incorporated into the biogenic-silica fraction, their low concentrations in bulk organic matter (table 5) suggest that the REE contents are very low in silica, possibly similar to those in biogenic calcite (Palmer, 1985).

Throughout the rest of this report, we present the content of each minor element in plankton as a single value that we consider to be best defined by average plankton, although it is unlikely to be a single value, nor is it well defined. We note that whereas the absolute content of a single minor element can vary by several orders of magnitude, the inter-element ratios vary by no more than a factor of approximately 20; therefore, we focus our attention on these ratios.

Table 5. End-member major-element-oxide and minor-element contents in sedimentary fractions of the Monterey Formation in comparison with standards.

[Major-element-oxide contents in weight percent; minor-element contents in parts per million. Dashes, not available. NASC, North American Shale Composite (Gromet and others, 1984); WSA, World Shale Average (Wedepohl, 1969–78). Values for detrital fraction of the Monterey Formation (in parentheses) represent minimums or single trends, calculated from plots of element or element oxide versus detritus; neither a minimum nor a single trend was recognized in several plots, in which case no value is listed. Contents of other minor elements in WSA and in detrital fraction (in parentheses) are as follows: Ag, — (0.5); As, 10 (10); Ba, 640 (670); Cs, 5.2 (5.4); Ga, 21 (22); Hf, 3.8 (4.0); Li, 60 (50); Sc, 13 (16); Sr, 125 (220); Th, 12 (10.5); Y, 26 (32). Data sources: Biogenic SiO₂, 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
	WSA or NASC (Monterey Formation)	Biogenic SiO ₂	Calcite	Organic matter	Apatite
Major-element oxides					
P ₂ O ₅ -----	0.16	—	—	1.74	40.7
TiO ₂ -----	.77 (0.81)	—	—	—	—
K ₂ O-----	3.2 (3.2)	—	—	—	—
CaO-----	3.09	—	56.0	—	55.5
Fe ₂ O ₃ -----	6.75 (6.33)	—	—	.050	—
Al ₂ O ₃ -----	17.1 (17.4)	—	—	—	—
SiO ₂ -----	58.4	100.0	—	—	—
Minor elements					
La-----	31.2 (31)	5.80	.128	.14	—
Ce-----	66.7 (61)	8.21	.105	.23	—
Pr-----	—	—	—	—	—
Nd-----	27.4 (24)	6.71	.106	.30	—
Sm-----	5.59 (5.3)	1.56	.019	—	—
Eu-----	1.18 (1.12)	.40	.004	—	—
Gd-----	—	1.78	.022	—	—
Tb-----	.85	—	—	—	—
Dy-----	—	1.69	.024	.01	—
Ho-----	—	—	—	—	—
Er-----	—	—	—	—	—
Tm-----	—	—	—	—	—
Yb-----	3.06 (3.0)	0.86	.015	—	—
Lu-----	.456 (0.45)	—	—	—	—
Cu-----	35.0	—	.700	11.0	—
Cd-----	.2	—	—	12.0	—
Co-----	19.0	—	—	1.0	—
Cr-----	83.0	—	—	2.0	—
Mo-----	2.6	—	—	2.0	—
Ni-----	44.0	—	—	7.5	—
Se-----	1.0	—	—	3.0	—
U-----	3.0	—	—	—	—
V-----	110	—	—	3.0	—
Zn-----	100	—	—	110.0	—

HYDROGENOUS SOURCE

Two mechanisms have been invoked by geochemists to account for the accumulation directly from seawater of minor elements in marine sediment. One mechanism involves equilibrium thermodynamics, first treated in depth by Krauskopf (1956) and Garrels and Christ (1965). The second mechanism, proposed by Goldberg (1954) to explain

the incorporation of seawater-undersaturated minor elements into the inorganic phases of pelagic sediment, promotes seawater scavenging throughout the water column by both organic and inorganic particulate matter.

The major seawater redox reactions that drive the precipitation-dissolution reactions of individual minor compounds can be written in a simplified form as follows (Froelich and others, 1979):

GEOCHEMISTRY OF MINOR ELEMENTS IN THE MONTEREY FORMATION, CALIFORNIA

Table 6. Major components in sedimentary rocks of the Monterey Formation at Naples Beach and Lions Head, Calif.

[All values in weight percent, calculated from major-element-oxide contents]

Sample (fig. 1)	Silica	Detritus	Apatite	Dolomite	Calcite	Organic matter
KG-1	3.35	31.92	5.16	1.43	37.76	15.03
KG-2	6.49	35.06	8.25	2.88	14.54	23.85
KG-3	4.85	64.40	6.30	7.01	.02	9.77
KG-4	5.11	55.66	1.54	1.40	2.60	24.60
KG-5	34.85	36.40	1.35	1.80	11.06	5.00
KG-6	9.70	64.96	.82	1.66	3.84	8.25
KG-7	36.07	49.34	.09	.46	.31	5.96
KG-8	12.50	61.60	1.53	2.24	1.27	8.69
KG-9	3.15	70.00	3.09	9.79	2.60	6.18
KG-10	20.46	30.46	.60	5.81	32.44	6.23
KG-11	45.82	18.37	.27	3.24	24.47	3.85
KG-12	28.3	57.12	.20	2.37	0	1.34
KG-13	32.51	51.18	0	1.85	0	1.34
KG-14	18.05	59.92	.16	5.72	7.58	3.53
KG-15	32.67	39.09	.68	6.17	13.02	5.88
KG-16	17.17	24.70	2.17	41.30	4.98	8.40
KG-17	30.18	19.71	8.60	.65	28.83	10.28
KG-18	11.52	19.66	.23	53.03	11.02	1.35
KG-19	2.32	2.07	.63	91.14	3.77	1.40
KG-20	15.45	67.76	.50	5.47	0	6.44
KG-22	24.45	24.25	4.34	6.36	29.30	9.84
KG-24	26.91	43.34	3.52	0	.55	22.20

Table 7. Weight ratios of minor elements (in parts per million) to Fe (in weight percent) in fecal matter, shale, and plankton.

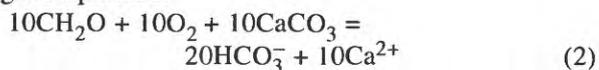
[Data on fecal matter from Fowler (1977); data on shale are for World Shale Average (WSA) from Wedepohl (1969-79) or, for rare-earth elements, for North American Shale Composite (NASC) from Gromet and others (1984). Fe contents (in weight percent): fecal matter, 2.4; WSA, 4.72; NASC, 4.43; plankton, 0.034]

	Cu	Zn	Cd	Sc	Cr	Mn	Co	Ni	Ce	Eu
Fecal material---	94	400	4.0	1.2	16	100	1.5	8.3	83	.28
Shale-----	6.8	20	.06	2.5	16	112	3.6	8.2	17	.30
Plankton-----	315	2,860	340	--	58	--	29	210	--	--

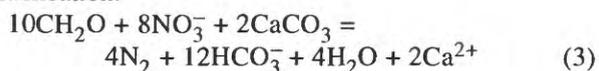
Table 8. Minor-element contents in organic matter (plankton) and seawater.

	Organic matter (ppm)	Element:P ratio (organic matter)	δ -seawater (weight ratio)	Seawater concentration at ~2,000-m depth (ppb)
Cd-----	12	1.6×10^{-3}	1.3×10^{-3}	.078
Co-----	<1	-	-	.0012
Cr-----	2.0	$.26 \times 10^{-3}$	1.6×10^{-3}	.21
Cu-----	11	1.40×10^{-3}	1.6×10^{-3}	.23
Mo-----	2	$.26 \times 10^{-3}$	-	10.60
Ni-----	7.5	1.0×10^{-3}	5.3×10^{-3}	.47
Se-----	3.0	$.40 \times 10^{-3}$	1.5×10^{-3}	.13
U-----	<1	-	-	3.00
V-----	3.0	$.39 \times 10^{-3}$	1.1×10^{-3}	1.80
Zn-----	110	14.00×10^{-3}	6.1×10^{-3}	.39
REE's (La)---	<1	-	-	.0052

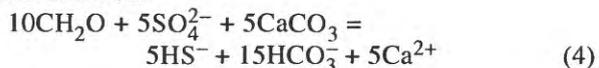
Oxygen respiration:



Denitrification:



Sulfate reduction:



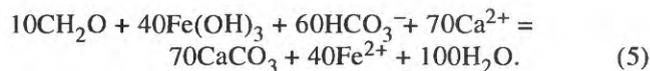
Organic matter, expressed here as CH_2O but better represented by the formula $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{15}(\text{H}_3\text{PO}_4)$ (minor elements)_{0.0X}, is the most important electron donor in the oceans, and O_2 , NO_3^- , and SO_4^{2-} are the most important electron acceptors. The hierarchy of these reactions is determined by the one 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 successively more favored electron acceptors with depth in the water column. These basins include the Golfo Dulce (Costa Rica), Baltic Sea, Black Sea, Cariaco Trench (Venezuela Shelf), and several fiords at high latitudes (Richards, 1965; Emerson and others, 1979; Jacobs and others, 1985, 1987; Emerson and Husted, 1991). 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; O_2 is present at a very low concentration at intermediate depths (Emerson and others, 1979) under conditions of denitrification, the depth interval over which NO_3^- shows a sharp decrease in concentration; and both O_2 and NO_3^- are virtually absent in the bottom water, under conditions of sulfate reduction (eq. 4), in the presence of H_2S . Sulfate reduction continues into the sediment until SO_4^{2-} is depleted in the pore water, at which depth the residual labile organic matter begins to be 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.

In contrast, the open ocean exhibits oxygen respiration virtually throughout the water column. Denitrification occurs in the oxygen-minimum zone (OMZ, fig. 3), 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 and Indian Oceans. 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 primary produc-

tivity in the photic zone such that bacterial oxidation of settling organic matter drives down the O_2 content of the water column within the OMZ to a value that promotes denitrification.

Several minor elements also serve as electron acceptors, including CrO_4^{2-} , $\text{Fe}(\text{OH})_3$, MnO_2 , MoO_4^{2-} , SeO_4^{2-} , $\text{UO}_2(\text{CO}_3)_2^{2-}$, H_2VO_4^- , and other components of seawater that might be reduced by way of oxidation of organic matter (table 9). By including the half-cell reaction for the oxidation of organic matter, as we did in equations 2 through 4, $\text{Fe}(\text{III})$ reduction can be written in the following form:



Its reduction occurs before that of sulfate (table 9) and toward the end of denitrification (Berner, 1980; Bender and others, 1989); SeO_4^{2-} and CrO_4^{2-} also are reduced under conditions of denitrification (table 9; Measures and others, 1983; Murray and others, 1983).

These minor elements contribute insignificantly to the actual oxidation of organic matter, owing to their low concentrations in seawater, but their accumulation on the sea floor, as a result of their reduction and (or) precipitation, contributes in a major way to our identification of past redox conditions in the water column. 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 fraction coprecipitates with Fe and Mn oxide phases or is scavenged by these oxides. Pelagic sediment, however, is a minor sink for many minor elements, except Mn (Lyle and others, 1984). Its high metallic-element contents reflect very low bulk-sediment-accumulation rates rather than high minor-element-accumulation rates.

Within basins that exhibit sulfate reduction in bottom waters, Fe^{2+} , Cu^+ , Cd^{2+} , and Zn^{2+} exhibit reduced concentrations in the bottom water (Brewer and Spencer, 1974; Jacobs and others, 1985, 1987), possibly owing to precipitation as sulfides; CrO_4^{2-} is reduced and precipitates as $\text{Cr}(\text{OH})_3$ (Emerson and others, 1979); and H_2VO_4^- should be reduced to V_2O_4 , or, possibly, $\text{V}(\text{OH})_3$ (Wanty and Goldhaber, 1992). Mo, Se, and U also show lower concentrations in the bottom water than in the oxic surface water (Bruland, 1983; Anderson and others, 1989a; Emerson and Husted, 1991); they too might precipitate, possibly by some form of the reactions listed in table 9.

Minor elements in the modern environment, however, seldom behave ideally, or simply. For example, the thermodynamic properties of U require that it is present in seawater as $\text{UO}_2(\text{CO}_3)_2^{2-}$ (Langmuir, 1978) and $\text{UO}_2(\text{CO}_3)_3^{4-}$; the one should be reduced under conditions of denitrification and the other under conditions of sulfate reduction (table 9). The

distribution of U in the Black Sea (Anderson and others, 1989) supports its reduction under conditions of sulfate reduction. It exhibits no variation through the intermediate zone of denitrification but shows a strong decrease in the bottom water. Isotopic evidence further suggests that reduc-

tion and precipitation of U actually occur in the sediment pore-water environment (Anderson and others, 1989a). This distribution indicates that the complex $UO_2(CO_3)_3^{4-}$ is the stable seawater species. Similarly, V should be reduced under strongly denitrifying conditions (table 9), but its dis-

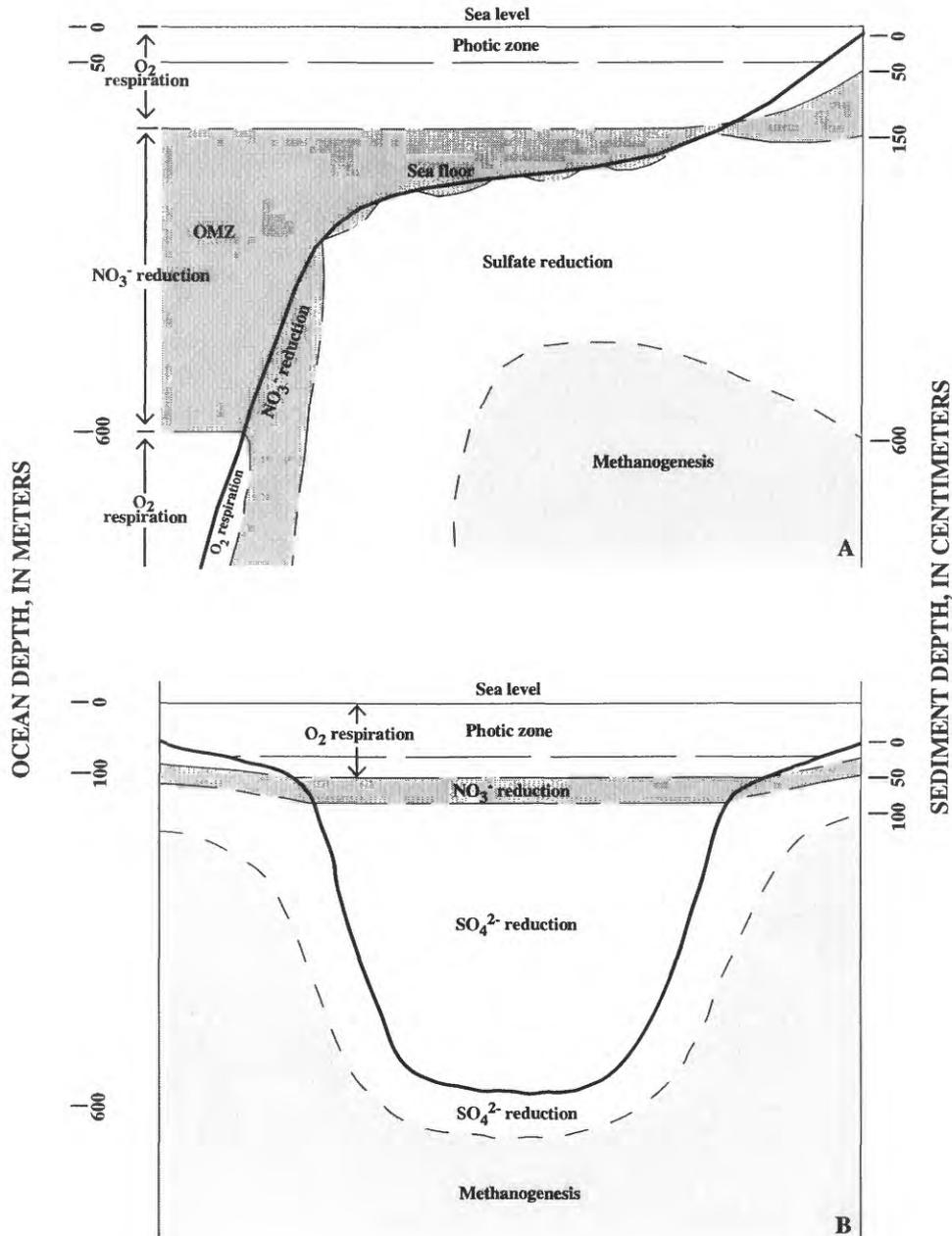


Figure 3. Schematic diagram illustrating seawater and sediment chemistry in a marine-shelf environment with high primary productivity and weak advection at intermediate depth (top), and in a shallow-silled basin with low to moderate primary productivity and extremely weak advection (bottom). Modern examples of shelf environment are the Peru and Namibia Continental Shelves, and of basin environment the Black Sea and the Cariaco Trench. Fundamental difference between these two environments is depth of most intense reduction in water column: at intermediate depth on shelf and at maximum depth in basin. Shaded area, oxygen-minimum zone (OMZ).

Table 9. Half-cell reactions, assuming standard-state conditions.

[**Boldface**, major reactions in oxidation of organic matter. 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	$3\text{Co}^{2+}_{(\text{aq})} + 4\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Co}_3\text{O}_4_{(\text{s})} + 2\text{e}^- + 8\text{H}^+_{(\text{aq})}$	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	$\text{Mn}^{2+}_{(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{MnO}_2_{(\text{s})} + 2\text{e}^- + 4\text{H}^+_{(\text{aq})}$	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 4	$\text{I}^- = 5.0 \times 10^{-9}$, $\text{IO}_3^- = 4.5 \times 10^{-7}$	1, 3
.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	$\text{Ce}^{3+}_{(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{CeO}_2_{(\text{s})} + \text{e}^- + 4\text{H}^+_{(\text{aq})}$	9	$\text{Ce}^{3+} = 1.0 \times 10^{-11}$	3, 8
.296	$\text{Fe}^{2+}_{(\text{aq})} + 3\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Fe}(\text{OH})_3_{(\text{s})} + \text{e}^- + 3\text{H}^+_{(\text{aq})}$	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 4.5	$\text{HCO}_3^- = 2.47 \times 10^{-3}$, $\text{UO}_2(\text{CO}_3)_2^{2-} = 1.26 \times 10^{-8}$	3, 5, 9
-.018	$2\text{Fe}^{2+}_{(\text{aq})} + 3\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Fe}_2\text{O}_3_{(\text{s})} + 2\text{e}^- + 6\text{H}^+_{(\text{aq})}$	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 4	$\text{HS}^- = 7.75 \times 10^{-25}$, $\text{SO}_4^{2-} = 2.8 \times 10^{-2}$	3, 5
-.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 2.5	$\text{SO}_4^{2-} = 2.8 \times 10^{-2}$, $\text{Cu}^+ = 3.59 \times 10^{-9}$	1, 3, 10
-.137	$\text{CdS}_{(\text{s})} + 4\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{SO}_4^{2-}_{(\text{aq})} + \text{Cd}^{2+}_{(\text{aq})} + 8\text{e}^- + 8\text{H}^+_{(\text{aq})}$	4 6	$\text{SO}_4^{2-} = 2.8 \times 10^{-2}$, $\text{Cd}^{2+} = 6.94 \times 10^{-10}$	1, 3, 5, 12
-.162	$\text{ZnS}_{(\text{s})} + 4\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{SO}_4^{2-}_{(\text{aq})} + \text{Zn}^{2+}_{(\text{aq})} + 8\text{e}^- + 8\text{H}^+_{(\text{aq})}$	4 6	$\text{SO}_4^{2-} = 2.8 \times 10^{-2}$, $\text{Zn}^{2+} = 5.97 \times 10^{-9}$	1, 3, 5
-.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 5	$\text{SO}_4^{2-} = 2.8 \times 10^{-2}$, $\text{MoO}_4^{2-} = 1.1 \times 10^{-7}$	3, 13, 14
-.188	$\text{NiS}_{(\text{s})} + 4\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{SO}_4^{2-}_{(\text{aq})} + \text{Ni}^{2+}_{(\text{aq})} + 8\text{e}^- + 8\text{H}^+_{(\text{aq})}$	4 6	$\text{SO}_4^{2-} = 2.8 \times 10^{-2}$, $\text{Ni}^{2+} = 8.01 \times 10^{-9}$	1, 3, 5, 10
-.209	$\text{FeS}_{(\text{s})} + 4\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{SO}_4^{2-}_{(\text{aq})} + \text{Fe}^{2+}_{(\text{aq})} + 8\text{e}^- + 8\text{H}^+_{(\text{aq})}$	4 6	$\text{SO}_4^{2-} = 2.8 \times 10^{-2}$, $\text{Fe}^{2+} = 1.20 \times 10^{-9}$	1, 3, 4
-.210	$\text{UO}_2_{(\text{s})} + 3\text{CO}_3^-_{(\text{aq})} \rightarrow \text{UO}_2(\text{CO}_3)_3^{4-}_{(\text{aq})} + 2\text{e}^-$	4.5 5.5	$\text{CO}_3^- = 1 \times 10^{-4}$, $\text{UO}_2(\text{CO}_3)_3^{4-} = 1.26 \times 10^{-8}$	3, 5, 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 4	$\text{HS}^- = 2.8 \times 10^{-25}$, $\text{SO}_4^{2-} = 4.3 \times 10^{-6}$	3, 5

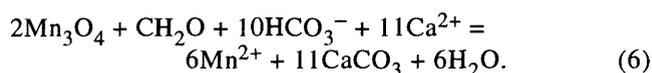
tribution in several basins (Emerson and Husted, 1991) suggests it is reduced only under sulfate-reducing conditions.

The concentration of Ni in seawater and the Eh conditions established in sulfate-reducing environments predict that Ni too should precipitate as a sulfide (table 9). At first glance, its depth profile in the water column, which shows no depletion in the bottom water relative to the surface water (Jacobs and others, 1985, 1987), suggests that it does not. However, the profile simply requires that Ni removal from bottom water is limited to the amount added to bottom water by way of bacterial oxidation of organic matter. Still, Ni should exhibit a depth profile similar to those of Cu and Cd. Several reasons likely account for its apparent nonideal behavior and the nonideal behavior of other minor elements. First, our calculations of stable species (table 9) are limited to those for which we have equilibrium constants, and these may not necessarily be the species that actually control the solubility of, for example, Ni and U. Second, the thermodynamic constants used in our calculations are from one of several recently published lists of values, which do not always agree. Third, we have not fully evaluated the effects of complexation (Kremling, 1983; Jacobs and others, 1985; Landing and Lewis, 1991), which would increase solubilities. Fourth, we have not considered diffusion across the benthic boundary layer (see below).

Under the intermediate redox condition of denitrification, metallic sulfides will not precipitate. Cr(OH)₃, however, is stable (Murray and others, 1983), and the thermodynamic properties of V (table 9) allow for its reduction from H₂VO₄⁻ to the more reactive ionic state VO₂⁺ (Sadiq, 1988) and to V₂O₄ near the NO₃⁻-SO₄²⁻-reduction boundary (table 9). The higher concentration of V in sea-water than of Cr (table 8) and the possible removal of V from the water column during denitrification make V a more conspicuous index of sediment from this environment than is Cr.

REE's respond still differently in seawater. They are adsorbed onto seawater particulate phases under oxic and denitrifying conditions and returned to seawater under sulfate-reducing conditions. Within the open ocean, acetic-acid-soluble particulate phases show an increase in REE content and increasingly positive Ce anomaly with depth (Sholkovitz and others, 1994); however, sediment-accumulation rates suggest the flux is quite low. Within the denitrification zone of the Cariaco Trench and the Black Sea, above the zone of sulfate reduction (Hashimoto and others, 1983; Codispoti and others, 1991), the 3+-valence-state (within the marine environment, all REE's except Ce) light REE's La, Pr, Nd, and Sm show strong concentration minimums, requiring their removal onto particulate phases (de Baar and others, 1988, German and others, 1991; Schijf and others, 1991). Toward the NO₃⁻-SO₄²⁻-reduction interface and into the sulfate-reducing water in both basins, their concentrations increase sharply. Within the denitrification zone of the OMZ in the eastern Pacific Ocean, the 3+-

valence-state REE's also show concentration minimums. They are scavenged by particulate phases, most likely oxyhydroxides of Mn (German and others, 1993) and Fe (Sholkovitz, 1993), more so under denitrifying than oxic conditions, and released to solution under sulfate-reducing conditions. The carrier phase in the denitrification zone in the OMZ of the eastern Pacific is unlikely to be an Mn phase. Dissolved Mn shows a concentration maximum, whereas REE's exhibit concentration minimums (Klinkhammer and Bender, 1980; de Baar and others, 1985; German and others, 1991). Particulate Mn is reduced, possibly by some form of the reaction



Thus, although the mechanism whereby the 3+-valence-state REE's are transferred to the sea floor within the hydrogenous fraction remains problematic, the redox conditions under which it is enhanced or diminished are well established.

Ce is somewhat more complex than the other REE's. Its occurrence as insoluble Ce(OH)₄ under oxic conditions (table 9) accounts for the negative Ce anomaly (see fig. 4 for definition) of seawater. Reduction back to a 3+ valence state under denitrifying conditions accounts for the increase in Ce concentration and for the more positive Ce anomaly of the OMZ in the eastern Pacific Ocean and the Cariaco Trench (de Baar and others, 1988). In the Black Sea, this trend is reversed (German and others, 1991; Schijf and others, 1991): In the denitrification zone, the Ce concentration decreases to a minimum, as does the Ce anomaly, paralleling the trends of the 3+-valence-state REE's.

Scavenging by the seawater particulate phases of other minor-element ions (Balistreri and others, 1981; Li, 1981; Whitfield and Turner, 1987; Clegg and Sarmiento, 1989) probably is equally complicated by such geochemically complex water columns as that in the Black Sea and Cariaco Trench, but the results of research into metallic-ion adsorption under oxic conditions clearly identify the importance of scavenging for many minor elements. Evaluating the importance of minor-element scavenging in the Monterey Formation, or in any ancient rocks, however, is hampered by the difficulty of identifying a marine fraction for those minor elements that have been well studied, are nonbioreactive, and are strongly scavenged. Th is the most intensively examined element in this group, but its high content in the detrital fraction of sediment and sedimentary rocks, relative to its concentration in seawater—that is, relative to a possible seawater contribution—makes it unlikely that we might identify a marine fraction for Th in the Monterey Formation from bulk analyses. Of the other minor elements for which we have analyzed, Zn and Cu also are likely to be scavenged, and Ni and Cd should not be, or much less so (Clegg

and Sarmiento, 1989; Balistreri and Murray, 1984). Thus, within the group of minor elements for which we have analyzed, hydrolytic scavenging should enrich Zn over Ni and Cd, owing to the greater tendency for Zn to be adsorbed onto particulate matter (under seawater oxic conditions) and its higher concentration in seawater (for example, 5 times that of Cd). The distributions of Zn, Ni, and Cd in the marine fraction of sediment of the Gulf of California (Brumsack, 1986), however, reflect a strong, possibly solely, biogenic input, suggesting that scavenging is a minor process under conditions of high primary productivity.

Interpretation of the accumulation of metallic elements in ancient rocks on the basis of their accumulation in modern sediment is further complicated by diffusion across the benthic boundary layer. Where O₂-depleted pore waters of organic-matter-enriched sediment are present close to the sea floor, Mo, U, V, and Cr can diffuse from seawater across the seawater-sediment interface and be retained in the sediment (Calvert, 1976; Manheim and Landergren, 1978; Brumsack, 1983, 1986; François, 1988; Pedersen and others, 1989; Emerson and Husted, 1991; Klinkhammer and Palmer, 1991), possibly independently of redox conditions of the bottom water. Near-surface sediment in the Gulf of California exhibits increasing concentrations of Mo, Cr, and V with depth. In absolute terms, however, this enrichment mechanism results in only slightly elevated minor-element contents (Brumsack, 1986); sediment on the Peru Shelf, which also accumulates under denitrifying conditions, shows no evidence of minor-element diffusion across the benthic boundary layer—minor-element concentrations are relatively constant in the uppermost 35 to 40 cm of sediment (Dean and Arthur, 1992).

The relative accumulation rates of metallic elements under these different redox conditions, in an area of high primary productivity, are summarized in figure 4. This diagram should be considered only in general terms because the elemental contribution of any single source changes with primary productivity, water depth, bulk-sediment-accumulation rate, and residence time of the bottom water, to name but four factors. Also, we exclude scavenging and diffusion as major mechanisms of minor-element enrichment under conditions of O₂ depletion in the bottom water, except for REE's, although scavenging could be important for some metallic elements, however difficult it is to evaluate. Figure 4 is intended to show that the hydrogenous flux of minor elements to the sea floor will be low under oxic conditions, except for Mn and Fe, with REE's exhibiting a widely varying, but commonly positive, Ce anomaly; it will be virtually zero for Mn and high for REE's (negative Ce anomaly), Cr, and V under denitrifying conditions; and it will be zero for Mn and REE's and high for Cr, V, Mo, Se, Fe, Cu, Cd, and Zn under sulfate-reducing conditions. Although Fe precipitates as a sulfide under sulfate-reducing conditions, detection of a hydrogenous fraction is hampered by detrital and organic inputs, even under conditions of the

lowest bulk-sediment-accumulation rates, as noted above for pelagic deposits.

The failure of seawater profiles of several minor elements in modern basins to reflect the geochemistry of the bottom water—that is, the apparent absence of approach toward equilibrium between dissolved and solid phases

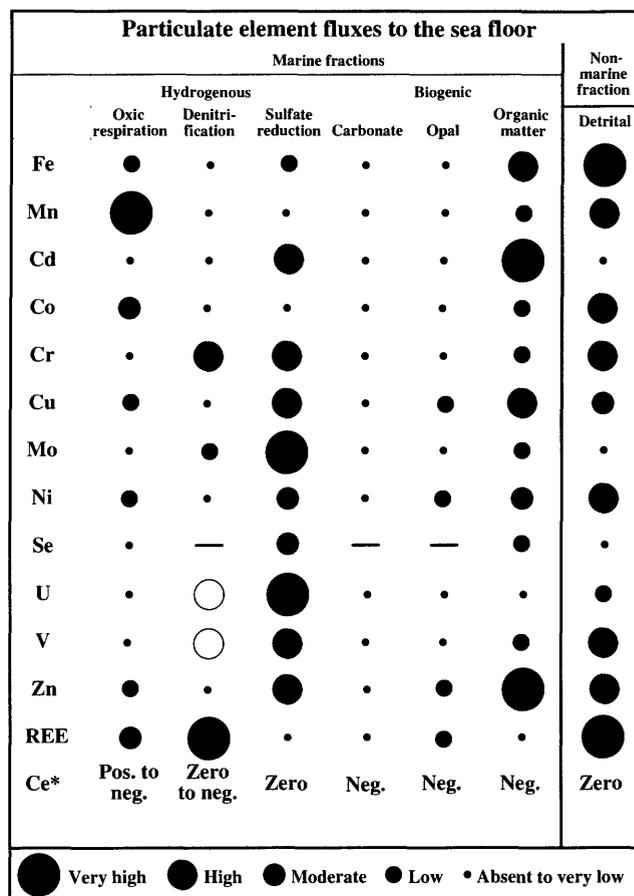


Figure 4. Generalized summary of elemental accumulation in marine sediment under conditions of high primary productivity in photic zone, where seawater (hydrogenous and biogenic) sources are not totally masked by detrital (terrigenous) source. Chart should be read across rather than down; for example, dominant sediment source of Cd under conditions of high primary productivity is organic matter. Under conditions of sulfate reduction in bottom water, as well as high primary productivity in photic zone, Cd also accumulates as an inorganic precipitate, CdS; its accumulation as an inorganic precipitate under bottom-water redox conditions of oxic respiration, or denitrification, is minor, as is its accumulation within detrital fraction of sediment under all conditions. Sizes of circles in any one row are unrelated, in absolute terms, to those in any other row; open circles are used in those cases for which theoretical considerations seem to conflict with observations. Ce*, Ce anomaly, defined as $\log [3\text{Ce}/(2\text{La}+\text{Nd})]$, in which all three REE's have been normalized on an element-by-element basis to North American Shale Composite (see table 1). Dashes, no information available on which to estimate accumulation rate.

(Cutter, 1982; Anderson and others, 1989a, b; Emerson and Husted, 1991)—urges further caution in the application of figure 4 to natural systems. One possible explanation for this apparent nonideality is suggested by the strong correlations in many samples of modern and ancient sediment between organic matter, albeit the residual fraction, and several minor elements, which should otherwise behave quite differently. We have stressed the transport of minor elements to the sea floor by organic matter, whose interelement ratios approach those of plankton. A second major role of organic matter is to supply minor elements to bottom waters by way of oxidized organic matter (Piper and Isaacs, 1995), again in the ratios of plankton. A third role of settling organic matter may be to provide a surface on which the actual reduction and (or) precipitation of minor elements occurs. The presence of the oxidized species U(VI) in the sulfate-reduction zone of water column in the Black Sea (Anderson and others, 1989a) might be explainable by this mechanism. If, as we suggest, reduction and precipitation of seawater-dissolved elements partly depend on reactions at the surfaces of organic debris, then the rate of minor-element accumulation in the sediment would depend on the settling rate of organic matter—again, primary productivity. The degree to which minor-element removal from the water column then reflects equilibrium depends on a balance between primary productivity in the photic zone and residence time of the bottom water, as well as on the physical chemical properties of the dissolved species. In possible support of this interpretation, Mo, U, and V are strongly depleted in the bottom water of the Black Sea (long residence time) but very weakly depleted in the bottom water of Saanich Inlet (short residence time). Still, the distributions of Mo and V in the bottom water of Framvaren Fiord demonstrate the full complexity of our problem: Mo is depleted, whereas V is not (Emerson and Husted, 1991). Thus, the enrichments of minor elements, as illustrated in figure 4, represent idealized cases of marine shelf-slope and basin environments for which the detrital contribution of minor elements does not totally mask that of the marine environment, and equilibrium between particulate and dissolved species in seawater is approached, if not actually attained.

DIAGENETIC OVERPRINT

The depth profile of Eh in sediment of the ocean margins resembles that in the water column of anoxic basins, such as the Black Sea (see eqs. 2–5). The pore water of the surface veneer of sediment has the same redox properties as that of the immediately overlying bottom water, and the pore water becomes more reducing with depth. Burial exposes each parcel of sediment to ever more reducing conditions than that under which it accumulated. Thus, deciphering the marine fraction of metallic elements in sedimentary rocks is further complicated by the changing redox condi-

tions to which the rocks were exposed immediately after deposition. The loss of a minor element from a sediment during early diagenesis can mask its source if its loss is substantial and differs from the relative loss of other elements. Sholkovitz (1973) reported a difference between the C:P ratio of sedimentary organic debris in the Santa Barbara Basin and that of plankton of 106:1 (Redfield and others, 1963). Interelement ratios of minor elements may be similarly decoupled from those in settling organic matter, through diagenesis (Shaw and others, 1990).

Within fully oxygenated sediment, Cu, as well as Cd, Cr, V, Zn, Ni, and organic P, are, indeed, recycled into the overlying water column during early diagenesis. Sediment-trap studies (Fischer and others, 1986) and pore-water studies of pelagic sediment (Callender and Bowser, 1980; Klinkhammer and others, 1982) reveal that as much as 90 percent of the Cu is recycled at the sediment surface. The absence of Cr and U in excess of a terrigenous contribution in oxic sediment (Piper, 1988) requires that virtually all of the seawater-derived fractions of these elements also are recycled. Even with this loss, the albeit-slight retention of several minor elements by the sediment in oxic environments, largely associated with Fe and Mn oxides in both concretions (Mero, 1965) and finely dispersed phases (Piper, 1988), is notable, owing to the very low rate of sediment accumulation in the pelagic environment rather than to a high flux of minor elements or a high retention efficiency on the sea floor of the deep ocean. Thus, different interelement ratios in the marine fraction of this sediment from those in marine organic matter and in the marine fraction of modern

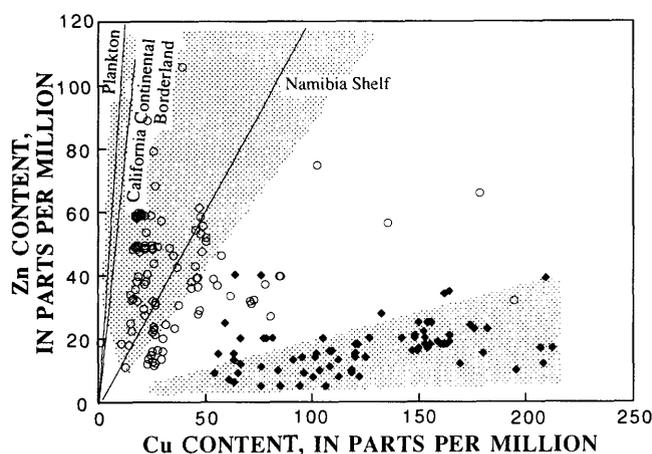


Figure 5. Zn:Cu interelement ratio in modern marine organic matter (shaded area on left), based on this ratio in plankton, in sediment from the Peru Shelf (circles), the Namibia Shelf, and the Santa Barbara Basin of the California Continental Borderland, and in fully oxic sediment (shaded area at bottom right) from a pelagic environment (diamonds). Labeled curves represent averages. See text for data sources.

sediment in ocean-margin areas (fig. 5), as discussed below, might allow for the identification of sedimentary rocks that accumulated under oxic conditions, on the basis of their current minor-element contents.

Profiles of the major oxidants (O_2 , NO_3^- , and SO_4^{2-}) in sediment on ocean margins are greatly steepened (Froelich and others, 1979; Berner, 1980; Claypool and Threlkeld, 1983; Bender and others, 1989; Shaw and others, 1990) over those in pelagic and hemipelagic sediment, somewhat independently of the organic-matter content. At one extreme is sediment on the Peru and Namibia Continental Shelves (Baturin and others, 1972; Calvert and Price, 1983; Burnett and Froelich, 1988), which contains as much as 20 weight percent organic carbon (30–40 weight percent organic matter). The surface sediment is exposed to oxic seawater conditions, or to denitrification over that area of the sea floor impinged by the core of the OMZ (fig. 3), and sulfate-reducing conditions extend upward to the surface of the sea floor in some areas (Froelich and others, 1988), owing to the high content of labile organic matter in the sediment and the low O_2 content in the overlying bottom water. Sediment of the Santa Barbara Basin shows a similar redox profile. The sulfate-reduction zone extends to within 2 cm of the surface (Sholkovitz, 1973), yet the sediment contains as little as 3 weight percent organic carbon.

Cu, Cd, Cr, Zn, and V are likely to be retained in this type of sediment, a conclusion supported by their behavior in sulfate-reducing seawater and in sediment pore water. Douglas and others (1986) and Shaw and others (1990) showed that Cu tends to be retained in the solid phases of such sediment. Cd and Zn are expected to behave similarly because of the low solubility of CdS and ZnS. The distributions of Cr and V in surface and near-surface sediment of the Gulf of California (Brumsack and Gieskes, 1983) reflect not merely their retention by, but their slight addition to, the sediment of O_2 -depleted environments, possibly owing to the reduction of Cr and V under denitrifying and more negative redox conditions (table 9). Their reduction, CrO_4^{2-} to $Cr(OH)_3$ and $H_2VO_3^-$ to VO^{2+} or V_2O_4 , results in their greater stability under reducing than oxidizing conditions (Sadiq, 1988), although the formation of metal-organic complexes (Douglas and others, 1986; Heggie and others, 1986; Breit and Wanty, 1991) and various other possible reactions greatly complicate their geochemical behavior.

Minor-element contents and interelement ratios in sediment on the Peru and Namibia Shelves and the California Continental Borderland (fig. 5) support our interpretation that minor elements are efficiently retained in mildly to strongly reducing sediment. Average interelement ratios of several elements in the marine fraction of sediment from these areas are comparable and similar to those in average plankton. Equally important, minor-element ratios in sediment from all of these environments differ significantly from those in the marine fraction of oxic pelagic sediment (fig. 5).

REE's are remobilized within sulfate-reducing sediment (Elderfield and Sholkovitz, 1987), an observation in agreement with their behavior in sulfate-reducing seawater (de Baar and others, 1988; German and others, 1991). Significant loss of REE's from the sediment, however, may not occur. Their incorporation into a stable solid phase, such as apatite, before the onset of sulfate reduction might enhance their retention in the sediment. In sediment on the Peru Shelf, pelletal carbonate-fluorapatite accretes in the surface and near-surface sediment (Burnett and others, 1988) and has a high REE content (Piper and others, 1988). A slightly negative Ce anomaly in several, but certainly not all, bulk-sediment samples (Piper and others, 1988; Dean and Arthur, 1992), similar to that in apatite pellets (Piper and others, 1988) and in seawater (de Baar and others, 1985), also requires retention of a seawater fraction, possibly within very fine grained apatite that is dispersed throughout the sediment (Burnett, 1977). Sulfate reduction in the water column and in the surface sediment would have prevented the retention of REE's in all marine fractions of the sediment, if not their initial accumulation (fig. 4).

This discussion of the behavior of minor elements within widely varying redox environments of the modern ocean—from seawater through the sea floor to burial—has allowed us to introduce a stoichiometric model for the minor-element contents of ancient sediment and, at the same time, to outline many of the limitations of this model. Though none too brief, our discussion is little more than a cursory summary of a vast literature that, even so, has yet to define fully this extremely complex environment. Our discussion can serve only as an introduction to the subjects of the sources of minor elements in marine sediment and of the behavior of minor elements during burial. It is surely but one small step, hopefully, in the right direction.

RESULTS: ELEMENTAL HOST PHASES—THE MONTEREY FORMATION

Rocks of the Monterey Formation consist of the following major components (Isaacs, 1980): biogenic silica (opal-A, opal-CT, and diagenetic quartz), calcite, dolomite, organic matter, and minor amounts of apatite and metallic sulfides—the marine fraction—and quartz, clay, and other Al silicates, such as feldspar and heavy minerals—the detrital fraction. Their abundances (table 6) were calculated by using the normative scheme for which $Al_2O_3 \times 5.7$ gives the amount of the detrital fraction. Comparison of the contents of other major-element oxides with those in WSA defines the contribution of these oxides by the detrital fraction in the Monterey Formation. The combination of "excess" SiO_2 , MgO, and P_2O_5 in each sample identifies the amounts of biogenic silica, dolomite, and apatite, respectively. The CaO in

excess of that present in detritus, dolomite (assuming stoichiometric dolomite), and apatite gives the amount of calcite present. The abundance of organic matter is calculated from the organic-carbon content (organic matter=organic carbon \times 1.5).

DETRITUS

Fe₂O₃, TiO₂, and K₂O correlate with Al₂O₃ (table 3). On a plot of these elements versus detritus (Al₂O₃ \times 5.6), the trends approximate those of WSA (figs. 6A–6C) and extrapolate to the origin. The agreements are especially close when we consider the range of rock compositions used to determine the composition of WSA (Wedepohl, 1969–78; Medrano and Piper, 1992) and the heterogeneity of the Monterey Formation. Several of the plots (fig. 6) suggest that the average composition of NASC (Gromet and others, 1984) more closely approaches that of the detrital fraction of the Monterey Formation than does that of WSA. Relative to the NASC standard, the Monterey Formation contains a slight excess of Fe₂O₃. Regardless of the standard used for comparison, however, the detrital fraction of the Monterey Formation appears to be uniform in composition. More analyses of the Rincon Shale and Sisquoc Formation are needed to fully evaluate their compositions relative to both the Monterey Formation and the two shale standards, but the two analyses of each unit suggest no significant differences.

Several minor elements, similar to K₂O and TiO₂, correlate strongly with detritus (tables 10, 11). The trends of elements versus detritus also approach those of WSA (figs. 6D–6F) and extrapolate to or near the origin. These elements include Li, Ga, and Co; additional elements that show this same strong trend with detritus (tables 10, 11) and with WSA are Hf, Sc, and Th (not shown) and the REE's La through Eu (figs. 6G–6I). The strength of these trends supports our use of WSA as a standard for the detrital host of minor elements in the Monterey Formation and our assumption that its composition is uniform. We can use the composition of WSA and the Al₂O₃ content in the Monterey Formation to estimate the detrital contribution of minor elements to their total inventory, even for those elements that do not correlate with detritus, including Cd, Cr, Cu, Mo, Ni, Se, U, V, and Zn; we consider below REE's as exceptions to this interpretation.

CARBONATES

Calcite has negligible contents of minor elements, except Sr (tables 10, 11), as also may be true for dolomite (table 11). These conclusions are supported by the sparse minor-element content in modern biogenic calcite (Palmer, 1985).

SULFUR PHASES

Sulfur is present in the Monterey Formation in amounts as high as 8 weight percent (table 1) but less than 4 weight percent in most samples (Leventhal, 1989; Zaback and Pratt, 1992). It exhibits a positive correlation with organic matter (fig. 7A), similar to the relation in core samples from the Santa Maria Basin near Orcutt, Calif. (Leventhal, 1989). A slight excess of 0.5 weight percent S at 0 weight percent organic matter was reported in samples from the Santa Maria Basin, as inferred by extrapolation of the trend of S versus organic matter; Leventhal (1989) attributed this excess to the presence of metallic sulfides, mostly pyrite. A similar trend is seen in our data (fig. 7A); however, by merely interchanging the axes, the curve defining the relation in the samples used in this study extrapolates onto the organic-matter axis at 0 weight percent S. Going through this same exercise with the data of Leventhal (1989) reduces the excess S in samples from the Santa Maria Basin virtually to zero, a reflection of the weakness of the correlation, plus very low pyrite.

The presence of pyrite was evaluated by comparing excess Fe₂O₃—that is, relative to NASC (fig. 6A)—with sulfur. Although the curve for pyrite (fig. 7B) defines a maximum for excess iron in the Monterey Formation, we are unable to say whether pyrite is actually present, although certainly it averages less than approximately 1.0 weight percent. Pyrite has been reported by researchers investigating the Monterey Formation, and it was observed in several of the samples in this study, in the range 1–2 volume percent (J. Rullkötter, verbal commun., 1993). Such a low concentration of pyrite likely hosts a minor fraction of minor elements.

Ba also correlates weakly with S (fig. 7C; table 10). The occurrence of Ba as barite (BaSO₄) is more strongly suggested by the much-reduced Ba content in samples analyzed by ICP versus those analyzed by NAA (fig. 2C). The lower La content in the ICP-analyzed than in the NAA-analyzed sample (KG–24, table 2) with the highest Ba content supports this interpretation of barite occurrence; marine barite is known to have an REE content of hundreds of parts per million (Piper, 1974; Church, 1979; Guichard and others, 1979). The barite (present in only 0.5 weight percent) and apatite in these samples likely represent the major hosts of the marine REE inventory.

ORGANIC MATTER

Several minor elements that do not correlate with detritus correlate strongly with organic matter (table 10), and the correlations are enhanced, albeit slightly, by subtracting the detrital contribution from their bulk contents (figs. 8, 9). Strong partitioning of minor elements into organic matter

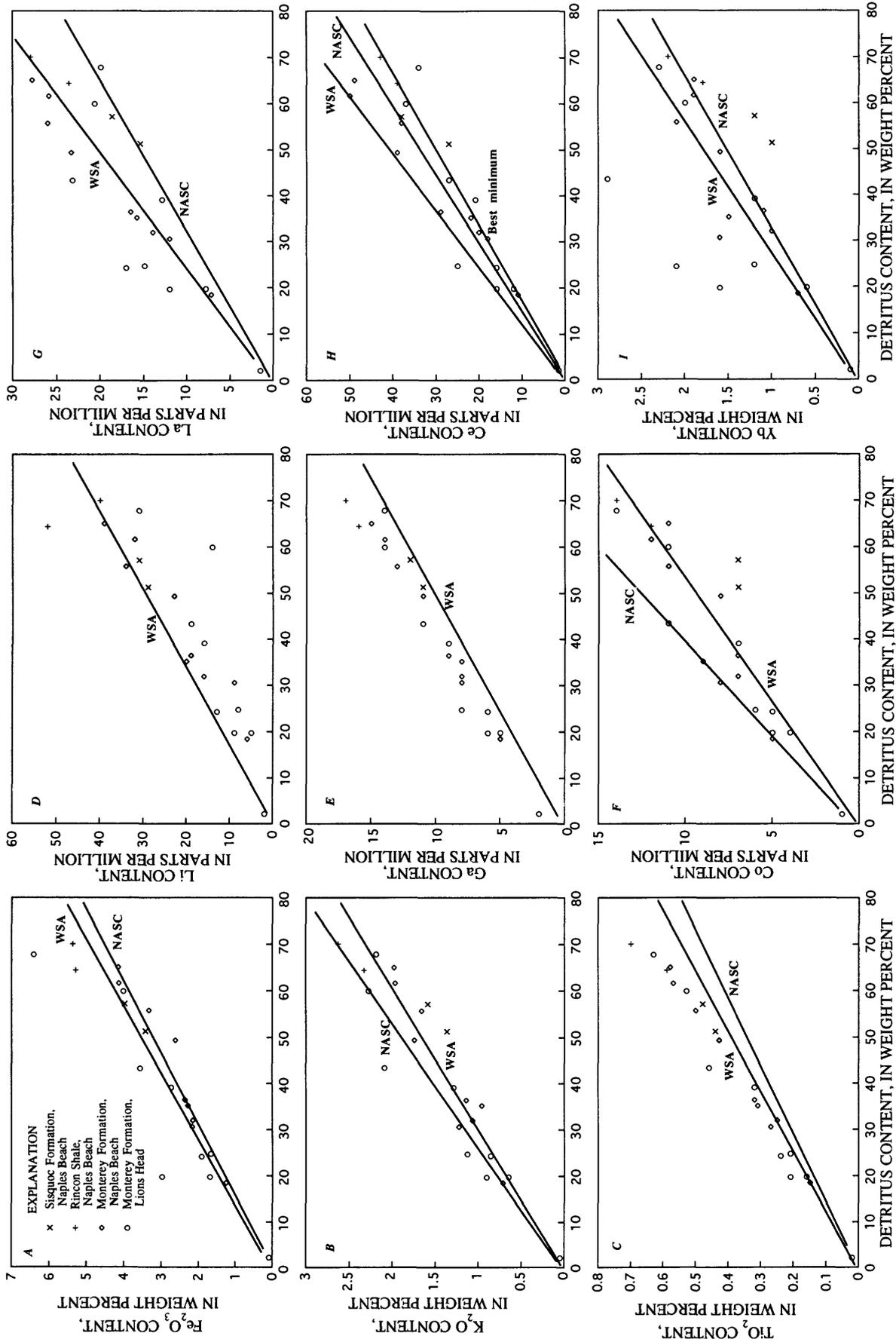


Figure 6. Contents of Fe_2O_3 (A), K_2O (B), TiO_2 (C), Li (D), Ga (E), Co (F), La (G), Ce (H), and Yb (I) versus detritus content ($Al_2O_3 \times 5.6$) in sedimentary rocks of the Monterey Formation. Curves represent averages for World Shale Average (WSA; Wedepohl, 1969-78) or North American Shale Composite (NASC; Gromet and others, 1984). WSA data in figures 6G through 6I from Piper (1974). In figure 6H, curve labeled "best minimum" is our estimate of Ce contribution by detrital fraction to each sample; extrapolation of curve gives a Ce content in detritus alone of 61 ppm.

Table 10. Correlation coefficients for major components and minor elements in the Monterey Formation.

	Silica	Detritus	Apatite	Dolomite	Calcite	Organic matter	Sulfur	Mn	As	Ba	Be	Cd	Ce	Co	Cr	Cu	Eu	Ga
Silica-----	1																	
Detritus-----	-.196	1																
Apatite-----	-.276	-.143	1															
Dolomite-----	-.355	-.565	-.204	1														
Calcite-----	.138	-.578	.371	-.132	1													
Organic matter--	-.321	.084	.592	-.341	.097	1												
Sulfur-----	-.089	.125	.408	-.288	0	.687	1											
Mn-----	-.221	.027	-.246	.310	-.156	-.256	-.087	1										
As-----	-.238	.462	.464	-.447	-.150	.643	.704	-.163	1									
Ba-----	-.065	.120	.336	-.279	-.083	.665	.804	-.066	.591	1								
Be-----	-.571	.636	.375	-.407	-.127	.443	.207	-.031	.568	.25	1							
Cd-----	-.133	.106	.406	-.168	-.080	.491	.407	-.148	.675	.461	.387	1						
Ce-----	-.172	.928	-.126	-.539	-.574	.116	.084	-.035	.347	.117	.671	.129	1					
Co-----	-.305	.904	.047	-.564	-.432	.333	.372	.009	.677	.320	.751	.270	.823	1				
Cr-----	-.316	.333	.517	-.419	-.083	.888	.771	-.177	.825	.794	.547	.504	.273	.590	1			
Cu-----	-.200	.130	.452	-.341	0	.910	.857	-.216	.720	.863	.365	.511	.146	.377	.916	1		
Eu-----	-.022	.722	-.158	-.525	-.287	.162	.439	-.033	.539	.285	.445	.059	.648	.758	.411	.32	1	
Ga-----	-.248	.982	-.105	-.531	-.565	.115	.160	.066	.501	.159	.700	.213	.932	.920	.371	.166	.699	1
Hf-----	-.055	.916	-.199	-.578	-.493	.016	.184	.053	.342	.115	.480	.011	.873	.760	.217	.104	.777	.877
La-----	-.211	.881	.052	-.603	-.479	.357	.336	-.090	.543	.315	.693	.242	.933	.862	.519	.402	.695	.904
Li-----	-.313	.882	.081	-.466	-.555	.177	.009	-.054	.516	.071	.677	.280	.830	.774	.355	.148	.468	.878
Lu-----	-.065	.616	.152	-.529	-.285	.461	.724	-.092	.717	.561	.439	.265	.579	.759	.681	.625	.815	.632
Mo-----	-.126	.073	.437	-.263	.004	.725	.717	-.182	.708	.833	.348	.790	.096	.275	.763	.860	.174	.150
Nd-----	-.143	.875	.072	-.613	-.469	.267	.318	-.131	.509	.231	.647	.208	.936	.836	.425	.317	.720	.888
Ni-----	-.229	.210	.516	-.425	-.002	.951	.805	-.229	.754	.795	.455	.507	.204	.473	.960	.969	.351	.239
Sb-----	-.052	.039	.464	-.318	-.020	.851	.788	-.249	.584	.684	.270	.378	.121	.281	.776	.887	.308	.055
Sc-----	-.146	.920	-.089	-.530	-.485	.063	.261	.073	.585	.175	.580	.139	.775	.929	.403	.158	.802	.916
Se-----	-.188	.053	.493	-.296	.017	.946	.827	-.227	.698	.771	.285	.51	.063	.300	.894	.972	.256	.079
Sm-----	-.186	.901	.057	-.628	-.463	.345	.416	-.086	.600	.334	.672	.249	.915	.899	.536	.414	.775	.916
Sr-----	-.152	-.349	.625	-.233	.856	.334	.013	-.181	.083	.059	.269	.144	-.358	-.164	.187	.147	-.295	-.319
Th-----	-.250	.923	-.131	-.517	-.555	.168	.047	-.032	.352	.114	.702	.126	.984	.843	.312	.166	.608	.927
U-----	-.335	.337	.549	-.346	-.187	.780	.540	-.177	.720	.578	.651	.717	.456	.515	.770	.755	.233	.423
V-----	-.075	.230	.334	-.385	-.153	.826	.768	-.234	.698	.740	.383	.517	.274	.465	.833	.892	.447	.255
Y-----	-.235	.526	.477	-.540	-.130	.677	.735	-.175	.819	.583	.574	.421	.480	.705	.837	.733	.606	.568
Yb-----	-.110	.642	.225	-.594	-.217	.512	.722	-.130	.761	.529	.529	.326	.606	.796	.701	.633	.818	.662
Zn-----	-.253	.278	.517	-.392	-.102	.893	.844	-.213	.849	.805	.482	.637	.262	.521	.951	.951	.400	.330

	Hf	La	Li	Lu	Mo	Nd	Ni	Sb	Sc	Se	Sm	Sr	Th	U	V	Y	Yb	Zn
Hf-----	1																	
La-----	.819	1																
Li-----	.714	.816	1															
Lu-----	.635	.779	.467	1														
Mo-----	.028	.297	.159	.438	1													
Nd-----	.850	.976	.791	.777	.214	1												
Ni-----	.154	.455	.228	.651	.788	.375	1											
Sb-----	.054	.327	.026	.570	.667	.306	.891	1										
Sc-----	.825	.785	.754	.734	.082	.794	.253	.072	1									
Se-----	.033	.321	.093	.555	.807	.248	.964	.917	.081	1								
Sm-----	.867	.984	.788	.838	.302	.979	.471	.347	.847	.337	1							
Sr-----	-.404	-.261	-.214	-.230	.173	-.295	.205	.055	-.307	.149	-.277	1						
Th-----	.826	.921	.843	.541	.103	.899	.235	.115	.758	.087	.891	-.304	1					
U-----	.222	.643	.496	.572	.753	.584	.787	.687	.290	.738	.600	.114	.471	1				
V-----	.204	.444	.175	.624	.770	.394	.899	.926	.248	.899	.472	-.025	.289	.719	1			
Y-----	.471	.744	.529	.897	.571	.712	.785	.622	.622	.691	.774	.058	.465	.751	.636	1		
Yb-----	.650	.802	.507	.986	.457	.805	.676	.582	.747	.572	.862	-.128	.572	.616	.638	.919	1	
Zn-----	.214	.527	.333	.721	.843	.454	.960	.832	.337	.933	.547	.112	.273	.838	.865	.858	.745	1

was also reported by Leventhal (1989) and Odermatt and Curiale (1991) for the Monterey Formation and by Swanson (1961) and Nissenbaum and Swaine (1976) for other rocks and modern sediment. Lewan (1984), Odermatt (1986), and Moldowan and others (1986) further examined fractionation of metallic elements between the various phases of organic matter. The actual slopes of the plots for minor elements and organic matter, however, bear no relation to the composition of the organic matter in marine plankton.

The different units of the Monterey Formation and the Rincon Shale exhibit nearly identical minor-element/organic-

matter trends (fig. 8), except possibly for slightly lower concentrations of several minor elements in the phosphatic shale unit of the Monterey Formation. Mere dilution by apatite alone is insufficient to account for these lower concentrations, although more analyses are required to confirm the trends. The two samples from the Sisquoc Formation contain less than 1.5 weight percent organic matter (table 6) and have low minor-element contents; data for these samples plot near the origin. Thus, we are unable to evaluate a partitioning of minor elements into a marine fraction, possibly organic matter, in these two samples.

Table 11. Factor analysis for major components in sedimentary rocks of the Monterey Formation, using the computer program StatView II (oblique-solution primary-pattern matrix).

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Silica-----	-0.133	-0.147	-0.108	-0.843	-0.231	-0.082
Detritus-----	-.054	.976	-.065	.017	.033	.017
Apatite-----	.348	-.074	.586	.067	.026	.252
Dolomite-----	-.127	-.662	-.424	.585	-.061	.127
Calcite-----	-.063	-.371	.827	-.187	-.077	-.225
Organic matter--	.874	.005	.129	.066	.331	-.013
Sulfur-----	.928	.050	.013	.037	-.303	-.170
Mn-----	-.090	-.023	-.138	.664	-.218	-.217
As-----	.599	.395	.163	.042	-.292	.298
Ba-----	.882	-.021	-.123	.006	-.073	.001
Be-----	.117	.685	.355	.279	.222	.194
Br-----	.186	.163	.185	-.015	.897	-.167
Cd-----	.382	.028	-.013	-.081	-.173	.779
Ce-----	-.039	.929	-.157	-.047	.222	.056
Co-----	.217	.889	.074	.120	-.046	-.008
Cr-----	.855	.261	.084	.117	.026	.042
Cu-----	.992	.016	-.029	.012	.087	-.031
Eu-----	.277	.759	.029	-.070	-.299	-.326
Ga-----	-.035	.958	-.075	.089	.001	.115
Hf-----	-.029	.917	-.089	-.076	-.055	-.150
La-----	.225	.891	-.062	-.034	.129	.024
Li-----	-.104	.848	-.024	.056	.149	.339
Lu-----	.584	.646	.031	-.061	-.313	-.196
Mo-----	.790	-.074	-.070	-.102	-.112	.332
Nd-----	.148	.909	-.052	-.091	.061	.026
Ni-----	.942	.119	.071	.018	.133	-.044
Sb-----	.966	-.042	-.095	-.088	.162	-.152
Sc-----	.021	.926	.057	.059	-.285	-.029
Se-----	.999	-.073	-.048	.012	.127	-.034
Sm-----	.254	.913	-.024	-.047	.005	-.022
Sr-----	-.026	-.181	.914	-.022	.141	.012
Th-----	-.027	.913	-.138	.007	.306	.050
U-----	.619	.289	.000	.053	.195	.404
V-----	.929	.104	-.177	-.098	.125	-.020
Y-----	.623	.551	.234	.025	-.190	-.008
Yb-----	.561	.680	.125	-.058	-.276	-.156
Zn-----	.902	.184	.026	.036	-.025	.125

For the samples from the Monterey Formation alone, those from the Lions Head section have slightly higher ratios of Cr, Cu, Se, V, and Zn to organic matter than those from the Naples Beach section (fig. 9). We can attach no significance to these differences, given the number of samples we examined and the magnitude of the differences.

APATITE

On a plot of the marine fraction of heavy metals against apatite (fig. 10), the samples follow two trends, a relation suggested by the organic-matter plots (fig. 8). The first trend is defined by the minimum of the plot of minor elements versus organic matter (curves labeled "organic matter," fig. 9). This trend was plotted in figure 10 by converting organic-matter to P content, on the basis of the C:P ratio in plankton of 0.019 to 0.0225 (Collier and Edmond, 1984; Brumsack, 1986), and then converting P to apatite content by assuming 17.7 weight percent P in apatite (table 5). The

success of this calculation in defining the organic-matter trend, particularly for Cr, Cu, Ni, and Zn, suggests that much of the P in excess of the detrital contribution might be organically bound, even though we have expressed it in figure 10 as an apatite equivalent. The second trend, referred to as the apatite trend (curves labeled "apatite," fig. 10), identifies samples with reduced minor-element contents. These same relations have been observed for the San Gregorio Formation (Piper, 1991), a phosphatic deposit of Oligocene to Miocene age in Baja California.

The degree of minor-element enrichment between these two trends, expressed by the relation

$$[\text{metal}/\text{P}]_{\text{apatite}} : [\text{metal}/\text{P}]_{\text{organic matter}} \quad (7)$$

is surprisingly similar for all minor elements; it varies over the limited range 0.16 (Cd)–0.22 (Cr). Although it is tempting to conclude that minor elements are incorporated into

these two major phases, organic matter and apatite, they also are probably present in minor phases, such as metallic sulfides. Otherwise, we might have expected such an ele-

ment as Cd, similar in ionic charge and radius to Ca^{2+} , to be the most strongly enriched of the minor elements in the phosphatic samples. If anything, the opposite is true: The ratio

$$[\text{Cd}/\text{P}]_{\text{apatite}} : [\text{Cd}/\text{P}]_{\text{organic matter}} \quad (8)$$

is smaller than those for other minor elements, which should substitute less strongly into the apatite phase.

The REE patterns (fig. 11) of the samples indicate that REE's are present in excess of a detrital contribution, despite strong correlations of individual REE's with detritus (fig. 6; table 11). The depletion of Ce relative to La and Nd in most samples, and a heavy-REE enrichment in several samples (for example, 2, 17, 22, 24, fig. 11), resemble the REE pattern of seawater (Goldberg and others, 1963; Høgdahl, 1967; de Baar and others, 1985). This pattern, which is unique to the marine environment, represents unequivocal evidence of a marine origin for some of the REE's in the Monterey Formation. Although apatite is known to host REE's in phosphate deposits (Altschuler and others, 1967; McArthur and Walsh, 1984; Wright and others, 1987; Piper, 1988, 1991; Piper and Medrano, 1991) and in modern sediment (Piper and others, 1988), its low content in these samples, the low content of REE's in the marine fraction of sediment, and the likely partitioning of some of this fraction in barite preclude our ascertaining the importance of apatite as REE host in the Monterey Formation.

An Eu anomaly exhibited by several samples (fig. 11) is possible further evidence of a marine fraction of REE's. Plots of this Eu anomaly against major components and minor elements, however, give no clue as to a possible phase that might be responsible for its occurrence.

Apparently, the REE contents in WSA overestimate the detrital contribution of REE's to the Monterey Formation. NASC also might not be totally representative of the detrital fraction. Although it defines a minimum for La and Yb contents (fig. 6G), a Ce content even lower than that in NASC (fig. 6H) is needed to define the minimum detrital Ce content. Using these minimums for the REE content in detritus—for La (31 ppm), Ce (61 ppm), and Nd (29 ppm)—we can calculate the REE content and Ce anomaly in the marine fraction alone (fig. 12). The Ce anomaly correlates, albeit weakly, with apatite, and the correlation is stronger than that between apatite and the Ce anomaly calculated by using bulk REE contents. Given the large error in this calculation due to the dominance of the detrital contribution to the light-REE inventory (figs. 6G, 6H), the improvement in the apatite trend is rather remarkable and seems to support our method of selecting Ce, La, and Nd contents in the detrital fraction of the Monterey Formation.

U correlates with organic matter (fig. 8) and weakly with apatite (tables 10, 11).

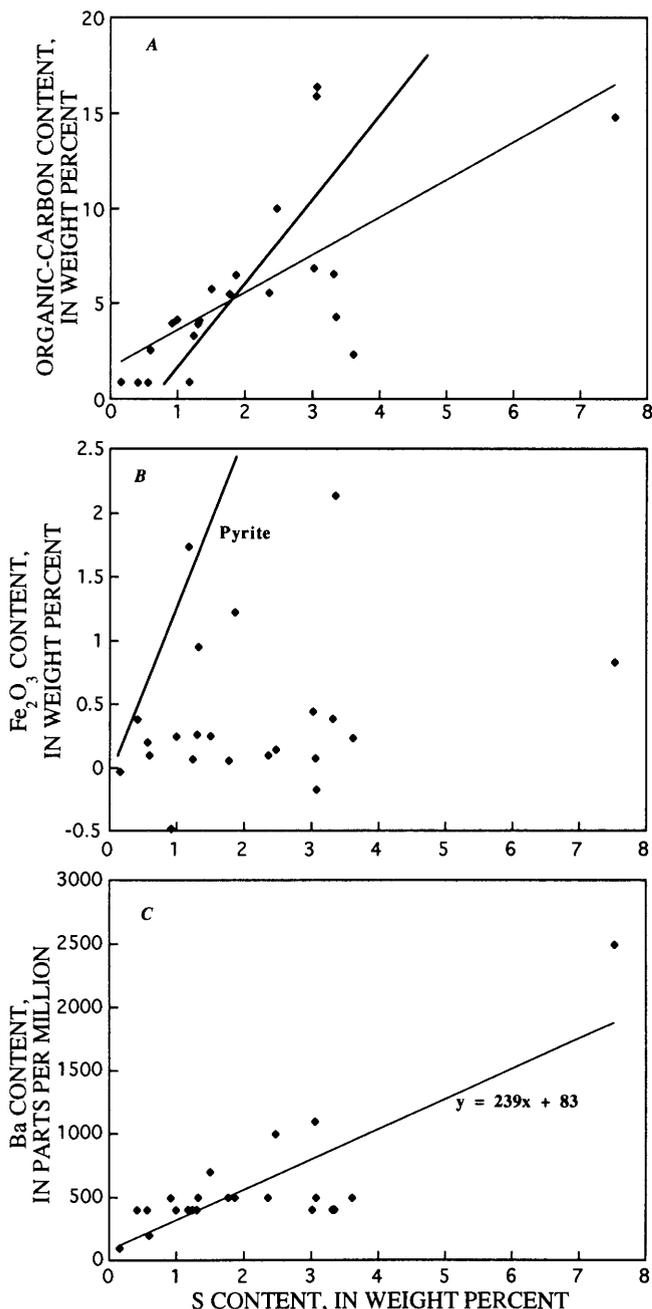


Figure 7. Organic-carbon content (A), Fe_2O_3 content in excess of a detrital contribution (B), and Ba content (C) versus S content in sedimentary rocks of the Monterey Formation. Two curves in 7A are best-fit lines, obtained by interchanging axes; they have same standard deviation (S.D.) of 0.65 and center of mass. S.D. of curve in figure 7C is 0.80.

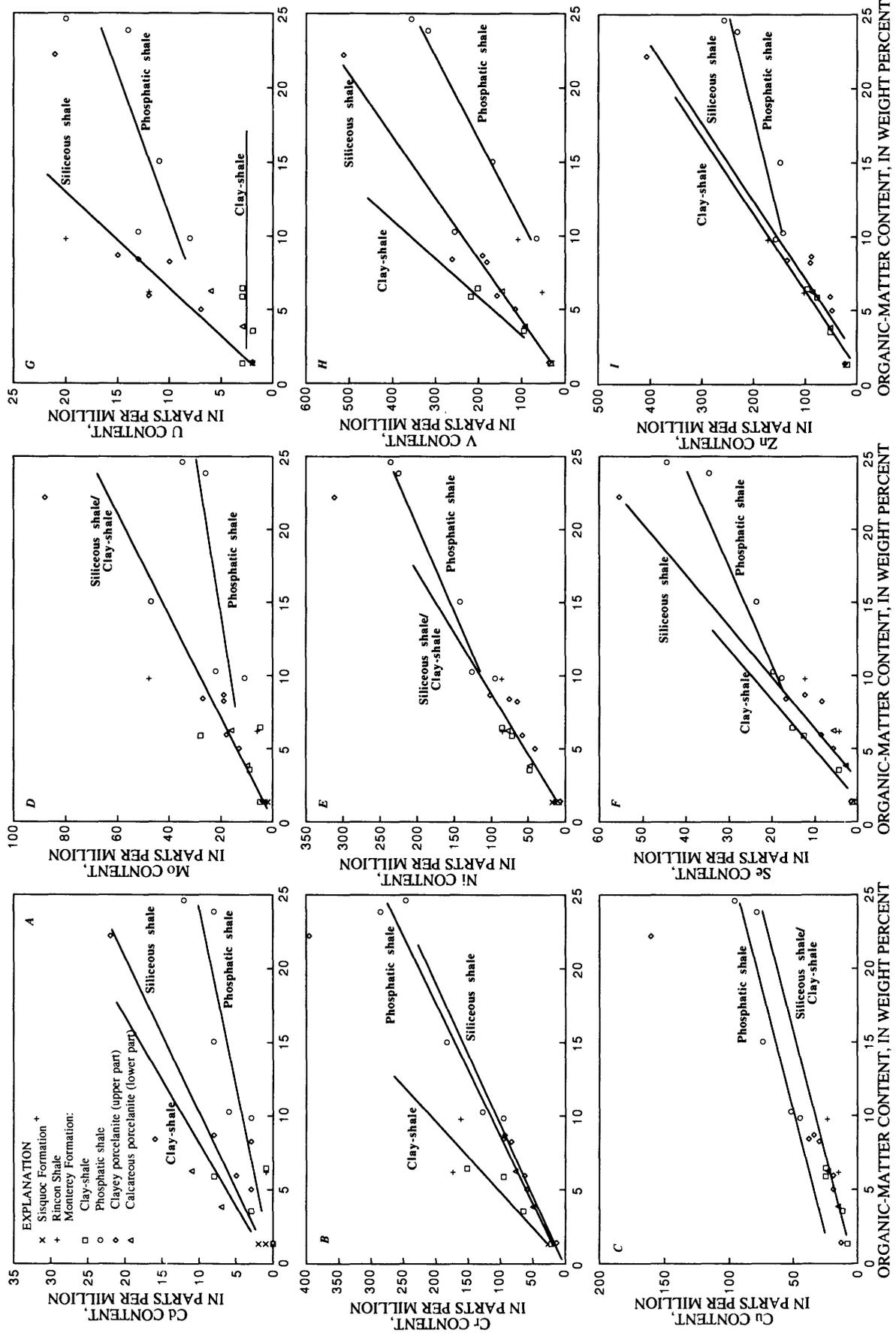


Figure 8. Contents of Cd (A), Cr (B), Cu (C), Ni (D), Se (F), U (G), V (H), and Zn (I) versus organic-matter content of marine fraction in sedimentary rocks of the Monterey Formation. Curves, which represent grouping of samples by lithology, are fitted to data visually.

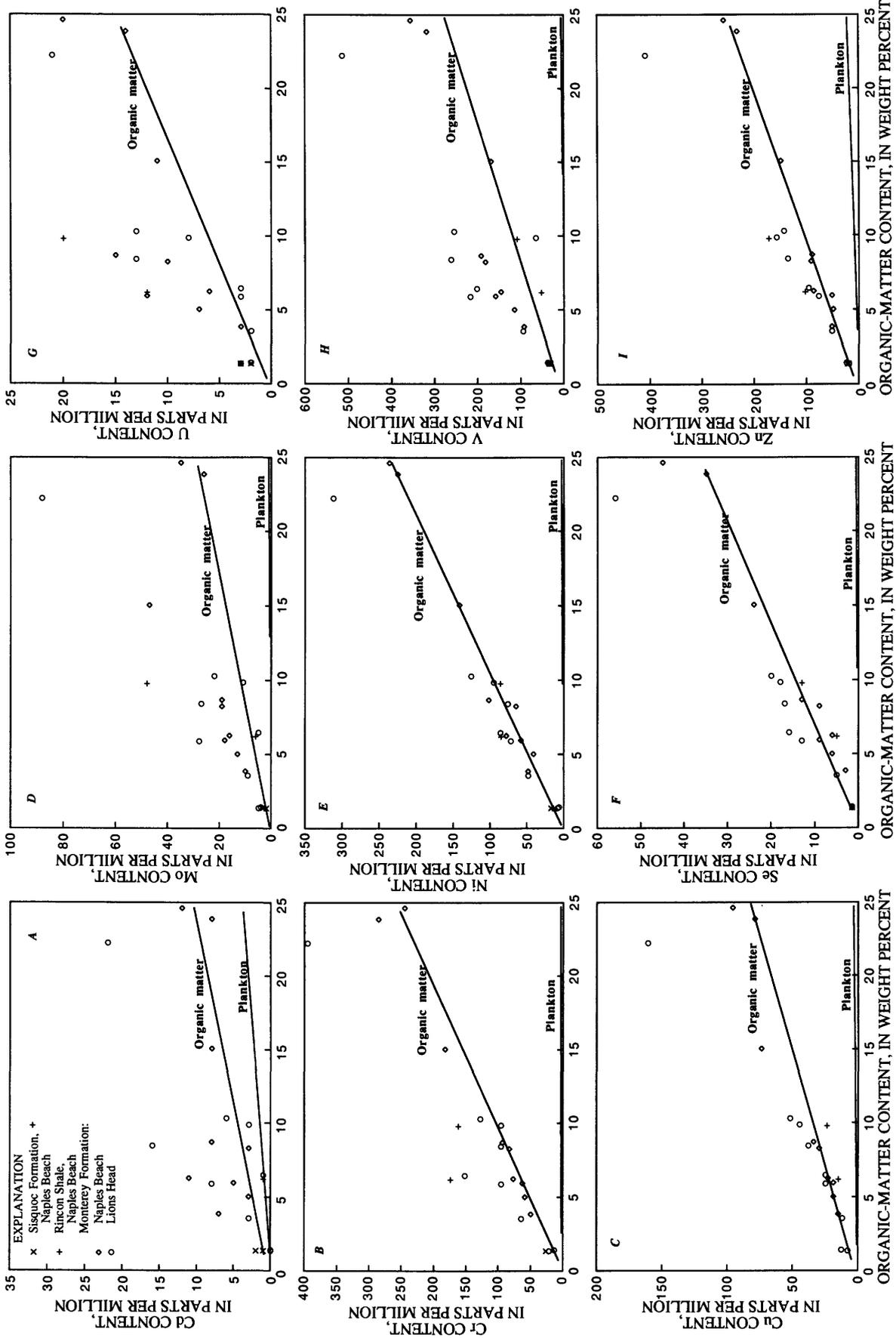


Figure 9. Contents of Cd (A), Cr (B), Cu (C), Mo (D), Ni (E), Se (F), U (G), V (H), and Zn (I) versus organic-matter content of marine fraction in sedimentary rocks of the Monterey Formation. Samples are grouped by site. Curves labeled "plankton" are based on minor-element content of marine organic matter (Martin and Knauer, 1973; Bruland, 1983; Collier, 1984; Collier and Edmond, 1984; Cutter and Bruland, 1984). Curves labeled "organic matter" represent our estimate of best minimum value for each element associated with organic matter in the Monterey Formation.

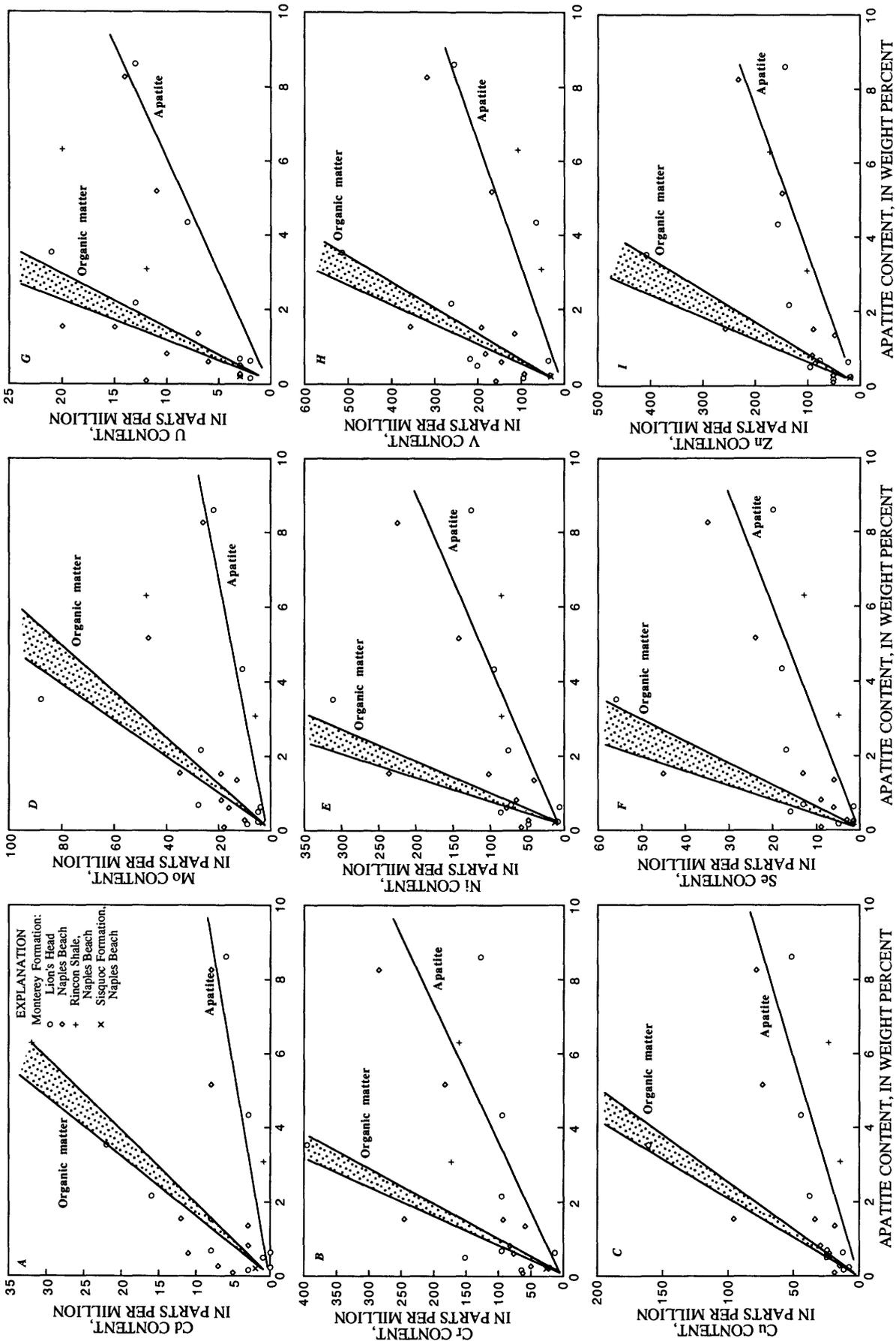


Figure 10. Contents of Cd (A), Cr (B), Cu (C), Mo (D), Ni (E), Se (F), U (G), V (H), and Zn (I) versus apatite content of marine fraction in sedimentary rocks of the Monterey Formation. Curve labeled "apatite" is fitted to data visually; dotted area between curves labeled "organic matter" is based on curve labeled "organic matter" in figure 9, after converting organic-matter to P-equivalent content (P:C ratio of 0.019-0.0225 in organic matter) and P-equivalent to apatite-equivalent content (P:apatite ratio of 0.177 in apatite).

MISCELLANEOUS

Several sample pairs, representing associated finely laminated versus massive units, were included in the samples analyzed (Isaacs and others, 1992). Although each massive unit has a higher metallic-element content within the marine fraction than its laminated pair (fig. 13), both plot close to a single organic-matter trend.

DISCUSSION: ELEMENTAL SOURCES—
THE MONTEREY OCEAN

Two slightly different approaches to the partitioning of minor elements between multiple marine sources offer a possible check on our determination of elemental sources to the Monterey Formation. Both approaches assume that the detrital fraction has a uniform composition comparable to

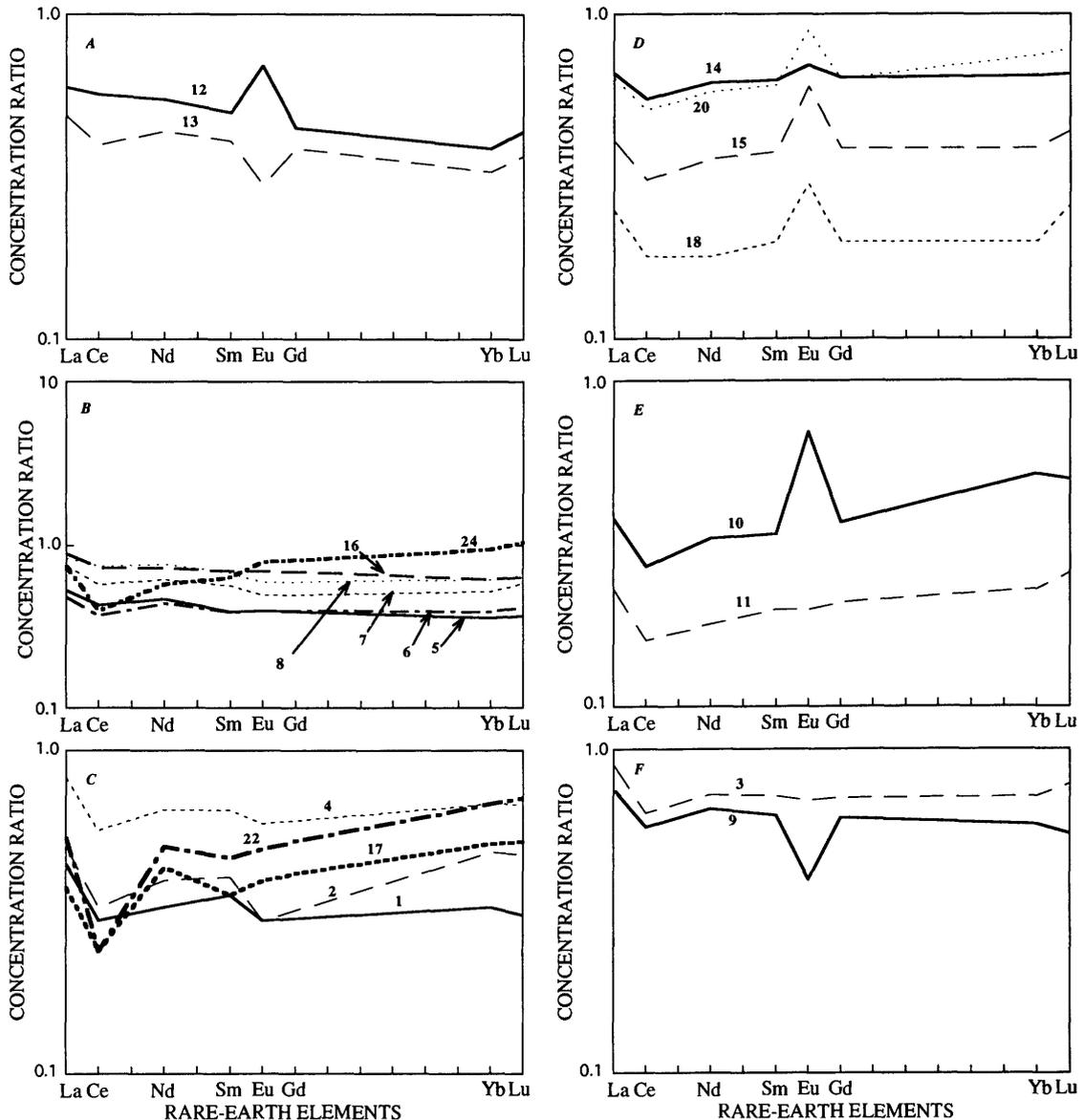


Figure 11. Rare-earth-element patterns for samples from the Monterey Formation. A, Sisquoc Formation. B, Siliceous shale (upper part). C, Phosphatic shale. D, Clay-shale. E, Siliceous shale (lower part). F, Rincon Shale. Patterns represent elemental contents normalized on an element-by-element basis to World Shale Average (Wedepohl, 1969–78; Piper, 1974) and plotted against atomic number. Normalizing values (in parts per million): La, 41; Ce, 83; Nd, 38; Sm, 7.5; Eu, 1.61; Yb, 3.53; and Lu, 0.61. Samples are grouped according to lithology, as in figure 8. Although data for Gd are unavailable, curves are drawn through a Gd value estimated by interpolation between Sm and Yb values. Purpose of interpolation is to emphasize anomalous behavior of Eu; however, we have made no attempt to evaluate Eu anomaly without actual Gd data.

that of some sedimentary-rock standard. The first approach computes the rate of accumulation of each element in the marine fraction by using the rate of accumulation of the rocks, which is determined by one of various methods. By

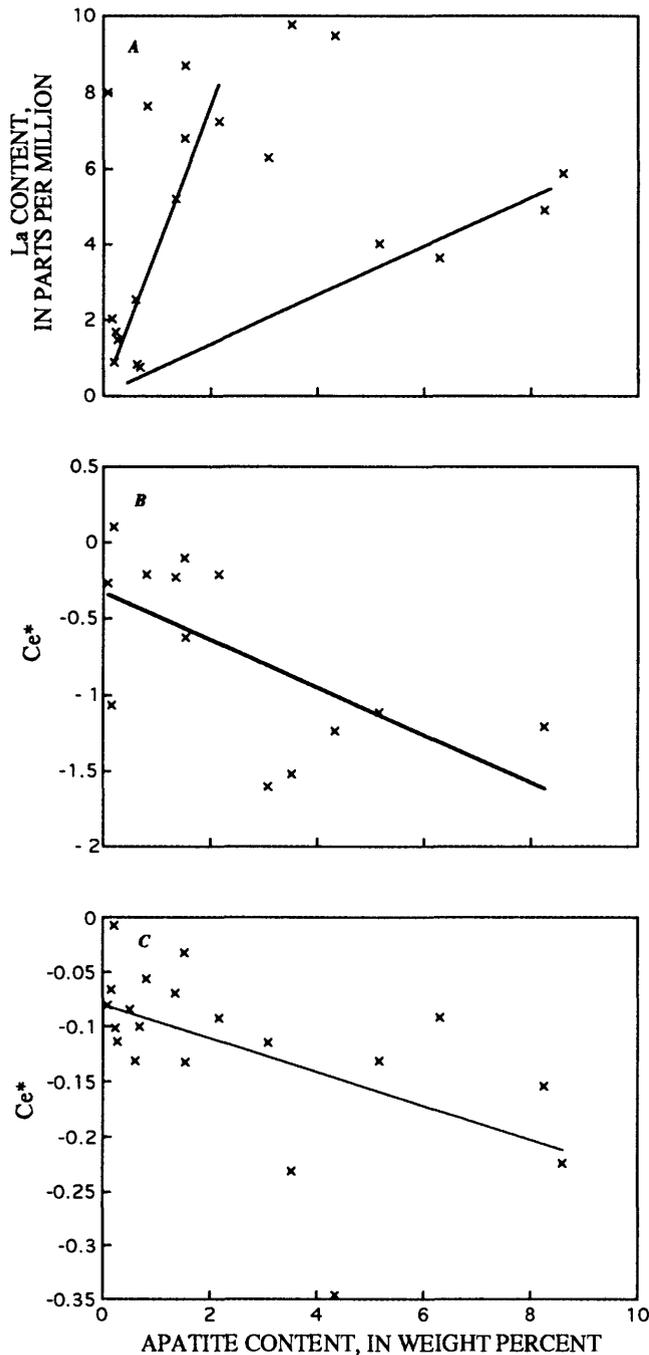


Figure 12. La content (A) and Ce anomaly (B) of marine fraction, and Ce anomaly in bulk sediment (C), versus apatite content in sedimentary rocks of the Monterey Formation. Curves in figure 12A represent apparent trends; curves in figures 12B and 12C are least-squares best-fit lines, with standard deviations of 0.65 (fig. 12B) and 0.54 (fig. 12C)

assuming a minor-element stoichiometry for Miocene organic matter, based on the minor-element content of modern plankton, the rate of accumulation of organic matter required to supply each minor element to the Miocene sea floor can be calculated. These values are compared with the rate of accumulation of organic matter on the sea floor of the modern ocean. Those elements that give higher rates than probable organic fluxes are interpreted to have accumulated directly from seawater as a hydrogenous fraction, in addition to having accumulated as a biogenic fraction. Their rate of accumulation within the hydrogenous fraction depends on such factors as water-column advection, metallic-element concentrations in seawater, and bottom-water redox conditions; and their rate of accumulation within the biogenic fraction depends mostly on primary productivity in the photic zone.

The varying rate of accumulation of sediment in the Monterey Formation (Isaacs, 1985) and the small number of samples analyzed in this study, alone, dissuaded us initially from emphasizing this first approach. However, the range of concentrations and average values measured in these samples agree closely with those of cored (max 3,320 m deep) rock samples from the Santa Maria Basin (Leventhal, 1989) and 35 additional surface samples from the Santa Barbara-Ventura Basin (C.M. Isaacs, unpub. data, 1993). Also, ratios of the major-element oxides and minor elements to Al_2O_3 in the detrital fraction and minor-element:minor-element ratios in the marine fraction are virtually identical in the three sets of samples. Agreement with the Santa Maria Basin samples further precludes major alteration by surficial weathering of the rocks examined in this study.

The second approach compares the relative contents of minor elements in the marine fraction of the rocks with their contents in modern plankton. This approach is greatly facilitated when the minor elements exhibit strong interelement

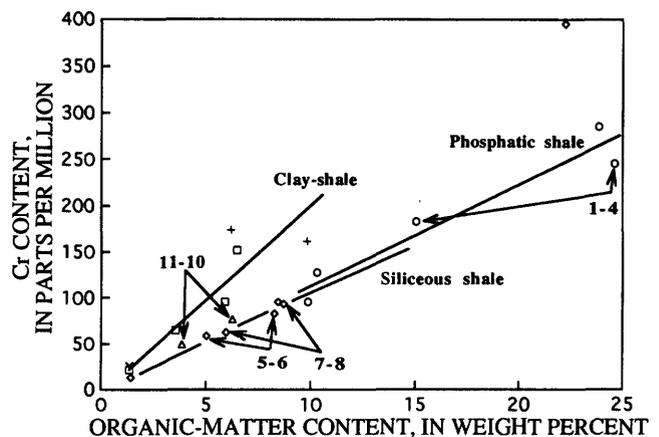


Figure 13. Cr versus organic-matter content of marine fraction in sedimentary rocks of the Monterey Formation (see fig. 8B). Numbered data points represent closely associated, finely laminated/massive sample pairs (see fig. 1 for locations).

correlations. From simple x - y plots, minor-element:minor-element ratios give the elements that are enriched above a biogenic contribution. This procedure, which is used in the absence of information on sediment-accumulation rates, points up the desirability of a master variable, or a single element, that defines the marine organic source, just as Al_2O_3 defines the terrigenous source. In this discussion, we resorted to using Cu as the master variable for the marine biogenic fraction. Several aspects of its chemistry recommend it.

1. It is a bioreactive element, with a concentration in plankton (table 5) that exceeds those of most other bioreactive minor elements (Martin and Knauer, 1973; Broecker and Peng, 1982; Bruland, 1983; Collier and Edmond, 1984; Brumsack, 1986). Thus, its biogenic signal should be strongly imprinted in rocks that were initially rich in organic matter.
2. Although it accumulates from oxic seawater (fig. 5) by a small fraction of its dissolved load being adsorbed onto other particulate matter (Boyle and others, 1977), more importantly, it precipitates under seawater sulfate-reducing conditions as a sulfide (Jacobs and others, 1985) virtually quantitatively. Its concentration in seawater should make this hydrogenous input to any sediment distinguishable from a biogenic or a detrital input. If we assume redox and advection conditions similar to those in the Cariaco Trench (Jacobs and others, 1987); a Cu concentration in seawater advecting into the basin equal to that of seawater at 2,000-m depth (table 8), and a bulk-sediment-accumulation rate of 3 mg/cm^2 per year, similar to that of the Monterey Formation in this area (Isaacs, 1985), then the content of Cu, which would have precipitated as a sulfide, would be approximately 30 ppm.
3. The organic-matter content of the Monterey Formation (table 6) is similar to that of surface and near-surface sediment accumulating currently on the Peru Shelf, in which sulfate-reducing conditions in the sediment pore water extend close to the benthic boundary layer in many areas (Froelich and others, 1988). Although Cu is quickly recycled into the overlying water under oxic conditions (Boyle and others, 1977; Fischer and others, 1986), it should be retained under sulfate-reducing conditions, owing to the low solubility of Cu_2S , as reflected by its precipitation under seawater sulfate-reducing conditions (table 9; Jacobs and others, 1985) and the immobility of Cu in sulfate-reducing sediment (Douglas and others, 1986).
4. The marine fractions of most minor elements in the Monterey Formation correlate strongly with Cu (fig. 14; table 10), allowing a precise comparison of the minor-element contents through simple x - y plots. The absence of such correlations, however, does not preclude the use of this approach, inasmuch as the strength of present correlations should depend more on the composition of host phases than of source phases. The compositions of

the host phases likely reflect diagenetic processes and (or) recent rock alteration, rather than depositional processes. For those minor elements for which such correlations are weak, more samples must be analyzed to fully document the interelement ratios.

We should add that both approaches are stoichiometric. They assume that the composition of detritus was the same as that of standard shale (WSA or NASC), the composition of deposited organic matter was the same as that of modern organic matter, and the metallic-element content in excess of these two sources is attributable to a hydrogenous source.

TERRIGENOUS SOURCE

Ratios of major-element oxides to detritus strongly indicate that the detrital fraction in the Monterey Formation has a uniform composition in the two sections sampled. They furthermore indicate that the detrital fraction had a predominantly terrigenous source, as opposed to a marine volcanoclastic source. Plots of the detrital fraction ($5.6 \times \text{Al}_2\text{O}_3$) versus TiO_2 and K_2O (figs. 6B, 6C) fall along single trends, have slopes approaching those for WSA, and extrapolate to zero. Thus, this fraction is both a current host phase and a source phase.

This interpretation extends to several minor elements. The Co: Al_2O_3 ratio in WSA is 1.13×10^{-4} , virtually the same as in the Monterey Formation (fig. 6F). The scatter of the data about the WSA line likely reflects uncertainties in the analytical procedures at low Co contents (table 4), rather than significant deviations in the Co content of any sample. This same relation extends to Li and Ga (fig. 6) and to Hf, Sc, and Th (table 10). Extrapolation of the curves to zero also supports the conclusion that the detrital fraction is the sole source of these minor elements. These relations support our use of WSA as a representative of the detrital source of the other minor elements under consideration, except REE's.

For those minor elements that correlate with organic matter (figs. 8, 9), their bulk content in most samples is large relative their content in the detrital fraction. Thus, a slight error in our estimate of the detrital contribution, based on the minor-element content in WSA and the Al_2O_3 content in the Monterey Formation samples, introduces a small error in our calculation of the marine fraction of minor elements.

MARINE SOURCE

Strong correlations between many minor elements (fig. 14; tables 10, 11) and the similarity in the partitioning of all minor elements into the organic-matter and apatite trends (fig. 10) suggest that the minor elements have undergone only limited remobilization since their initial accumulation on the sea floor. Adsorption onto residual organic matter, apatite, and, possibly, sulfide precipitates within the fine

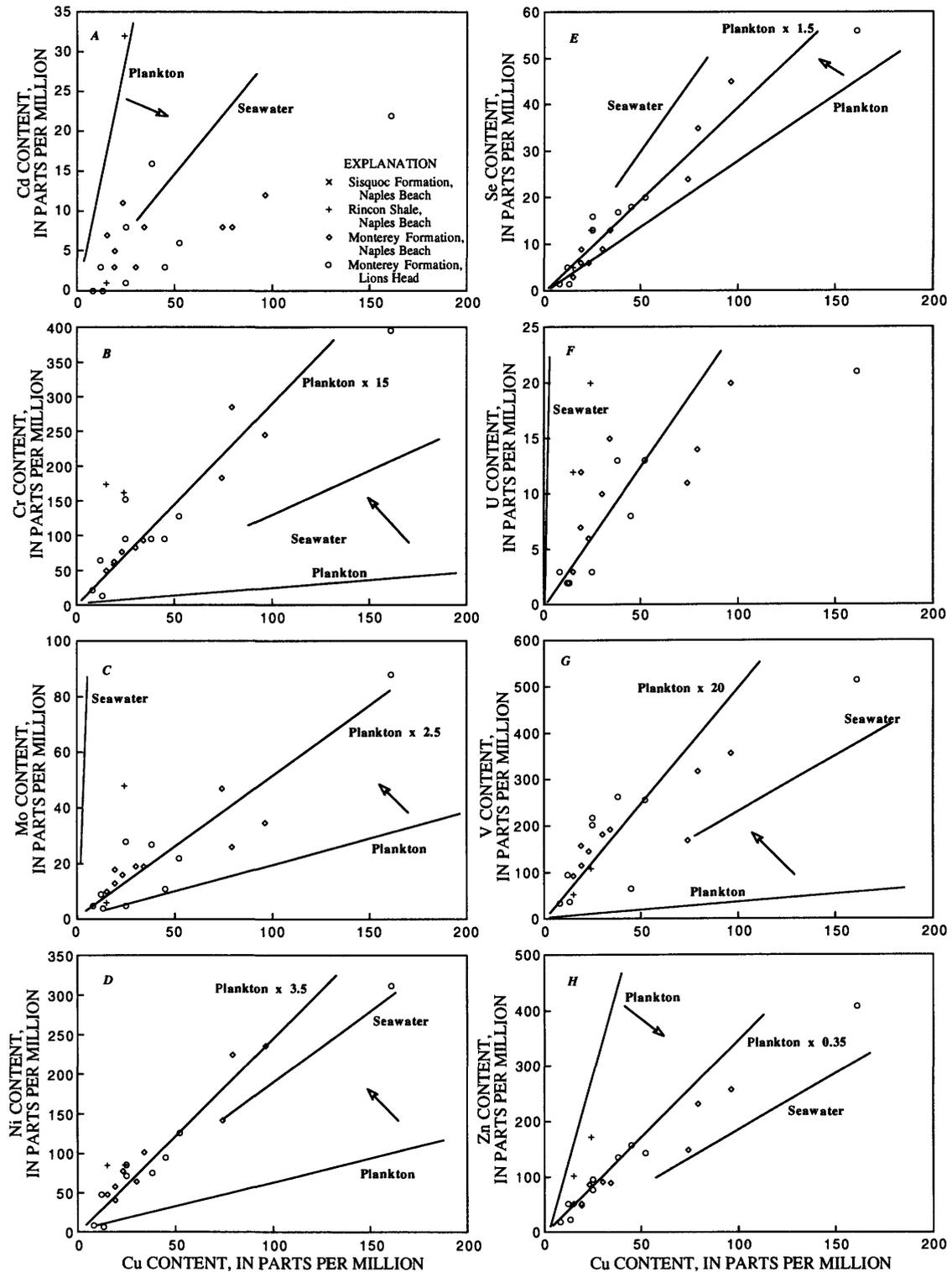


Figure 14. Contents of Cd (A), Cr (B), Mo (C), Ni (D), Se (E), U (F), V (G), and Zn (H) versus Cu content of marine fraction in sedimentary rocks of the Monterey Formation. Samples are grouped by site. Curve labeled "plankton" represents our best estimate of trend for modern plankton, extrapolated into field of the Monterey Formation; curve labeled "seawater" represents ratio for seawater (table 8), also extrapolated into field of the Monterey Formation; curve labeled "plankton×..." represents data for the Monterey Formation, along with its deviation from plankton.

unconsolidated sediment apparently removed minor elements from pore water as they were released during diagenesis from the labile fraction of organic matter and any labile hydrogenous fractions.

Although the marine fraction of several minor elements correlates strongly with organic matter (fig. 8), a curve that defines the approximate average minimum minor-element content in organic matter (curves labeled "organic matter," fig. 9) lies well above that for modern plankton in all cases, by approximately 3- to 300-fold. If the sedimenting organic matter had the same stoichiometry as modern plankton, then clearly a major readjustment to the minor-element:organic-carbon ratio occurred during sedimentation and burial. Depth profiles of organic carbon in modern sediment (Douglas and others, 1986; Froelich and others, 1988; Calvert, 1990), which has an organic-matter content similar to that of the Monterey Formation, strongly suggest that some organic matter was lost during early diagenesis as HCO_3^- , rather than that minor elements were gained. Possible exceptions are Cr, Mo, U, and V, which might have diffused across the benthic boundary layer (Brumsack, 1983; François, 1988; Emerson and Husted, 1991).

Sediment-trap studies of pelagic environments further support the loss of organic matter during early diagenesis (Fischer and others, 1986). Settling particulate matter collected at greater than 3,000-m depth contains approximately 5 times more organic matter than detritus, whereas surface sediment at the same sites contains approximately 100 times more detritus than organic matter. Approximately 95 to 99 percent of the organic matter that rains out of the water column is, thus, oxidized at and very near the surface. Ocean-margin areas will have an even larger flux of organic matter to the sea floor, owing to shallower sea floor (Sarnthein and others, 1988), higher primary productivity (Berger and others, 1988; Pedersen and Calvert, 1990), and a positive relation between the relative rain rate of organic matter from the photic zone and primary productivity (Baines and others, 1994).

To differentiate between minor-element contributions to the Monterey Formation by (1) a biogenic source and (2) a hydrogenous source, we first ascertain the biogenic contribution. The minor-element contribution by organic matter (plankton) alone can be evaluated by comparing the rate of accumulation of organic matter necessary to deliver the now-observed metallic-element contents in the Monterey Formation with modern sedimentary environments. The rate of primary productivity of organic matter in the photic zone of the Peru Shelf today, an area of exceptionally high primary productivity, is approximately 200 mg/cm^2 per year (Chavez and Barber, 1987), of which approximately 15 to 45 percent settles out of the photic zone (Dugdale and Goering, 1970; Von Bockel, 1981). As much as 8 percent escapes oxidation in the water column and benthic boundary layer altogether and accumulates within the sediment (Reimers and Suess, 1983). An even larger amount must

settle (that is, rain) onto the sea floor, as is the case in the pelagic environment (Fischer and others, 1986; Sarnthein and others, 1988). For the Monterey Formation, Isaacs (1985) estimated a bulk-sediment-accumulation rate of 3 to 5 mg/cm^2 per year, although this rate varied spatially and temporally. By considering that (1) the average Cu content in the marine fraction of the Monterey Formation is 37 ppm (fig. 14) and (2) the stoichiometry of accumulating organic matter was the same as that of modern plankton (table 5), we calculate the rate of accumulation of organic matter required to deliver Cu to the sea floor at 10 to 15 mg/cm^2 per year. A calculation based on the Fe content (fig. 7B) in excess of the terrigenous contribution (NASC curve, fig. 6A) and the Fe content of plankton (table 5) gives a similar accumulation rate for organic matter. Cd and Zn require slightly lower rates, and Mo and Se slightly higher rates. Thus, the sediment raining onto the sea floor consisted of approximately 80 percent organic matter. Our interpretation is that primary productivity significantly lower than the current rate on the Peru Shelf could have provided this amount and the total marine fraction of Cu, Cd, Mo, Se, Zn, and Fe to the Monterey sea floor.

If the sole source of these minor elements was organic matter and minor elements were retained in the sediment after deposition, then a projection of the interelement ratio for any pair of minor elements in plankton should extend into the field of concentrations for the Monterey Formation. In fact, all the values are displaced slightly from the minor-element:Cu trend of plankton (fig. 14). The shift in trends away from the ratios in plankton is toward the seawater-concentration ratios, suggesting that a small part of the marine fraction may be attributable to the accumulation of a hydrogenous fraction.

Unlike the Cd:Cu, Mo:Cu, Se:Cu, Zn:Cu, and Fe:Cu trends, the shifts in minor-element:Cu trends for Cr, V, REE's (not shown), and U away from the organic-matter trends are extreme and must be explained largely by inorganic processes. For Cr, U, and V, their diffusion across the benthic boundary layer into a pore-water system that was O_2 depleted offers one possible explanation (Brumsack and Gieskes, 1983; Brumsack, 1986; Emerson and Husted, 1991; Klinkhammer and Palmer, 1991). This same explanation might also account for the slight enrichment of Mo relative to Cu (fig. 14). All else being equal, we might have expected the order of enrichment in the rocks to reflect, in part, their seawater concentrations: $\text{Mo} \gg \text{U} > \text{V} > \text{Cr}$; but this is not the case. In absolute terms, V is somewhat more enriched in rocks of the Monterey Formation than is Cr, and both elements are much more strongly enriched than are Mo and U (fig. 8). Their enrichments, over and above a biogenic contribution and relative to their seawater concentrations, follow the trend $\text{Cr} > \text{V} \gg \text{U} \approx \text{Mo}$.

The thermodynamic properties of these elements (table 9) allow Cr and V to precipitate under conditions of denitrification in the OMZ of the water column, as well as under

lower redox conditions, but these same properties restrict Mo precipitation to sulfate-reducing conditions. Thus, bottom-water conditions of denitrification can explain the much greater enrichments of Cr and V. These two metallic elements would have been strongly enriched in sediment underlying such an OMZ, more so than other minor elements, by precipitation as oxyhydroxides and (or) adsorption onto particulate phases within seawater, but unlikely by diffusion across the benthic boundary layer. The absence of a strong enrichment of U apparently is due to its occurrence in seawater as $\text{UO}_2(\text{CO}_3)_3^{4-}$, rather than as $\text{UO}_2(\text{CO}_3)_2^{2-}$. The slight Mo enrichment probably reflects diffusion across the benthic boundary layer, but we cannot dismiss the possibility of brief periods of sulfate reduction in the bottom water, as occur on the Peru Shelf (Dugdale and others, 1977).

Establishment of denitrification in the bottom water constrains bottom-water advection. If we assume that the denitrifying part of the water column was 250 m thick and that approximately 25 percent of surface productivity was oxidized in the bottom water—conditions similar to those on the Peru Shelf today—a residence time for the bottom water of approximately 5 yr would be required to establish denitrification. Although this value will change by adjusting the various parameters, the instability of the water column of the present-day Santa Barbara Basin (Sholkovitz and Gieskes, 1971) clearly suggests a residence time in this modern, open-oceanic, denitrifying basin on the order of years. This calculation should apply to “bottom” waters, whether we are considering a basin environment or an open-shelf environment, as illustrated in figure 3.

The Cr content of the Monterey Formation also limits the residence time of the bottom water at the time of deposition. Assuming that (1) the thickness of denitrifying water was 250 m, as above; (2) the initial Cr concentration in the water advecting into the basin was 0.21 ppb (table 8), 25 percent of which was removed to the sea floor, the approximate maximum amount of Cr(III) in the OMZ of the eastern Pacific Ocean (Murray and others, 1983); (3) the average Cr content in the marine fraction of the Monterey Formation is 102 ppm, 90 percent of which accumulated as a hydrogenous fraction (fig. 8); and (4) the sediment-accumulation rate was 3 mg/cm² per year (Isaacs, 1985), then the maximum residence time for bottom water in the basin is also calculated at 5 yr. Adjusting the thickness of the denitrifying section of the water column changes the residence time proportionally but does not alter the agreement between the calculation based on the accumulation of Cr and the above calculation of the oxidation of organic matter. Although this calculation is simplistic, the result is consistent with our interpretation of bottom-water denitrification.

The residence time for bottom waters in permanently sulfate reducing basins is considerably greater than this: in the Black Sea about 375 to 1,000 yr (Östlund, 1974; Murray and others, 1991) and in the Cariaco Trench 100 to 200 yr (Jacobs and others, 1987). Although sulfate reduction in the

bottom waters of such fiords as Saanich Inlet can be seasonal (Anderson and Devol, 1973), several aspects of these small inland basins suggest that they are unlikely to be analogs of a large, open-ocean basin. For example, much of the organic matter settling into the bottom water might be terrigenous rather than marine, forcing sulfate reduction at a much greater rate than that predicted by surface-water productivity alone. Also, flushing apparently reestablishes denitrification, rather than oxygen respiration, in the bottom water of Saanich Inlet. Thus, the mean residence time of the bottom water is more than merely 1 yr, and the water is poised to almost immediately reestablish sulfate reduction with the secession of flushing. Although we cannot dismiss the dynamics of this basin as one possible explanation, the longer bottom-water residence time required for the establishment of sulfate reduction in such larger basins as the Black Sea, and the significantly shorter residence time for bottom water of the Miocene basin (or open shelf), seems to preclude sulfate reduction in the bottom water of the Santa Barbara-Ventura Basin during Miocene time.

Field studies of REE's have established their removal from denitrifying seawater and their dissolution under conditions of sulfate reduction (de Baar and others, 1988; German and others, 1991). Sulfate reduction in the bottom water would have required sulfate reduction in the pore water of the surface sediment as well. Such a system should have precluded any enrichment of REE's above a detrital contribution, and yet REE's are enriched in the sediment, although this conclusion is based more on the seawater-type pattern of several samples (fig. 11) than on their absolute contents (fig. 6). Nonetheless, denitrification in the bottom water and sulfate reduction restricted to the near-surface pore water could have allowed the accumulation of REE's from the water column. The content of marine La (fig. 12A) supports this interpretation: Its content in the marine fraction of the Monterey Formation and its content in seawater (table 8) give a bottom-water residence time of 5 yr, the same as did Cr. Thus, REE's should have been no more enriched than by the slight amount we observe.

Scavenging of additional minor elements in the water column, particularly Th, Sc, Be, Ga, and Hf, by particulate phases is clearly an important process on a global scale (Li, 1981; Balistrieri and Murray, 1984; Clegg and Sarmiento, 1989). The mere absence of these elements in the marine fraction of the Monterey Formation, however, may not allow us to dismiss scavenging as an important minor-element-enrichment mechanism in the Monterey Formation. The low concentrations of Th and other elements of this group in seawater should preclude our identification of a hydrogenous fraction within bulk analyses. Leaching experiments, which we have not pursued to date, might identify such a fraction.

Although Cd, Cu, Ni, and Zn are slightly enriched above their biogenic input, scavenging cannot explain the slight shifts in minor-element:Cu ratios toward their values

in seawater (fig. 14). Ni should be only weakly scavenged from seawater, whereas Cu and Zn should be scavenged more efficiently (Clegg and Sarmiento, 1989); yet Ni is the more strongly enriched above a biogenic source. Also, scavenging should have shifted the Zn:Cd ratio away from the stoichiometric value in organic matter of about 9.2 (table 5), which is not observed (compare figs. 14A and 15 with fig. 14H). Evidence against scavenging is also provided by the metallic-element content of fecal material (table 7). Its high Cd, Cu, and Zn contents indicate these minor elements are strongly scavenged by fecal debris, but an Ni:Fe ratio approximating that in WSA suggests a detrital origin for Ni (Piper, 1991). The low organic-carbon content (approx 5 weight percent; Youngbluth and others, 1989), and high clay content (approx 85 weight percent; Dunbar and Berger, 1981) in fecal material emphasize the need for a complete chemical analysis to fully account for the partitioning of metallic elements between the various fractions of fecal material. Even in the absence of such data, the enrichment of Ni in the Monterey Formation over both Zn and Cu is evidence against a major role for seawater scavenging in the enrichment of minor elements in these rocks.

Accumulation within biogenic silica, in addition to organic matter, might account for the displacement of these minor-element ratios away from the plankton value. The enrichment of Zn in biogenic silica is supported by the similarity of the distribution of Zn in seawater to that of $\text{Si}(\text{OH})_4$ (Sclater and others, 1976). Analyses of biogenic silica (Martin and Knauer, 1973), however, show that Cu is even more enriched in this phase, which has a Zn:Cu ratio of about 0.7. Accumulation of this phase on the sea floor, then, followed by its dissolution and the retention of Cu and Zn could explain the shift in the Zn:Cu trend in the rocks away

from the ratio in plankton of 10 (fig. 14H). The Zn:Cu ratios in plankton, silica, and the Monterey Formation actually suggest that silica supplied a major part of minor elements to the sediment. This same mechanism might also contribute to the low Cd contents, but a sampling bias also contributes to the lower than expected average Cd content. The Cd-Cu relation has two separate trends (fig. 9A). The samples with the lower Cd:Cu ratios (phosphatic samples) seem to be disproportionately represented. Additional analyses for the Santa Barbara-Ventura Basin (C.M. Isaacs, unpub. data, 1993) and the analyses by Leventhal (1989) for the Santa Maria Basin (fig. 15) also show these two trends, but most samples plot along the siliceous-shale trend.

An Ni content in biogenic silica needed to explain the shift in the Ni:Cu ratio (fig. 14D) seems to be much higher than we might expect to observe. Thus, the strong enrichment of Ni in these rocks must remain enigmatic until its distribution in biogenic phases is more fully evaluated. Its behavior during early diagenesis (Shaw and others, 1990) seems only to add to the problem; it is apparently remobilized under O_2 -depleted pore-water conditions.

The slight shift of Cd:Cu, Mo:Cu, Se:Cu, U:Cu, and Zn:Cu ratios all away from their plankton values, toward seawater values (fig. 14), might also be explained by a very brief excursion of bottom-water redox conditions into the field of sulfate reduction, as mentioned above. Just as the OMZ on the Peru Shelf can become sulfate reducing for brief periods of time (Dugdale and others, 1977), so might have the bottom water of this Miocene sea. A simple calculation, similar to that made for Mo accumulation in early Quaternary sediment from the Sea of Japan (Piper and Isaacs, 1995), limits sulfate-reducing conditions in the bottom water considered here to less than about 1 percent of the time. Thus, accumulating organic matter remains the dominant source of these elements.

The variation in bottom-water redox is expressed by the difference in V contents in the phosphatic unit and the shale units (fig. 14G). The higher values in the shale units require accumulation under more strongly reducing bottom-water conditions (table 9), an interpretation that seems to conflict with the sulfur-isotopic data (Zaback and Pratt, 1992).

Our stoichiometric approach clearly has many problems because it is a simplified representation of an extremely complex system. Froelich and others (1979, 1988), Bender and others (1989), Jahnke (1990), and Ingall and Van Cappellen (1990) revealed the complex geochemistry of major nutrients during diagenesis, from oxygen respiration, through manganese reduction, denitrification, Fe(III) reduction, and sulfate reduction, to methanogenesis. The behavior of minor elements during early diagenesis is likely to be equally complex (Shaw and others, 1990). As future research better defines the geochemistry of minor elements in the modern marine environment, our interpretation of their distributions in sedimentary rocks will surely require adjustment.

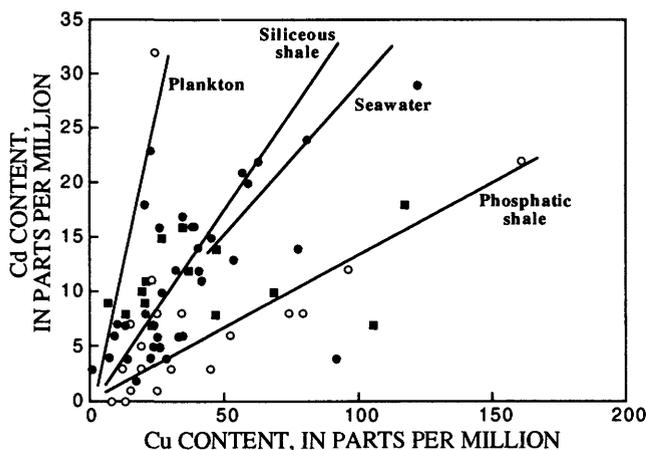


Figure 15. Cd versus Cu contents of marine fraction in sedimentary rocks of the Monterey Formation. Labeled curves represent averages. Data sources: circles, this study; squares, Leventhal (1989); dots, C.M. Isaacs (unpub. data, 1993).

PALEOCEANOGRAPHY

The late Miocene ocean is commonly considered as representative of an ocean that underwent a global anoxic event—that is, sulfate-reducing conditions much more widespread in bottom water of the ocean than they are today. Evidence generally cited for this representation is the seemingly vast areal extent of formations of this age with high organic-matter and minor-element contents, similar to those of the Monterey Formation, and on the interpretation that sedimentary rocks of this composition accumulated under seawater sulfate-reducing conditions. This environment has a very limited areal extent in the ocean today, and yet its accumulating sediment represents a major sink for several minor elements (Kolodny and Kaplan, 1970; Bertine and Turekian, 1973; Cutter, 1982; Jacobs and others, 1987; Emerson and Husted, 1991; Klinkhammer and Palmer, 1991). Sediment within this environment may or may not have high minor-element contents, depending on the rate of accumulation of the detrital fraction (dilution), but it will have high minor-element-accumulation rates. The Monterey Formation has high minor-element contents but minor-element-accumulation rates that were typical of the modern shelf environment.

The effect of a global anoxic event on the distribution of minor elements in seawater would be drastic. In response to their accumulating over a much larger area of the sea floor, minor-element residence times and concentrations in the ocean would decrease sharply. The decrease would be felt worldwide and virtually instantaneously, owing to the very short residence times of most minor elements (Goldberg, 1963b). Piper and Codispoti (1975) suggested that NO_3^- might have the same fate, with the somewhat-unexpected consequence that if organic-matter enriched sedimentary rocks represent periods of global anoxia, they must also represent times of reduced global primary productivity.

The geochemistry of the Monterey Formation suggests another interpretation for its high contents of organic matter and minor elements. The high organic-matter content of this formation and, possibly, of rocks of correlative age results from low bulk-sediment-accumulation rates, that is, slight dilution by detrital phases and biogenic carbonates and silica, not from any significant change in primary productivity or in the geochemistry of the world's ocean. Locally, primary productivity during much of the time represented by the Monterey Formation was probably no higher than it is today in the California Current. Similarly, high minor-element contents reflect this moderate primary productivity and low accumulation rate of diluting sediment fractions. The accumulation rates of Cr and V, alone, required a somewhat-expanded distribution of denitrifying bottom water, from its current restricted distribution in the Santa Barbara Basin. This local expansion of O_2 -depleted bottom water, however, probably had no global significance. Interelement ratios of all minor elements in the Monterey Formation can be ex-

plained by accumulation from a seawater with minor-element contents similar to those in the North Pacific Ocean today; in fact, interelement ratios in the Monterey Formation require such an ocean.

CONCLUSIONS

Analysis of 9 major-element oxides and 33 minor elements in 22 samples of the Sisquoc and Monterey Formations and Rincon Shale were carried out in three laboratories by ICP, NAA, and XRF methods. The precision of most analyses, on the basis of agreement of the results between laboratories, was better than 5 percent, allowing us to identify contributions of the minor elements by terrigenous debris, marine-biogenic matter, and marine hydrogenous phases.

The interelement ratios between major-element oxides (Al_2O_3 , K_2O , TiO_2) and minor elements (Co, Cs, Ga, Hf, Li, Sc, Th) closely approach those of NASC and (or) WSA standards. These ratios indicate that the detrital fraction was the sole source for these elements and that it itself had a terrigenous source. The strength of these relations allows us to determine the detrital contribution to the total inventory of other minor elements (Cd, Cr, Cu, Mo, Ni, Se, U, Zn, REE's) and Fe_2O_3 from the Al_2O_3 :minor-elemental ratios in the standards and the Al_2O_3 content of each individual sample. The residual content of this group of minor elements and Fe_2O_3 represents, then, the marine contribution.

The interelement ratios between Cd, Cu, Mo, Se, Zn, and Fe in this marine fraction of the rocks approximate the corresponding interelement ratios in modern plankton, suggesting that these minor elements had a predominantly biogenic source. During Monterey time, the rate of accumulation of organic matter on the sea floor of the Miocene Santa Barbara-Ventura and Santa Maria Basins necessary to provide these elements to the sediment was approximately equal to that on the present-day California Continental Shelf, an area of moderately intense coastal upwelling and primary productivity in the photic zone of the water column.

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. Their rates of accumulation in Monterey sediment limited the residence time of bottom water in the basin to a maximum of approximately 5 yr. This residence time is the same as that necessary to establish denitrification in the bottom water by way of the oxidation of settling organic matter.

Sulfate reduction was not established in the bottom water through bacterial respiration, an interpretation based on the preservation of a seawater-derived enrichment of REE's in the Monterey Formation, the absence of a strong

marine input of U, and the absence of enrichments of Cu, Cd, Se, Zn, and, particularly, Mo above a biogenic input. Otherwise, Cu, Cd, Se, Zn, and Mo would have accumulated as inorganic sulfides, in addition to accumulating in an organic fraction, 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 is 5 to 50 times more abundant in seawater than V and Cr and 2,000 more abundant than REE's (La), 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 overlying water column.

In the ocean today, no single environment represents a perfect analog of the Monterey Formation. The chemical and biologic processes and bathymetry that controlled the overall composition of these rocks do occur, but only within several shelf-slope environments. Also, the Monterey Formation was deposited over several million years, during which time the rocks recorded significant local oceanographic changes. The minor-element content of the Monterey Formation, however, requires that the chemistry of the open ocean during late Miocene time was identical to that of today.

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