

TRACE ELEMENT VARIATIONS IN SOME
CENTRAL PACIFIC AND HAWAIIAN SEDIMENTS

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By

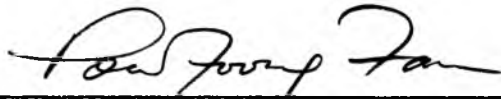
William C. Burnett

Thesis Committee:

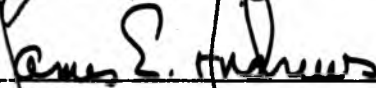
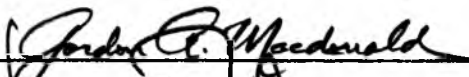
Pow-Foong Fan, Chairman
Gordon A. Macdonald
James E. Andrews

We certify that we have read this thesis and that
in our opinion it is satisfactory in scope and quality
as a thesis for the degree of Master of Science in
Geosciences--Geology.

THESIS COMMITTEE



Chairman



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ABSTRACT

The abundance of Rb, Sr, Ba, Cr, Co, Ni, Cu and Zn from the tops of cores raised from the Central and western equatorial Pacific have been determined by rapid instrumental techniques. A wide variety of sediment types occurs in the area studied, enabling contrasts to be made on a lithologic as well as a regional basis. A series of elemental variation maps are presented to show regional patterns of distribution for these trace elements. The distribution patterns for Ba and Cu clearly show an enrichment of these two elements in areas of high organic productivity. When only the biogenically-derived sediments are considered, there is a strong positive correlation between Ba and Cu. Rb appears to follow its geochemically related element, K. The K/Rb ratios are lowest in the carbonate oozes and highest in the brown clays. The average K/Rb ratio for all samples is 255, only slightly higher than the average crustal value. Cr contents are generally about the same as values reported for crustal rocks with the exception of some volcanic sediments near the Hawaiian Islands. These sediments contain Cr in excess of 180 ppm. Zn is homogeneously distributed throughout much of the area studied although a possible relation between high Zn values and proximity to island phosphorite (guano) deposits has been noted.

The average abundance of each trace element in 19 brown clays has been compiled and a comparison is made with the results reported by several other authors. Generally, the averages reported here agree well with previous estimates of the trace element composition of a typical pelagic clay. Co and Ni, however, show distinctly lower values than previously reported. In order to show the degree of fractionation that occurs between an average brown clay and normal crustal material, these values are also compared to average trace element contents of igneous rocks. All the trace elements studied here are enriched in pelagic clays relative to average crustal values except Cr, which is about the same, and Sr which is significantly lower.

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INTRODUCTION

A. Purpose of study

This study was initiated in order to investigate the elemental abundance of certain trace metals in surface sediments from the region of the Hawaiian Islands and the Central Pacific. The elements studied fall into two groups: (1) the alkali and alkaline-earth metals Mg, K, Ca, Rb, Sr and Ba; and (2) the transitional metals Cr, Fe, Co and Ni. Cu and Zn, which are often associated with these elements, were also investigated.

Although there have been several studies made on the geochemistry and trace element distribution in Pacific sediments (Goldberg and Arrhenius, 1958; and El Wakeel and Riley, 1961) this study is unique in several ways: (1) trace element abundances are determined on a wide variety of sediment types including biogenic siliceous and calcareous oozes; (2) elemental distributions are contrasted by a comparison of the abundances as found in a shallow water environment (the Hawaiian Islands) to those found in a pelagic-type environment; and (3) most studies up to now have limited themselves to spectrographic data rather than to the more modern methods of analysis. One important exception to this last statement is the work of Boström et al. (1966, 1969) on the metalliferous zone of the East Pacific

Rise which used essentially the same instrumental procedures as described here.

Another obvious reason for this study is a paucity of any data of this type from the area studied. The sample locations are shown in Figure 1 with a more detailed index map of the Hawaiian Islands presented in Figure 2. The majority of the papers that have appeared in the literature (Goldberg and Arrhenius, 1958; El Wakeel and Riley, 1961; Young, 1968; and Cronan, 1969) which deal with elemental distributions in surface sediments of the Pacific, report on pelagic clays that have been sampled in the eastern or northeastern Pacific. Very little data currently exist for the western equatorial Pacific. Even the major elemental distribution here is not well known; Boström and Peterson (1969) show no data available here for the distribution of Al, Fe and Mn in the surface sediments.

B. Previous work

In a study of some minor elemental distributions in Atlantic bottom samples Wedepohl (1960) has presented three results which are significant to this study: (1) the average abundances of Rb and Cr are the same in near-shore and pelagic clays within the limits of analytical error; (2) Ba is as abundant in near-shore clays as in pelagic clays from the Atlantic but is more abundant in the Pacific; and (3) Co, Ni, Cu and Zn increase from near-shore muds to Atlantic clays and from these to Pacific clays regardless of other

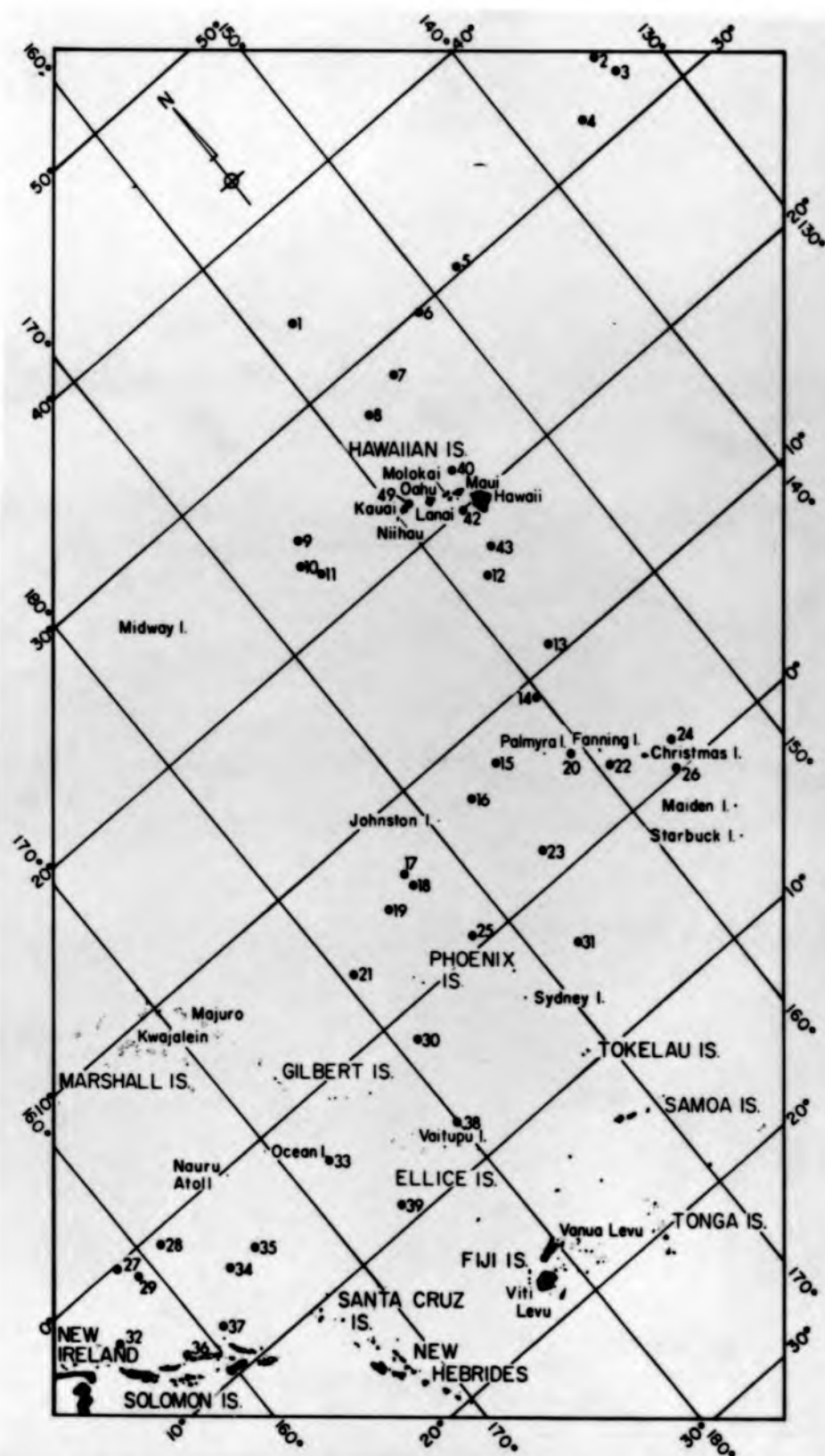


Figure 1. Index map showing sample locations and numbers. See Figure 2 for more detail around the Hawaiian Islands.

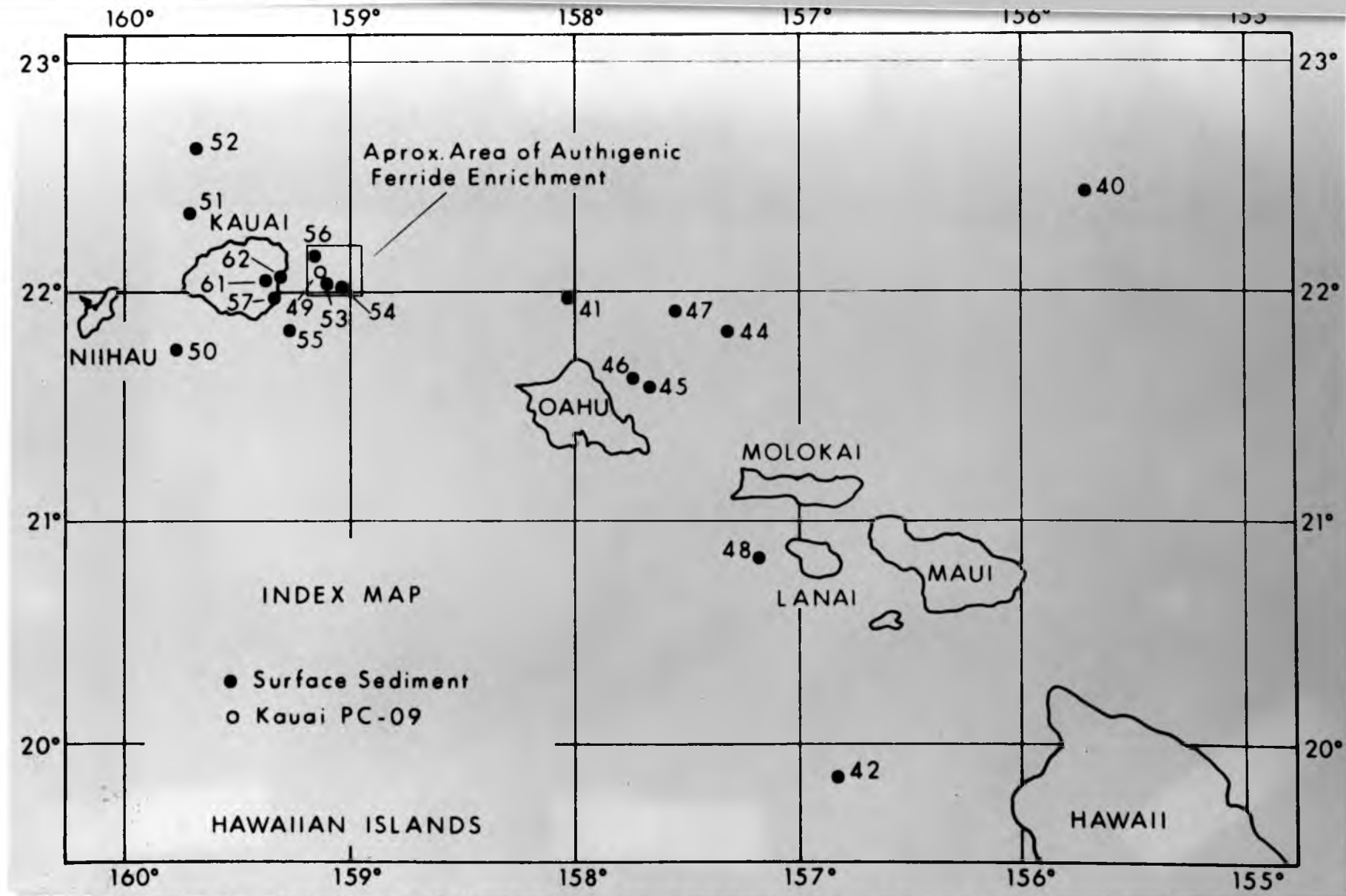


Figure 2. Index map of Hawaiian Islands showing sample locations and numbers.

similarities in their chemical composition. Wedepohl (1960) proposes that this enrichment in the Pacific pelagic clays might be caused by more intense submarine volcanic activity in this ocean. He sees this as an attractive source for these elements since the average values in pelagic sediments exceed the values required for balance computations of weathered average crustal material. It has also been shown (Chester and Hughes, 1966) that extraterrestrial material cannot significantly compensate for this overabundance.

Turekian and Imbrie (1966) studied the distribution of Ba, Cr, Co, Ni, Cu, Pb, Mn and Sn in deep-sea sediments of the Atlantic Ocean. A statistical analysis of the data was made to determine whether any associations of trace elements with other elements, water depth, calcium carbonate, or mineralogy existed. Surprisingly, no association at all was indicated between the trace element content and the mineralogy (mineralogy from Biscaye, 1965). Also, no correlations between trace element content and water depth were noted. The only two strong correlations found in this analysis were: (1) a strong covariance between the elements Mn, Ni and Co; and (2) a similar one between Cu and CaCO_3 . High concentrations of Mn, Ni and Co were shown to occur in regions of low clay accumulation rates as along the axis of the Mid-Atlantic Ridge. According to Turekian and Imbrie (1966) the high concentrations are probably related to the

deposition of fine material with high concentrations of these elements transported from the continents. The apparent relationship between Cu and CaCO_3 cannot be contained in the lattice of the carbonate tests themselves, it must be biologically associated in some way and extracted from sea water and preserved with the calcium carbonate fraction.

An investigation of the geochemistry of Pacific pelagic sediments has been made by Goldberg and Arrhenius (1958). These authors have presented an extensive treatment of the chemistry of both the major and some minor elements in deep-sea sediments from the eastern Pacific. Both bulk analyses and separated fractions were reported, giving a good indication of the distribution of the elements between the various constituents of the sediments. Some important results from their work which are significant to this study follow. (1) They have shown that the rate of accumulation of Ba (normalized to TiO_2) is a function of the rate of organic production in the euphotic zone. They showed this by plotting the rate of Ba accumulation (expressed as BaO/TiO_2) as a function of latitude, across the zone of high organic productivity in the equatorial divergence. (2) In their discussion of Cr, these authors noted that this element is often associated with volcanic debris. They concluded that an excess of this element above approximately 100 ppm in pelagic sediments is a

useful indication of the presence of altered or unaltered basaltic pyroclastics. (3) In the discussion of Mn and associated elements, it was noted that these elements occur in relatively large amounts in the most fine-grained part of the sediment. The absence of any tendency to form soluble complexes (resistant to dissolution in EDTA) indicates that the insoluble Mn, Ni, Co, Cu and Cr in the colloidal range possibly proxy for the main cations in clay minerals. Finally, (4) these authors also noted the fact that Cu, like Ba, is often associated with organic productivity.

Chemical and spectrographic analyses are presented for the major and several minor elements in various types of sediments from the Atlantic, Pacific and Indian Oceans and the Mediterranean Sea by El Wakeel and Riley (1961). Generally, their results for the minor elements followed those of Goldberg and Arrhenius (1958) for Pacific sediments. It was noted that the only difference in the chemical composition of the $< 2 \mu$ fraction of near-shore clays as compared to deep-sea argillaceous sediments was the higher ferrous iron and organic carbon contents. In attempting to explain the observed high concentrations of Pb and the transitional elements, these authors suggest that the sediments acquire their content of these elements from sea water by absorption or scavenging.

In order to explain the anomalously high values of Mn, Ni and Fe in deep-sea sediments, Chester and Hughes (1966) investigated the occurrences of these elements in a core from the North Pacific. The analyses were performed on separated fractions of the sediment, following basically the same type of procedure as Goldberg and Arrhenius (1958). Their conclusions showed that in this particular core, approximately 88% of the Mn, 56% of the Ni, and only about 5% of the Fe is of hydrogenous origin. The remaining portions of these elements are considered to have a lithogenous source and are incorporated into the sediment in detrital clay minerals.

Two other papers that report on trace element work in Pacific sediments are by Young (1968) and Cronan (1969). Young presents spectrographic data for Cr, Ni and Cu (among others) for three siliceous oozes, six red clays, three volcanic muds, three calcareous oozes and one manganese nodule from the Pacific. Cronan presents analytical data for Cr, Fe, Ni, Co and Cu (among other elements) for twenty-six Pacific pelagic clay samples. He uses these data together with previously published results to compute new averages for the abundance of each of these elements in Pacific clay sediments.

In a more specialized type of study on the geochemistry of sediments from the East Pacific Rise, Boström and Peterson (1966) have shown that heavy metals such as Fe, Mn,

Pb and Cr are concentrated in areas of high heat flow associated with active oceanic rises. These same sediments are also significantly depleted in Al, Ti, and Si. In a later paper, Boström and Peterson (1969), interpreted the simultaneous occurrence of high heat flow, ocean-floor spreading and the unusual composition of these sediments as noted above as most likely due to interconnected processes and not to a fortuitous coincidence. They believe that the very high concentration of Fe, Mn, As, Cr, B, V, and Cd in these sediments is due to emanations from the upper mantle and that only a minor fraction has been leached out of buried sediments.

Bender and Schultz (1969) studied the distribution of trace elements in deep-sea sediments from the Indian Ocean and noted that the Mn, Ni, Co and Cu content of these sediments increases from low to moderate near the continents to very high at the center of the ocean basin. The higher concentrations of trace elements seemed to correlate well with the finer grain size of the sediments in that area. This is in agreement with Turekian and Imbrie (1966) who had proposed that the high concentration of these elements along the crest of the Mid-Atlantic Ridge (discussed earlier) was a consequence of a hypothetical fine-grained silicate fraction that tended to accumulate along topographic highs. Boström and Peterson (1969) do not speculate on the possibility that the type of enrichment they observed on the East

Pacific Rise is analogous to the relative enrichments that Turekian and Imbrie (1965) have observed along the Mid-Atlantic Ridge, but this certainly must be considered a possibility and will most likely be investigated in the near future.

Angino (1966), in an investigation of the geochemistry of Antarctic sediments, studied the question of how to recognize glacial marine sediments when present in a "normal" sedimentary sequence. He suggests that trace element geochemistry is one approach and his results look encouraging. It was discovered that for glacial marine sediments as a type, the elements Cr, Ni, Ti, Fe, and Al are deficient when compared to crustal abundances. It was also noted that the elemental ratios Mn/Ti, Ni/Co, and Ni/Al in this type of sediment were distinctively different from those calculated for deep-sea clays. This study illustrates one way in which trace element geochemistry can be a useful tool as an environmental indicator.

C. Geological setting

As can be seen from the index map (Figure 1) the samples selected for this study are located on a line that runs roughly northeast-southwest from an area on the Murray Fracture Zone to just north of the Solomon Islands. The major structural and tectonic features of this area of the Pacific are shown in Figure 3 (data from Menard, 1964).

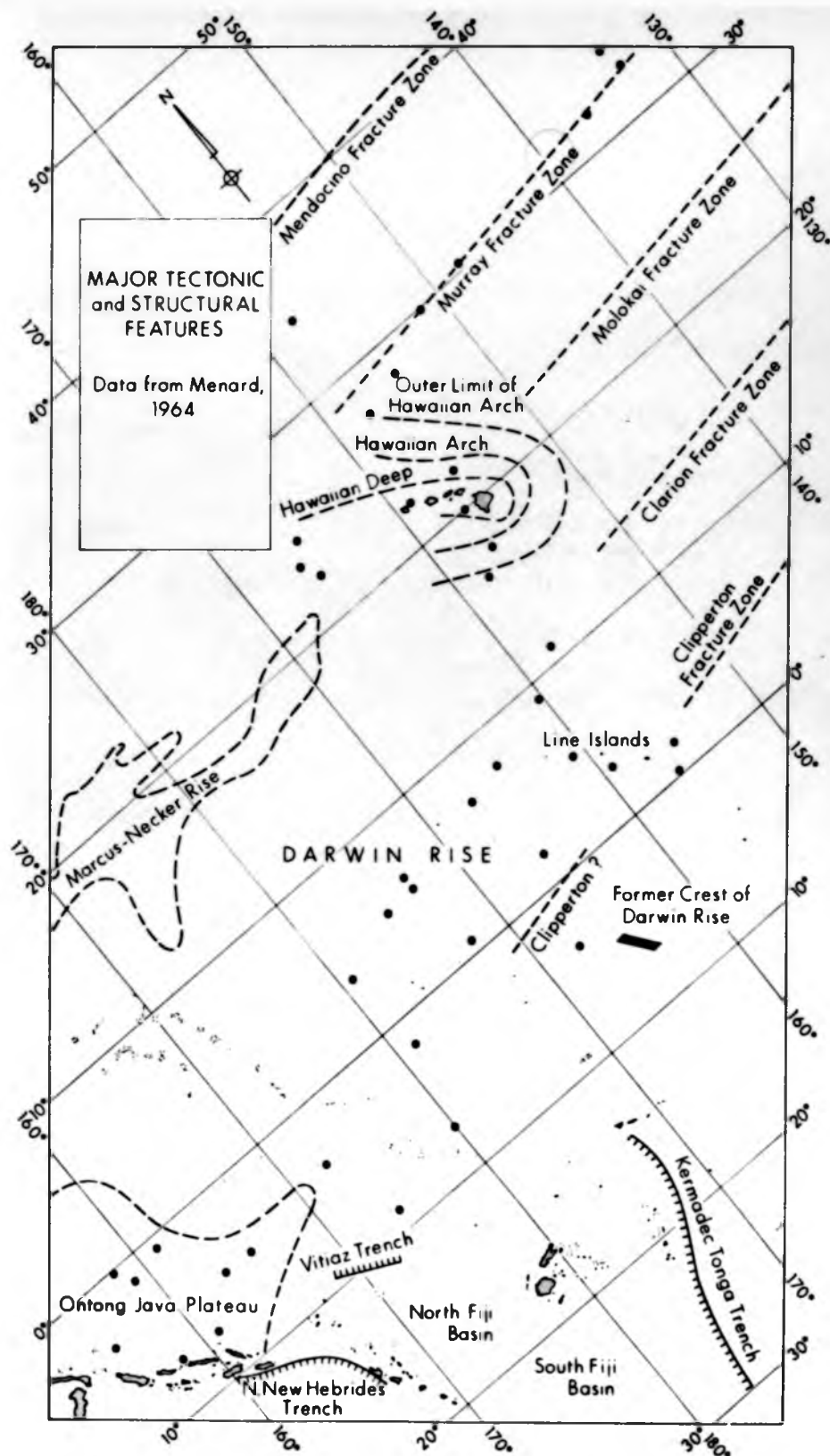


Figure 3. Major tectonic and structural features of the Central Pacific (data from Menard, 1964; possible extension of Clipperton from Rosendahl, personal communication).

Two of these features, the Hawaiian Ridge and the Darwin Rise, will be briefly discussed here.

The Hawaiian Islands are the surface expression of a large submarine ridge 160-320 km wide and 3200 km long which itself rests on a broad "swell" on the ocean floor. A deep, called the Hawaiian Deep (Hamilton, 1957), lies between the ridge and swell in the southeastern part of the island chain, but is absent in the northwestern part. The deep and swell suggest some sort of a failure of the crust to support the load of the islands. Moberly and McCoy (1966) consider that the processes of volcanism, isostatic adjustment and sedimentation determine the marine geology of the sea floor adjacent to Hawaii.

The Western Central Pacific contains the highest concentration of flat-topped seamounts (guyots) and atolls found anywhere in the world. It was in this area that Darwin on H.M.S. Beagle made his observations and formulated his now-accepted theory on the origin of atolls. Hamilton (1956), in an investigation of several guyots west of Hawaii (Mid-Pacific Mountains), found shallow-water fauna, rounded basalt pebbles and pieces of vesicular basalt in dredges taken from the tops of some of these seamounts, substantiating Darwin's theory that a major portion of this area of the Pacific had undergone subsidence.

It is now generally accepted that the numerous flat-topped seamounts of the Western Equatorial Pacific represent

sunken former islands. On the basis of a study of the relative heights of these seamounts above the adjacent sea floor and assuming that all of the islands existed simultaneously, Menard (1964) deduced the former existence of a broad, now subsided uplift called the Darwin Rise. Heezen et al. (1966) showed from seamount data that the deep-sea floor surrounding the Manihiki Plateau has subsided approximately 1.5 km in the last 10^8 years. Although there is no seamount data for the Plateau itself, a subsidence of about 3800 m is suggested by the bevelled platform. The occurrence of Cretaceous fossils dredged from the plateau indicates that the bevelling occurred before or during this Period.

Based primarily on the agreement between the 3.5 km depth of the basement of the Manihiki Plateau and the 3.5 paleo-isobath of the Darwin Rise, Heezen et al. (1966) suggest that the Manihiki Plateau may be an unsubsided remnant of this ancient uplift.

The Darwin Rise today appears to be bounded by a rhombic pattern of ridges. The Marcus-Necker Ridge corresponds roughly to the northern boundary; the Line Islands to the eastern boundary; the Marshall, Gilbert and Ellice Islands Ridge to the western boundary; and the Manihiki-Tokelau Plateau appears to lie on the axis of the rise. It has been suggested (Woollard and Sutton, 1969) that these ridges may represent post-Darwin Rise fractures

that developed in conjunction with subsidence of the rise on or from a later tectonic stress pattern.

The relief today of the Darwin Rise is almost entirely volcanic in origin. The dominant mode of this vulcanism is in the form of vast floods of very fluid lava which buried abyssal hills and built smooth archipelagic aprons. The average crustal section over the Darwin Rise contains a thick layer of volcanic rock, a consequence of the development of these aprons. In a composite crustal section across the northeastern half of the Darwin Rise, Woollard and Sutton (1969) have shown that the mean crustal velocity, crustal thickness and mantle velocity tend to decrease towards the northeast. The depth to mantle in the area of the thickest crustal section was 14 km and this was found over the postulated axis of the Darwin Rise. All indications to date show that the Darwin Rise area is characterized by about average heat flow.

D. Sediment type

The sediments investigated here may be grouped into the following lithologic types: (1) brown clay, (2) siliceous ooze, (3) coccolith ooze, (4) foraminiferal ooze and (5) detrital muds (mostly volcanic debris admixed with shallow-water carbonate). The distribution pattern of the surface sediments over the study area is shown in Figure 4. All data for this map were taken from Andrews (1970) and all the points represent samples used in this study. Some additional

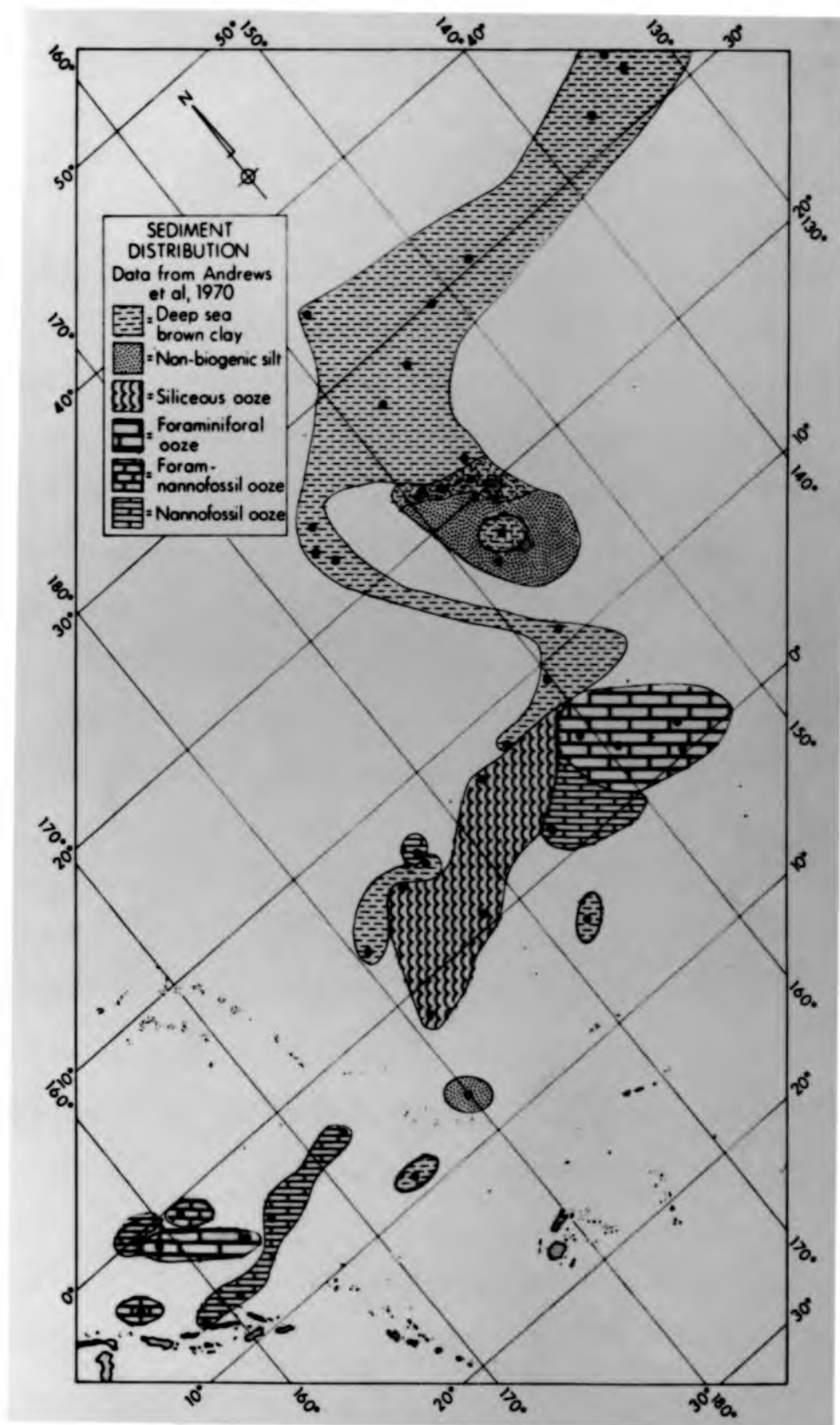


Figure 4. Sediment distribution in the Central Pacific. Data from Andrews (1970) and Coulbourn (personal communication). See Table 1 for more detail on samples.

data around the Line Island group were provided by W. Coulbourn (personal communication).

The pelagic brown clays are found primarily in the northern section of this area. The major contributor to these clays is probably eolian transport (Rex and Goldberg, 1958; and P. Fan, personal communication). The siliceous oozes are found in the equatorial region where the water depth is greater than about 4800 m. There is a high rate of organic productivity in this area due to equatorial upwelling and consequently the sediments are almost wholly made up of biogenic debris. The siliceous oozes consist chiefly of radiolarian fragments but also contain other forms such as sponge spicules and diatoms. The coccolith oozes are found on both sides of the area characterized by the siliceous ooze where the water depth is shallower. Foraminiferal oozes are found primarily around the Line Islands and on the Ontong Java Plateau.

The mineralogy of the non-biogenic fraction of these sediments from the equatorial Pacific has recently been discussed by Heath (1969). He suggests that the modern equatorial Pacific deep-sea sediments are mixtures of three main components: (1) "continental," that fraction dominated by quartz, illite, and alkali feldspar; (2) "oceanic," those deposits rich in montmorillonite and often containing the authigenic zeolites phillipsite and clinoptilolite-heulandite; and (3) "island arc," those

sediments containing abundant chlorite and pyroxene and having a pyroxene:plagioclase ratio of about 1:4. This last group of sediments is most important in the western and southwestern equatorial Pacific.

The distribution of clay minerals in the Pacific has been discussed by Griffin and Goldberg (1963) and again by Griffin et al. (1968). Briefly, in the North Pacific, illite is the dominate clay mineral with the abundances of montmorillonite, chlorite, and kaolinite being a function of location (proximity to continents, etc.). In the South Pacific montmorillonite is the most abundant clay mineral. The montmorillonite:illite ratio is always greater than 1 and no apparent variation with geographical position was noted.

The mineralogy and sedimentology of the area around the Hawaiian Islands has been studied by many authors. Rex and Goldberg (1958) observed that the quartz content of the sediments increased with distance from the island of Oahu. They interpreted this as a decrease in the dilution of an eolian-transported component by the island-derived material. Moberly (1963) and Moberly et al. (1968) discuss the mineralogy of the clays off eastern Oahu, with particular reference to the possible formation of authigenic illite from amorphous aluminosilicates in the marine environment. Fan and Grunwald (in preparation) show the general sediment distribution pattern in the Hawaiian Islands.

E. Samples

All the samples used in this study were taken on various cruises by the two research vessels of the Hawaii Institute of Geophysics, the R/V MAHI and the R/V TERITU. The samples used were all recovered from near the tops (usually in the upper 15 cm) of sediment cores. The samples were originally taken as a small plug of about 12 grams for porosity, bulk density, and void ratio measurements by the Core Analysis Laboratory. In making these measurements, a known volume of sediment is sampled, weighed and then dried at approximately 105°C. The samples are then weighed again and the weight loss per unit volume recorded, marked, and stored for later use. In order to insure against contamination for this study, the outside of each plug was carefully shaved and discarded leaving about 10 grams of useful, contamination-free sample. These were then ground in a mortar and pestle to approximately 250 mesh and stored in plastic vials. Subsequently, all splits for chemical analysis were taken from these vials. The preparation of these samples for each type of analysis will be discussed in the next section. The locations, depth and sediment type for all the samples used in this study are shown in Table I. Locations and depth were taken from sampling logs kept on board ship and the sediment type is from Andrews (1970), Belshé (1968) and M. Morgenstein (personal communication).

Table I: Location, depth and sediment type for all samples

Sample No.	Log No. ^a	Latitude	Longitude	Depth (m)	Sediment Type
1	AH -FFC-8	35°47'N	157°43'W	5569	deep-sea brown clay
2	MFZ-1-008	33°50'N	133°11'W	5140	deep-sea brown clay
3	MFZ-1-007	32°38'N	132°55'W	4640	deep-sea brown clay
4	MFZ-2-002	31°47'N	136°23'W	4550	deep-sea brown clay
5	MFZ-6-006	30°42'N	148°17'W	5500	deep-sea brown clay
6	MFZ-4-004	29°58'N	151°22'W	5633	deep-sea brown clay
7	MFZ-6-012	28°36'N	155°18'W	5160	deep-sea brown clay
8	Navy 782NE	27°33'N	157°42'W	3800	deep-sea brown clay
9	MFZ-3-002	24°58'N	165°55'W	5100	deep-sea brown clay
10	MFZ-3-003	23°32'N	167°09'W	3100	deep-sea brown clay
11	MFZ-3-005	22°41'N	165°48'W	3250	deep-sea brown clay
12	S68-FFC-1	16°03'N	157°58'W	5330	non-biogenic silt
13	S68 -PC-1	11°03'N	158°00'W	5150	deep-sea brown clay
14	S68-PC-28	08°55'N	160°34'W	4805	deep-sea brown clay
15	S68-PC-29	07°40'N	164°50'W	4970	deep-sea brown clay
16	S68-PC-30	07°00'N	167°31'W	4775	siliceous ooze
17	S68-PC-35	06°11'N	173°01'W	4890	nannofossil ooze
18	S68-PC-31	05°27'N	173°05'W	5740	deep-sea brown clay
19	S68-PC-34	04°43'N	175°18'W	5100	siliceous ooze
20	LIR-1-004	04°40'N	161°00'W	na ^b	foraminiferal ooze
21	S68-PC-33	03°52'N	179°32'W	5428	deep-sea brown clay
22	LIR-1-011	03°00'N	159°17'W	na	foraminiferal ooze
23	S68-PC-27	02°15'N	166°31'W	5520	nannofossil chalk ooze
24	LIR-1-006	01°40'N	155°36'W	na	foraminiferal ooze
25	S68-PC-25	00°35'N	172°11'W	5620	siliceous ooze
26	LIR-1-008	00°15'N	156°34'W	na	foraminiferal ooze

Table I (continued) Location, depth and sediment type for all samples

Sample No.	Log No.	Latitude	Longitude	Depth (m)	Sediment Type
27	S68-PC-11	00°26'S	158°17'E	3900	nannofossil chalk ooze
28	S68-PC-12	00°52'S	161°13'E	3430	nannofossil-foram ooze
29	S68-PC-16	01°36'S	158°46'E	2020	foram chalk ooze
30	S68-PC-24	02°03'S	178°45'W	5273	siliceous ooze
31	S68-PC-02	03°48'S	168°11'W	5520	deep-sea brown clay
32	S68-PC-18	04°13'S	155°36'E	2580	nannofossil-foram chalk ooze
33	S68-PC-21	04°20'S	172°04'E	3875	siliceous nannofossil ooze
34	S68-FFC-26	04°44'S	163°29'E	2240	foram chalk ooze
35	S68-FFC-34	04°55'S	165°41'E	2850	nannofossil chalk ooze
36	S68-FFC-15	07°00'S	158°11'E	2475	nannofossil chalk ooze
37	S68- PC-06	07°15'S	161°17'E	1628	nannofossil chalk ooze
38	S68- PC-03	07°06'S	179°50'E	5450	non-biogenic silt
39	S68-PC-04	09°07'S	173°50'E	5250	deep-sea brown clay
40	HIG-650125-8	22°23'N	155°46'W	4540	deep-sea brown clay
41	HIG-650125-3	21°59'N	158°01'W	4005	volcanic mud w foram tests
42	HIG-670313-3	19°51'N	156°51'W	4780	pyroclastic silt
43	HIG-670123-2	17°35'N	157°10'W	4750	brown clay w ash layers
44	SUBCAN-FFC-1	21°50'N	157°21'W	4310	volcanic mud w carbonate
45	SUBCAN-FFC-2	21°37'N	157°45'W	1102	carbonate w volcanic mud
46	SUBCAN-FFC-4	21°39'N	157°47'W	1420	volcanic mud
47	SUBCAN-FFC-6	21°55'N	157°33'W	4126	volcanic mud
48	SUBSHELF-1-1	20°49.5'N	157°11.5'W	1097	carbonate w volcanic mud
49	*KAUAI-PC-9a	22°04.7'N	159°08.4'W	2348	indurated siltstone
50	KAUAI-PC-2	21°46.5'N	159°46.1'W	2546	volcanic mud w carbonate
51	KAUAI-GC-2	22°16.7'N	159°41.2'W	1750	carbonate w green clay
52	KAUAI-GC-4	22°36.8'N	159°39.0'W	4630	volcanic mud w carbonate
53	TE-2-08	22°03.5'N	159°08.0'W	2120	manganese crust
54	TE-2-11	22°02.5'N	159°00.5'W	2230	foram-Mn sand & altered volcanics

Table I (continued) Location, depth and sediment type for all samples

Sample No.	Log No.	Latitude	Longitude	Depth (m)	Sediment Type
55	TE-2-12	21°52'N	159°16'W	2400	carbonate sand w volcanic debris
56	TE-2-14	22°08'N	159°11'W	2200	carbonate sand w volcanic debris
57	beach sand #1			-	carbonate sand
58	*KAUAI-PC-9b	22°05'N	159°08'W	2348	pyroclastic arenite
59	*KAUAI-PC-9c	22°05'N	159°08'W	2348	muddy arenite
60	*KAUAI-PC-9d	22°05'N	159°08'W	2348	pyroclastic arenite
61	Wailua River #1	-	-	-	stream sediment
62	Wailua River #5	-	-	-	stream sediment

^aLog Number refers to the sample designation as recorded on board ship and used by the Core Analysis Laboratory.

^bna = not available.

*KAUAI-PC-9: a=surface; b=46cm; c=54cm; d=65cm.

ANALYTICAL TECHNIQUES

A. General

The desire to analyze a relatively large number of samples for several different elements required the use of rapid instrumental techniques throughout. The major elements Fe, K, and Mg and the trace elements Co, Cr, Cu, Ni and Zn were determined by atomic absorption spectrography. Ba, Rb and Sr were analyzed by X-ray fluorescence spectrography. Because of difficulty with the Ni analyses (due to interference most likely related to the iron content) by atomic absorption, this element was repeated by X-ray fluorescence. In order to show a further comparison between the two techniques, a major element, K, was also determined by both methods. The values for K as determined by X-ray fluorescence were systematically lower in the concentration ranges below 1.25%, while they were systematically higher for any values above this. A check by atomic absorption on four previously analyzed basalts (provided by Charles Fein) produced extremely good agreement and it was decided to report all the K values as determined by this method. This probably implies that some type of rotational adjustment was needed for the X-ray working curve. On the other hand, the X-ray values for Ni appeared to be more reliable and are used exclusively except in a few cases where the sample in question was not available for this type of analysis.

B. Standards

For all the X-ray fluorescence work, the six new U.S.G.S. rock standards (Flanagan, 1969) and G-1 (Westerly granite, used as an international rock standard; Fleischer, 1969) were used as primary standards. W-1 (standard diabase) was run as an unknown for a check on accuracy. In the case of major elements, and a few trace elements, the HIG standards were also used. These rocks, all Hawaiian volcanics, have been analyzed twice for major elements; once by the Japan Analytical Chemistry Research Institute and once by the U.S.G.S. laboratory in Denver. Trace elements have also been determined for these rocks by a six-step spectrographic technique by Harriet Neiman (U.S.G.S.) once in 1965 and again in 1966. Two additional rock standards were obtained from Dr. Bernard Leake (University of Bristol); BL 2/3571 and JWA 601 (Leake et al., 1970) and were used for the Rb and Sr determinations.

The author recognizes the fact that there are inherent difficulties in the use of rock standards for primary calibration. Foremost among these difficulties, especially in trace element work, is that the recommended or "best" values for G-1 and W-1 and the average values for the new U.S.G.S. rocks are often just an approximation of the real or "true" value and it must be recognized that there is considerable divergence in many of the reported analyses of these rocks. To illustrate this, Table II reports the

Table II: Ranges in reported values for G-1 and W-1 and the six new U.S.G.S. rock standards. Data from Flanagan (1969) and Fleischer (1969).
All values in ppm.

Element	G-1	W-1	G-2	GSP-1	AGV-1	PCC-1	DTS-1	BCR-1
Ba	1039-1850	140-229	1500-3000	855-2000	1047-2700	-	-	480-1230
Co	2-3	33-54	2-21	<3-22	10-30	80-3000	96-200	29-60
Cr	9-43	76-148	5-29	5-18	8-45	1840-4780	2840-5560	8-45
Cu	8-20	100-140	<2-17	15-54	52-83	5-16	<2-15	7-33
Ni	1-21	29-110	2-14	3-25	11-27	1750-3400	1770-3300	8-30
Rb	210-260	18-35	108-513	200-690	68-130	-	-	45-150
Sr	250-346	85-210	235-680	148-400	348-1050	-	-	244-525
Zn	25-55	43-95	42-138	54-340	64-304	24-100	22-140	94-278

ranges of a dozen or more analyses of all the minor elements investigated in this study. As can be seen the disagreement is considerable, most often by a factor of two or three and many by a factor of ten or more. This table may be slightly misleading in view of the fact that it is reporting the range of all values (Flanagan, 1969 and Fleischer, 1969) and does include some highly inaccurate values that would ordinarily be ruled out. The situation is not as bad for the major elements and their values may be considered fairly well known. In most cases the recommended values of all the elements looked at in this study in G-1 and W-1 are probably fairly reliable, although Fleischer (1969) still considers the agreement for the reported values of Ba, Ni, and Sr as poor. The effect this has on the Sr determinations will be discussed in a later section.

In addition to the difficulties already mentioned it has recently been shown beyond almost any doubt (Shaw, 1969) that some trace elements are not homogeneously distributed throughout the rock matrix and that some reported variations in trace-element content may in fact be real.

In spite of these various problems, the author still believes that there is a good case for the use of these standards as a means of calibration. The main advantages may be summarized as follows: (1) the major elements,

especially in G-1 and W-1, are now well enough known that any variance would most likely fall within the margin of error of most rapid techniques; (2) they give the individual analyst the opportunity to compare his results with those from laboratories all over the world; (3) although certainly not eliminating interferences (such as matrix effects) in absorption and emission spectrography, at least a geological sample may now be calibrated against a material which is at least fairly similar to itself in composition. For example, the basalt, BCR-1, or the diabase, W-1, are somewhat similar chemically to the pelagic brown clays looked at in this study; (4) rock standards should tend to eliminate some systematic errors that may occur with the exclusive use of synthetic standards. As an example, a stock solution of some metal or metals that has been incorrectly prepared will propagate its error throughout all dilutions but will still produce a straight working curve which could easily mislead the analyst into believing his calibration is correct; and (5) in the absence of any other well-calibrated standards these rocks have provided some much needed overall control on reported results.

As the best compromise that appeared valid to this author, it was decided to use synthetic standards (prepared from Beckman standard solutions) in addition to rock standards for all the trace elements done by atomic absorption. This procedure has the advantage that it will

show conclusively whether or not any matrix effects or other interferences have been introduced with the geochemical samples. No synthetic standards were prepared for X-ray analysis, principally because of the difficulty involved in homogenization of powdered samples. It is hoped that the large number of rock standards prepared and run by this method will tend to balance out any inherent errors in the standards themselves.

In the following sections some details of the various methods of analysis will be presented along with some typical working curves from each technique. The determination of Cu by atomic absorption and the Rb - Sr determinations by X-ray fluorescence will be shown as illustrations of the general type of procedure used for each technique. The carbonate determinations will also be discussed briefly, followed by a short discussion on the estimated precision and accuracy achieved in this study.

C. Atomic absorption spectrometry

The theory and practice of atomic absorption spectrometry with regards to geochemical samples has received great attention in the last few years. Angino and Billings (1967) have treated the subject quite thoroughly, so this discussion will be limited to specifics of this study only. The major elements Fe, Mg, and K; and the minor elements Co, Cr, Cu, and Zn were analyzed by this method.

The samples were prepared by the method of Bernas (1968). Briefly, this method involves the dissolution of the dried and powdered sample by hydrofluoric acid in specially designed teflon crucibles enclosed in an acid digestion bomb. Quantitative decomposition was found to occur in approximately 40 minutes (for a 200 - 250 mg sample in 5 - 10 ml of HF) at a temperature of 110°C. In order to dissolve the insoluble metal fluorides that precipitate during this process, boric acid is added which results in the formation of fluoboric acid by a slightly exothermic reaction. The metal fluorides dissolve at this stage and a clear, homogeneous sample solution results. The fluoboric-boric acids system permits contamination-free sample handling in glass equipment, ensures sample solution stability, and also contributes to signal stability (Bernas, 1968).

All atomic absorption measurements were carried out on a Perkin-Elmer model 303 spectrometer. The instrumental conditions for each analysis are summarized in Table III.

Some typical working curves are presented in Figures 5 (zinc), 6 (chromium), and 7 (potassium). Where rock standards are used they are indicated in each figure, all other points represent synthetic standards. Figures 5 and 6 show that there is no serious interference with the introduction of natural metals for zinc and chromium. As already mentioned, rock standards were used exclusively for

Table III: Instrumental conditions for elemental analysis by atomic absorption spectrography

Element	Atomic No.	Range	Wavelength (m μ)	Slit (mm)	Fuel flow ^a	Oxidizer flow ^a
Mg	12	UV ^b	285	3	9	8
K	19	VIS ^c	383	1	9	9
Cr	24	UV	358	.3	9	7.5
Fe	26	UV	248	.3	9	9
Co	27	UV	241	.3	9	9
Ni	28	UV	232	.3	9	9
Cu	29	UV	325	1	9	9
Zn	30	UV	214	3	9	9

^aFlow rates in units of p.s.i.g.

^bUltraviolet

^cVisible

Acetylene fuel with air as an oxidizer used exclusively. Hollow cathode source used throughout.

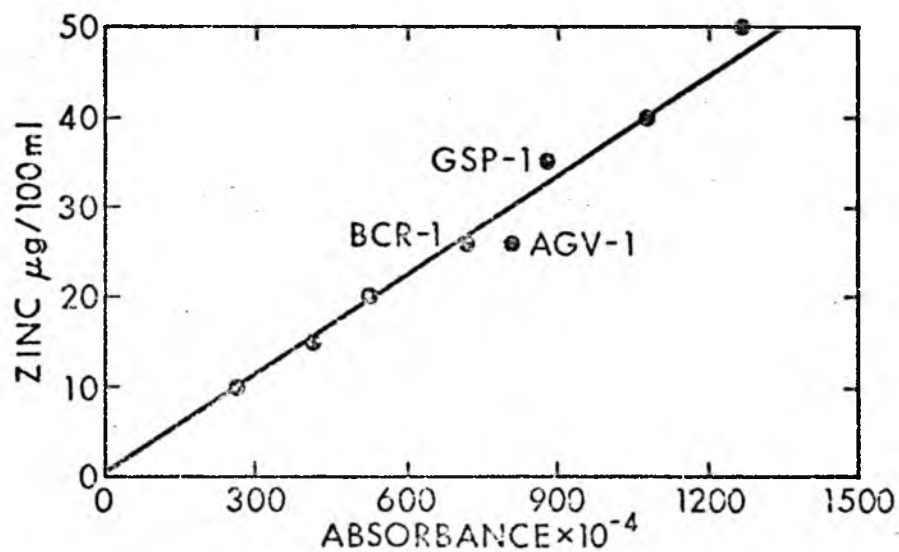


Figure 5. Working curve for zinc.

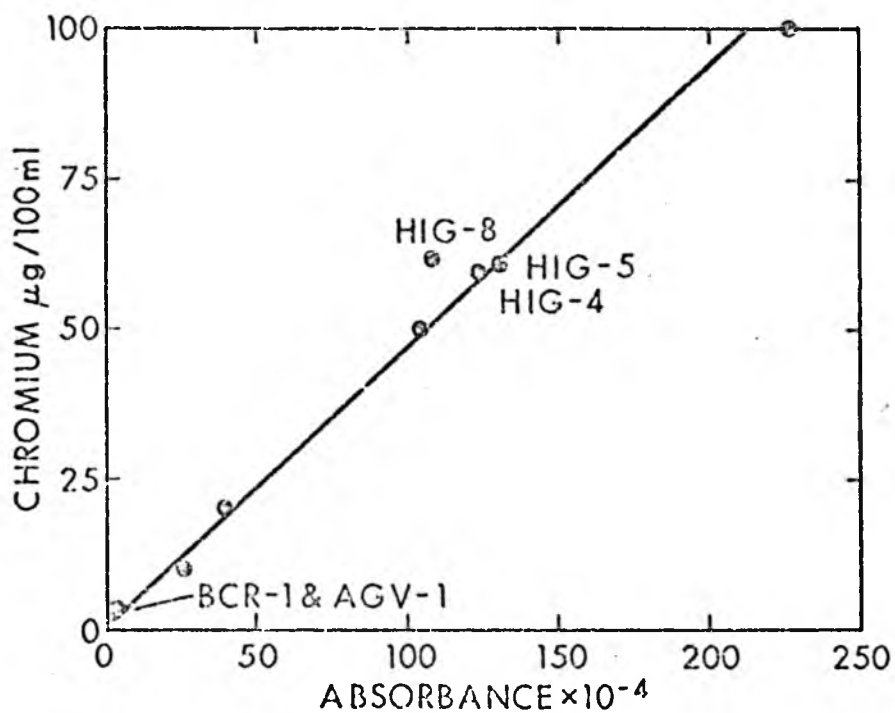


Figure 6. Working curve for chromium.

the major elements and, as seen in Figure 7, they provided a suitable working curve for potassium, as they did for magnesium and iron (not shown).

The determination of copper deserves special mention here because interference effects have definitely complicated the situation. Although Belt (1967) reported that the amounts of Na, K, or Ca normally found in silicate rocks do not interfere with the determination of Cu, it is this author's feeling that he overlooked the important interfering element, iron.

To insure that all the reported values for Cu in the rock standards used here were reasonable, the technique of standard additions was used as a check on the HIG standards. This is a standard technique for analysis when interference is suspected (a good treatment of this method appears in Willard, Merritt, and Dean, 1965). Two of these determinations by addition are shown in Figure 8. All rock standards as well as a suite of synthetic standards were then plotted on a conventional working curve (concentration in solution vs absorbance). As can be seen in Figure 9, the natural standards are displaced towards the lower absorbance values in some type of coherent manner. It also appears that the ones most affected are those richest in total iron (shown as Fe_2O_3). The exact nature of this interference is not known. Fletcher (1970) reports that although background absorption was detected in the region of the

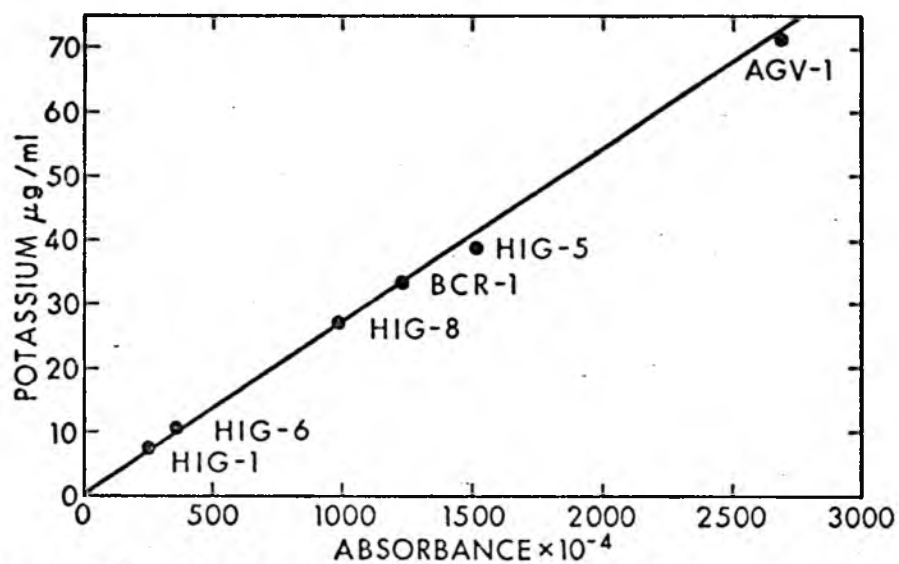


Figure 7. Working curve for potassium.

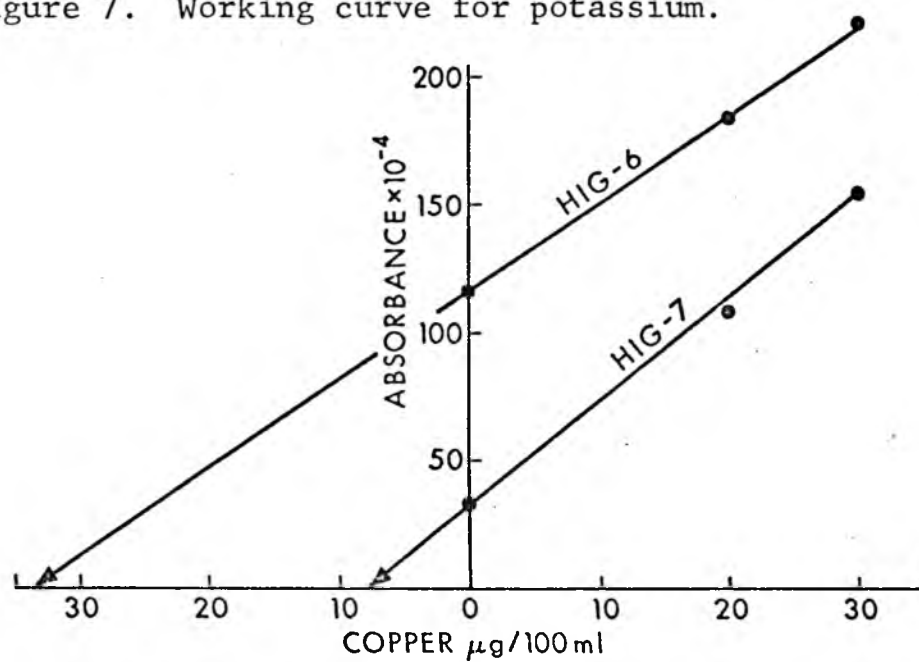


Figure 8. Standard addition analysis for copper.

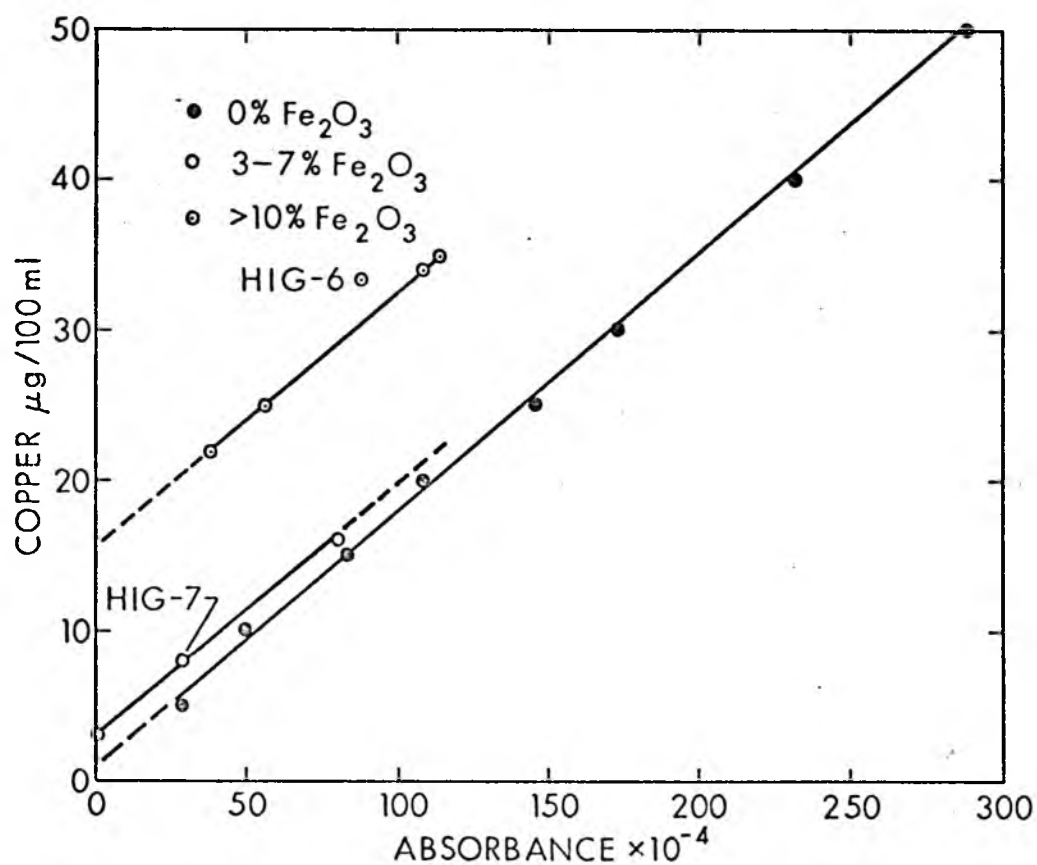


Figure 9. Working curve for copper showing how interference is related to iron content. See text for discussion.

copper line (325 mμ), the differences this produced between the corrected and uncorrected values were negligible. Perhaps some type of chemical interference produced the effect observed here, i.e., Cu combining with another element present in the natural samples would produce a negative error in absorption if this combination does not break down in the flame to produce ground state atoms.

In Belt's (1964) work on the determination of copper and zinc in various silicate rocks, the precision for copper ranged from 34% at 5 ppm to 3.3% at 210 ppm. Duplicate runs on three different samples in this study produced a range in precision from 28.6% at 21 ppm to 2.1% at 191 ppm. A further discussion of the precision and accuracy in this study will be presented in a later section.

In the analysis of unknowns for Cu, the total iron (as Fe_2O_3) content was used to determine which line on the working curve to use. Those samples with < 3% Fe (as the carbonate oozes) were picked off the synthetic curve; those with Fe concentrations in the range 3 - 7% (most of the brown clays) or > 10% (some brown clays and most detrital muds) were picked off the corresponding curves. Those unknowns that contained between 7 - 10% total Fe, in the range where no rock standards occurred, were picked off the curve that most closely duplicated their Fe concentration.

The analyses of Co and Ni by atomic absorption produced a situation somewhat similar to that just described

for Cu, although not in such a coherent manner. Fletcher (1970) mentions that background absorption was particularly severe for the resonance lines of Ni, Co, and Pb. This has the effect of producing spuriously high values (in contrast to lower values for the uncorrected Cu determinations) for the metal content. This appears to be the case for Co and Ni here, and it is therefore considered to be a different type of interference than that observed for Cu. The interference was corrected for by using the working curve which followed the geochemical standards.

D. X-ray fluorescence spectrometry

The use of X-ray fluorescence spectrometry, both from a theoretical and practical point of view, has been extensively treated in Jenkins and DeVries (1967). More recently, an exhaustive study on the analysis of 38 different elements in rock powders by this method has been presented by Leake et al. (1970). K, Rb, Sr, Ba, and Ni were analyzed by this method.

All X-ray determinations were made on a Norelco Universal Vacuum Spectrograph Type No. 52530. The instrumental conditions for each element analyzed by this method are summarized in Table IV.

Sample preparation was somewhat similar to that followed by Ball (1965) and Wolfe (1969). This method involves mixing the dried and powdered sample with methyl cellulose in a 1:1 ratio, homogenizing the mixture for

Table IV: Instrumental conditions for elemental analysis
by X-ray fluorescence spectrography

Element Atomic No.	K 19	Ni 28	Rb 37	Sr 38	Ba 56
Peak	K_{α}	K_{α}	K_{α}	K_{α}	L_{β}
Tube	Cr	W	W	W	W
Volts (kV)	45	48	47	47	50
Current (mA)	20	20	20	20	50
Atmosphere	vacuum	air	air	air	helium
Collimator	coarse	fine	fine	fine	coarse
Crystal	LiF	LiF	LiF	LiF	LiF
Detector	GFPC	SC	SC	SC	GFPC
Voltage	1800	1040	1040	1040	1595
PHA: base	5 v	6 v	9 v	9 v	1.5 v
PHA: window	15 v	11 v	11 v	11 v	4 v

GFPC = gas flow proportional counter;
SC = scintillation counter

approximately 40 minutes in a mechanical mixer and then drying the mixture for at least twelve hours at about 110°C. The sample is then transferred to a stainless steel die, leveled off, and approximately 3 grams of boric acid added to serve as a backing for mechanical strength. The die is then subjected to about 23,000 psi on a hydraulic press. The result is a two-layer briquette which is easily handled, has a surface for marking, and is extremely durable (samples prepared over 12 months ago are still in excellent condition). The manufactured briquettes are then marked and transferred to petri dishes to prevent surface damage and stored in a dessicator to prevent moisture absorption and swelling. This method proved to be very satisfactory in that it insured the stability of the sample when used in a vacuum, the briquettes possessed adequate mechanical strength, and by dilution with a standard additive (cellulose) the differences in sample composition or "matrix" effects were somewhat buffered. Adding a dilutant, however, does diminish the intensity of the secondary radiation; so the 1:1 ratio selected here is somewhat of a compromise.

The determination of Rb and Sr by X-ray techniques has received much attention in the literature (Champion et al., 1966; Chappell et al., 1969; and Leake et al., 1970). This attention is a result of the importance of Rb and Sr in geochronology. The major problem that arises in the analysis of these two elements is the determination of

the background profile in the 2θ region where the Rb and Sr K_{α} peaks occur. Since the peak-to-background ratios are often very small when these elements are present only in trace amounts, the background count is an essential step in the quantitative analysis (Fairbairn, 1966).

Figure 10 shows that the background level slopes (toward the low energy direction) in the 2θ region investigated. As a consequence, several background positions must be chosen to arrive at a good estimate of the background intensity under each peak. The optimum positions were located by drawing a line tangent to the three inter-peak valleys located between 23° and 28° 2θ on a dozen or more rock standards and using an average value for each of the three background positions, i.e., one before the Rb K_{α} peak, one in the valley between the Rb and Sr K_{α} peaks, and finally one after the Sr K_{α} peak. With background intensities at these three positions, the actual background under both peaks may be estimated with a fair degree of confidence.

Correcting for background by this procedure is justified with the assumption that the background intensity is a linear function of 2θ in this region. Although this is not necessarily correct, it probably is true to at least a first approximation. Fortunately, a standard (U.S.G.S., DTS-1) was available which contained less than 1 ppm of both Rb and Sr. This, therefore, may serve as a "blank" to

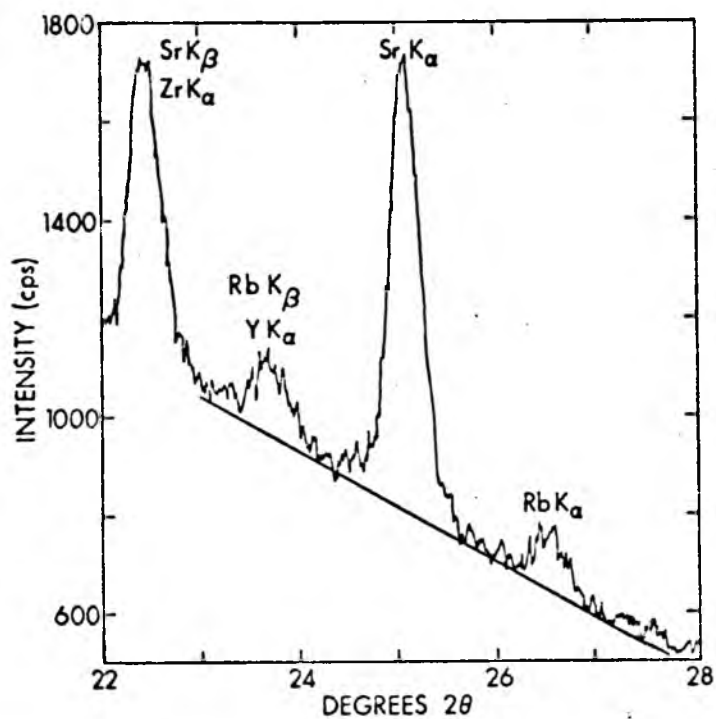


Figure 10. 2θ scan of U.S.G.S. rock standard BCR-1

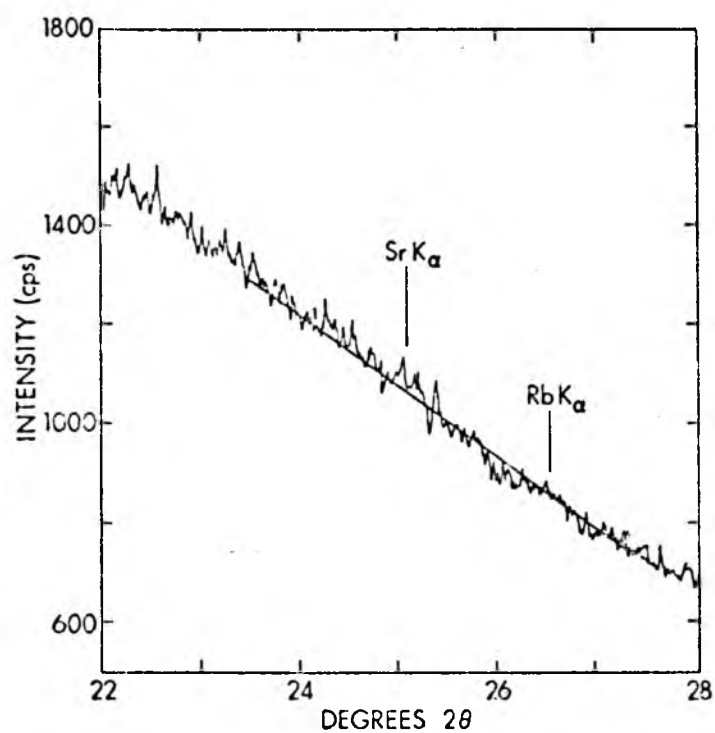


Figure 11. 2θ scan of U.S.G.S. rock standard DTS-1

test the supposition that the background intensities here, are in fact, a linear relationship. Figure 11 shows a scan of this standard over the same region studied and it appears fairly obvious that this assumption is valid.

Working curves for Rb and Sr are presented in Figures 12 and 13. Net intensity (peak and any deadtime correction¹ minus estimated background) vs. concentration produces a reasonably good line in both cases. Note that the scatter in the Sr calibration is probably a combination of inaccurate reported values for the rock standards, as mentioned earlier, with a matrix effect; i.e., points below the line are all intermediate to granitic rocks while those above are more basic basalts and diabases. A least squares line seems justifiable in view of the fact that the samples picked for analysis are of widely divergent matrix. The least squares analysis was run by computer on a program slightly modified from Wolfe (1969). The failure of either of these working curves to intercept the origin must imply that the background effect was not completely removed by this procedure. Because of this, the practical detection limits for these two elements are at about 15 and 18 ppm for Rb and Sr respectively.

¹The inability of a counter to resolve rapidly occurring pulses is known as the "deadtime" loss.

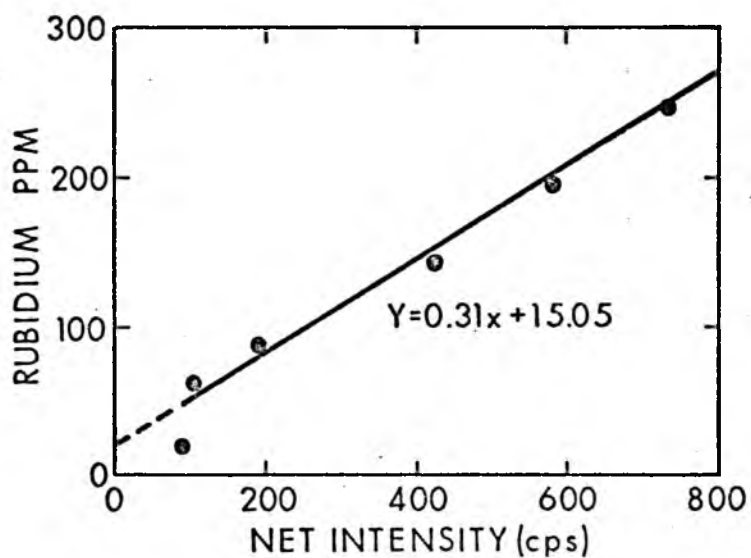


Figure 12. Working curve for rubidium.
Line drawn by least squares fit.

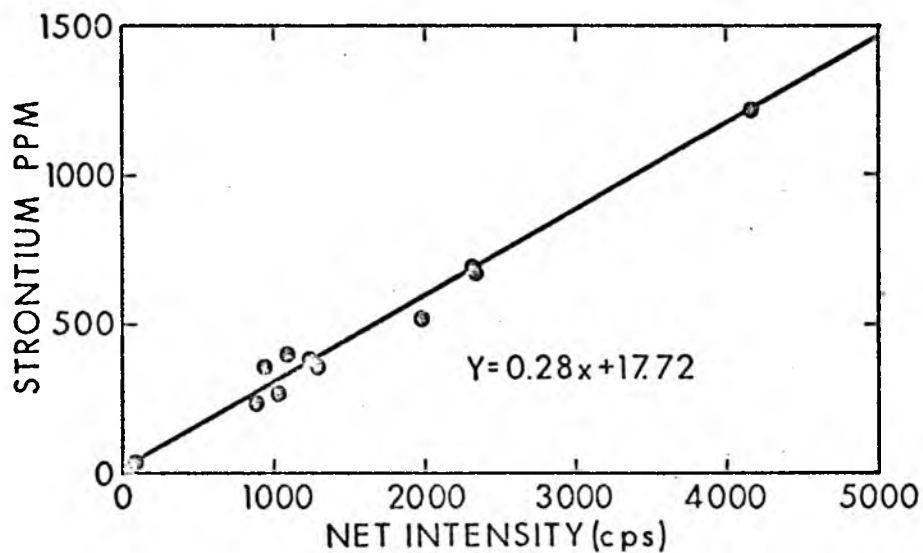


Figure 13. Working curve for strontium.
Line drawn by least squares fit.

Another interesting feature was noted during the X-ray determination of Ni. After running a whole suite of rock standards, it appeared that the net intensity of the Ni K_{α} line was very sensitive to the absolute iron concentration. Higher Fe concentrations resulted in lower intensity readings. This is probably the result of the Fe K absorption edge being only 0.085 Å above the Ni K_{α} line. Therefore, as in the case of Cu by atomic absorption analysis, knowing the iron content of the unknown enables a more precise determination of Ni. Andermann and Kemp (1958) also noted this effect and used scattered X-rays as an internal standard to correct for this interference. They discovered that a ratio of Ni K_{α} to scattering at 0.6 Å is almost independent of the iron concentration.

E. Carbonate analysis

Many techniques are currently available for the measurement of CaCO_3 in unconsolidated sediments. These methods include simple EDTA titrations (Turekian, 1956) to more elaborate methods using automatic carbon analyzers such as a LECO or CHN analyzer. These are also used for looking at the organic carbon content. Most of the gravimetric and volumetric methods for carbonate determinations rely on the reaction:



Clearly, the amount of CO_2 evolved by this reaction is directly proportional to the CO_3^{2-} concentration. If the

volume of CO_2 liberated by a known amount of powdered sample can be measured, then the calculation of the carbonate ion concentration may be based on the Gas Law: $pV=RT$.

This led Hülsemann (1966) to develop an apparatus in which the volume of CO_2 evolved after acidification of the sample (by 2N HCl) could be easily measured. Briefly, this apparatus consists of a gas generating system connected to a manometer where the volume of CO_2 can be read by the displacement of a column of mercury.

Hülsemann (1966) presents the Gas Law in a more convenient form for the calculation of $\%\text{CaCO}_3$:

$$\%\text{CaCO}_3 = \frac{v \cdot (P - M)}{W \cdot (T + t)} \cdot 0.1603$$

where

v = observed volume of CO_2 in ml,

P = barometric pressure in mm Hg,

M = vapor pressure of water in mm Hg,

W = weight of the sample in grams,

T = room temperature in $^{\circ}\text{C}$,

$t = 273.16$ (constant for conversion to absolute temperature scale).

0.1603 is a constant resulting from the conversion of the barometric pressure to c.g.s. units, the Gas Constant, and the molecular weight of CaCO_3 .

If $\% \text{CaCO}_3 = 100$, then W = weight in grams of CaCO_3 ; assuming a constant temperature of 26°C and a barometric pressure of 770 mm of Hg (these were the average conditions on the days of observation), the above equation is plotted as a function of ml of CO_2 evolved vs. weight in grams on Figure 14. Also shown here is an experimental curve run with Reagent grade CaCO_3 under similar conditions to that given for the Gas Law calculation. The reason these two curves are not coincident must be a consequence of moisture absorbed by the Reagent grade calcite causing systematically high weight values.

Using the calibration curve determined experimentally, sample # 15 (which had been dried once previously but not dessiccated during storage) produced the following results: 16.6, 18.0, 18.3, 16.1 and 16.3 % CaCO_3 . These values have a mean (\bar{x}) of 17.1%; a standard deviation (s) of 1.02%; and a coefficient of variation (C) of 5.97%. Sample # 20 provided results of 93.7, 92.6, 93.7 and 92.7 % CaCO_3 , or $\bar{x} = 93.2\%$, $s = 1.21\%$, and $C = 1.30\%$. Another split of sample # 15 was then taken and dried overnight at about 110°C and kept in a desiccator until weighing. Its carbonate content as determined by the Gas Law was 16.2%, within the standard deviation as noted above. Thereafter, all unknowns were determined by use of the experimental curve. It is hoped that differences between the water content of the samples and the Reagent calcite will not significantly

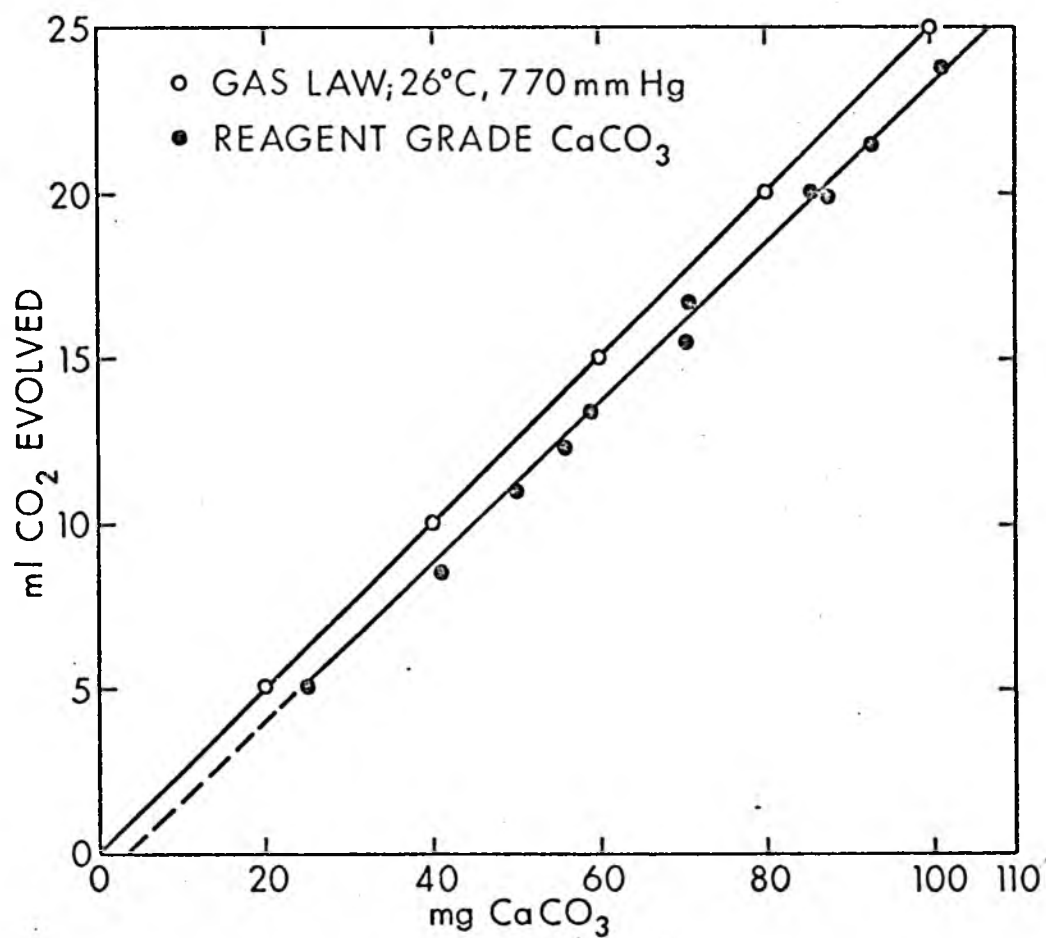


Figure 14. Working curve for calcium carbonate determinations showing variance between theoretical and experimental data. See text for explanation.

effect these determinations. M. Valencia (personal communication) reports approximately 13% variance at the 95 % confidence level using the same equipment below a 10 ml displacement; above 10 ml, however, the error decreases to less than 3%.

F. Precision and accuracy

During the course of the atomic absorption measurements, three samples (No.'s 30, 51 & 58) were made up in duplicate and run at various times during the course of the analyses. The value each replicate produced together with the variance and coefficients of variation (expressed as a percent) are presented in Table V. Generally, the precision seems to vary almost as much with the particular sample involved (appearing to be best for sample # 58) as it does for any one element. This is interpreted as meaning that the precision here must be related to sample preparation as much as to errors inherent in the instrumental procedure itself. From Table V, it appears that the highest precision was attained for Fe: C = 0.25 % at 15.5 % Fe; and for Zn: C = 0.54 % at 183 ppm. The two worst estimates for precision were both for Cr: C = 47.0 % at 57 ppm and C = 30.8 % at 107 ppm.

The U.S.G.S. rock standard W-1 was run as an unknown on all X-ray and atomic absorption measurements as a check on accuracy. The results for each element determined in

Table V: Data on duplicate runs of three samples from this study. Fe, Mg, and K reported as weight percent; all others as parts per million

Element	Sample No. 30				Sample No. 51				Sample No. 58			
	1	2	s	C	1	2	s	C	1	2	s	C
Fe	5.52	5.09	.45	8.19	2.69	2.88	.19	6.81	15.42	15.49	.07	.25
Cr	71	44	27	47.0	90	123	33	30.80	654	639	15	2.31
Co	73	81	8	10.38	36	39	3	8.00	97	101	4	4.04
Ni	212	-	-	-	17	13	4	26.66	756	769	13	1.70
Cu	365	340	25	7.08	24	18	6	28.57	193	189	4	2.09
Zn	-	-	-	-	-	-	-	-	183	182	1	0.54
Mg	4.12	3.87	.25	6.25	3.59	3.72	.13	3.55	9.05	9.66	.61	6.51
K	1.24	1.13	.11	9.24	0.19	0.14	.05	29.41	0.65	0.57	.08	13.11

Numbers 1 & 2 refer to the original and replicate runs respectively on each sample;

s = standard deviation or variance;

C = coefficient of variation expressed as a percent.

this study are compared with the recommended or "best" values for W-1 as reported in Fleischer (1969) in Table VI. All the results are in fairly good agreement, with Cr, Cu, Sr and Ba producing the best results. Notice that the Ni value determined by X-ray fluorescence is closer to the recommended value of W-1 than that determined by atomic absorption spectrometry.

Table VI: Comparison of analytical results from this study to the recommended values of U.S.G.S. rock standard W-1

W-1	% Fe ₂ O ₃	ppm					
		Cr	Co	Ni ^a	Ni ^b	Cu	Zn
This study	11.28	120	45	66	131	110	95
Fleischer, 1969	11.09	120	42	78	78	110	82
	% MgO K ₂ O		ppm Rb Sr Ba				
This study	6.38	0.51	30	182		181	
Fleischer, 1969	6.62	0.64	22	180		180	

^aNickel determined by X-ray fluorescence spectrography.

^bNickel determined by atomic absorption spectrography.

RESULTS AND DISCUSSION

A. General

The main feature of this section will be a series of elemental variation maps for each trace element and related major elements. Data from the literature are added when available. The variation maps are similar in style to those used by Turekian and Imbrie (1966) to show the patterns of trace element distribution in the Atlantic. The main purpose of the maps is to show the concentration of each element as a function of location. Each element was grouped into three, and in a few cases four, concentration ranges. It is felt in each case that a more refined grouping would not contribute to a more meaningful pattern. All elements except Sr are shown as calculated on a carbonate-free basis, i.e., all elements except Sr are assumed to be associated with the "clay" fraction of the sediments. Sr, due to its geochemical similarity to Ca, is known to be concentrated in the carbonate fraction of sediments (Turekian and Kulp, 1956). Ba, although strongly associated in some way with the calcareous sediments, is probably not incorporated to any significant extent into a calcite crystal lattice because of its large ionic radius.

B. Distribution of some alkali and alkaline-earth elements

The bulk concentrations of CaCO_3 , MgO , and K_2O (reported as weight percent) and Rb, Sr and Ba (reported as parts per million) are shown in Table VII for all samples analyzed. The concentrations of MgO , K_2O , Rb and Ba on a carbonate-free basis are shown in Table VIII. The K/Rb ratios for all samples are also reported in Table VIII. It should be pointed out that the relative error in the calculation to a carbonate-free basis increases greatly with samples containing very high carbonate values. This has apparently caused a large error in the carbonate-free determinations of sample number 22, which was reported at 99.4% CaCO_3 . The unrealistic high values which resulted here might have been satisfactory if the carbonate determination had been just a few percent lower.

The distribution of rubidium strongly follows that of its geochemically related element, potassium. The ratio of these two elements is extremely constant throughout the rock cycle and apparently only extreme conditions have an effect on the K/Rb ratio in any geochemical sample. Even in the extremely fractionated Skaergaard intrusion of Greenland the K/Rb ratio remains constant throughout (Heier and Adams, 1963). The significance of the K/Rb ratios in deep-sea sediments will be discussed in a later section.

Because of its similarity to K, Rb does not form minerals of its own but is camouflaged in K-minerals. The

Table VII: Concentration of calcium carbonate and some alkali and alkaline-earth metals from all samples analyzed

Sample No.	%			ppm		
	CaCO ₃	MgO	K ₂ O	Rb	Sr	Ba
1	0.52	3.70	3.95	167	176	1370
2	0.0	3.56	3.43	142	177	2270
3	0.18	3.78	3.35	142	221	3170
4	0.30	3.66	3.58	145	220	3320
5	0.0	3.43	3.96	171	157	1070
6	0.1	3.53	4.08	161	164	950
7	0.2	3.41	3.79	160	176	1595
8	0.1	3.77	4.08	160	169	1150
9	0.6	3.76	3.71	146	212	2030
10	0.1	3.88	3.47	137	195	1570
11	1.0	4.57	2.70	91	279	2070
12	0.0	8.82	0.76	24	218	334
13	0.7	3.43	2.81	104	251	2370
14	5.1	3.57	2.27	77	375	4270
15	16.9	2.93	2.08	76	418	2470
16	26.1	2.45	1.44	63	438	3046
17	71.8	1.07	0.25	16	761	847
18	0.32	3.42	2.32	79	194	1570
19	1.4	4.67	1.66	57	403	5896
20	93.2	0.61	0.06	nd ^a	1091	317
21	0.8	3.58	1.99	83	191	950
22	99.4	0.86	0.09	nd	1133	457
23	85.5	1.28	0.25	18	1141	497
24	93.0	0.80	0.15	nd	1214	477
25	0.7	2.86	1.91	73	204	1181
26	88.6	0.95	0.15	nd	1213	367
27	85.1	1.25	0.24	18	1113	367
28	85.1	0.99	0.25	18	1120	487
29	93.6	1.08	0.15	15	1035	282
30	0.5	4.12	1.24	50	210	776
31	0.0	4.13	2.11	72	257	870
32	42.0	1.53	1.59	32	907	557
33	82.9	1.29	0.32	15	1156	457
34	93.3	0.74	0.13	15	1043	277
35	85.8	1.00	0.21	nd	1049	547
36	53.4	2.03	0.62	24	910	527
37	79.1	1.56	0.32	nd	1138	437
38	0.4	4.18	2.16	68	245	914
39	1.1	4.16	1.49	41 _b	270	720
40	0.4	4.09	2.62	-	-	-
41	17.9	3.18	0.93	-	-	-
42	1.4	5.77	1.10	-	-	-

Table VII (continued) Concentration of calcium carbonate and some alkali and alkaline-earth metals from all samples analyzed

Sample No.	%			Rb	ppm	
	CaCO ₃	MgO	K ₂ O		Sr	Ba
43	1.1	7.73	0.82	-	-	-
44	64.7	2.84	0.21	nd	2101	154
45	53.7	2.03	0.23	17	1750	319
46	9.5	3.80	1.16	38	339	1404
47	6.0	6.36	0.76	24	413	674
48	47.9	2.75	0.36	nd	1522	364
49	1.0	7.49	1.28	-	-	-
50	33.0	5.17	0.58	20	478	474
51	63.2	3.59	0.19	nd	2473	nd
52	43.7	3.13	0.29	20	536	644
53	0.0	1.44	0.33	-	-	-
54	35.1	11.70	0.27	-	-	-
55	80.8	1.54	0.12	-	-	-
56	44.9	5.46	0.42	-	-	-
57	90.8	3.97	0.02	-	-	-
58	3.3	9.05	0.65	23	215	309
59	35.5	8.75	0.28	-	-	-
60	4.2	11.38	0.49	-	-	-
61	0.0	3.91	0.17	-	-	-
62	0.0	9.71	0.19	-	-	-
Method	GAS ^c	AA ^d	AA	XRF ^e	XRF	XRF

^and = not detected

^b- = not looked for

^cGAS = gas volumetric

^dAA = atomic absorption spectrography

^eXRF = X-ray fluorescence spectrography

Table VIII: Concentration of some alkali and alkaline-earth metals on a carbonate-free basis

Sample No.	%		ppm			K/Rb
	MgO	K ₂ O	Rb	Sr ^a	Ba	
1	3.72	3.97	168	176	1377	236
2	3.56	3.43	142	177	2270	242
3	3.79	3.36	142	221	3176	237
4	3.67	3.59	145	220	3330	248
5	3.43	3.96	172	157	1070	230
6	3.53	4.08	161	164	951	253
7	3.42	3.80	160	176	1598	238
8	3.77	4.08	160	169	1151	255
9	3.78	3.73	147	212	2042	254
10	3.88	3.47	137	195	1572	253
11	4.62	2.73	92	279	2091	297
12	8.82	0.76	24	218	334	317
13	3.45	2.83	105	251	2387	270
14	3.76	2.39	81	375	4499	295
15	3.53	2.50	91	418	2972	275
16	3.32	1.95	85	438	4122	229
17	3.79	0.89	57	761	3006	156
18	3.43	2.33	79	194	1575	295
19	4.74	1.68	58	403	5980	290
20	8.97	0.88	nd ^c	1091	4662	- ^d
21	3.61	2.01	84	191	958	239
22	* ^b	*	*	*	*	*
23	8.83	1.72	124	1141	3428	139
24	11.43	2.14	nd	1214	6814	-
25	2.88	1.92	74	204	1189	259
26	8.33	1.32	nd	1213	3219	-
27	8.39	1.61	121	1113	2463	133
28	6.64	1.68	121	1120	3268	139
29	16.88	2.34	nd	1035	4406	-
30	4.14	1.25	50	210	780	250
31	4.13	2.11	72	257	870	293
32	2.64	2.74	55	907	960	498
33	7.54	1.87	88	1156	2673	213
34	11.04	1.94	nd	1043	4134	-
35	7.04	1.48	nd	1049	3852	-
36	4.36	1.33	52	910	1131	256
37	7.46	1.55	nd	1138	2091	-
38	4.20	2.17	68	245	918	319
39	4.21	1.51	41	270	728	368
40	4.11	2.63	-	-	-	-
41	3.87	1.13	-	-	-	-
42	5.85	1.12	-	-	-	-

Table VIII (continued) Concentration of some alkali and alkaline-earth metals on a carbonate-free basis

Sample No.	MgO	K ₂ O	ppm			K/Rb
			Rb	Sr ^a	Ba	
43	7.82	0.83	-	-	-	-
44	7.99	0.59	nd	2101	436	-
45	4.38	0.50	37	1750	689	135
46	4.20	1.28	42	339	1551	305
47	6.77	0.81	26	413	717	312
48	5.28	0.69	nd	1522	699	-
49	7.57	1.29	-	-	-	-
50	7.72	0.87	30	478	707	290
51	9.76	0.52	nd	2473	nd	-
52	5.56	0.52	36	536	1144	144
53	1.44	0.33	-	-	-	-
54	18.03	0.42	-	-	-	-
55	8.02	0.63	-	-	-	-
56	9.91	0.76	-	-	-	-
57	43.15	0.22	-	-	-	-
58	9.36	0.67	25	215	320	268
59	13.57	0.43	-	-	-	-
60	11.88	0.51	-	-	-	-
61	3.91	0.17	-	-	-	-
62	9.71	0.19	-	-	-	-

^aSr values reported without conversion to carbonate-free basis.

^bInaccurate carbonate determination gave unrealistic values here.

^cnd = not detected

^d- = not looked for

important K-bearing clay mineral, illite, is a major constituent of marine sediments (Biscaye, 1965). The distribution of illite in the Pacific, as discussed earlier, appears to be the controlling factor in the distribution of K (shown in Figure 15) and, thus, of the distribution of Rb (Figure 16). The brown clays north of the Hawaiian Islands, which have been shown to be rich in illite (Griffin and Goldberg, 1963), contain the highest concentration of both of these elements.

Hirst (1962) reports an enrichment of Rb relative to K in clays from the Gulf of Paria. This may be due to the lower ionic potential of Rb which could result in a greater tendency of interstitial capture in clay minerals. Generally, the sediments from around the Hawaiian Islands are low in both K and Rb. This may be a reflection of the low values for both of these elements in the volcanic rocks of the Hawaiian Islands. Macdonald (1968) reports an average of 0.4% K from 200 Hawaiian tholeiites and olivine tholeiites. Hubbard (1967) shows generally low values for Rb in the majority of Hawaiian rocks that he studied.

Strontium is most similar to calcium in chemical properties and is usually concentrated in Ca, K, and Ba minerals. Goldberg and Arrhenius (1958) have shown that only 13 % of the total Sr content occurs in the sorbed state in pelagic clays. The remaining Sr fraction is dispersed in calcite, apatite, phillipsite and other such minerals. The

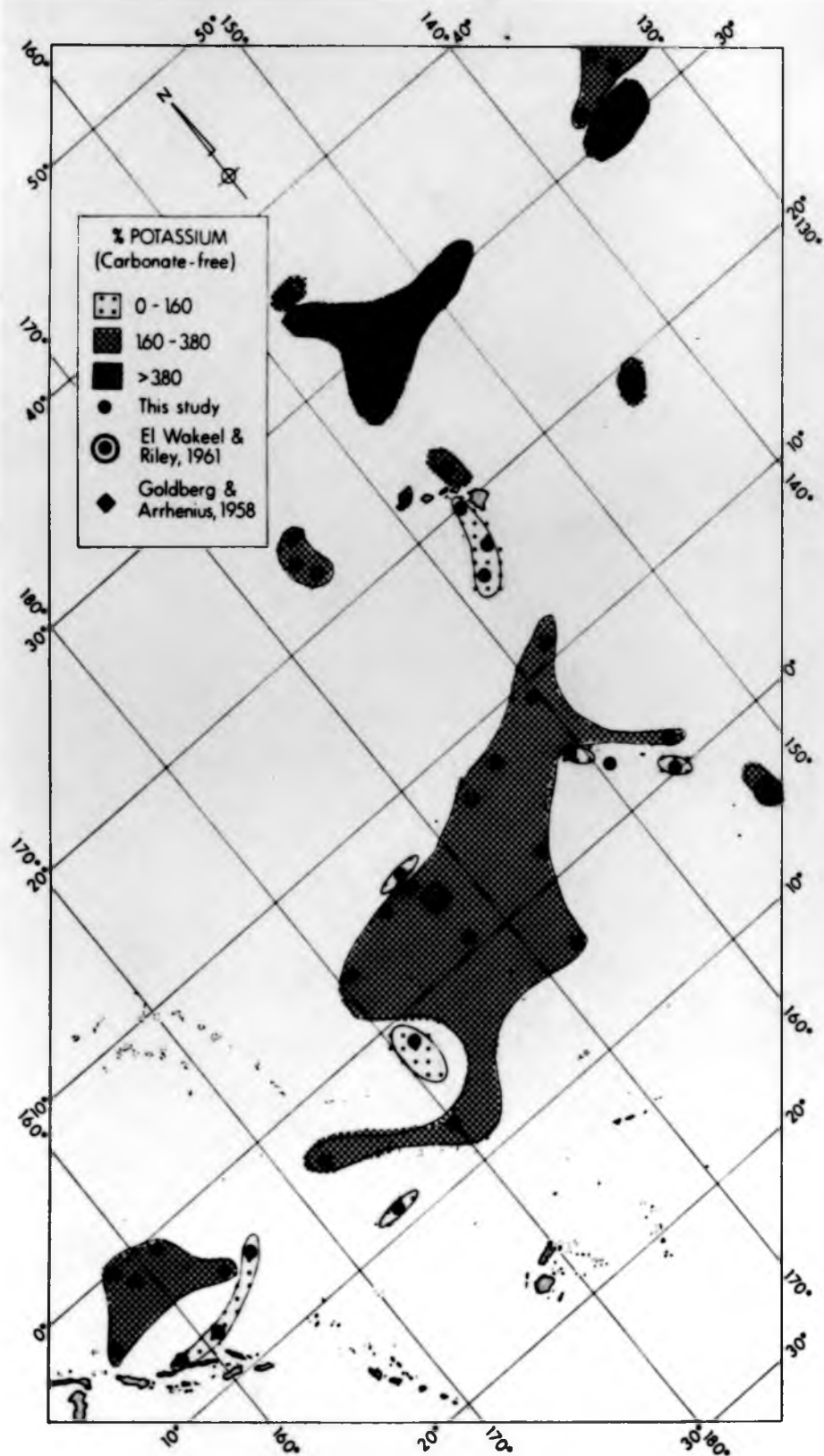


Figure 15. Variation map for potassium.

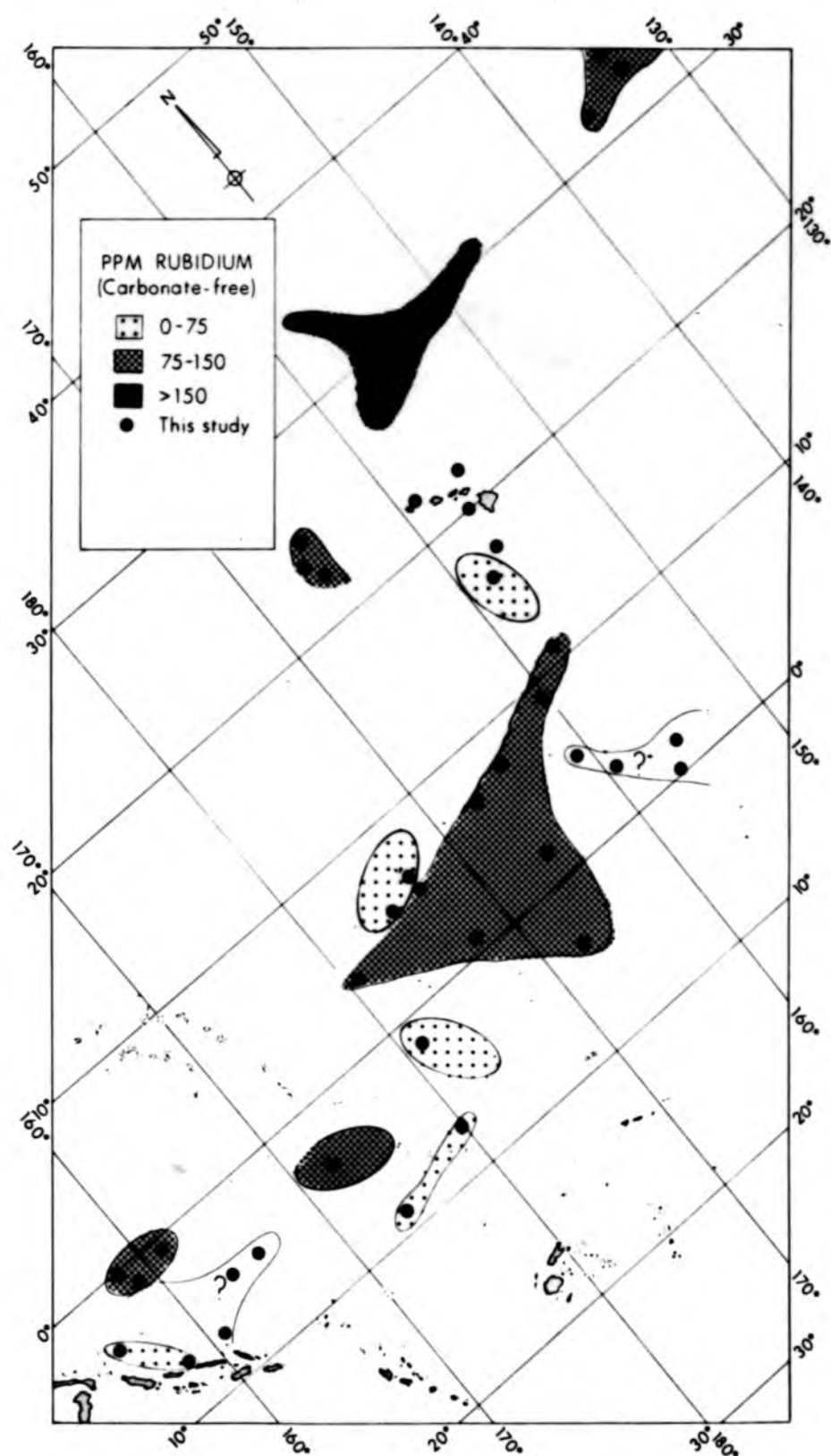


Figure 16. Variation map for rubidium.

major sink for Sr in the oceans must be the extensive calcareous oozes that usually occur at moderate depths in the ocean basins. Turekian (1964) reports an average content of about 1200 ppm Sr in foraminiferal tests. An average of 2080 ppm Sr for calcareous deep-sea sediments averaging 88 % total carbonate has been reported by Turekian and Kulp (1956). The distributions of Ca, as CaCO_3 , and Sr in the area studied are shown in Figures 17 and 18.

It is evident from these two maps that a major control on the distribution of Sr in bottom sediments is the carbonate content at any particular location. The highest concentrations of both components are found in the Line Island area and on the Ontong Java Plateau, both of which are characterized by extensive carbonate sedimentation. Turekian (1964) has mentioned that deep-sea clays are not a very efficient sink for Sr in the oceans. This is supported by the fact that Sr values in pelagic clays are generally lower than those from shales deposited on the continental margins. Turekian and Kulp (1956) have previously reported an average Sr content of 250 ppm for shales with less than 0.4 % Ca. All of the brown clays investigated in this study are about equal to or less than this value (average of 19 brown clays = 228 ppm Sr).

Particularly high Sr contents have been reported for aragonitic skeletons (Vlasov, 1966). This is probably because the more open structure of aragonite (orthorhombic)

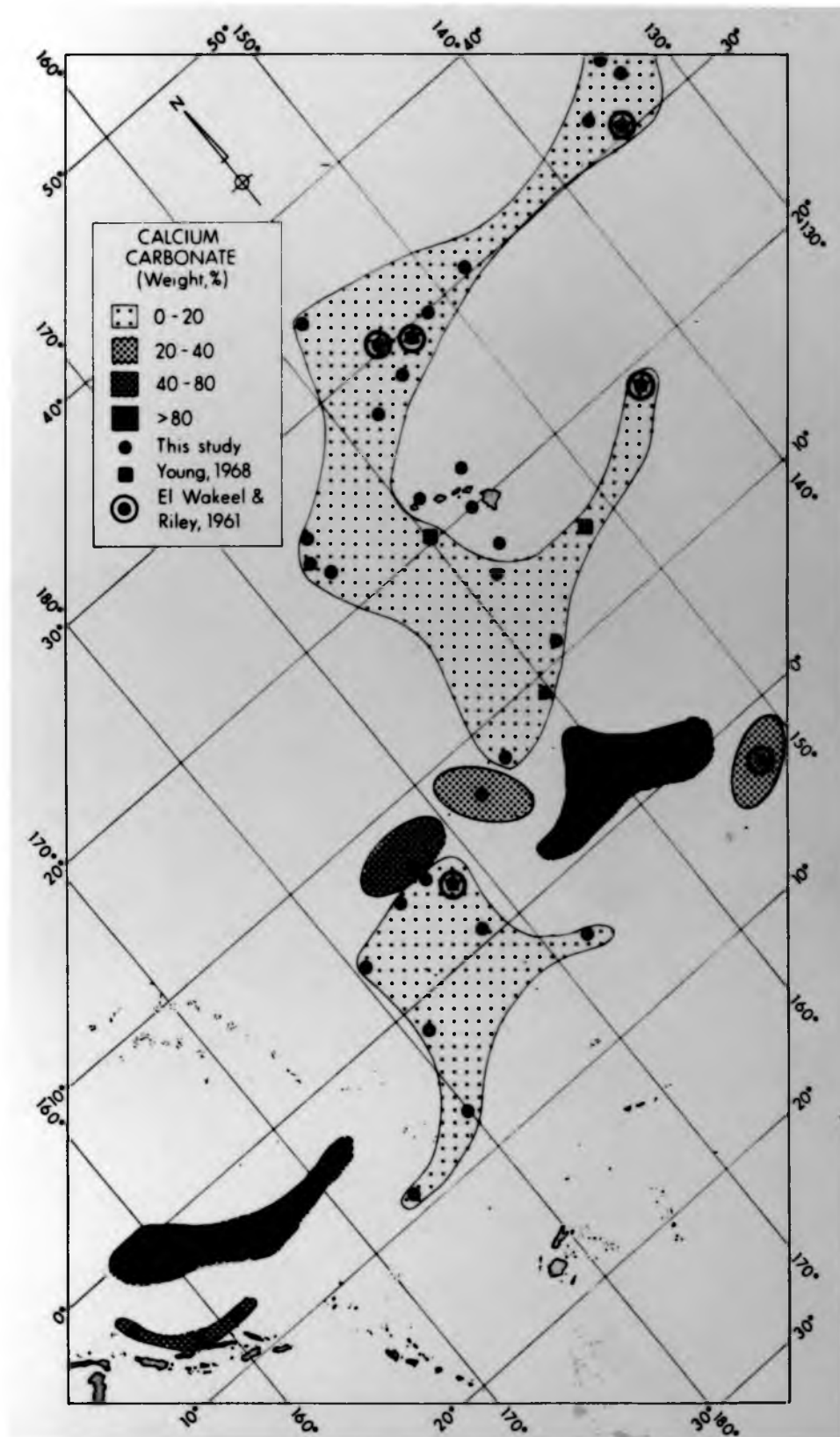


Figure 17. Variation map for calcium carbonate.

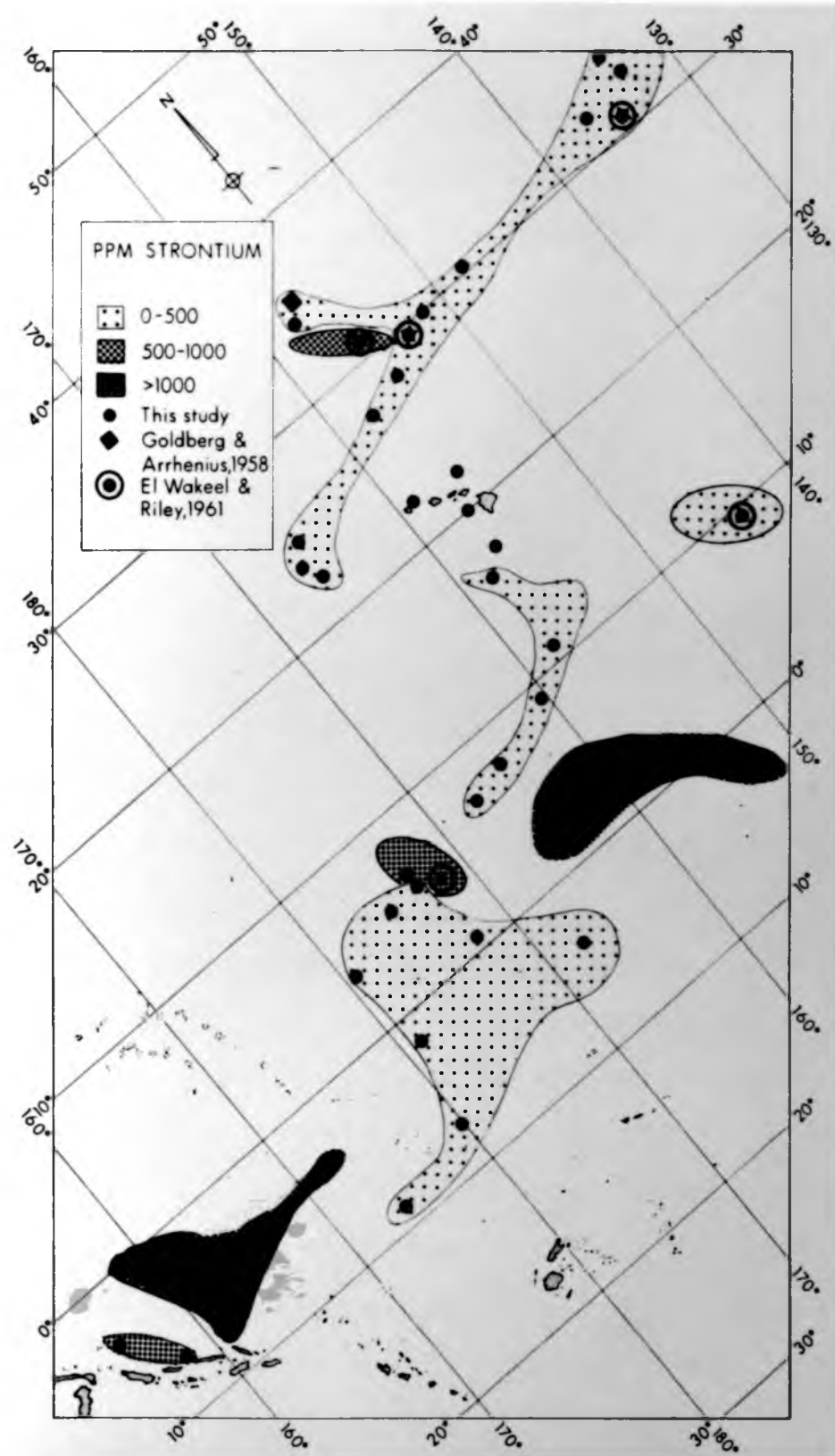


Figure 18. Variation map for strontium

can accommodate the larger-sized Sr^{2+} ion while this diadochic replacement of Ca^{2+} by Sr^{2+} is more restricted in the rhombohedral calcite structure. The high Sr values of some of the sediments around the Hawaiian Islands are probably caused by the inclusion of shallow-water aragonitic carbonates in the sediment.

Barium is geochemically similar to the major elements Ca and K. Because of its large ionic radius, Ba does not generally replace Ca but is extensively substituted for K in igneous silicates. Turekian and Armstrong (1960) have shown, however, that the Ba:Ca ratio is higher in marine shells than in sea water. Clearly, some other controls rather than just simply atomic substitution of a major element must be operative in the marine deposition of Ba. Goldberg and Arrhenius (1958) have found that the Ba (normalized to TiO_2) content in Pacific pelagic sediments is a function of latitude across the equatorial zone of high organic productivity. Turekian and Tausch (1964) discovered a similar relationship in the Atlantic Ocean, i.e., the highest Ba concentrations occurred in an area of prominent upwelling off south-west Africa. Arrhenius and Bonatti (1965) have reported that small spindle-shaped crystals of barite are present in moderate to high concentrations in the equatorial sediments of the Pacific. Barite (BaSO_4) probably exists as a solid solution with celestite (SrSO_4), which is a more soluble phase in sea water and is

not substantially preserved. Barite, being relatively insoluble, appears to crystallize readily wherever there is a source for Ba. Arrhenius and Bonatti (1965) attribute the major source to volcanism, while Turekian (1968) ascribes the production of BaSO_4 crystals to an association with planktonic productivity. It has been noted a few times (Revelle et al., 1955; El Wakeel and Riley, 1961) that there is a fairly strong covariance between biogenous Cu and Ba. The exact nature of this association is not completely understood at this time but there appear to be good arguments in favor of organic controls on the distribution of Ba in marine sediments.

The variation map for Ba appears as Figure 19. All of the samples from this study which contained greater than 4000 ppm Ba on a carbonate-free basis were located around the equatorial region of high productivity. Generally, the values are higher in the eastern portion of this area around the Line Island group. Two data points from El Wakeel and Riley (1961) show very high values for Ba north of 15°N . Both of these samples were reported as brown clays, so these high values are either suspicious or these samples happened to contain a Ba-mineral such as barite (unlikely at these depths) or harmotome. The data points which show low Ba values in a band just south of the equator are all deep-water non-calcareous sediments. The data here support the view that Ba is associated with the calcium carbonate

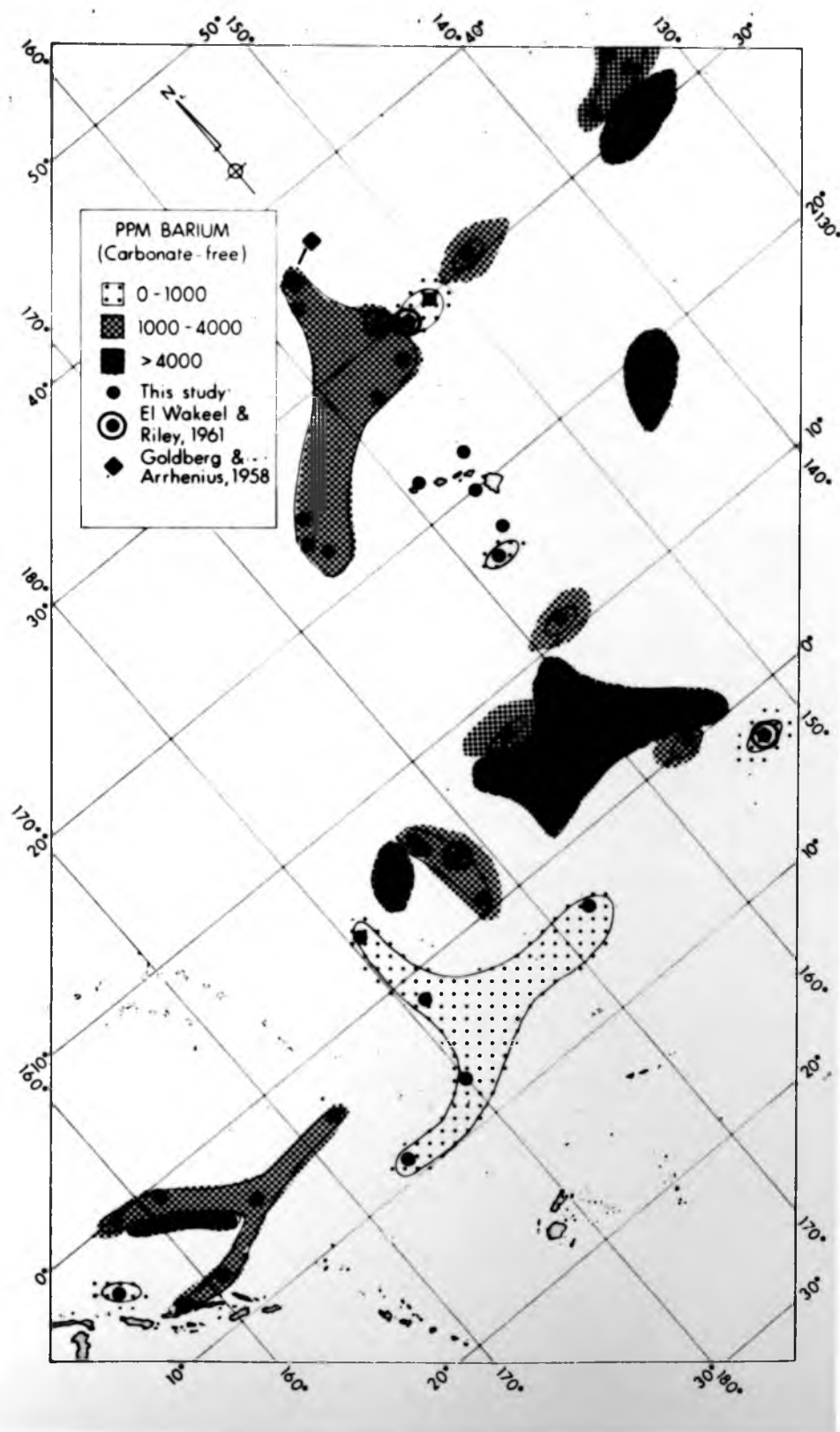


Figure 19. Variation map for barium.

fraction of the sediments and the production of barium sulfate crystals which probably dissolve at great depths.

C. Distribution of some transitional elements and Cu and Zn

The bulk analyses of Fe, Cr, Co, Ni, Cu and Zn are reported in Table IX. Total Fe is reported as percent Fe_2O_3 ; all others are shown as parts per million. All of these elements are presented in Table X on a carbonate-free basis; these values are used in the construction of all the variation maps in this section. Sample number 22 again appears to suffer from an inaccurately high carbonate determination. Contamination, possibly from the acid digestion bomb, was somewhat of a problem for Zn determinations. Several samples showed extraordinarily high Zn contents which later proved to be incorrect when the samples were prepared again under more carefully controlled conditions.

The ability of chromium to replace ferric iron and aluminum diadochically accounts for the majority of Cr in the lithosphere. Because of the strong resemblance of the ionic charge and radius to those of Fe^{3+} and Al, Cr follows these elements in the weathering cycle.

El Wakeel and Riley (1961) report that the average abundance of Cr in bottom samples from the Pacific was significantly lower than the mean for crustal rocks. As can be seen from Figure 20, most Cr values from the area

Table IX: Concentration of some transitional elements and Cu & Zn from all samples analyzed

Sample No.	Fe_2O_3 % ^a	ppm				
		Cr	Co	Ni	Cu	Zn
1	7.20	110	50	71	184	125
2	7.76	159	67	140	187	129
3	8.21	151	59	142	197	140
4	7.75	128	75	141	183	153
5	7.56	131	61	138	185	126
6	7.56	101	52	110	174	142
7	7.69	101	57	111	204	196
8	7.50	100	59	118	176	180
9	7.92	113	56	145	185	138
10	7.89	116	44	150	189	157
11	9.92	227	14	128	233	145
12	10.91	289	31	284	266	120
13	7.10	55	98	195	419	212
14	5.23	36	64	176	412	221
15	4.55	60	30	120	287	207
16	3.38	25	18	150	343	144
17	0.63	20	9	15	76	79
18	5.70	30	44	151	265	101
19	6.69	31	55	350	553	240
20	0.08	nd ^b	19	nd	23	8
21	6.23	90	63	135	330	105
22	0.20	nd	19	nd	26	20
23	0.75	13	20	11	55	117
24	0.45	5	20	14	42	10
25	5.56	63	51	120	304	199
26	0.36	8	19	14	43	63
27	1.28	nd	22	15	57	62
28	0.96	32	10	17	45	252
29	0.84	20	13	11	26	163
30	5.52	71	73	160	365	369
31	9.24	110	50	105	298	130
32	2.89	50	39	21	50	50
33	1.71	nd	32	18	75	179
34	0.74	nd	10	14	47	78
35	1.04	16	10	14	36	20
36	3.60	nd	45	19	78	88
37	2.02	nd	16	18	36	57
38	9.98	60	74	187	379	135
39	11.13	50	60	191	491	153
40	10.11	154	38	77*	232	159
41	10.45	211	41	123*	267	157

Table IX (continued) Concentration of some transitional elements and Cu & Zn from all samples analyzed

Sample No.	Fe ₂ O ₃ ^a	ppm				
		Cr	Co	Ni	Cu	Zn
42	8.96	198	38	106*	195	99
43	9.86	216	48	206*	237	119
44	4.30	112	62	29	41	49
45	4.78	75	64	32	56	70
46	11.23	313	53	150	241	134
47	11.92	411	46	176	231	152
48	6.45	110	75	45	72	80
49	14.78	599	205	366*	320	383
50	10.62	474	107	186	180	140
51	2.69	90	36	28	24	673
52	7.34	245	72	124	101	110
53	19.93	nd	4864	2805*	528	535
54	9.69	355	183	641*	129	127
55	2.46	36	35	40*	23	385
56 ^c	10.45	423	150	6735*	526	60
57	1.39	5	27	77*	13	45
58	15.42	654	97	490	193	183
59	7.49	339	91	299*	47	90
60	14.56	522	87	920*	155	206
61	16.34	677	66	509*	206	149
62	15.60	698	75	750*	185	165
Method	AA ^d	AA	AA	XRF ^e	AA	AA

^aTotal iron reported as Fe₂O₃^bnd = not detected^csample possibly contaminated^dAA = Atomic absorption spectrography^eXRF = X-ray fluorescence spectrography

* = Nickel determinations by AA

Table X: Concentration of some transitional elements
and Cu & Zn on a carbonate-free basis

Sample No.	% Fe_2O_3^a	ppm				
		Cr	Co	Ni	Cu	Zn
1	7.24	111	50	71	185	126
2	7.76	159	67	140	187	129
3	8.22	151	59	142	197	140
4	7.77	128	75	141	184	153
5	7.56	131	61	138	185	126
6	7.57	101	52	110	174	142
7	7.71	101	57	111	204	196
8	7.51	100	59	118	176	180
9	7.97	114	56	146	186	139
10	7.90	116	44	150	189	157
11	10.02	229	14	128	235	146
12	10.91	289	31	284	266	120
13	7.15	55	99	196	422	213
14	5.51	38	67	185	434	233
15	5.48	72	36	144	345	249
16	4.57	34	24	203	464	195
17	2.23	71	32	53	270	280
18	5.72	30	44	151	266	101
19	6.78	31	56	355	561	243
20	1.18	nd ^c	279	nd	338	118
21	6.28	91	64	136	333	106
22 ^b	33.33	nd	3167	nd	4333	3333
23	5.17	90	138	152	379	807
24	6.43	71	286	57	600	143
25	5.60	63	51	121	306	200
26	3.16	70	167	123	377	553
27	8.59	nd	148	97	383	416
28	6.44	215	67	114	302	1691
29	13.13	313	203	172	406	2547
30	5.55	71	73	161	367	371
31	9.24	110	50	105	298	130
32	4.98	86	67	35	86	86
33	10.00	nd	187	105	439	1047
34	11.04	nd	149	209	701	1164
35	7.32	113	70	99	254	141
36	7.73	nd	97	40	167	189
37	9.67	nd	77	86	172	273
38	10.02	60	74	188	381	136
39	11.25	51	61	193	496	155
40	10.15	155	38	77	233	160
41	12.73	257	50	150	325	191

Table X (continued) Concentration of some transitional elements and Cu & Zn on a carbonate-free basis

Sample No.	% Fe_2O_3^a	ppm				
		Cr	Co	Ni	Cu	Zn
42	9.09	201	39	108	198	100
43	9.97	218	49	208	240	120
44	12.18	317	176	82	116	139
45	10.32	162	138	69	121	151
46	12.41	346	59	166	266	148
47	12.68	437	49	187	246	162
48	12.38	211	144	86	138	154
49	14.93	605	207	370	323	387
50	15.85	707	160	277	269	209
51	7.31	245	98	76	65	1829
52	13.04	435	128	220	179	195
53	19.95	nd	4864	2805	528	535
54	14.93	547	282	988	199	196
55	12.81	188	182	208	120	2005
56 ^d	18.97	768	272	12223	955	109
57	15.11	54	293	837	141	489
58	15.95	676	100	782	200	189
59	11.61	526	141	464	73	140
60	15.20	545	91	960	162	215
61	16.34	677	66	509	206	149
62	15.60	698	75	750	185	165

^aTotal iron reported as Fe_2O_3 .

^bUnrealistically high values may be due to inaccurate carbonate analysis.

^cnd = not detected

^dContamination was evident in this sample

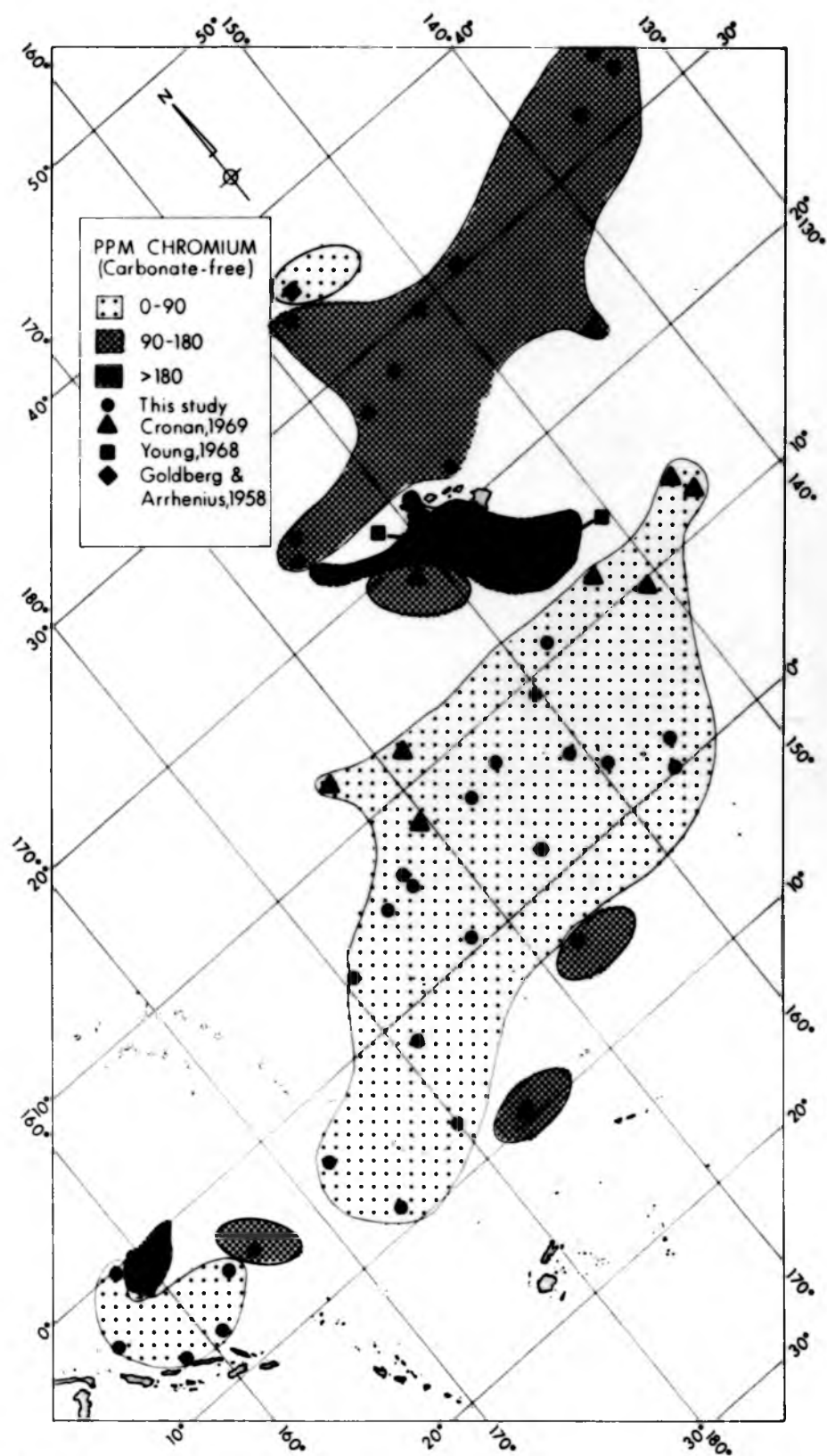


Figure 20. Variation map for chromium

studied here are low. El Wakeel and Riley (1961) suggest that these low values in pelagic sediments may be a result of oxidation of Cr to the hexavalent state, which increases its mobility and may cause partial loss from the sediment.

Goldberg and Arrhenius (1958) reported the highest concentrations of Cr occurring in samples containing pyroclastic material. This agrees with the results reported here, which show the highest concentration of Cr in a band south of the Hawaiian Islands. All the sediments from the area contain volcanic debris, usually in the form of ash layers. Perhaps most of the Cr is incorporated in the octohedral layers of montmorillonite, which is an alteration product of volcanic glass. Goldberg and Arrhenius (1958) propose that an excess above 100 ppm Cr is a useful indication of the presence of basaltic pyroclastic material. Although this general relation appears to be correct, the present author suggests a somewhat higher value, about 180 ppm Cr, for this distinction.

High carbonate-free concentrations of Cr were found in two samples (numbers 28 and 29) which are relatively pure calcareous oozes. On a carbonate-free basis, these samples are also high in Sr and Ba. This may indicate that a celestobarite (Ba, SrSO_4) phase is present here. If so, it could account for the higher concentration of Cr, as Arrhenius and Bonatti (1965) have suggested that Cr as $(\text{CrO}_4)^{2-}$ may substitute for $(\text{SO}_4)^{2-}$ in the celestobarite structure.

Turekian and Imbrie (1966) have shown that cobalt and nickel, as well as Mn and Cu, are significantly enriched in the shallower, mid-oceanic regions of the Atlantic. The variation maps for Co and Ni are shown in Figures 21 and 22. The patterns of distribution (especially for Ni) are not readily discernible. However, there are a few points which are worth mentioning.

The main feature of these maps which strikes the author is the apparent separation of Co and Ni in the sediments. The volcanic sediments south of the Hawaiian Islands are relatively rich in Ni but depleted in Co. Data points in the Line Island area show an enrichment of Co but a deficiency in Ni. The only similarity of abundances appears to be in the brown clays north of Hawaii and the calcareous oozes on the Ontong Java Plateau, which show intermediate values for both elements. This apparent separation is a little surprising in view of the fact that these elements are closely associated chemically and show a strong correlation with Mn in marine sediments (Turekian and Imbrie, 1966).

The distribution of Co, and particularly Ni, appears most complex in the biogenic sediments of the equatorial region. Perhaps biological activity is responsible in part for the mixed patterns seen there. As discussed in an earlier section, the sediments there consist of calcareous and siliceous oozes with the siliceous ooze occurring at

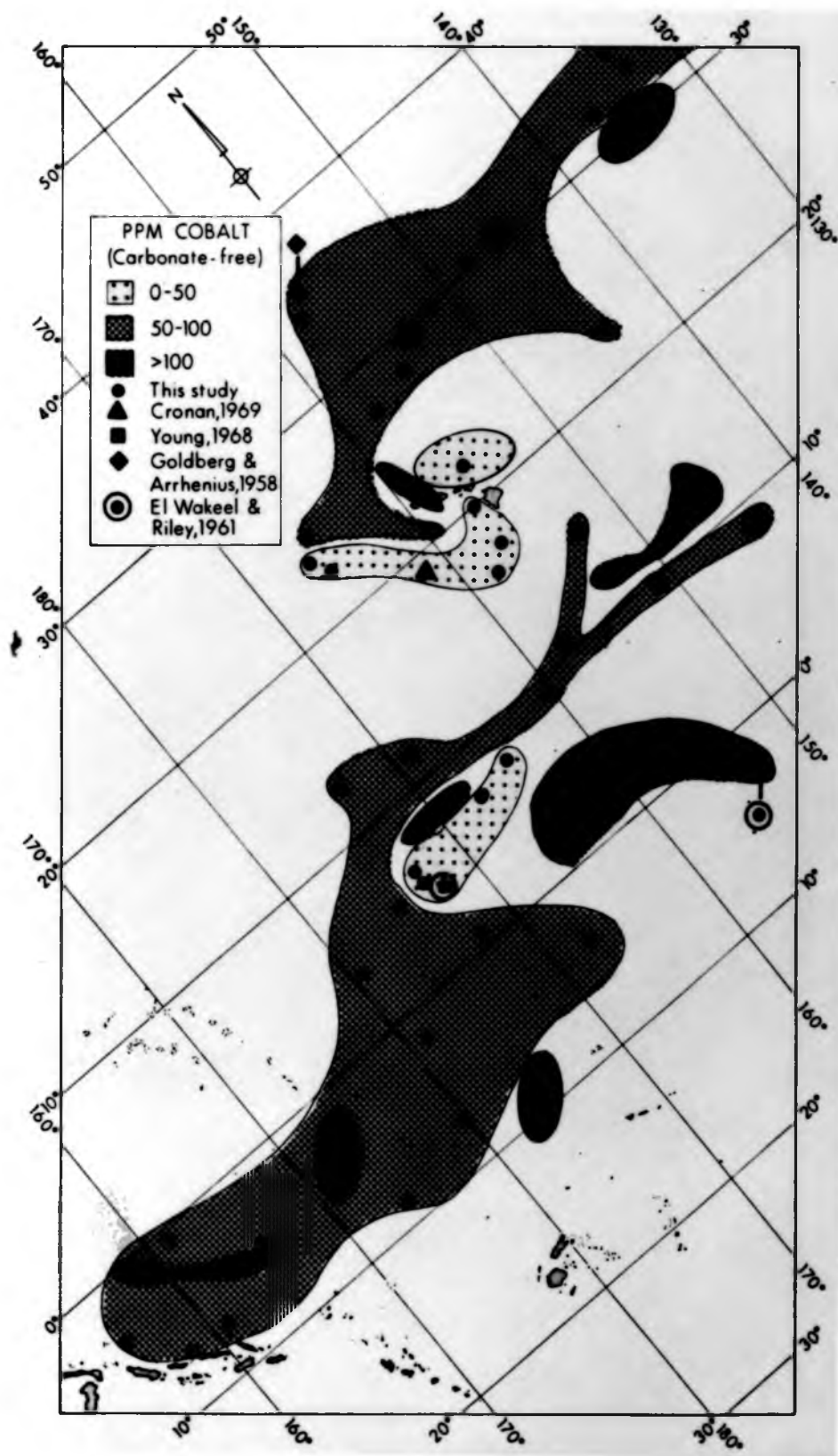


Figure 21. Variation map for cobalt.

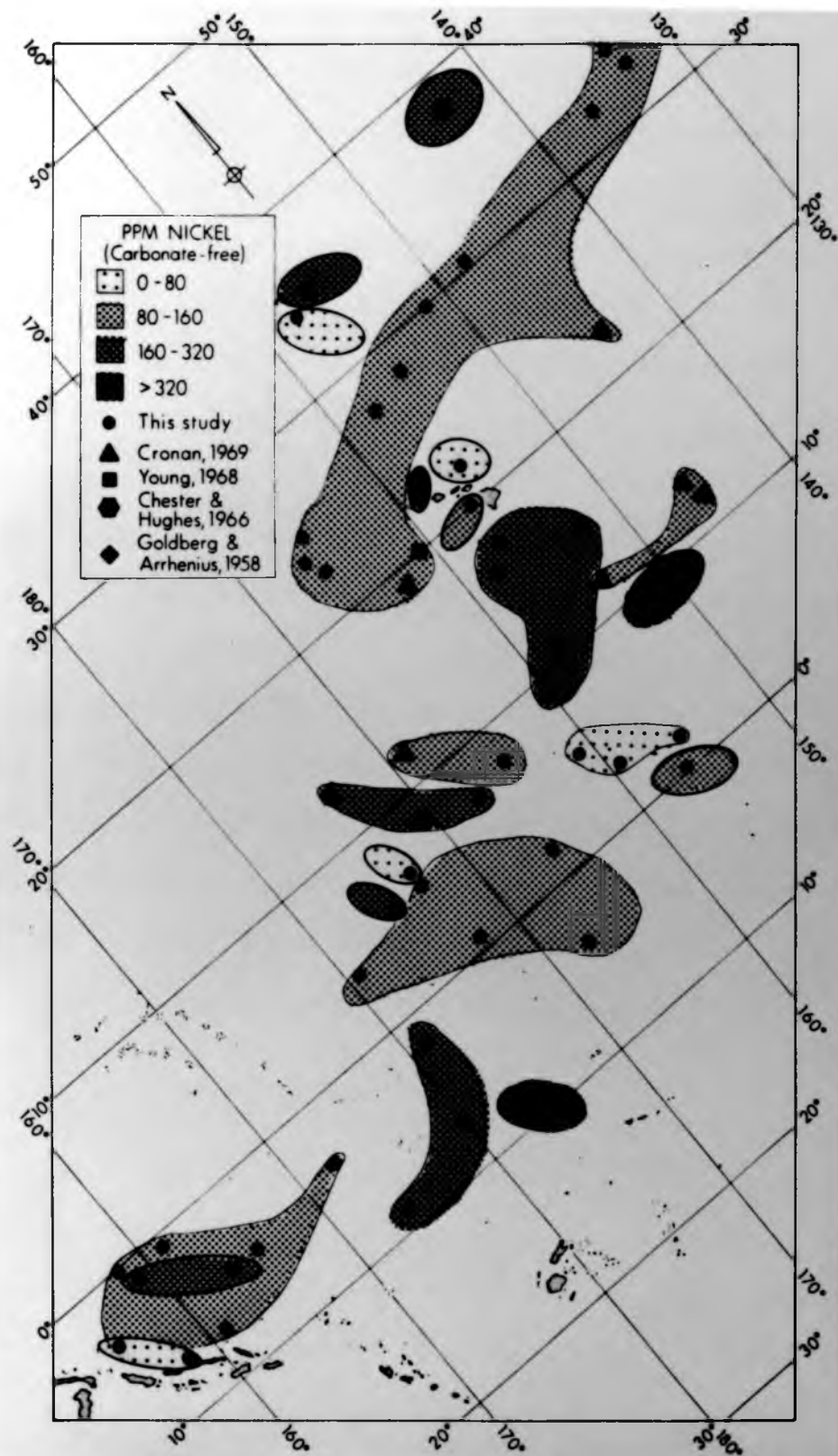


Figure 22. Variation map for nickel.

depths greater than about 4800 m. The role that organic molecules play in the addition to, or redistribution of, rare metals in pelagic sediments is generally unknown. Baturin and Kochenov (1967) show a distinct correlation, however, between organic carbon and Co and Ni (as well as Mo and V) in sediments from many localities. These authors feel that the mechanism for concentration of rare metals in bottom sediments cannot be explained by the simple extraction of these metals from sea water by combination with organic molecules. They propose that diagenetic redistribution of metals within the sediment is promoted by dissolved organic matter and that interstitial solutions tend to migrate towards layers with a high organic content. Apparently, these processes occur not only in sediments undergoing reduction but in sediments undergoing oxidation which have retained some organic matter. Thus it appears possible that these types of reactions may be responsible for the apparent random distribution of Co and Ni in these biogenic sediments.

The non-biogenic sediments such as the brown clays and volcanic muds show a more normal content of Co. The Co is enriched in the brown clays relative to the volcanic sediments, while the reverse is true for Ni. Chester and Hughes (1966) have shown in a study of a deep-sea core from the Pacific that approximately 56 % of the Ni was located in micro-manganese nodules (EDTA soluble portion) and that the

remaining 44 % was bound in the lattice structure of clay minerals. Van der Waijden et al. (1970) noted a good correlation between Co and Al from Atlantic bottom sediments indicating an association of Co with the clay fraction. They do not speculate, however, on whether Co is incorporated in or adsorbed onto the clay particles. Hirst (1962) showed that the loosely bound (acid soluble) portion of Co in clays from the Gulf of Paria is invariably higher than that of Ni. Thus it appears that a significant amount of Co may be adsorbed onto clay surfaces directly from sea water while non-hydrogenous Ni is probably restricted to structural positions.

Geochemically, copper has an affinity for sulfur but its distribution in marine sediments is certainly not completely controlled by sulfide deposits. The Cu concentration in the oceans appears to be controlled by the adsorption on, or possible combination with marine organisms. The biogeochemistry of Cu in the oceans may be the most important consideration in determining its distribution in marine sediments. This appears to be the case in the Central Pacific, as shown in Figure 23. Cu appears to be homogeneously distributed in the brown clays of the northern latitudes, while it is greatly enriched in the non-carbonate fraction of the calcareous oozes and slightly enriched in the siliceous oozes of the equatorial region.

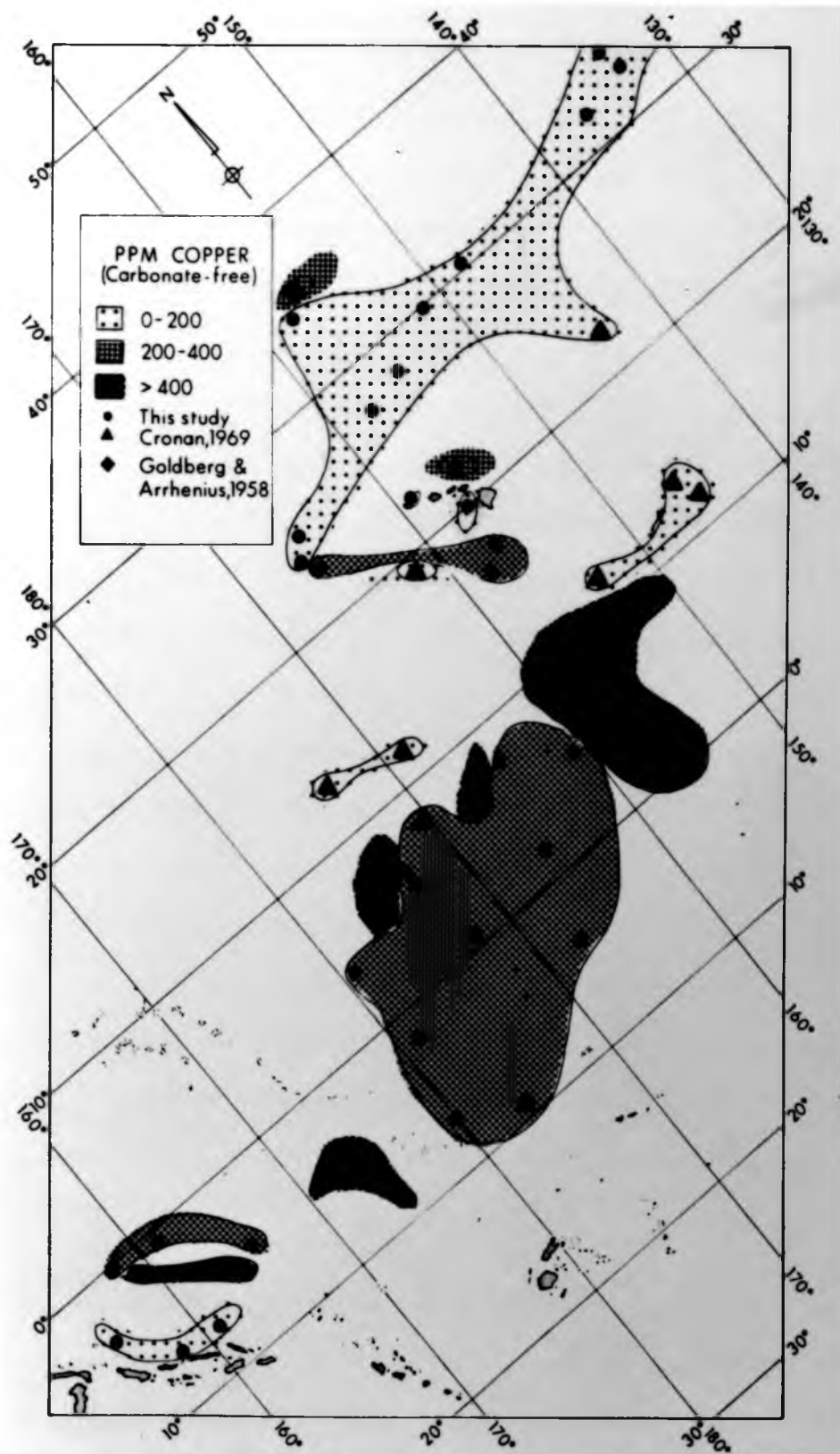


Figure 23. Variation map for copper

Although Cu certainly may occur as a hydrogenous deposit, as shown by its high concentration in manganese nodules, the organically-contributed Cu must be the important constituent in areas of high productivity. It has been suggested by Revelle et al. (1955) that the accumulation rate of biogenetic Cu is in general proportional to the rate of deposition of calcareous tests. This appears to be the case here, with the highest concentrations of non-carbonate Cu occurring around the Line Island group and on the Ontong Java Plateau. Turekian and Imbrie (1966) also noticed this association between Cu and the calcium carbonate fraction of the sediments from the Atlantic. These authors point out that Cu is not contained in the lattice of the carbonate tests but is in some unknown association with them. It is well known that Cu is an essential element in the respiratory pigment called hemocyanin found in the blood of many marine invertebrates. It has also been suggested (Rankama and Sahama, 1950) that Cu may form a complex with large organic molecules to form insoluble salts or coordination compounds which are only very slightly dissociated, such as the protein molecules.

The manner of occurrence of zinc in the lithosphere is determined by its property of diadochically replacing ferrous iron and magnesium in mineral structures. Zn goes readily into solution during weathering as a sulfate or chloride.

Apparently, the Zn^{2+} ion is very mobile and extensive migration is possible (Rankama and Sahama, 1950).

Zn is homogeneously distributed throughout much of the area studied here. The distribution of Zn is shown in Figure 24. There is little variation in the Zn content north of about 15°N but there are some significant enrichments in the carbonate-free fraction of the sediments around the Line Islands, the Ontong Java Plateau and near Ocean Island. The source of these enrichments is not clear but one possibility occurs to this author. It has been reported (Brundin, 1933; in Rankama and Sahama, 1950) that Zn is greatly enriched in sedimentary phosphorites of organic origin (guano) from South Pacific Islands. These guano deposits are known to occur on Fanning Island (K. Roy, personal communication), and on Ocean Island and Nauru Atoll (Bateman, 1950). All of the sediments studied here which have a Zn content, on a carbonate-free basis, greater than 800 ppm occurs near at least one of these islands. It seems reasonable to suspect, then, that a detrital component from one of these islands may have influenced the trace element content of the surrounding areas.

D. Trace elements in Hawaiian sediments

Twenty-three samples from the Hawaiian Islands area were analyzed for their trace element content (see index map; Figure 2). Four of these samples were from a single

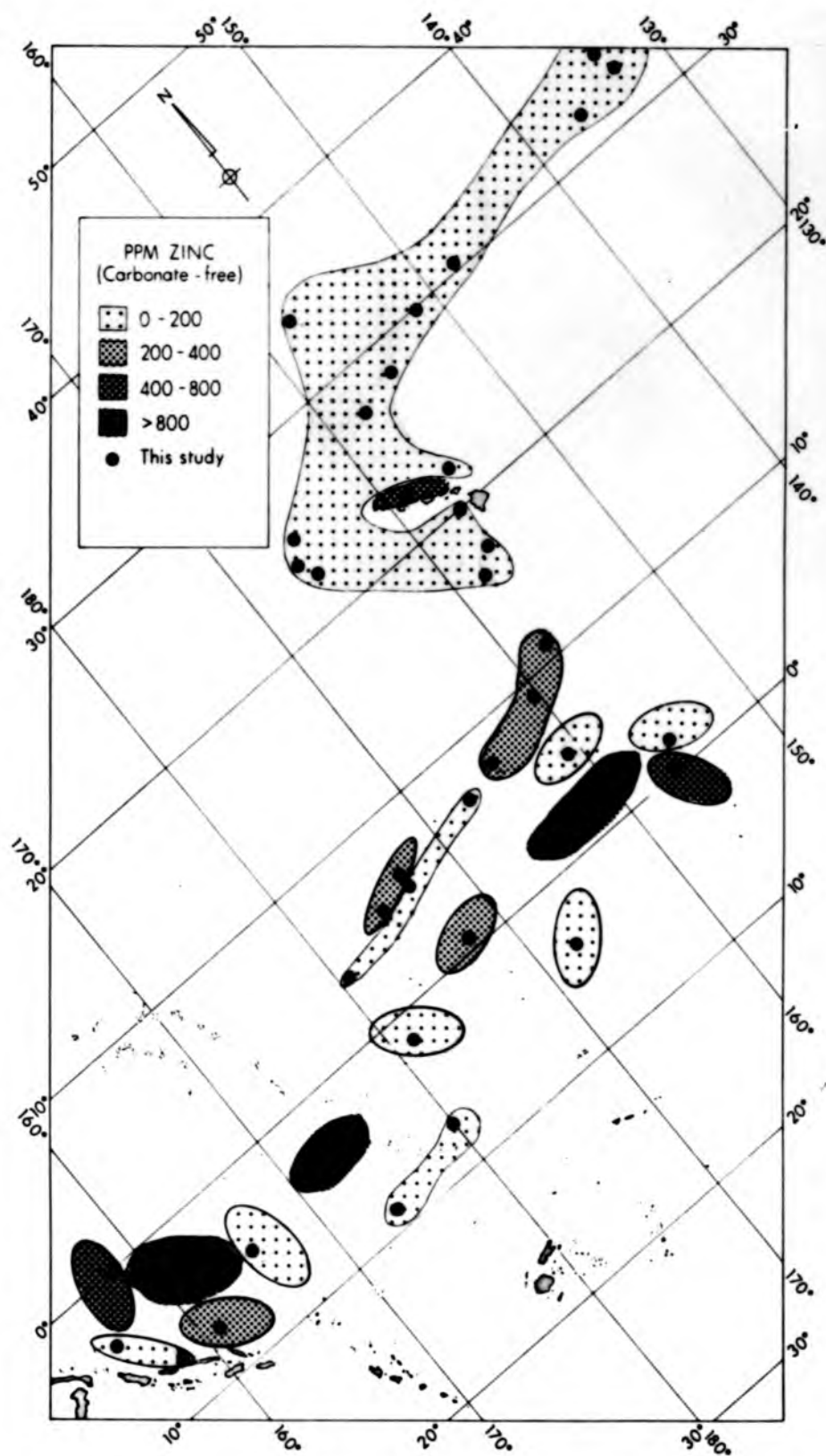


Figure 24. Variation map for zinc.

sediment core (KAUAI PC -09), two were river sediments from the Wailua River, Kauai, and one was a beach sand from Nawiliwili Harbor, Kauai. The distributions of MgO, total Fe, Cr, Co, Ni, Cu and Zn from some Hawaiian sediments are shown in Figures 25 through 31. All elements, except Mg, are reported on a carbonate-free basis in order to subtract the effect of carbonate dilution. Mg is not reported in this way because it is a major constituent in some shallow-water carbonates.

The heavy concentration of sampling sites near the island of Kauai is a result of an investigation currently in progress on the origin of manganiferous sediments in the Kauai Channel. These sediments often contain indurated siltstones and manganese crusts interlayered with pyroclastic arenites and detrital muds. The chemistry of the bottom sediments here is apparently a result of a combination of the deposition of subaerially weathered products admixed with the hydrogenous disposition of Mn and associated elements during periods of low sedimentation rates and rapid bottom currents (M. Morgenstein, personal communication).

This area will be referred to here as an area of authigenic ferride enrichment. Its approximate areal extent is outlined on the index map of the Hawaiian Islands (Figure 2). Four surface samples are located within this area (numbers 49, 53, 54 and 56) and the average trace

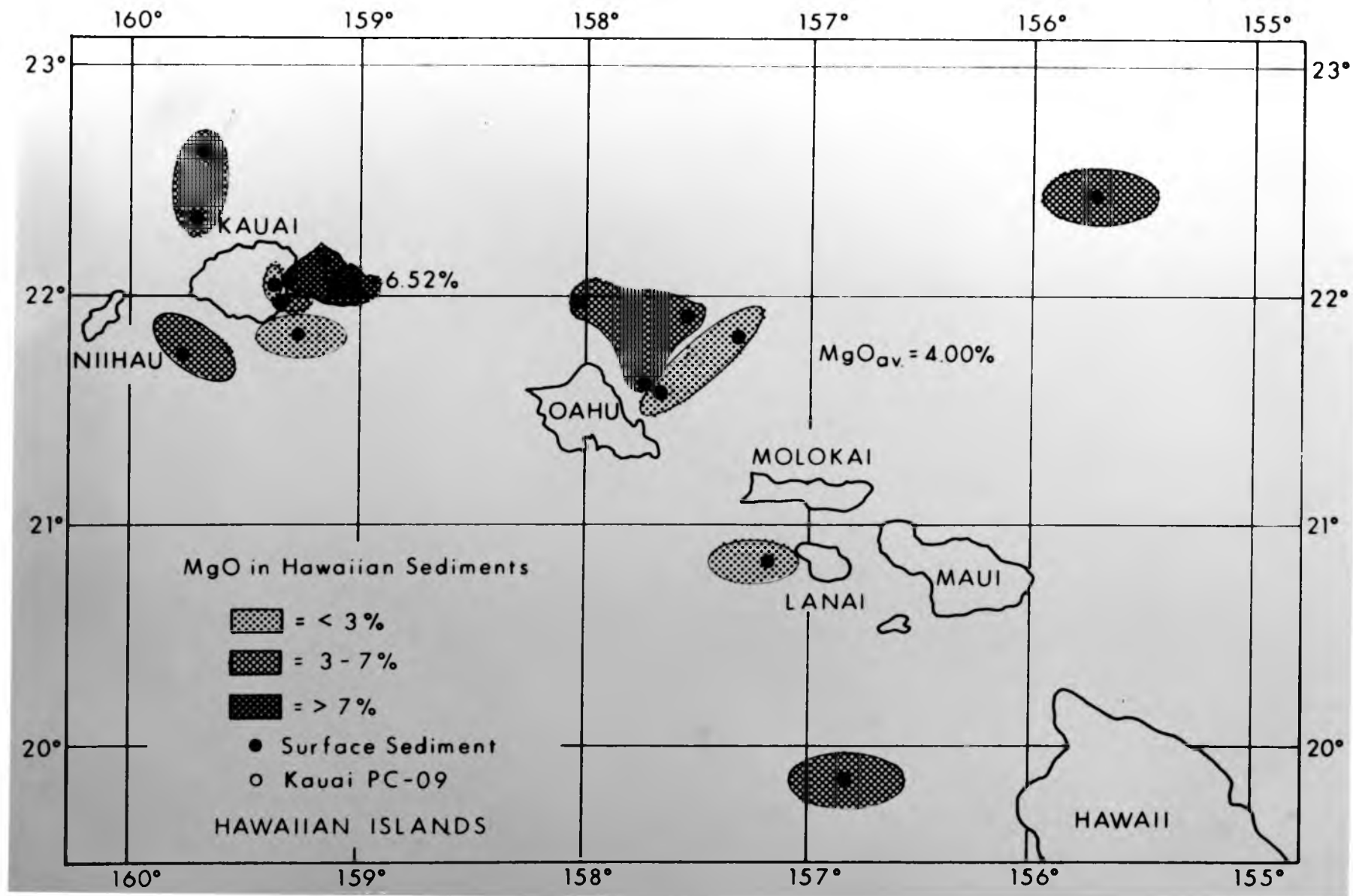


Figure 25. Variation of magnesium in Hawaiian sediments.

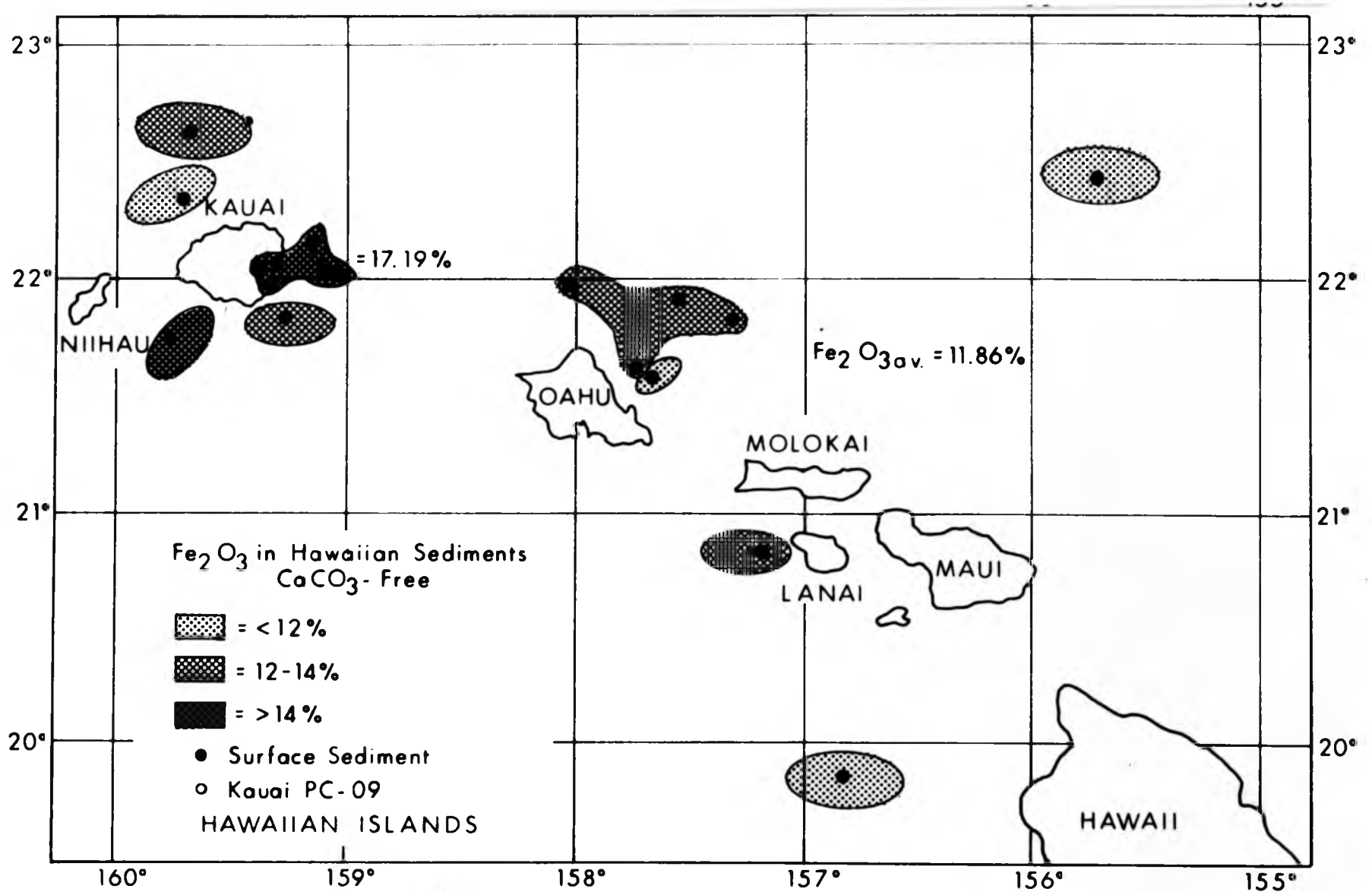


Figure 26. Variation of total iron in Hawaiian sediments.

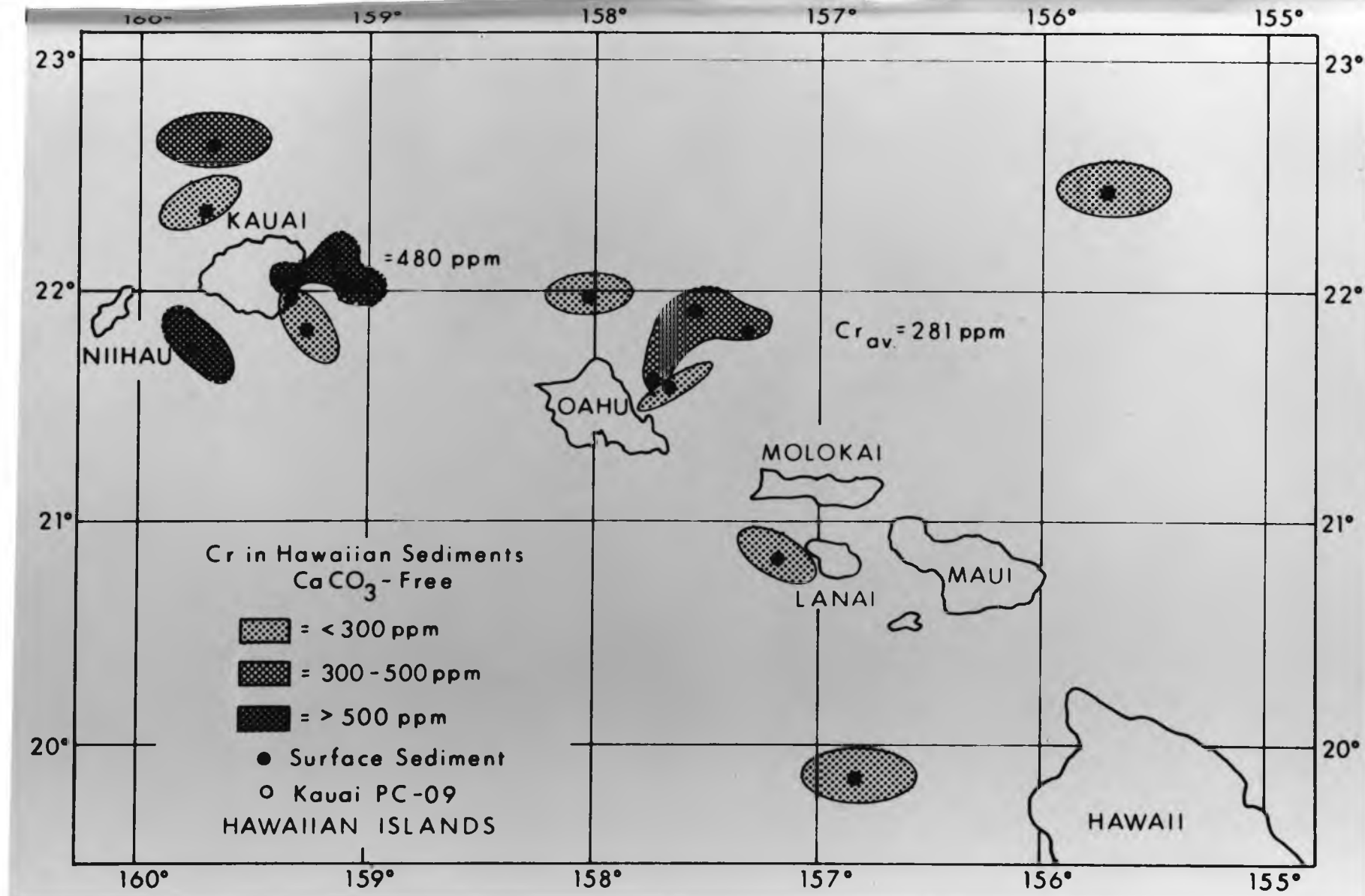


Figure 27. Variation of chromium in Hawaiian sediments.

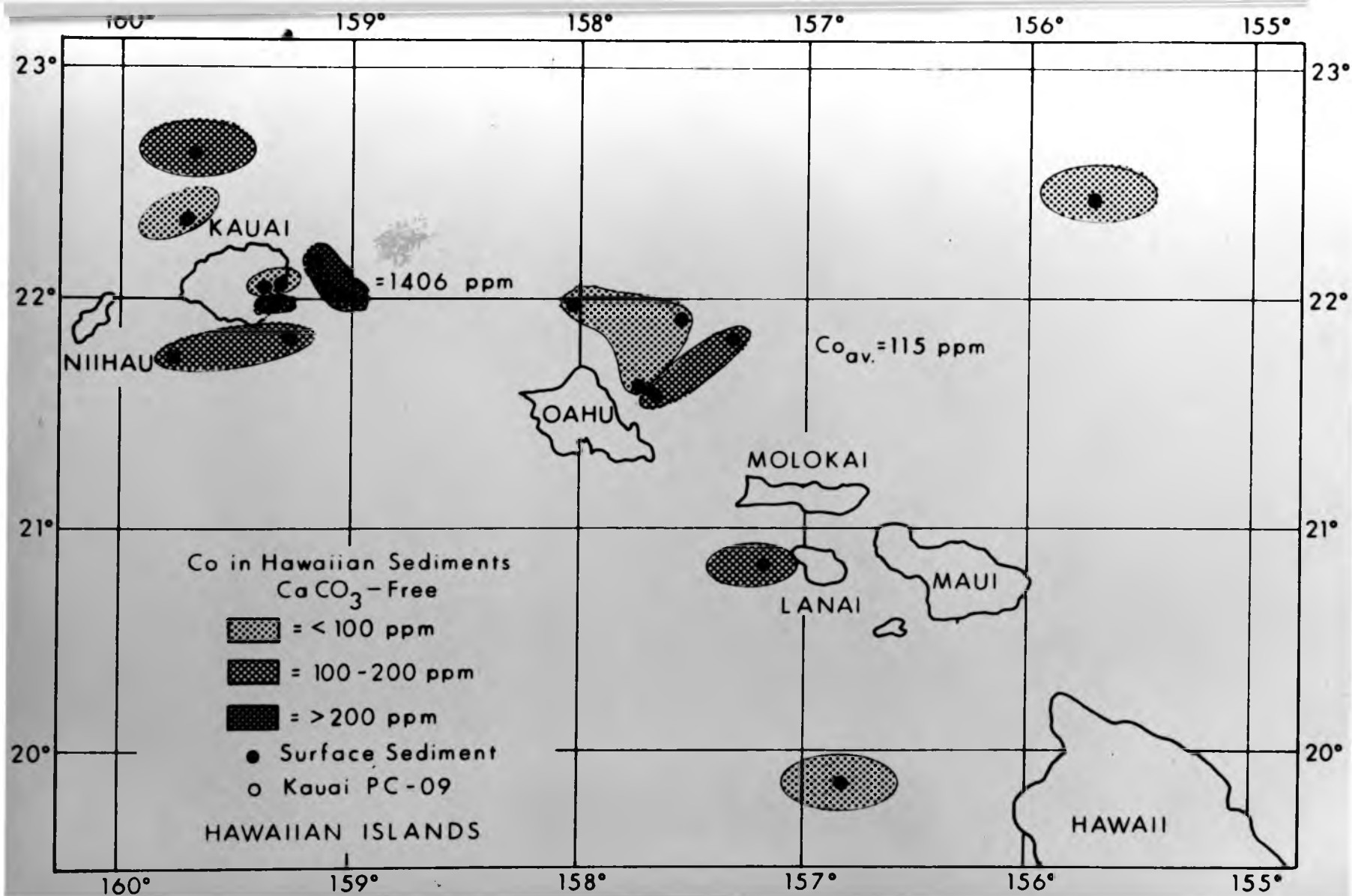


Figure 28. Variation of cobalt in Hawaiian sediments.

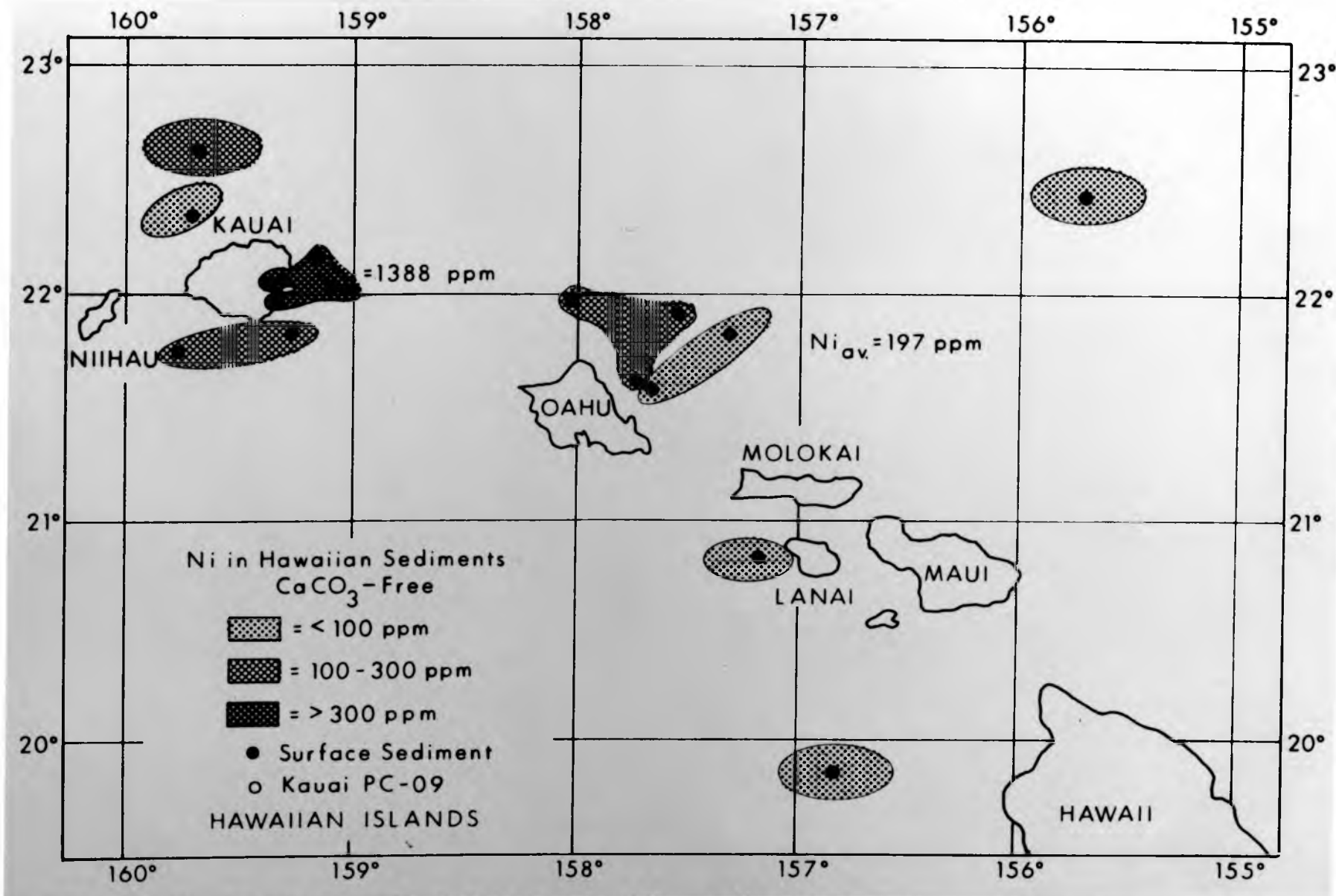


Figure 29. Variation of nickel in Hawaiian sediments.

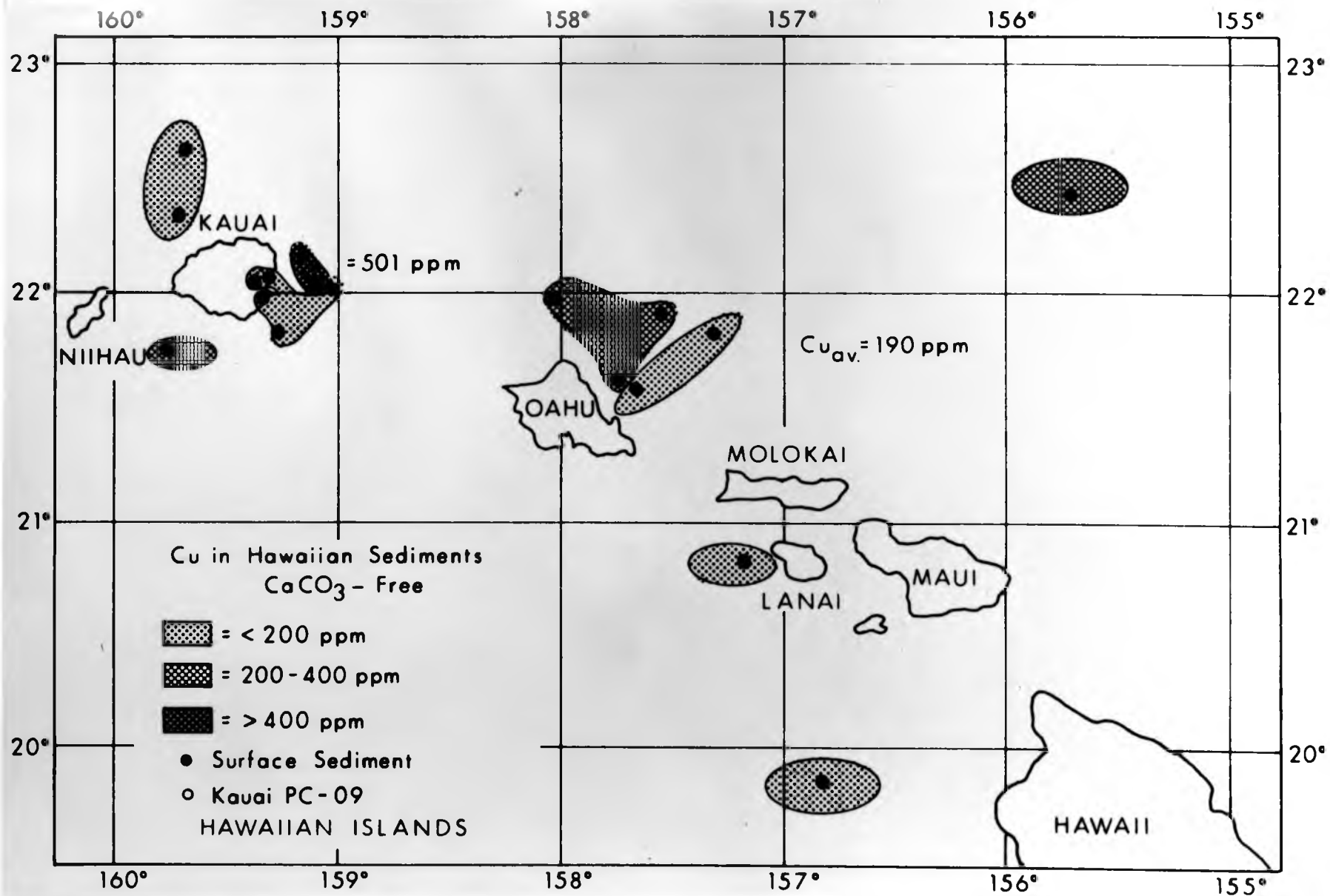


Figure 30. Variation of copper in Hawaiian sediments.

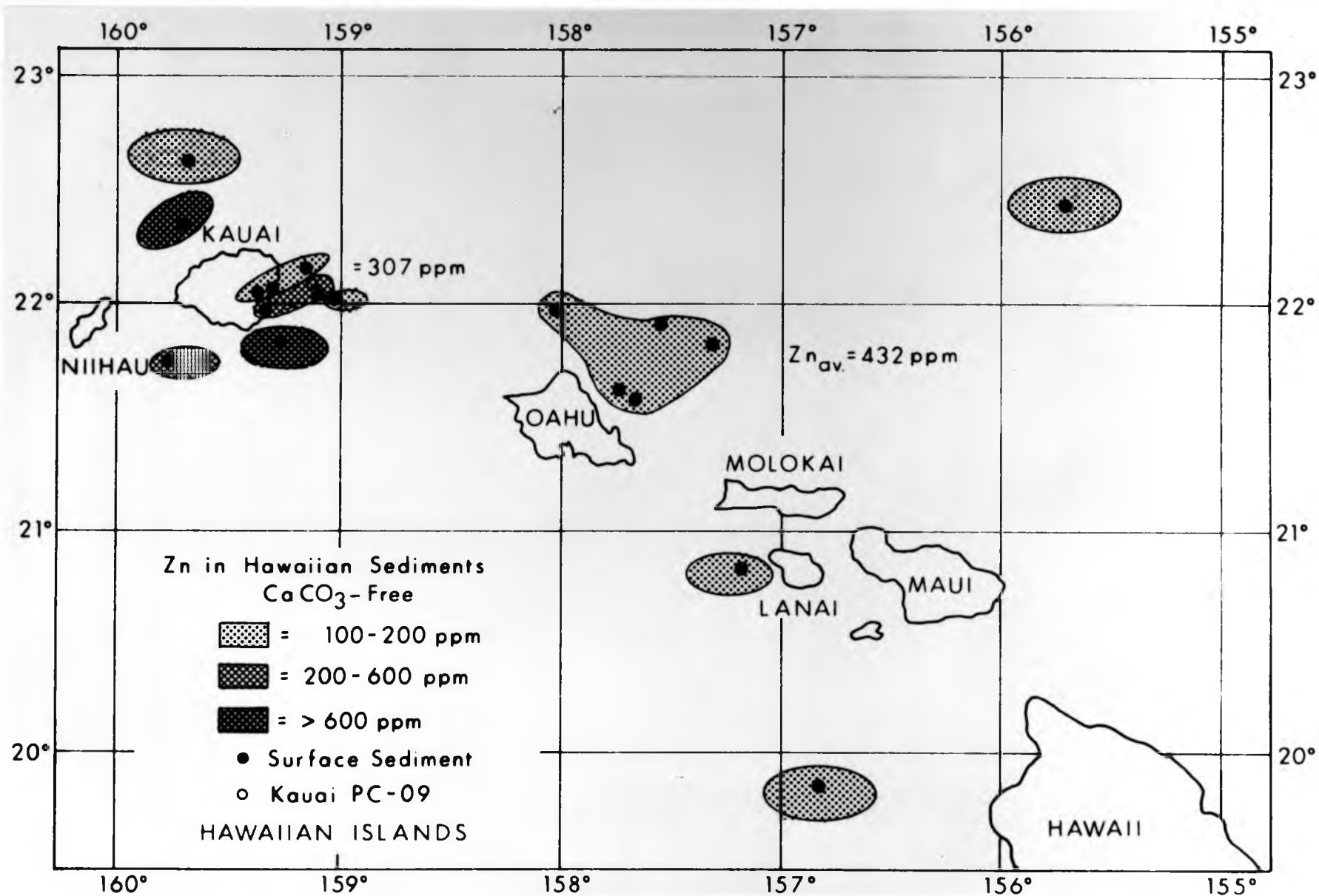


Figure 31. Variation of zinc in Hawaiian sediments.

element abundance for this region is indicated on each variation map. The average elemental abundances for all the other "normal" Hawaiian sediments are also shown for comparison. All the elements reported here except Zn are enriched in this area relative to other Hawaiian sediments. The greatest enrichment appears to be for Co which is concentrated by about a factor of 10.

The purpose of analyzing the stream sediments and beach sand from Kauai was to determine the importance of detrital contributors to this system. All elements except Cr have significantly higher concentrations in the zone of ferride enrichment relative to either the stream sediments or the beach sand. Arrhenius and Bonatti (1965) have reported that Cr remains in solution while Mn and Fe hydrolyze upon oxidation. This is probably due to the extreme mobility of Cr when oxidized to the hexavalent state. Sample number 53, which was a fragment of Mn crust recovered from this area, contained no detectable Cr (detection limit for Cr < 5 ppm). It appears that the trace element content of this Mn crust is in accord with that expected for a normal hydrogenic manganese deposit.

The trace element distribution has also been investigated in a short sediment core (KAUAI PC-09) located in the area of ferride enrichment. The distribution of CaCO_3 , Fe, Mg and some rare metals down the length of the core is shown in Figure 32. All metals are shown on a

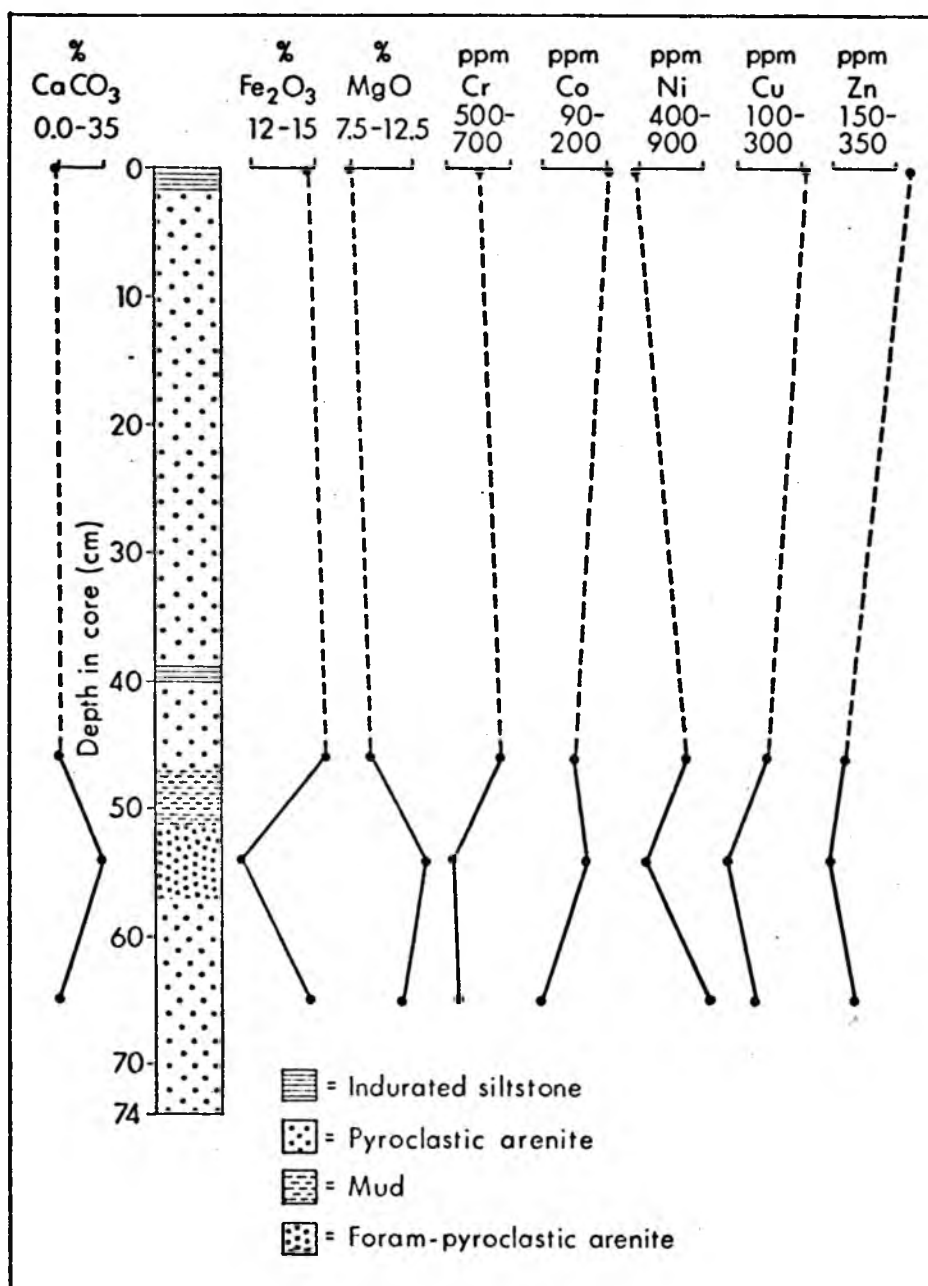


Figure 32. Elemental variations in Kauai PC-09.

carbonate-free basis. Notice that the indurated siltstone (surface) contains extreme values for all elements shown except for Cr. The Fe, Co, Cu and Zn contents are the highest, or nearly so in the case of Fe, while Mg and Ni values are the lowest in the core. Down the core there appears to be an extreme partition of Co and Ni, perhaps indicating the relative differences in the mobilities of these two elements during the sedimentary and hydrogenic sequences. Cr, Cu and Zn appear to follow Fe in this succession while Co shows a slight tendency to follow Mg.

E. Average trace element abundances in Pacific pelagic clays

The average trace element concentrations in nineteen brown clay samples from this study are presented in Table XI. Averages obtained by several other authors are also shown here along with Taylor's (1964) averages for abundances in the crust as a whole. Little work has been done on the determination of Rb and Zn in pelagic clays. The values reported in this study for these two elements are surprisingly close to Turekian and Wedepohl's (1961) values for the average pelagic clay.

In general, there is good agreement between all authors shown here for the average abundance of Rb, Ba, Cr and Zn. There is a larger spread in the estimates of Sr and Cu but the agreement would be considerably improved by deleting the averages taken from Goldberg and Arrhenius (1958). The results of these authors appear systematically high and may

Table XI: Average trace element abundances in pelagic clays; average crustal abundances also shown for comparison. All concentrations in ppm except Fe which is shown as wt. %.

Element (ppm)	1	2	3	4	5	6	7
Rb	110	-	-	-	-	120	90
Sr	180	710	450	250	-	228	375
Ba	2300	3900	2000	1750	-	1877	425
Cr	90	93	55	110	102	106	100
Co	74	160	100	51	101	55	25
Ni	225	320	300	125	211	134	75
Cu	250	740	400	181	323	239	55
Zn	165	-	-	-	-	154	70
Fe %	6.50	6.50	5.76	5.00	5.06	5.39	5.63

- 1 = Average chemical composition of pelagic clay (Turekian and Wedepohl, 1961).
2 = Average Pacific pelagic clay (Goldberg and Arrhenius, 1958).
3 = Average of 12 samples (El Wakeel and Riley, 1961).
4 = Average of 7 samples (Swanson *et al.*, 1967).
5 = Average Pacific pelagic clay (Cronan, 1969).
6 = Average of 19 brown clays, this study.
7 = Average crustal abundances (Taylor, 1964).

be an effect of the sample locations. Most of the samples were from the eastern Pacific and as Boström and Peterson (1969) have recently shown, trace elements may be greatly enriched along the crest of the East Pacific Rise. The elements which are related to organic productivity, such as Ba and Cu, would also tend to be higher in the eastern areas of the Pacific where the productivity is highest.

Two elements, Co and Ni, appear suspiciously low in the present work when compared to the values reported by other authors. The values of Swanson et al. (1967), however, agree very well with the results reported here for these two elements. The samples reported in that work were taken on a line between southern Alaska and the Hawaiian Islands along the 160°W meridian. The majority of the brown clays reported in the present study were located north of Hawaii, between 130°-160°W; so there is some overlapping of sampling areas. It appears, then, that these values for Co and Ni are real for this area of the Pacific.

In order to illustrate how these elements are distributed in the weathering-sedimentary sequence of the geochemical cycle, the average crustal abundance (Taylor, 1964) of each element has been included in Table XI. Taylor (1964) uses a 1:1 mixture of basalt and granite as a crustal model. Assuming that these values are probably nearly correct, it can be seen that the contents of Ba, Co, Ni, Cu and Zn are significantly enriched in Pacific brown clays relative to

average crustal values. Rb appears to be only slightly enriched and Cr does not appear to be fractionated at all. Sr is the only element studied here which exhibits a depletion in pelagic clays relative to an average crustal rock. Sr, however, does occur in high concentrations in calcareous sediments, as was discussed earlier. The fact that Sr is a major constituent in sea water (Culkin, 1965) may be a result of the inability of pelagic silicates to absorb this element in significant amounts.

TRACE ELEMENT ASSOCIATIONS AND CONCLUSIONS

A. Inter-element associations

In the discussion of trace element variations in natural materials it is often constructive to investigate how they are related to other elements or components in the same geochemical system. A recent treatment of elemental associations in pelagic deposits has been presented by Cronan (1970). For reasons mentioned earlier, many elements have been calculated on a carbonate-free basis on the assumption that these elements are associated with the "clay" fraction of the sediments. Figures 33 and 34 show the relationship of Co and Ni to the portion of the sediments insoluble in acid. The correlation for Co is quite good but the concentration of Ni, under about 50 ppm, appears to be independent of the insoluble fraction. This suggests that some mechanism apart from simple dilution of the sediments by a carbonate influx is responsible for the content of these elements (especially Ni) in pelagic sediments.

The relation between CaCO_3 and Sr in the sediments from this study is presented in Figure 35. In general, a strong positive correlation exists between these two parameters. However, several samples appear to be greatly enriched in Sr relative to the carbonate content. Two of these samples (numbers 32 and 36) are shown on this plot; other samples are so high in Sr that they fall outside the region of this

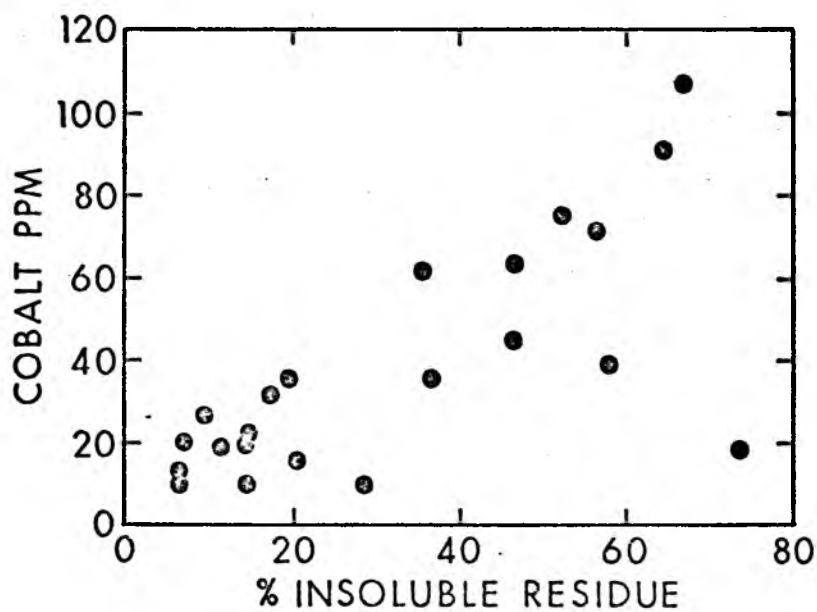


Figure 33. Scatter diagram for Co concentration vs percent acid-insoluble residue.

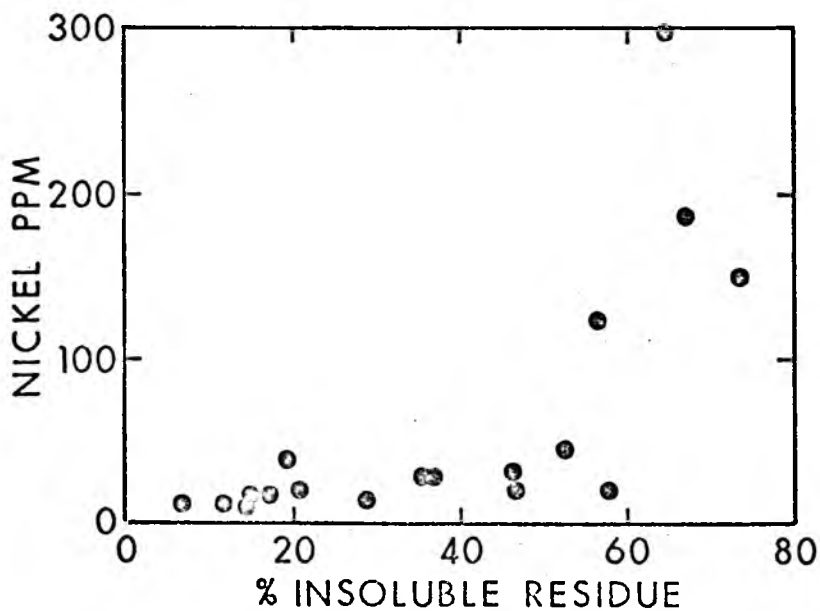


Figure 34. Scatter diagram for Ni concentration vs percent acid-insoluble residue.

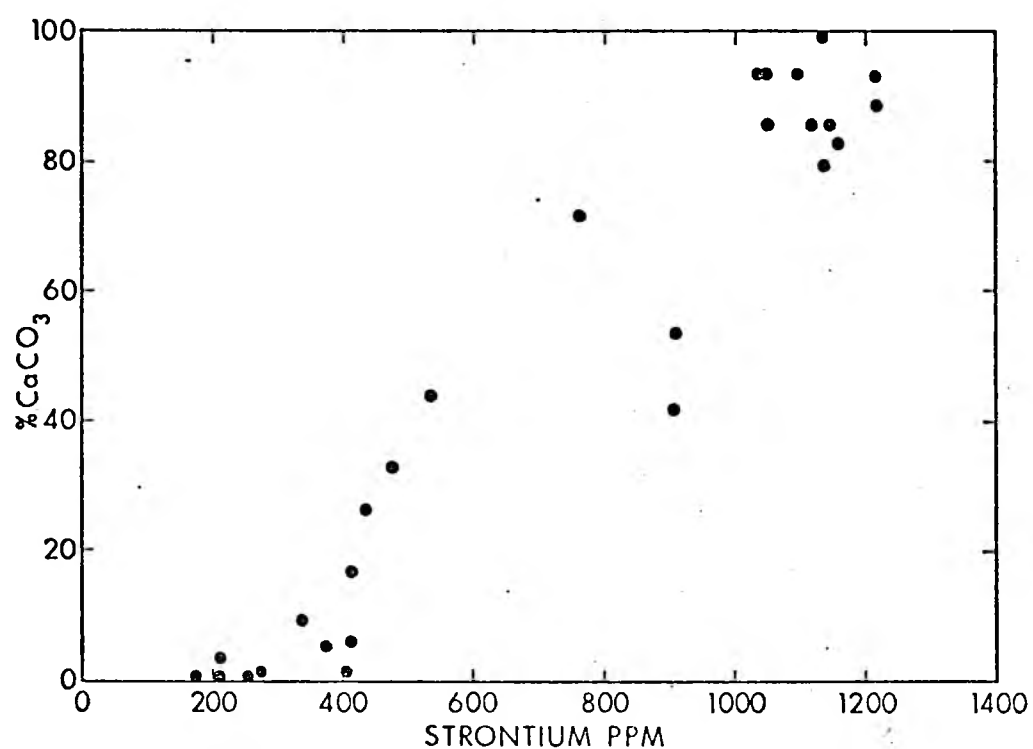


Figure 35. Scatter diagram showing relationship between Sr concentration and percent calcium carbonate in marine sediments from this study.

graph. All of the Sr-enriched samples are from near-shore localities and it may be presumed that their high Sr values are related to an increase of aragonite in these particular samples (see discussion on p. 58).

Turekian and Kulp (1956) have shown that while some differentiated basaltic bodies show a covariance between Sr and Ca (usually a negative correlation) there is no universal correlation of these two elements in basaltic rocks. They attribute this to regional variations in the concentrations of these two elements. This author suspects that there is a fairly good positive correlation between Sr and Ca in the calcitic remains of marine organisms found in pelagic sediments. This is probably a consequence of the extreme constancy of the initial abundance of Sr in the marine system. Since marine organisms derive their Sr directly from sea water, regional variations should be unimportant, as the Sr content of sea water is remarkably uniform at approximately 8 mg/l (Culkin, 1965). It has also been shown (Turekian, 1964) that the Sr/Ca ratio in sea water has probably remained constant during Phanerozoic time. So it can be expected that the Sr/Ca relationship, apart from the effects of recrystallization, should be quite constant within any one biogenic group both in recent and fossil forms.

A very interesting interelement association exists between Cu and Ba in the carbonate sediments studied. These two elements are not associated either chemically or

geochemically in crystalline rocks. Ba has a much larger ionic radius than Cu and is considered lithophile. It has been shown in the previous section, however, that both these elements are associated with the biologically derived fraction of marine sediments. A plot of Cu vs. Ba from the carbonate-free fraction of the biogenic sediments from this study is presented in Figure 36. The pelagic muds have been excluded from this plot because it was felt that much of the Cu there would be associated with the hydrogenous (Mn-micronodule) phase of these sediments. All the points in Figure 36 represent samples which contain at least 25 % calcium carbonate. The relationship shown here leaves little doubt that these two elements are concentrated in marine sediments by a similar process, most likely biological. The incorporation of Cu and perhaps Ba into some type or types of organic complexes that are not completely disassociated on their descent to the ocean floor is possibly a reasonable, although very incomplete, explanation of this mechanism. It is also possible that some type of diagenetic redistribution of these elements occurs after deposition. Baturin and Kochenov (1967) have suggested that organic molecules play a major role in the concentration of some rare metals during diagenesis. It is this author's opinion, however, that the concentration of these two elements is a primary feature, i.e., occurring before or during deposition. The concentration of Ba is probably related to the formation of

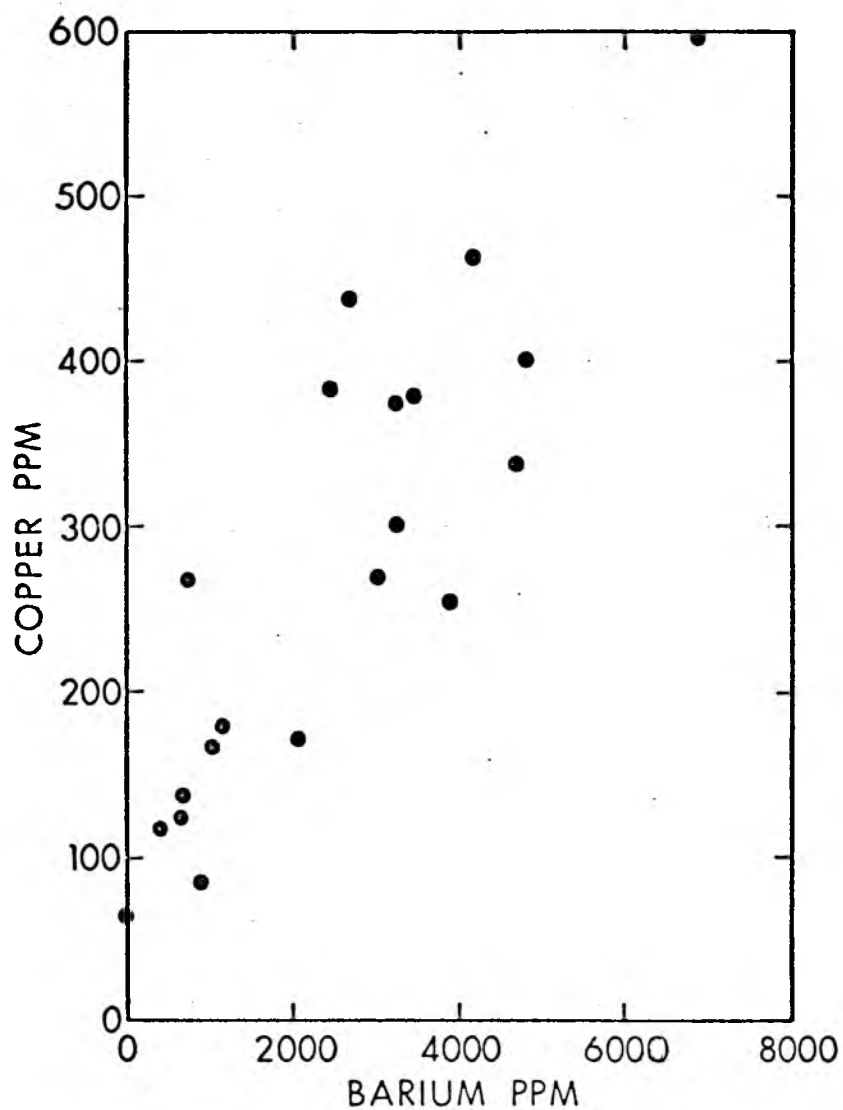


Figure 36. Scatter diagram for concentration of Cu vs concentration of Ba in all samples with greater than 25 % calcium carbonate.

relatively insoluble BaSO_4 crystals during the dissolution of carbonate tests in their descent through the ocean water. Cu, concentrated in the blood of marine invertebrates, may form complexes with some organic molecules after the death of the organism. Chave (1965) and Suess (1968) have shown that carbonate tests often have an organic coating that may inhibit carbonate-sea water interactions.

The relationship between Rb and K in geochemical materials is an extremely coherent one. Ahrens et al. (1952) have reported that the "normal" K/Rb ratios in igneous rocks and meteorites range between 115-460 with an average of 230. The crustal average of Turekian and Wedepohl (1961) is 253; that of Taylor (1964) is 232. Only one sample from this study (number 32; K/Rb = 498) falls outside of the limits set by Ahrens et al. (1952) and the mean for all sediments here is 255. Generally, the carbonate oozes have the lowest K/Rb ratios (mean of 4 values = 142) while the brown clays show the highest (mean of 18 samples = 265). This relationship between Rb and K is shown graphically in Figure 37; values for average crustal rocks and an average deep-sea clay and carbonate ooze from Turekian and Wedepohl's (1961) compilation are shown for comparison. From the data presented here it is difficult to support the suggestion of Gast (1965) that there is some enrichment of Rb relative to K during sedimentation and diagenesis, i.e., a lower K/Rb ratio in sediments. In contrast, if the average K/Rb ratio

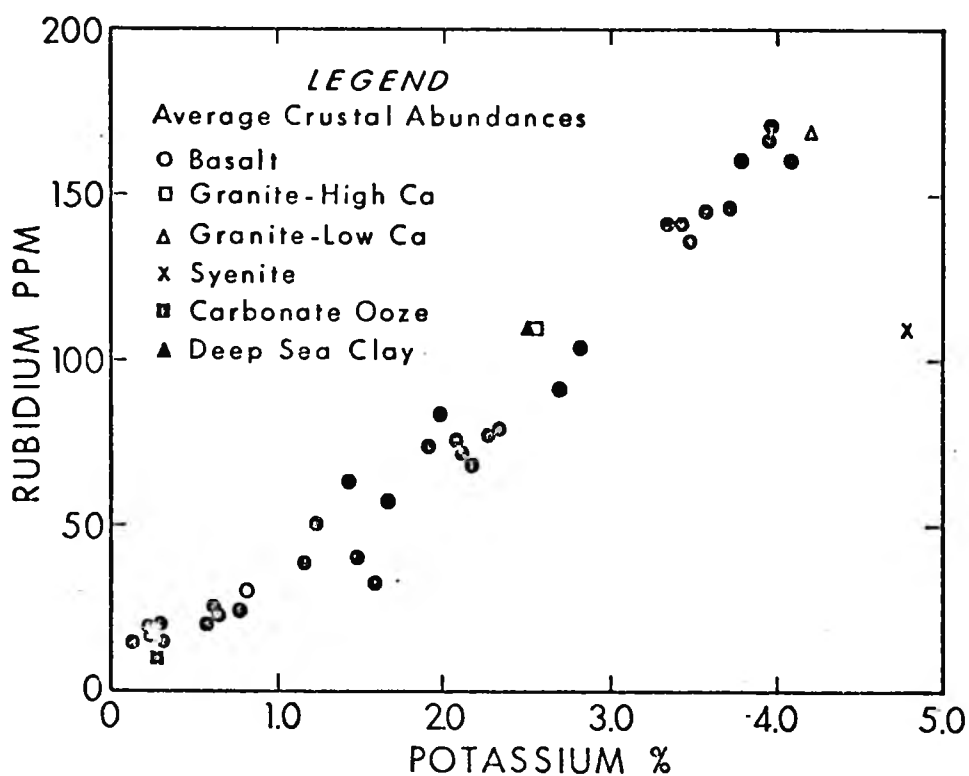


Figure 37. Relation of Rb to K in marine sediments from this study. Average values for crustal rocks shown for comparison. Data for average crustal abundances from Turekian and Wedepohl (1961).

for all sediments here has any significance, a slight enrichment of K relative to Rb has occurred. If Turekian and Wedepohl's (1961) value of 227 for deep-sea clay is a better estimate of the typical K/Rb relationship in marine clays, then a very slight relative increase in Rb content is suggested.

B. Sources and fixation of trace elements in marine sediments

By far the most important sources of material delivered to the ocean are the suspended and dissolved constituents of streams draining the continental areas of the world (Mackenzie and Garrels, 1966). Because the rate of supply per unit area is smaller in the Pacific than the Atlantic Ocean, sedimentation rates are slower in the Pacific and other more minor sources become important. Wind-derived continental material certainly accounts for a substantial portion of some pelagic deposits of the Pacific (Rex and Goldberg, 1958). Eolian material is most significant in the South Pacific where sedimentation rates are generally lowest. Another source of questionable importance (at least volumetrically) is submarine vulcanism and the associated emanations. Boström and Peterson (1969) have shown very good evidence for the addition of rare metals over an area of high heat flow on the East Pacific Rise by emanations from the mantle. Hubred (1970) investigated the transition metal content of manganese nodules associated with an abyssal hill of probable volcanic origin in the North Pacific. He concluded

that volcanism has contributed to the formation of these nodules by supplying nuclei and transition elements. The effect these sources have on the total material balance of the oceans is probably limited but may be very significant in volcanic areas where there is little supply from other sources. The addition of trace elements by meteoritic sources, as suggested by Pettersson (1959) as an explanation for the apparent overabundance of Ni in pelagic clays, is probably very minor (Chester and Hughes, 1966). Glacially transported sediments are probably only significant today in latitudes above 50° (Griffin, et al., 1968) and so are of little consequence to the overall system.

Perhaps a more important problem than defining the sources for trace elements in the ocean is defining the manner in which these elements are concentrated in marine sediments. Table XI shows that the average trace element content of a typical brown clay greatly exceeds that of average crustal rock. Many mechanisms have been proposed for trace element enrichment in marine sediments. Turekian (1968) has suggested that very fine-grained pelagic material has the ability to adsorb a large number of metallic cations due to its large surface area. Nicholls (1967) has considered the influence of pressure in controlling trace element concentrations and concluded that it is small and inadequate to explain the observed trace element content in pelagic clays. It is the present author's opinion that there are

several mechanisms for the fixation of trace elements in marine sediments. A list of six mechanisms for this process with examples from this study follows:

- 1) Trace element occurring as a major element of a mineral, e.g., Ba, Sr (?)
- 2) Trace element incorporated into the lattice structure of a clay mineral, e.g., Cr, Ni
- 3) Trace element adsorbed or exchanged on the surface of a clay mineral, e.g., Rb, Co, Zn
- 4) Occlusion of trace elements with precipitated iron or manganese oxides, e.g., Ni, Co, Cu, Zn
- 5) Formation of immobile metallo-organic complexes, e.g., Cu
- 6) Concentration of trace elements during diagenesis, e.g., Ni (?), Co (?)

These suggested mechanisms are fairly independent of each other and probably occur in various combinations, depending on the situation. While some elements are probably only affected by one or a few of these mechanisms, other elements may be controlled by several, if not all, of them. The deciding factors appear to be the regional and environmental situations in which they occur. More specifically, such factors as depth, rate of supply, productivity, and proximity to volcanism are responsible for the dominant mode of fixation of trace elements in marine sediments.

C. Conclusions

- 1) Rb follows its geochemically related element, K, in marine sediments. The mean K/Rb ratio of 37 samples is 255, possibly indicating a slight enrichment of K relative to Rb in marine sediments.
- 2) Sr is concentrated in the calcareous oozes found in the shallower regions of the equatorial Pacific. There appears to be a fairly good positive correlation between Sr and Ca in the calcitic marine deposits.
- 3) Ba is concentrated in zones of high organic productivity in the equatorial Pacific. The siliceous oozes of the same area show the highest concentrations of Ba, possibly indicating the formation of barite crystals during the dissolution of calcium carbonate tests at great depths.
- 4) Cr is concentrated in the volcanic sediments south of the Hawaiian Islands. A concentration in excess of 180 ppm may indicate the presence of basaltic volcanic debris in the sediments.
- 5) There is an extreme partition in the distributions of Co and Ni in the sediments studied here. This

may be a reflection of the different modes of fixation that these two elements follow in marine sediments.

- 6) Besides being associated with clay minerals and manganese deposits, Cu is also concentrated by marine organisms. There is a good positive correlation between Cu and Ba in the biogenic sediments studied here.
- 7) Zn is homogeneously distributed throughout much of the study area, possibly an expression of the extreme mobility of the Zn^{2+} ion. All the highest Zn values occurred near known phosphorite deposits on oceanic islands and atolls.
- 8) The contents of Ba, Co, Ni, Cu and Zn are significantly enriched in Pacific brown clays relative to average crustal values. Rb appears to be only slightly enriched and there is no apparent fractionation of Cr. Sr is depleted in marine clays relative to igneous rocks, but is greatly enriched in carbonate oozes.

REFERENCES

- Ahrens, L.H., Pinson, W.H. and Kearns, M.M., 1952. Association of rubidium and potassium and their abundance in common igneous rocks and meteorites. *Geochim. et Cosmochim. Acta*, v. 2, pp. 229-242.
- Andermann, G. and Kemp, J.W., 1958. Scattered X-rays as internal standards in X-ray emission spectroscopy. *Anal. Chem.*, v. 30, pp. 1306-1309.
- (Andrews, J.E.), 1970. Sediment core descriptions: Solomon Islands 1968-1969 and Murray Fracture Zone 1967. Hawaii Institute of Geophysics Report No. 70-25.
- Angino, E.E., 1966. Geochemistry of antarctic pelagic sediments. *Geochim. et Cosmochim. Acta*, v. 30, pp. 939-961.
- Angino, E.E. and Billings, G.K., 1967. Atomic Absorption Spectrometry in Geology. Elsevier Publ. Co., Amsterdam; 144 p.
- Arrhenius, G. and Bonatti, E., 1965. Neptunism and vulcanism in the ocean. In Progress in Oceanography, M. Sears, editor, Pergamon Press, New York.
- Ball, D.F., 1965. Rapid analysis for some major elements in powdered rock by X-ray fluorescence spectrography. *Analyst*, v. 90, pp. 258-265.
- Bateman, A.M., 1950. Economic Mineral Deposits. John Wiley & Sons, Inc., New York: 916 p.
- Baturin, G.N. and Kochenov, A.V., 1967. Relation between some rare metals and organic matter in marine sediments. *Oceanology*, v. 7, pp. 797-802.
- Belshe, J.C., 1968. Ocean sediments sampled during 1964-1967 in the Hawaiian Archipelago. *Applied Oceanography Series No. 6*, Hawaiian Institute of Geophysics Report No. 68-7, 52 p.
- Belt, C.B., 1964. Atomic absorption spectrophotometry and the analysis of silicate rocks for copper and zinc. *Econ. Geol.*, v. 59, pp. 240-258.
- _____, 1967. Partial analysis of silicate rocks by atomic absorption. *Anal. Chem.*, v. 39, pp. 676-678.

- Bender, M.L. and Shultz, C., 1969. The distribution of trace metals in cores from a traverse across the Indian Ocean. *Geochim. et Cosmochim. Acta*, v. 33, pp. 292-297.
- Bernas, B., 1968. A new method for decomposition and comprehensive analysis of silicates by atomic absorption spectrometry. *Anal. Chem.*, v. 40, pp. 1682-1686.
- Biscaye, P.E., 1965. Mineralogy and sedimentation of Recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans. *Geol. Soc. Amer. Bull.*, v. 76, pp. 803-832.
- Boström, K. and Peterson, M.N.A., 1966. Precipitates from hydrothermal exhalations on the East Pacific Rise. *Econ. Geol.*, v. 61, pp. 1258-1265.
- _____, 1969. The origin of aluminum poor sediments in areas of high heat flow on the East Pacific Rise. *Marine Geology*, v. 7, pp. 427-447.
- Champion, K.P., Taylor, J.C. and Whitten, R.N., 1966. Rapid X-ray fluorescence determination of strontium in samples of biological and geological origin. *Anal. Chem.*, v. 38, pp. 109-112.
- Chappell, B.W., Compston, W., Arriens, P.A., and Vernon, M.J., 1969. Rubidium and strontium determinations by X-ray fluorescence spectrometry and isotope dilution below the part per million level. *Geochim. et Cosmochim. Acta*, v. 33, pp. 1002-1006.
- Chave, K.E., 1965. Calcium carbonate: association with organic matter in surface seawater. *Science*, v. 148, pp. 1723-1724.
- Chester, R. and Hughes, M.J., 1966. The distribution of manganese, iron and nickel in a North Pacific deep-sea clay core. *Deep-Sea Research*, v. 13, pp. 627-634.
- Cronan, D.S., 1969. Average abundances of Mn, Fe, Ni, Co, Cu, Pb, Mo, V, Cr, Ti and P in Pacific pelagic clays. *Geochim. et Cosmochim. Acta*, v. 33, pp. 1562-1565.
- _____, 1970. Inter-element associations in some pelagic deposits. *Chemical Geology*, v. 5, pp. 99-106.

- Culkin, F., 1965. The major constituents of sea water. Chapter 4 in Chemical Oceanography, v. 1, J.P. Riley and G. Skirrow, editors, Academic Press, London and New York.
- El Wakeel, S.K. and Riley, J.P., 1961. Chemical and mineralogical studies of deep-sea sediments. *Geochim. et Cosmochim. Acta*, v. 25, pp. 110-146.
- Fairbairn, H.W., 1966. Progress report on determination of Rb/Sr ratios by X-ray fluorescence. Mass. Inst. of Technology Fourteen Ann. Report, pp. 187-191.
- Fan, P.F. and Grunwald, R.R., in preparation. Sediment distribution pattern near the Hawaiian Islands.
- Flanagan, F.J., 1969. U.S. Geological Survey standards - II. First compilation of data for the new U.S.G.S. rocks. *Geochim. et Cosmochim. Acta*, v. 33, pp. 81-120.
- Fleischer, M., 1969. U.S. Geological Survey standards - I. Additional data on rocks G-1 and W-1, 1965-1967. *Geochim. et Cosmochim. Acta*, v. 33, pp. 65-81.
- Fletcher, K., 1970. Some applications of background correction to trace element analysis of geochemical samples by atomic absorption spectrometry. *Econ. Geol.*, v. 65, pp. 588-591.
- Gast, P.W., 1965. Terrestrial ratio of potassium to rubidium and the composition of earth's mantle. *Science*, v. 147, pp. 858-860.
- Goldberg, E.D. and Arrhenius, G.O.S., 1958. Chemistry of Pacific pelagic sediments. *Geochim. et Cosmochim. Acta*, v. 13, pp. 153-212.
- Griffin, J.J. and Goldberg, E.D., 1963. Clay mineral distributions in the Pacific Ocean. In M.N. Hill, editor, The Sea, v. III, Interscience Publ., New York: 963 p.
- Griffin, J.J., Windom, H. and Goldberg, E.D., 1968. The distribution of clay minerals in the world ocean. *Deep-sea Research*, v. 15, pp. 433-459.
- Hamilton, E.L., 1956. Sunken islands of the Mid-Pacific Mountains. *Geol. Soc. Amer. Mem.* 64, 97 p.
- _____, 1957. Marine geology of the southern Hawaiian Ridge. *Bull. Geol. Soc. Amer.*, v. 68, pp. 1011-1026.

- Heath, G.R., 1969. Mineralogy of Cenozoic deep-sea sediments from the equatorial Pacific Ocean. *Geol. Soc. Amer. Bull.*, v. 80, pp. 1997-2018.
- Heezen, B.C., Glass, B. and Menard, H.W., 1966. The Manihiki Plateau. *Deep-sea Research*, v. 13, pp. 445-458.
- Heier, K.S. and Adams, A.S., 1963. Geochemistry of the alkali metals. In Physics and Chemistry of the Earth, v. 5, L.H. Ahrens, editor, Pergamon Press: New York.
- Hirst, D.M., 1962. The geochemistry of modern sediments from the Gulf of Paria II. The location and distribution of trace elements. *Geochim. et Cosmochim. Acta*, v. 26, pp. 1147-1187.
- Hubbard, N.J., 1967. Some trace elements in Hawaiian lavas. Unpublished PhD dissertation, University of Hawaii, 123 p.
- Hubred, G.L., 1970. Relationship of morphology and transition metal content of manganese nodules to an abyssal hill. *Seagrant Report 70-5*, University of Hawaii, 38 p.
- Hülsemann, J., 1966. On the routine analysis of carbonates in unconsolidated sediments. *Jour. Sed. Petrology*, v. 36, pp. 622-625.
- Jenkins, R. and De Vries, J.L., 1967. Practical X-ray Spectrometry, Philips Technical Library, The Netherlands: 182 p.
- Leake, B.L., Hendry, G.L., Kemp, A., Plant, A.G., Harvey, P.K., Wilson, J.R., Coats, J.S., Aucott, J.W., Lunel, T., and Howarth, R.J., 1970. The chemical analysis of rock powders by automatic X-ray fluorescence. *Chemical Geology*, v. 5, pp. 7-86.
- Macdonald, G.A., 1968. Composition and origin of Hawaiian lavas. *Geol. Soc. Amer., Mem.* 116, pp. 477-522.
- Mackenzie, F.T. and Garrels, R.M., 1966. Chemical mass balance between rivers and oceans. *Amer. Jour. Sci.*, v. 264, pp. 507-525.
- Menard, H.W., 1964. Marine Geology of the Pacific. McGraw-Hill Book Co., New York: 271 p.
- Moberly, R., 1963. Amorphous marine muds from tropically weathered basalts. *Amer. Jour. Sci.*, v. 261, pp. 767-772.

- Moberly, R. and McCoy, F.W., 1966. The sea floor north of the eastern Hawaiian Islands. *Marine Geology*, v. 4, pp. 21-48.
- Moberly, R., Kimura, H.S. and McCoy, F.W., 1968. Authigenic marine phyllosilicates near Hawaii. *Geol. Soc. Amer. Bull.*, v. 79, pp. 1449-1460.
- Nicholls, G.D., 1967. Trace elements in sediments: an assessment of their possible utility as depth indicators. *Marine Geology*, v. 5, pp. 539-555.
- Pettersson, H., 1959. Manganese and nickel on the ocean floor. *Geochim. et Cosmochim. Acta*, v. 17, pp. 209-313.
- Rankama, K. and Sahama, Th.G., 1950. Geochemistry. University of Chicago Press, Chicago: 912 p.
- Revelle, R., Bramlette, M., Arrhenius, G. and Goldberg, E.D., 1955. Pelagic sediments of the Pacific. In *Geol. Soc. Amer. Spec. Paper* 62, pp. 221-236.
- Rex, R.W. and Goldberg, E.D., 1958. Quartz contents of pelagic sediments of the Pacific Ocean. *Tellus*, v. 10, pp. 153-159.
- Swanson, V.E., Palacas, J.G. and Love, A.H., 1967. Geochemistry of deep-sea sediment along the 160°W meridian in the North Pacific Ocean. *U.S. Geol. Surv. Prof. Paper* 575-B.
- Shaw, D.M., 1969. Evaluation of data. In Handbook of Geochemistry, v. 1, K.H. Wedepohl, editor; Springer-Verlag, Berlin: pp. 324-374.
- Suess, E., 1968. Calcium carbonate interaction with organic compounds. PhD dissertation, Lehigh University, 153 p.
- Taylor, S.R., 1964. Abundance of chemical elements in the continental crust: a new table. *Geochim. et Cosmochim. Acta*, v. 28, pp. 1273-1285.
- Turekian, K.K., 1956. Rapid technique for determination of carbonate content of deep-sea cores. *Am. Assoc. Petroleum Geologists Bull.*, v. 40, pp. 2507-2509.
- _____, 1964. The marine geochemistry of strontium. *Geochim. et Cosmochim. Acta*, v. 28, pp. 1479-1496.
- _____, 1968. Deep-sea deposition of barium, cobalt and silver. *Geochim. et Cosmochim. Acta*, v. 32, pp. 603-612.

- Turekian, K.K. and Armstrong, R.L., 1960. Magnesium, strontium and barium concentrations and calcite-aragonite ratios of some recent molluscan shells. *Jour. Mar. Research*, v. 18, pp. 133-151.
- Turekian, K.K. and Imbrie, J., 1966. The distribution of trace elements in deep-sea sediments of the Atlantic Ocean. *Earth Planet. Sci. Letters*, v. 1, pp. 161-168.
- Turekian, K.K. and Kulp, J.L., 1956. The geochemistry of strontium. *Geochim. et Cosmochim. Acta*, v. 10, pp. 245-296.
- Turekian, K.K. and Tausch, E.H., 1964. Barium in deep-sea sediments of the Atlantic Ocean. *Nature*, v. 201, pp. 696-697.
- Turekian, K.K. and Wedepohl, K.H., 1961. Distribution of the elements in some major units of the earth's crust. *Bull. Geol. Soc. America*, v. 72, pp. 175-192.
- Van der Weijden, C.H., Schuiling, R.D. and Das, H.A., 1970. Some geochemical characteristics of sediments from the North Atlantic Ocean. *Marine Geology*, v. 9, pp. 81-99.
- Vlasov, K.A., 1966. Geochemistry of Rare Elements. Trans. from Russian by Z. Lerman; Israel Program for Scientific Translations, 688 p.
- Wedepohl, K.H., 1960. Trace element analyses in Atlantic deep-sea clays. *Geochim. et Cosmochim. Acta*, v. 18, pp. 200-231.
- Willard, H.H., Merritt, L.L. and Dean, J.A., 1965. Instrumental Methods of Analysis. D. Van Nostrand Co., Inc., Princeton: 784 p.
- Wolfe, L.A., 1969. X-ray spectroscopic method for the analysis of manganese in marine sediments. M.S. Thesis, University of Hawaii, 70 p.
- Woollard, G.P. and Sutton, G.H., 1969. A geophysical and geological study of the Darwin Rise. Research proposal, N.S.F., 19 p.
- Young, E.J., 1968. Spectrographic data on cores from the Pacific Ocean and the Gulf of Mexico. *Geochim. et Cosmochim. Acta*, v. 32, pp. 466-472.