

Chemical Composition of Surface Sediments on the Sea Floor

Walter E. Dean and James V. Gardner

Summary and Introduction

Sediments cover most of the sea floor in the Gulf of the Farallones, with a few areas of exposed bedrock. To help determine the origin and distribution of these sediments, 112 core samples were taken by the U.S. Geological Survey at sites on the sea floor from the shallow shelf down to a water depth of about 3,000 m (10,000 ft). These samples were analyzed for 28 major and trace elements, organic carbon, and calcium carbonate.

Many factors have affected the history, transport, and distribution of sediments in the Gulf of the Farallones, including the shape of the sea floor, sea-level fluctuations, and current patterns. The Continental Shelf in much of the gulf has a low gradient of about 0.1° , and water depth ranges from less than 50 m (160 ft) to about 120 m (400 ft). The Continental Slope in much of the gulf has a steeper gradient of about 3° , and water depth reaches about 3,200 m (10,500 ft) at its base. Although the shelf is uncut by channels and canyons, the upper slope is incised with numerous gullies and submarine canyons, including Pioneer Canyon (fig. 1).

Before 500,000 years ago, the main sources of sediment to the Gulf of the Farallones were the nearby onshore areas with their variety of sedimentary, metamorphic, and igneous rocks. About 500,000 years ago, drainage from interior California broke through to the Pacific Ocean at the Golden Gate, providing additional sources of sediment from as far away as the Sierra Nevada. The Continental Shelf between the Golden Gate and the Farallon Islands is covered with sandy sediment, which has been repeatedly reworked by fluctuations in sea level and great (100-year) storms. Major lowerings of sea level during global glaciations have exposed the shelf in the gulf as dry land several times, most recently from about 20,000 to 15,000 years ago. In these glacial periods, sea level was lowered by hundreds of feet, because of the large amount of water tied up in ice sheets on land. During these lowstands, a river probably coursed across all of what is now the Continental Shelf in the gulf, although no channel has yet been identified. About 15,000 years ago, rising sea level caused by the melting of the ice sheets once again drowned the Continental Shelf.

Water movement in the Gulf of the Farallones affects the distribution of sediment on the sea floor and the movement of sediment across the Continental Shelf to the deep sea (see chapter on Current Patterns over the Continental Shelf and Slope). The main oceanographic influences on circulation in the gulf include the southward-flowing California Current during the winter and the northward-flowing California Undercurrent during the summer (fig. 1). Strong offshore currents can also be caused by summer northwesterly winds, leading to coastal upwelling of cold water. Currents generated by tides also help account for the seaward transport of sediment in the gulf.

The results of chemical analysis of the core samples collected from the sea floor in the Gulf of the Farallones can be used as “fingerprints” to identify sources and transport patterns of sediment (see chapter on Heavy-Mineral Provinces on the Continental Shelf). The sandy sediments on the Continental Shelf between the Golden Gate and the Farallon Islands contain abundant heavy minerals that are rich in iron, magnesium, titanium, phosphorus, and many trace elements. The sediments immediately adjacent to the Farallon Islands contain low concentrations

of heavy minerals and the chemical elements associated with them; instead, these sediments are rich in silica (SiO_2). Sediments deposited on the Continental Slope have higher contents of organic matter and clay and, consequently, have higher concentrations of elements associated with clay minerals, such as aluminum, lithium, potassium, and sodium. Calcium carbonate (CaCO_3), mainly from the shells of pelecypods (oysters, clams, and mussels), is a very minor constituent of surface sediments in the gulf.

Methods

A total of 93 Soutar Van Veen cores were collected from the shelf in 1989, and 19 gravity cores were collected from the slope in 1990 (fig. 1). Surface grain-size measurements were made on samples from all Van Veen and gravity cores (Maher and others, 1991; Karl, 1992). Splits of the Van Veen and gravity core samples for geochemical analyses were air dried and ground in a ceramic mill. Concentrations of 10 major elements (Si, Al, Fe, Mg, Ca, Na, K, Ti, P, Mn) were measured by wavelength-dispersive X-ray-fluorescence spectrometry. Concentrations of 27 major and trace elements (Al, Fe, Mg, Ca, Na, K, Ti, P, Mn, Ba, Ce, Co, Cr, Cu, Ga, La, Li, Nd, Ni, Pb, Sc, Sr, Th, V, Y, Yb, Zn) were determined by inductively coupled argon-plasma emission spectrometry (Baedecker, 1987). Results of these analyses were reported by Dean and Gardner (1995), along with a discussion of the precision and accuracy of the analytical methods.

Concentrations of total carbon and carbonate carbon were determined by coulometry (Engleman and others, 1985) on splits of the geochemistry samples. Organic-carbon contents were determined by the difference between total carbon and carbonate carbon. Calcium carbonate (CaCO_3) content was calculated by dividing the carbonate-carbon content by 0.12, the mole fraction of carbon in CaCO_3 .

Multivariate analysis of the geochemical data was carried out by *Q*-mode factor analysis. The computer program used is a modified version of the extended CABFAC program (Klovan and Miesch, 1976; Miesch, 1981).

Distribution of Grain Size

Grain-size measurements of surficial sediment on the continental margin in the Gulf of the Farallones study area were reported by Maher and others (1991) and Karl (1992). Very fine sand dominates the inner shelf and margin (fig. 2), whereas fine to medium sand occurs in a central area of the shelf directly offshore from the Golden Gate. This distribution of coarser sediment on the shelf west of the Golden Gate probably reflects relict sediment from a lowstand deposit or a winnowed lag of San Joaquin-Sacramento River sediment reworked by strong tides and major storms. The area of finer grain size between the Golden Gate and Half Moon Bay probably represents winnowed material that was transported in suspension in the nearshore zone away from the coarser material that lies to the northwest. Some fine sediment is carried as suspended sediment across the San Joaquin-Sacramento River delta, through the Golden Gate, and across the Continental Shelf. As expected, the mean grain size decreases with increasing depth on the slope, with generally coarser grain sizes in Pioneer Canyon (fig. 1).

Distribution of Element Concentrations

A multivariate *Q*-mode factor analysis was performed on the geochemical data to determine associations among elements and to objectively determine geographic groupings of samples over

the Gulf of the Farallones study area, on the basis of geochemical similarities. The factor analysis reduces the 31 geochemical variables (elements or element oxides) to a much smaller number (typically, three to five) of composite geochemical variables called “factors” based on statistical groupings of elements. The “concentrations” of these composite geochemical variables are called the factor loadings. Several computations were made by using two different similarity coefficients (correlation coefficient and cosine theta) and three different types of factor axes in multidimensional space (principal components, varimax rotation, and oblique rotation). Most runs produced two dominant factors: an iron–titanium–rare-earth-element (REE) factor and an organic-clay factor. Most other factors were expressing the variance in one or two elements. The best results were obtained using the correlation coefficient as a measure of similarity together with a four-factor model and varimax rotation in four-dimensional space to maximize the variance in the normalized data. To determine which geochemical variables had the most influence in each factor, the factor loadings were correlated with the concentration of each geochemical variable. The results of this correlation analysis are listed in table 1.

Table 1 shows that factor 1 loadings have high correlation coefficients ($r > 0.5$) with many geochemical variables. Those variables (elements or element oxides) with the most influence on factor 1, in order of decreasing importance (decreasing value of correlation coefficient, table 1), are Nd, Fe₂O₃, Ce, TiO₂, V, La, Y, Yb, MnO, Th, Sc, Cr, Co, P₂O₅, Zn, and MgO. Contour maps of factor 1 loadings and concentrations of three representative factor 1 element oxides (Fe₂O₃, TiO₂, MnO) over the continental margin in the study area are shown in figure 3.

Sediment with the highest factor 1 loadings (fig. 3A), as typified by Fe₂O₃ contents greater than 5.0 weight percent and TiO₂ contents greater than 1.4 weight percent (figs. 3B, 3C), has maximum concentrations of factor 1 elements in an area between the Golden Gate and the Farallon Islands. Some of the factor 1 elements, illustrated by MnO in figure 3D but also by La, Ce, Th, and Cr (table 1), show a minor concentration of factor 1 centered on the Farallon Islands, whereas other factor 1 elements (Fe₂O₃, TiO₂, P₂O₅, MgO) have low concentrations in sediment around the Farallon Islands. This distribution of factor 1 sediment falls within the sand-rich belt around the Farallon Islands and reflects deposits of heavy-mineral components in relict sediment that has been continuously reworked by fluctuations in sea level and major (100 yr) storms. The heavy minerals probably were derived from metamorphic rocks of the Franciscan terranes that the San Joaquin-Sacramento River system traverses as it approaches San Francisco Bay. The bull’s-eye of relatively low values of Fe₂O₃ and TiO₂ (figs. 3B, 3C), as well as P₂O₅ and MgO, around the Farallon Islands probably reflects the composition of sand derived from the granitic Farallon Islands.

Those variables (elements or element oxides) with the most influence on factor 2, in order of decreasing importance (decreasing value of correlation coefficient, table 1), are Li, organic C, Na₂O, Cu, Ni, Ba, Zn, K₂O, Al₂O₃, and MgO. Contour maps of factor 2 loadings and concentrations of three representative factor 2 elements (Li, organic C, Cu) over the continental margin in the study area are shown in figure 4.

The distribution of sediment with high factor 2 loadings (fig. 4A) reflects the downslope decrease in grain size (fig. 2) and the concomitant increase in organic-carbon content (fig. 4B). This relation can be seen in a plot of mean grain size versus organic-carbon content (fig. 5A). The finer sediment (higher phi values) contains more organic carbon. The finer sediment contains more clay minerals that commonly are enriched in Li (figs. 4C, 5B), Na₂O, K₂O, Al₂O₃, and MgO. Thus, these elements and element oxides had major influences on factor 2 loadings (table 1). The higher Cu, Ni,

and Zn contents in factor 2 sediment are related to enrichment of these metals in organic-carbon-rich sediment (Vine and Tourteot, 1970; Holland, 1979). The relations between organic-carbon content and the concentrations of these three metals (fig. 6) are clearer in the finer, organic-carbon-rich slope sediment. The organic-carbon contents (fig. 5B) are relatively high for a continental shelf and margin, reflecting the high productivity supported by the nutrient-rich seasonal upwelling of the California Current system. Higher Ba contents associated with siliceous biogenic debris (Dymond and others, 1992) probably account for the higher Ba contents in organic-carbon-rich factor 2 sediment. MgO is associated with both factors 1 and 2 (table 1), reflecting Fe- and Mg-rich heavy minerals in shelf sand (factor 1) and clay minerals in slope mud (factor 2).

Calcium carbonate is a minor constituent of surficial sediment in the Gulf of the Farallones study area, with values of mostly less than 1 weight percent over the entire continental margin (fig. 7). The distribution of CaCO_3 is dominated by a bull's-eye in the northern part of the study area, probably caused by a few bivalve shell fragments. Factor 3 loadings reflect this distribution of CaCO_3 (table 1). Although the Sr content also is correlated with factor 3 loadings (table 1), the distribution of Sr in surficial sediment differs considerably from that of CaCO_3 , suggesting that most of the Sr is contributed from detrital clastic material rather than from the very little CaCO_3 that is present.

Table 1 shows that most of the contribution to factor 4 loadings is from SiO_2 . Minor contributions to factor 4 loadings also come from CaO, TiO_2 , MnO, Ce, La, and Nd, but the variance in these elements and element oxides is mainly accounted for by factor 1 or, for CaO, by factor 3. The SiO_2 content over the continental margin in the Gulf of the Farallones study area is mapped in figure 8.

SiO_2 contents are generally 67 to 69 weight percent on the shelf and distinctly higher (max 77 weight percent) adjacent to the Farallon Islands, reflecting silica-rich granitic sand shed from the islands. SiO_2 contents also tend to decrease downslope, reflecting the downslope increase in clay minerals that generally contain less SiO_2 and more Al_2O_3 than do quartz-rich silt and sand. The higher SiO_2 contents on the slope at the south end of the study area probably reflects larger amounts of sand moving down Pioneer Canyon. The contrast in composition between quartz-rich granitic sand and heavy-mineral-rich sand is clearly shown in figure 9 by the negative correlation between SiO_2 and Al_2O_3 , Fe_2O_3 , and MgO in shelf sand. Al_2O_3 , Fe_2O_3 , and MgO contents in the fine slope mud are fairly constant, indicating that this mud is more homogeneous than the shelf sand that tends to have pockets of heavy minerals.

Conclusions

The Continental Shelf between the Golden Gate and the Farallon Islands is covered with relict sandy sediment that has been repeatedly reworked by fluctuations in sea level and major (100-yr) storms. This sand contains abundant heavy minerals that are rich in Fe, Mg, Ti, P, and many trace elements. The sediments immediately adjacent to the Farallon Islands contain low concentrations of heavy minerals and the chemical elements associated with them. Instead, these sediments are rich in SiO_2 . Sediments deposited on the Continental Slope (water deeper than 120 m) have higher contents of organic matter and clay, and, consequently, of elements associated with clay minerals, such as Al, Li, K, and Na. A very minor constituent of surface sediments in the Gulf of the Farallones is CaCO_3 , which constitutes less than 1 percent of sediment over the entire Continental Shelf and Slope in the region.

Further Reading

- Baedecker, P.A., ed., 1987, Geochemical methods of analysis: U.S. Geological Survey Bulletin 1770, 129 p.
- California Division of Mines and Geology, 1980, Geologic map of California, San Francisco sheet: Sacramento, scale 1:250,000.
- Dean, W.E., and Gardner, J.V., 1995, Geochemistry of surface sediments in the Gulf of the Farallones: U.S. Geological Survey Open-File Report 95-527, 57 p.
- Dymond, J., Suess, E., and Lyle, M., 1992, Barium in deep-sea sediment; a geochemical proxy for paleoproductivity: *Paleoceanography*, v. 7, p. 163-181.
- Engleman, E.E., Jackson, L.L., Norton, D.R., and Fischer, A.G., 1985, Determination of carbonate carbon in geological materials by coulometric titration: *Chemical Geology*, v. 53, p. 125-128.
- Hall, J.F., 1966, Fleishacker Zoo to Mussel Rock (Merced Formation)—a Plio-Pleistocene nature walk: California Division of Mines, Geological and Mineral Information Service, v. 19, p. S22-S25.
- Holland, H.D., 1979, Metals in black shales—a reassessment: *Economic Geology*, v. 74, p. 1676-1679.
- Huyer, A., Kosro, P.M., Fleischbein, J., Ramp, S.R., Stanton, T., Washburn, L., Chavez, F.P., Cowles, T.J., Pierce, S.D., and Smith, R.L., 1991, Currents and water masses of the coastal transition zone off northern California, June to August, 1988: *Journal of Geophysical Research*, v. 96, p. 14809-14832.
- Karl, H.A., ed., 1992, Comprehensive geological and geophysical survey of the gulf of the Farallones Region, central California: U.S. Geological Survey administrative report to U.S. Environmental Protection Agency, 188 p.
- Klován, J.E., and Miesch, A.T., 1976, Extended CABFAC and QMODEL computer programs for *Q*-mode factor analysis of compositional data: *Computers and Geosciences*, v. 1, p. 161-178.
- Maher, N.M., Karl, H.A., Chin, J.L., and Schwab, W.C., 1991, Station locations and grain-size analysis of surficial sediment samples collected on the continental shelf, Gulf of the Farallones during cruise F2-89-NC, January, 1989: U.S. Geological Survey Open-File Report 91-375-A, 42 p.
- Miesch, A.T., 1981, Computer methods for geochemical and petrologic mixing problems, *in* Merriam, D.F., ed., *Computer applications in the earth sciences*: New York, Plenum, p. 244-265.
- Noble, M., and Gelfenbaum, G., 1990, A pilot study of currents and suspended sediment in the Gulf of the Farallones: U.S. Geological Survey Open-File Report 90-476.
- Noble, M., Ramp, S.R., and Kinoshita, K., 1992, Current patterns over the shelf and slope adjacent to the Gulf of the Farallones; executive summary: U.S. Geological Survey Open-File Report 92-382, 26 p.
- Ramp, S.R., Jessen, P.F., Brink, K.H., Niiler, P.P., Daggett, F.L., and Best, J.S., 1991, The physical structure of cold filaments near Point Arena, California, during June, 1987: *Journal of Geophysical Research*, v. 96, p. 14859-14884.
- Strub, P.T., Kosro, P.M., and Huyer, A., 1991, The nature of the cold filaments in the California Current system: *Journal of Geophysical Research*, v. 96, p. 14743-14768.
- Vine, J.D., and Tourtelot, E.B., 1970, Geochemistry of black shales—a summary report: *Economic Geology*, v. 65, p. 253-272.
- Washburn, L., Swenson, M.S., Largier, J.L., Kosro, P.M., and Ramp, S.R., 1993, Cross-shelf sediment transport by an anticyclonic eddy off northern California: *Science*, v. 261, p. 1560-1564.

Table 1. Correlation coefficients between loading for factors 1 through 4.

Factor	1	2	3	4
Major-element oxides				
Silicon (SiO ₂)	0.167	-0.627	-0.027	0.692
Aluminum (Al ₂ O ₃)	-.214	.626	-.040	-.502
Iron (Fe ₂ O ₃)	.855	-.049	-.096	.217
Magnesium (MgO)	.570	.587	-.244	-.154
Calcium (CaO)	.249	-.102	.576	.470
Sodium (Na ₂ O)	-.069	.791	.060	-.372
Potassium (K ₂ O)	-.252	.643	.221	-.500
Titanium (TiO ₂)	.843	-.496	-.098	.383
Phosphorus (P ₂ O ₅)	.614	.280	.010	-.409
Manganese (MnO)	.774	-.527	-.119	.483
Organic C	.292	.830	-.223	-.451
CaCO ₃	.035	.127	.807	.362
Trace elements				
Barium (Ba)	0.009	0.747	-0.056	-0.190
Cerium (Ce)	.845	-.521	-.026	.399
Cobalt (Co)	.624	.058	-.213	.212
Chromium (Cr)	.659	-.416	-.081	.268
Copper (Cu)	.428	.782	-.247	-.149
Gallium (Ga)	-.094	.312	-.263	-.524
Lanthanum (La)	.837	-.540	-.026	.403
Lithium (Li)	.299	.841	-.229	-.561
Neodymium (Nd)	.860	-.473	-.019	.362
Nickel (Ni)	.462	.781	-.339	-.361
Lead (Pb)	.109	-.102	.068	-.076
Scandium (Sc)	.680	-.100	-.187	.100
Strontium (Sr)	-.281	.023	.671	.268
Thorium (Th)	.749	-.341	-.003	.321
Vanadium (V)	.840	-.120	-.217	.244
Yttrium (Y)	.825	-.410	-.117	.216
Ytterbium (Yb)	.788	-.274	-.093	.154
Zinc (Zn)	.583	.744	-.269	-.256

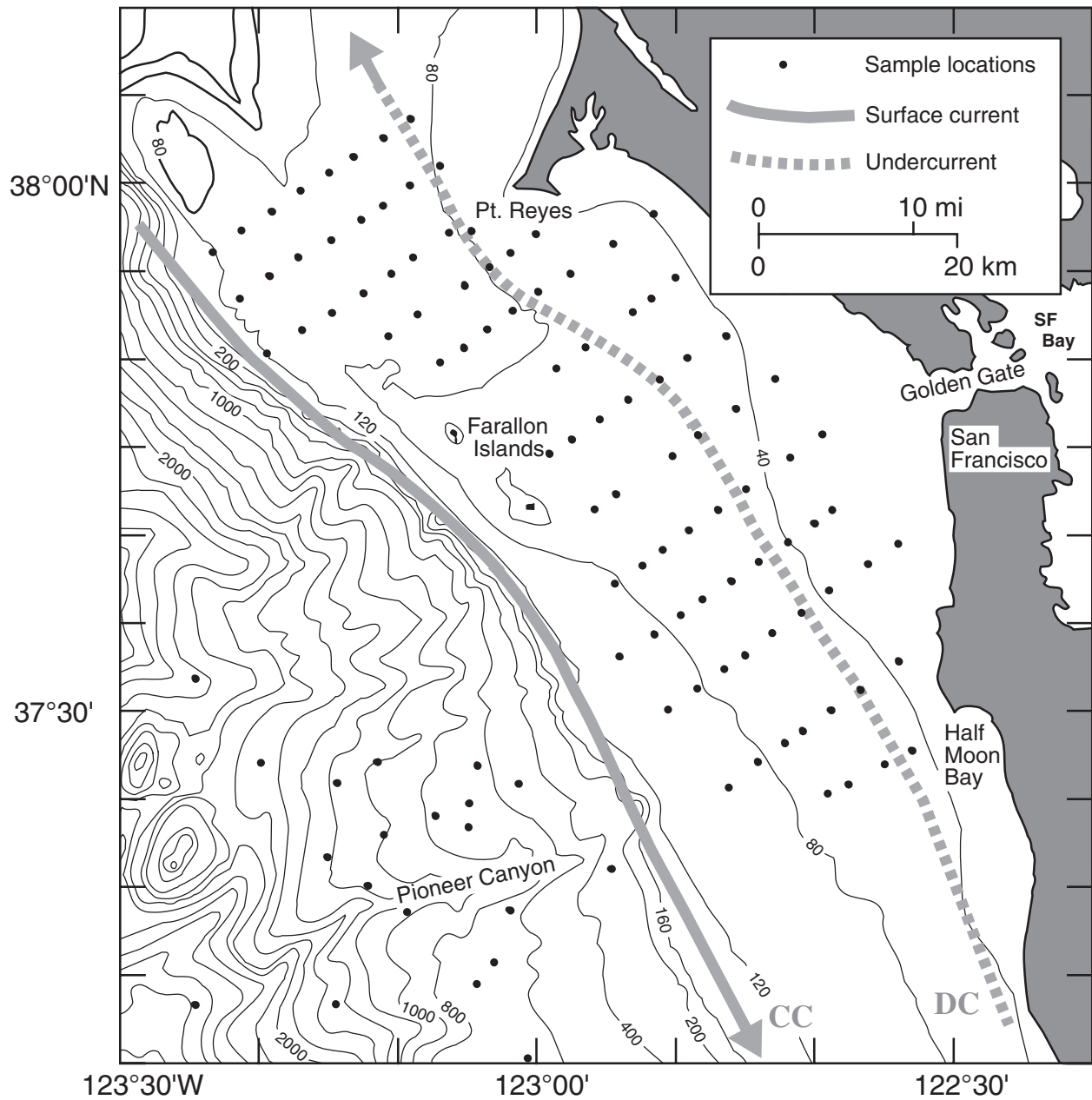


Figure 1. Gulf of the Farallones study area, showing locations of cores, bathymetry, surface currents, and shorelines of the California margin from latitude 37°10' to 38°10' N. and from long 122°20' to 123°30' W. CC, average position of the California Current; DC, seasonal location of the California Undercurrent. Outer edge of the Continental Shelf is at about 120 m (400 ft) water depth. Bathymetry in meters (1 m = 3.281 ft).

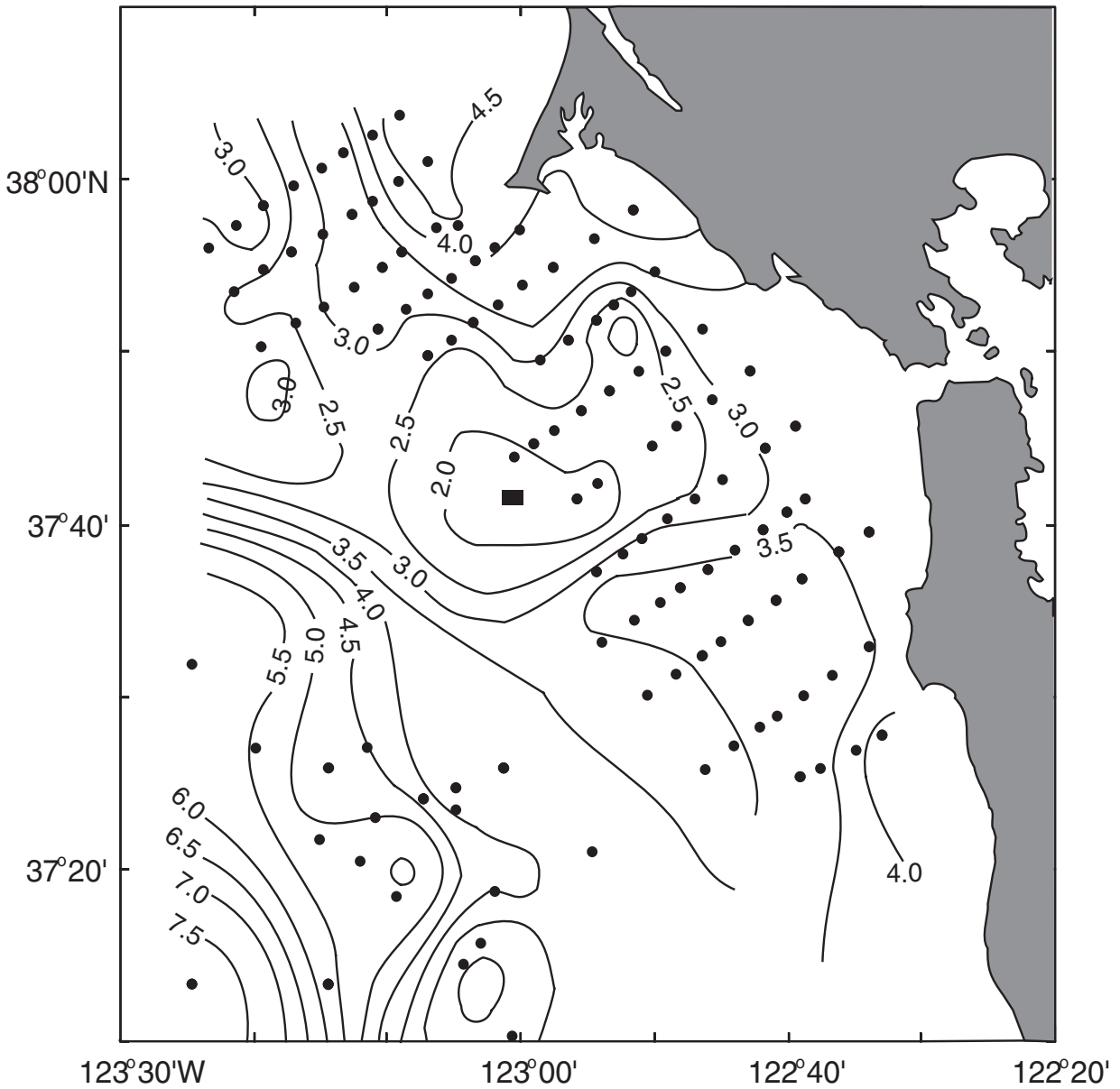


Figure 2. Gulf of the Farallones study area, showing contours of mean grain size (in phi units) of surficial sediment: 2–3, fine sand; 3–4, very fine sand; 4–6, coarse silt; 6–7, medium silt; 7–9, fine silt. Rectangle, the main Farallon Islands.

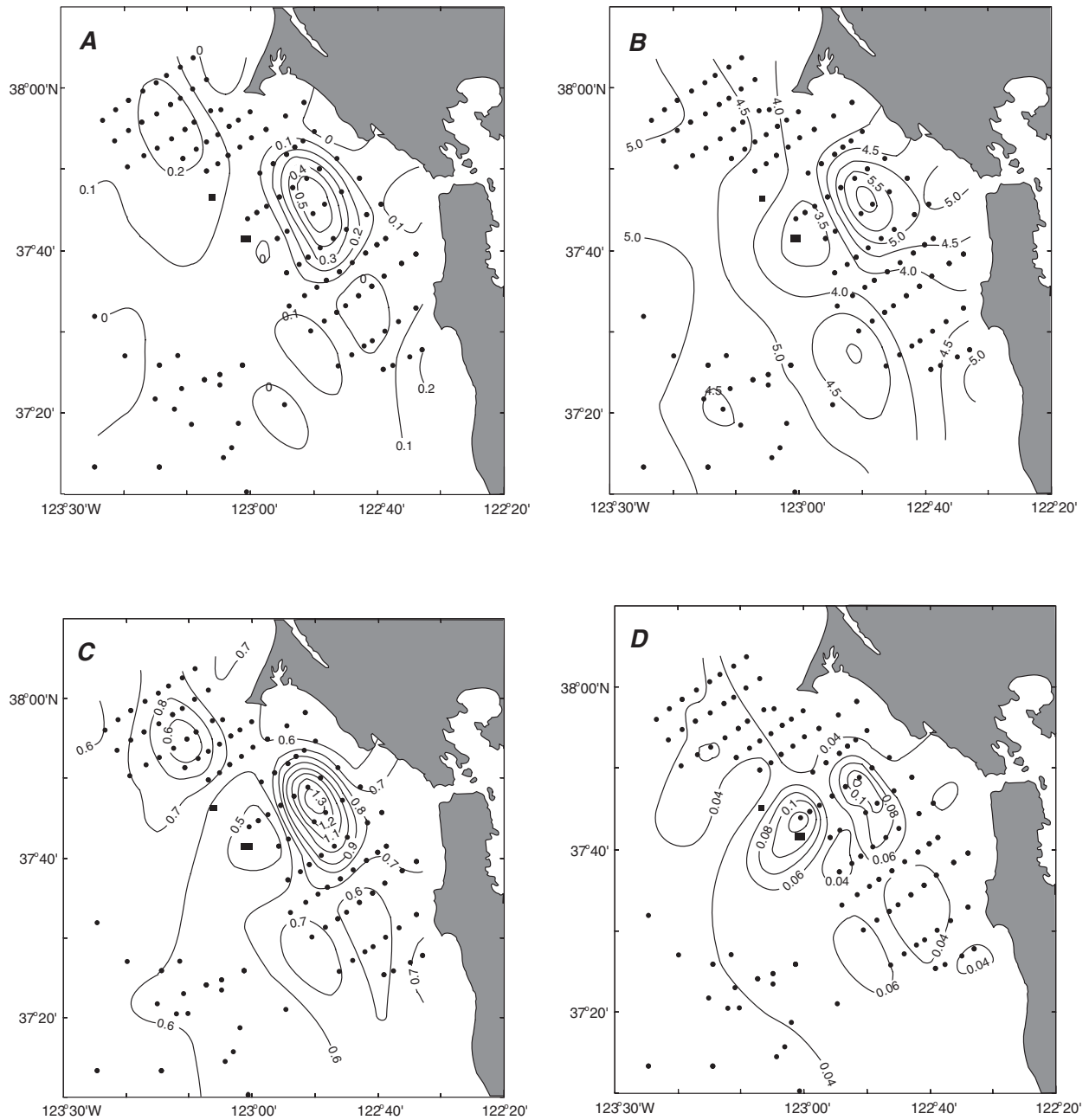


Figure 3. Gulf of the Farallones study area, showing contours of factor 1 loadings (A, in phi units), Fe_2O_3 content (B, in weight percent), TiO_2 content (C, in weight percent), and MnO content (D, in weight percent) in surficial sediment. Rectangles, Farallon Islands. Note concentration of factor 1 sediment between the Golden Gate and the Farallon Islands, reflecting heavy minerals derived from metamorphic rocks of the Franciscan terranes that the San Joaquin-Sacramento River system traverses as it approaches San Francisco Bay.

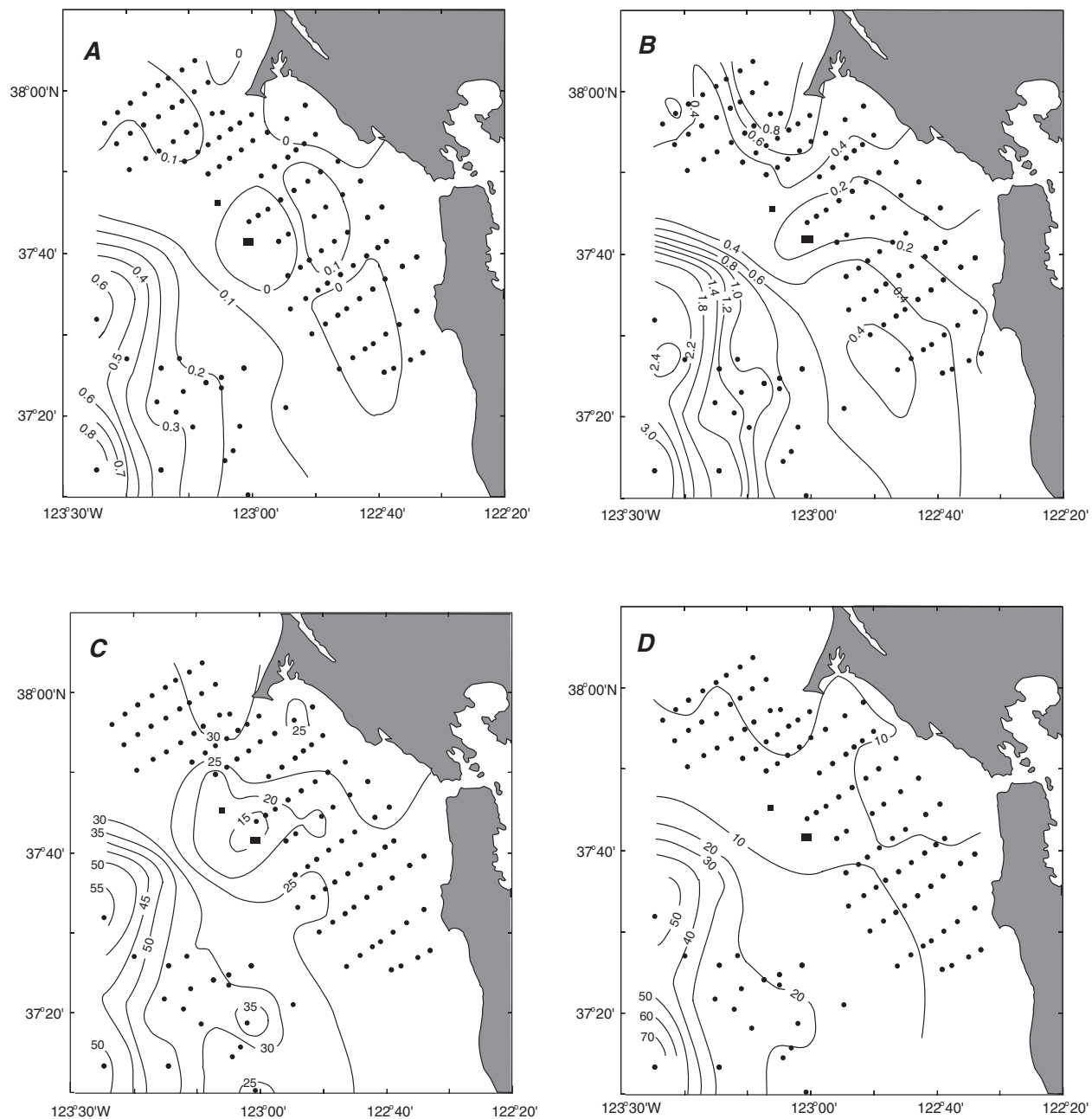


Figure 4. Gulf of the Farallones study area, showing contours of factor 2 loadings (A, in phi units), organic-carbon content (B, in weight percent), Li content (C, in parts per million), and Cu content (D, in parts per million) in surficial sediment. Rectangles, Farallon Islands. Concentration of factor 2 sediment on the Continental Slope reflects finer sediment that is deposited there with higher concentrations of clay minerals (richer in such elements as Li) and organic carbon (richer in such trace elements as Cu).

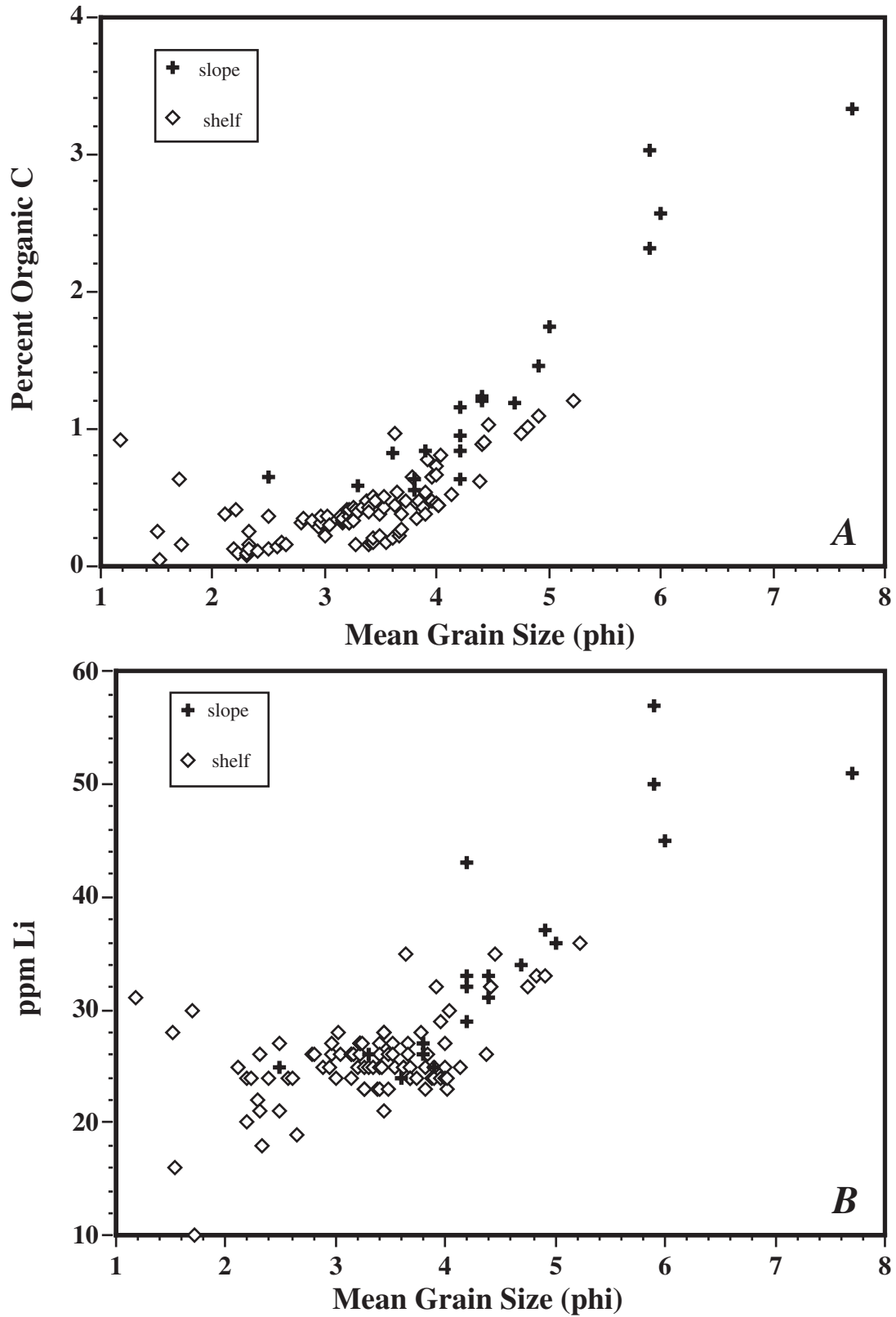


Figure 5. Mean grain size of surficial sediment in Gulf of the Farallones study area from shelf and slope cores (see fig. 2) versus organic-carbon content (A) and Li content (B). Finer sediment (higher phi values) concentrates more clay minerals (richer in such elements as Li) and organic carbon.

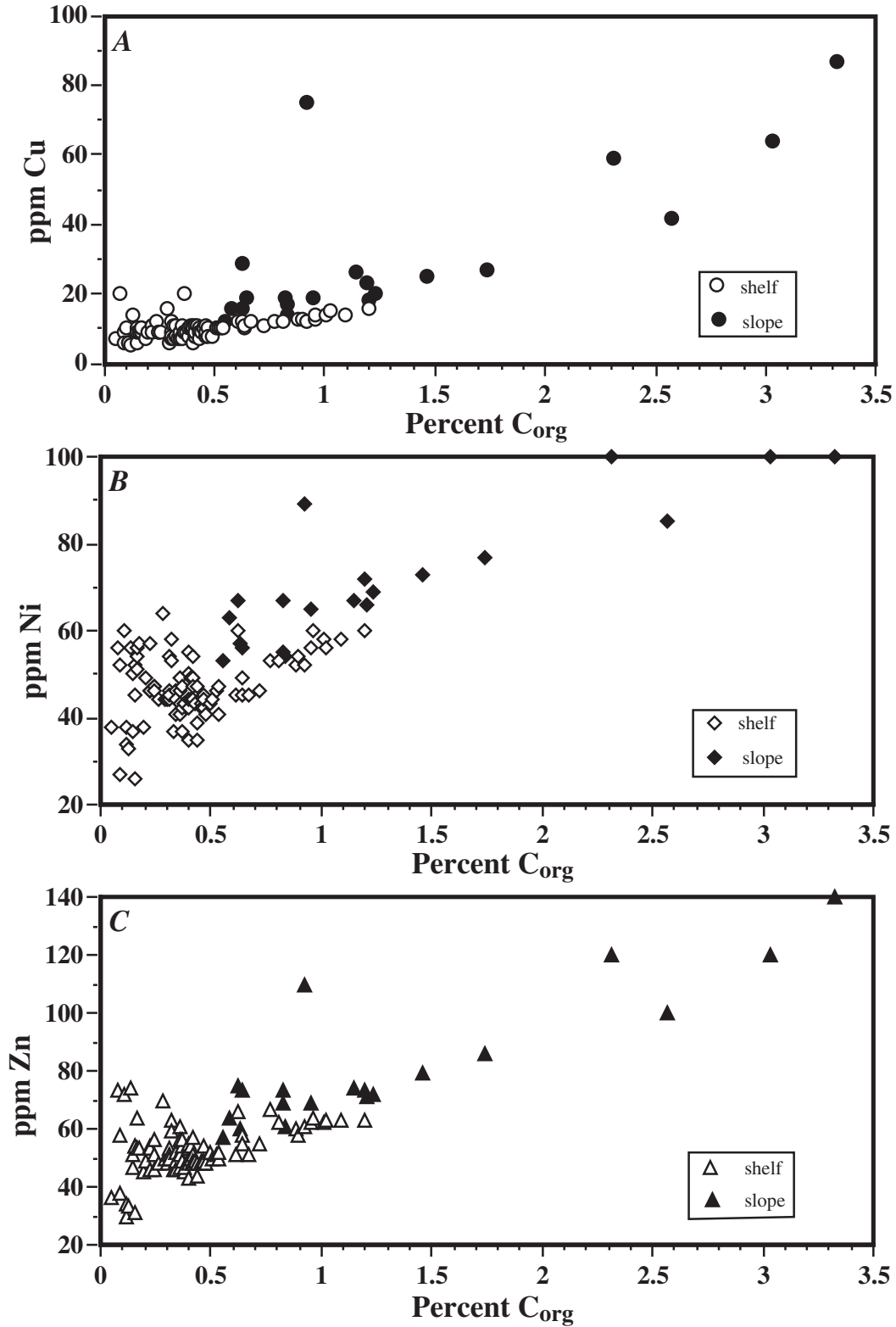


Figure 6. Organic-carbon content versus Cu (A), Ni (B), and Zn (C) contents of surficial sediment in Gulf of the Farallones study area from shelf and slope cores. Organic-carbon-rich sediment commonly is enriched in certain trace elements, such as Cu, Ni, and V.

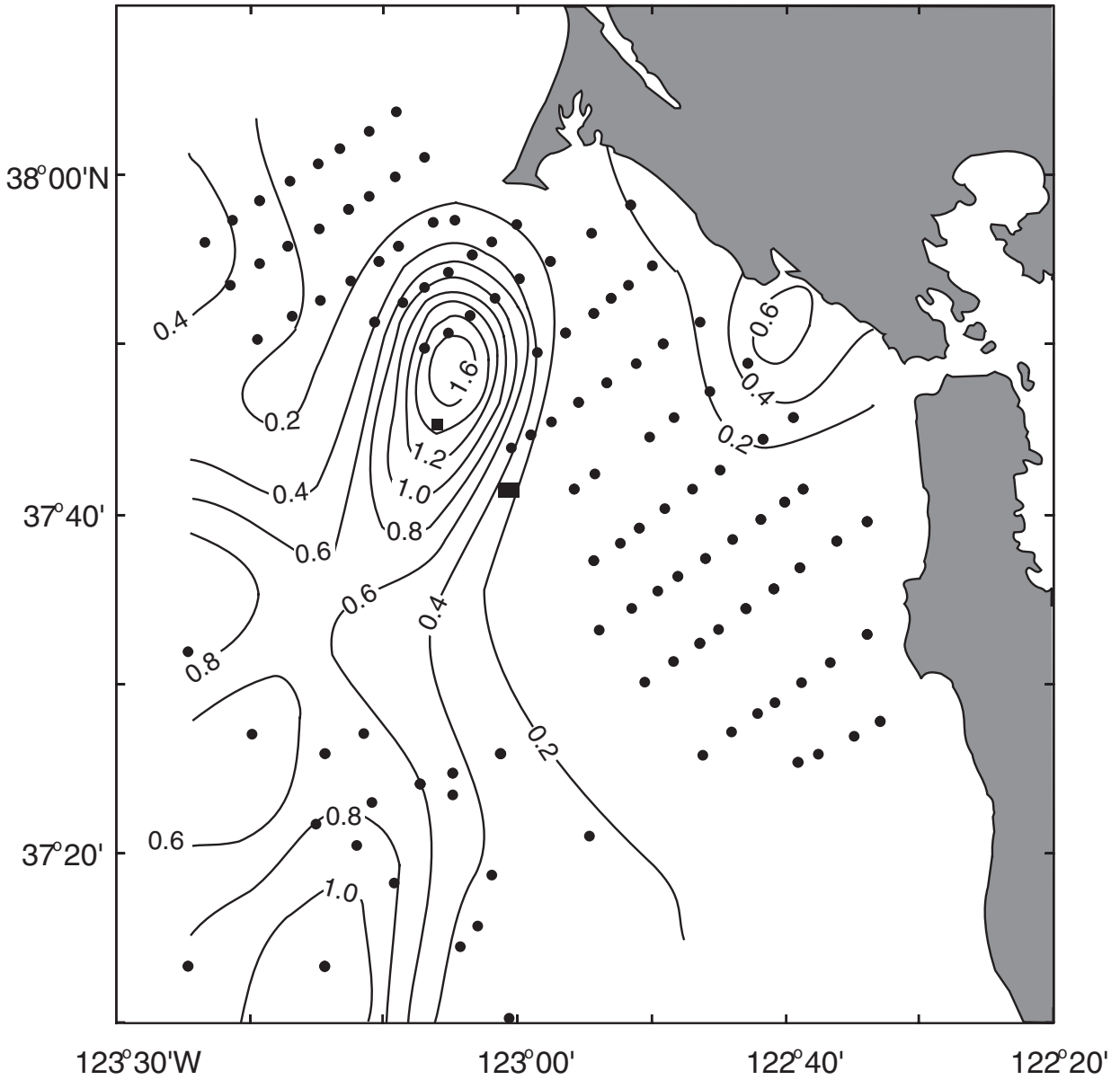


Figure 7. Gulf of the Farallones study area, showing contours of CaCO₃ content (in weight percent) of surficial sediment. Rectangles, Farallon Islands. Most sediment in study area has very low CaCO₃ content, and any CaCO₃ that is present is probably from shell fragments.

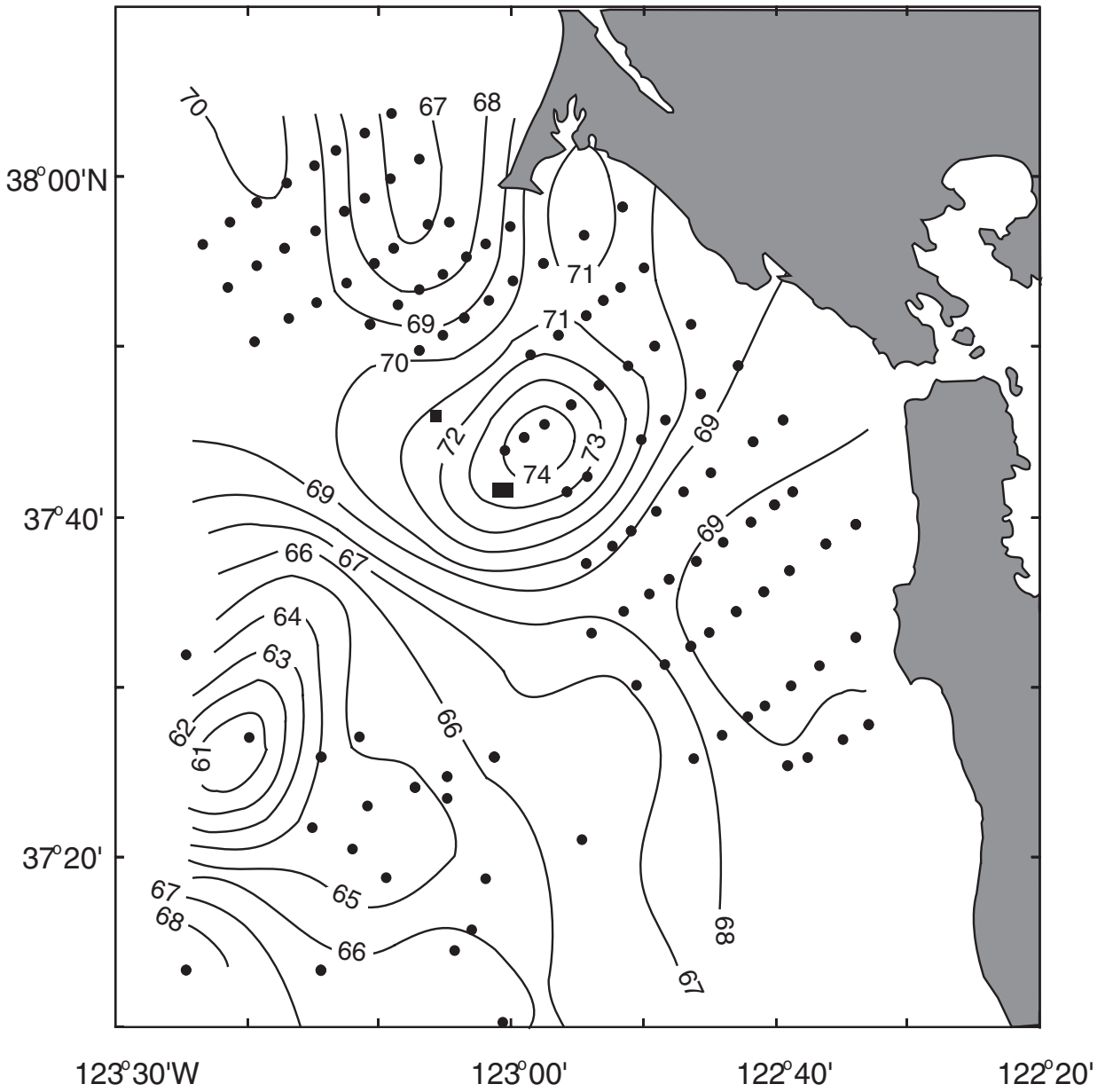


Figure 8. Gulf of the Farallones study area, showing contours of SiO₂ content (in weight percent) of surficial sediment. Rectangles, Farallon Islands. SiO₂-rich sediment near the Farallon Islands reflects quartz-rich sand derived from erosion of granitic rocks that make up the islands.

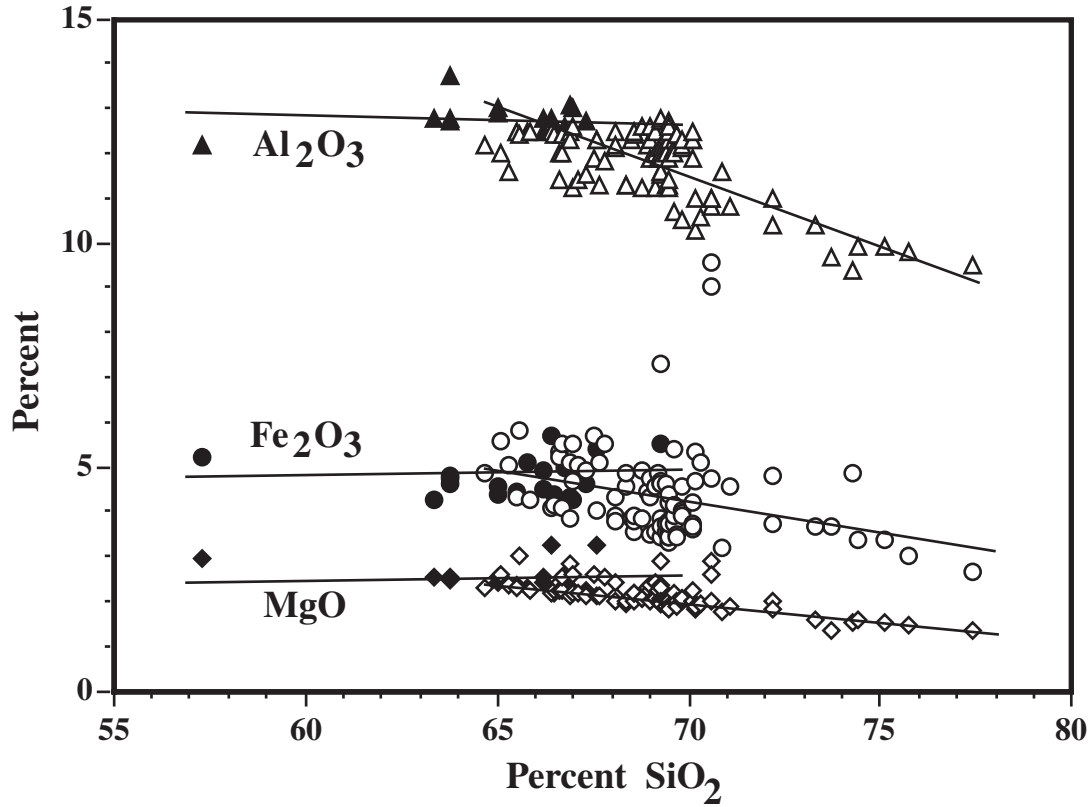


Figure 9. SiO₂ content versus Fe₂O₃ (circles), MgO (diamonds), and Al₂O₃ (triangles) contents of surficial sediment in Gulf of the Farallones study area from shelf (open symbols) and slope (solid symbols) cores. Lines through slope and shelf data are linear regressions. Quartz-rich shelf sand, such as that near the Farallon Islands (fig. 8), has lower concentration of heavy minerals rich in Fe₂O₃, MgO, and Al₂O₃. Heavy-mineral-rich shelf sand and clay-rich slope mud are relatively poor in quartz and have higher Fe₂O₃, MgO, and Al₂O₃ contents. More nearly constant composition of slope mud (little variation in Fe₂O₃, MgO, and Al₂O₃ contents) is due to mud being more homogeneous than shelf sand, which tends to have pockets of heavy-mineral-rich or quartz-rich sand. Most variation in SiO₂ content of slope mud is probably due to variation in amount of biogenic silica derived from siliceous algae (diatoms) that are predominant phytoplankton on northern California margin.