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ABSOLUTE DATING OF OCEAN SEDIMENTS BY USE OF Th-230/Pa-231 RATIO AND GEOCHEMICAL STUDIES OF LIMITING BOUNDARY CONDITIONS WITH SPECIAL ATTENTION TO EXOTIC ENVIRONMENTS

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Abstract

This report is a resumé of research carried out in 1966-1971 under the sponsorship of the U.S. Atomic Energy Commission, Grant AT-(40-1)-2411.

The project was Absolute Dating of Ocean Sediments by the use of Th-230/Pa-231 ratio--and Geochemical Studies of Limiting Boundary Conditions, with Special Attention of Exotic Environments.

One of the foremost interests of the principal investigator was the dating of the Pleistocene epoch.

The chronology and trend of climatic changes are best known for the recent past, up to 40,000 years by the method of C-14 dating. The climatic changes during the [illegible] Pleistocene is documented by the O-18/O-16 method (Emiliani, 1955, 1966). The time scale for three Caribbean cores were provided by the Th-230/Pa-231 method. This method was first proposed by Scakett (1960) and independently developed by Rosholt (1961). Briefly, Th-230, daughter of U-234, and Pa-231, daughter of U-235, both produced in sea water, are almost immediatedly precipitated to the ocean floor by adsorption on mineral particles. The decay of the unsupported Th-230 and Pa-231 leads to a change of their ratio, which is a function of time alone. The ages are calculated by the equation:

$$t = 8.26 \ln \left(0.106 \frac{\text{Th-230}}{\text{Pa-231}}\right) \times 10^4 \text{ years}$$

Despite quite extensive previous research, the assignment of age values on the basis of activity measurements is hampered by lack of knowledge of the geochemistry of the uranium and thorium isotopes, and of protactinium, and of their chemical distribution at zero time and possible chemical and physical processes that could affect their distribution at later time. We, therefore, tried a different approach by

investigating the geochemistry of these elements under conditions which differ, in some cases extremely, from those in the open sea. Such conditions can be found in basins with stagnant sea water, in which oxygen is depleted and pH and Eh are lower than in the open sea.

Landlocked sea water of Norwegian fjords, the Cariaco Trench off the continental shelf of Venezuela, and the Black Sea, the largest body of stagnant sea water, have been chosen for such investigation.

Introduction

Undisturbed sections of oceanic sediments of globigerina ooze contain a unique record of the events which occurred during the time of sediment deposition. Among the parameters which are recorded and which can be analysed are the surface and bottom temperature (by O-18/O-16 analysis), the direction of the earth's magnetic field, the influx of wind-borne particles from the continent and of cosmic materials from outer space (mainly spherules), the variation of geochemical components, the rates of evolution of represented fossils, etc. In order to evaluate the time derivative of these various parameters, a time as accurate as possible is necessary.

Among the methods available to date the Pleistocene deep sea cores, the C-14 method has a severe time limitation of about 40,000 years. Using the method based on the ratio of Th-230/Pa-231 the time scale can be extended to 200,000 years. By using these methods the most consistent results obtained are from deep sea cores, from the Caribbean Sea.

Three cores have been dated: P6304-8, P6304-9 (Rona and Emiliani, 1969) appended to the Progress Report 1969, and P6304-1 appended to this report, see Table 2b. The analytical and counting techniques are presented in: The Technical Report, Quantitative Radiochemical Methods for the Determination of Uranium, Thorium isotopes, and Protactinium; appended to the Annual Progress Report, 1969. All three cores have been analysed in considerable detail both isotopically (O-18/O-16) and micropaleontologically (by Emiliani and Rona, 1969). Th-230/Pa-231 analysis has been performed on the three cores mentioned and on three Caribbean cores analyzed by Rosholt *et al*. (1961, 1962).

All cores agree well in Th-230/Pa-231 chronology and in C-14 ages on the common range of the two methods. However, cores taken from nearby locations are found to be undatable.

A long piston core, P6304-14 (14°30'N, 67°20'W, 5056 m. deep) taken from the deepest part of the Venezuelan Basin was analyzed. The depth is sufficiently great to result in appreciable dissolution of some of the carbonate components. Wide semicyclic variations of the carbonate from 0 to 40% are shown in Fig. 1. Si (45-55%) and Al(15-20%) were found to vary opposite to carbonate (Fig. 1). The variations probably resulted from climatic effects during the portion of the Pleistocene time, represented by this core. By analogy with other Atlantic and Caribbean cores, the high $CaCO_3$ intervals are attributed to Pleistocene interglacials. The concentrations of various elements, on a carbonate free basis, are higher during glacial periods. About twenty elements were analyzed by Bonatti (unpublished). The higher concentration can be explained, assuming that during glacial periods rainfall is highest in tropical or semi-tropical areas, such as the Caribbean; as a consequence weathering is highest in adjacent lands. Mn-$CaCO_3$ correlation may be caused by the same controlling climatic factor. The concentrations of terrigenous minerals, such as quartz and muscovite is highest during interglacials, suggesting that conditions were drier, favoring transports of detritals. Much of the foraminifera component in this core has been dissolved because of the great depths of the core. Therefore, it is not possible to establish a correlation with other cores based on O-18/O-16 ratio or C-14 methods. The only method feasible is that based on the Th-230/Pa-231. Dating was tried on this sediment, and the results are presented in Table 1.

This core is greatly disturbed. Dissolution of $CaCO_3$ alone cannot explain why the Th-230 is low; it is more likely that a sudden change was brought about by turbidity currents transporting detrital material to the sites.

Core P6304-7 (16°06'N, 69°38'W, 3929 m. depth) was chosen because it contains a section of Globigerina ooze shown to be undisturbed by O-18/O-16 analysis and because of its location near two cores (P6304-8 and P6304-9) which gave internally consistent results. The results are presented in Table 2. The Th-230 and Pa-231 concentrations are comparable to those obtained for the datable cores; however, the uranium concentrations in the first twenty centimeters are so high that a correlation to obtain unsupported (authigenic) Th-230 and Pa-231 is not feasible. The low U-234/U-238 ratios should also be noted. A ratio of 0.4 is to our knowledge the lowest published in the literature for marine sediments.

A core from the Southwest Pacific, between Antarctica and New Zealand MSN-96 (57°34'S, 172°15'W), was analyzed for uranium and thorium isotopes and protactinium. This core, investigated in our institute (Bonatti, unpublished), shows a sequence of alternating layers of diatomaceous ooze and radiolaria, terrigenous brown inorganic clays, and ice rafted fragments. The sequences are presumably connected with the climatic fluctuation of the Quaternary. The variation of opaline silica in the core is related to the production of radiolaria and diatoms in the overlaying water masses, which varies with the temperature of water, circulation patterns and nutrient supplies that is--indirectly with the climate. Concentrations of quartz, micas and other terrigenous minerals might be related to the variation of transport agents, such as ice, wind, and ocean currents. The foraminifera concentration is too low to assess the climatic conditions either by the 0-18/0-16 or C-14 methods. An attempt was made to assess this condition by the Th-230/Pa-231 method. The results are given in Table 3.

It is not feasible to date this Pacific core using Th-230/Pa-231 method. The ratio of these two radionuclides is less than the calculated ratio of 10.8 for the production rate of Th-230 relative to Pa-231 all along the length of the core sampled by us. The relatively high Pa-231 concentration can be explained by the preferential scavenging of manganese, which was already observed by Sackett (1966). The floor of the Pacific and Indian Oceans are covered with manganese, whereas in the Atlantic Ocean and Caribbean Sea, deep sea ocean floor manganese is found primarily dispersed through the sediment. This may be the reason why the theoretical Th-230/Pa-231 of 10.8 is attained in some cores taken from the Atlantic and Caribbean Seas as Turekian (1971) suggested. The sedimentation rates calculated from unsupported Pa-231 resulted in 5.5 mm/thousand years for the first 40 cm. and to 4.8 mm/1000 y from surface to 80 cm. From a core taken from the same location Lal found 2.3 mm/1000 y calculated from unsupported Th-230 (personal communication).

The method of the Th-230/Pa-231 ratio for dating marine sediments rests on a few assumptions which have to be met. The rate of sedimentation must be undisturbed, continuous, and synchronous with the deposition of Th-230 and Pa-231. The change of concentration of these two radionuclides depends on the rate of radioactive decay only if they are deposited simultaneously. These conditions are not often met and it is not surprising that sediments which can be dated are the exception and not the rule.

The physical disturbances mentioned above can be brought about by burrowing organisms, by advection of reworked, e.g. older, clays in an otherwise undisturbed sediment and thus increase the age. Turbidity currents can transport material (e.g. small particle clays) from long distances to the deep parts of the sea.

The chemistry of Th-230 and Pa-231 is somewhat similar, both easily hydrolize and their residence time in sea water is short (about 50 years). Both have only one valence state, four and five, respectively. Most of the thorium compounds are more soluble than those of protactinium and are probably adsorbed on different mineral particles. The strong scavenging of protactinium by manganese is well known (Sackett, 1966).

Besides Th-230 and Pa-231, their parents U-234 and U-235 have to be considered. These two isotopes do not enter into the calculation of age but to obtain the amount of unsupported (authigenic) Th-230 and Pa-231 a correction must be made for their parent uranium which is allogenic and deposited on the sediments by winds and rivers. Uranium-235 for protactinium correction is calculated from U-238 as their activity ratio is unity (Rosholt, et al., 1961).

If the activity ratio of the uranium isotopes U-238 and U-234 is not unity, the correction for Th-230 and Pa-231 is different, such as is experienced in core P6304-7 (Table 2). The departure from unity of the ratio of the two isotopes is brought about by the nuclear property of U-234. U-238 decays by alpha particle emission to the beta emitters, Th-234 and Pa-234 ($T_{1/2}$ = 24 days and 1.18 min. resp) to U-234. Chemical bonds are broken and U-234 produced in situ is in the sixth valence state. According to Rosholt (1966), only U-234, which is produced in situ, is leachable. Easy removal of U-234 by leaching is also due to the recoil of the relatively high energy (4.7 MeV) alpha particles of U-234. When U-234 is removed under some hydrographic conditions, it leaves the sediment with a U-234/U-238 ratio lower than one (core P6304-7). The leached U-234 might be transported to a new sight, producing a ratio higher than one.

Geochemistry of the Black Sea:

The Black Sea offers a unique opportunity to study a rapidly, but well documented change in marine environment. It is the largest anoxic basin, containing salt water and covering 420,000 km^2 and more than 2000 meter deep. It has both continental shelves and a deep basin. Its single connection with the Mediterranean Sea is long, narrow and shallow through the Bosporus, where a ridge rises within 40 m. of surface, and the width of the Strait is only 3 km. The sea level was about 120 meters lower during the ice ages (the last one about 20,000 years ago). When the sea level was lowered and river discharge remained the same, the water of the Black Sea became less salty, with a salinity of 16 to 18o/oo. Lowered sea levels reduced the mixing of waters across the Bosporus. Winter turbulence of the surface water does not make it dense enough to sink through the underlying Mediterranean water; therefore, the deep water in the basin is not disturbed and only an extremely low overturn takes place. The inflow is so small in proportion to the total volume of the Black Sea that complete renewal of the water below 30 meters would take about 2500 years. This is in good agreement with Östlund's (1965) dating of Black Sea water of 2165 m to 2230 years B.P. by the C-14 method. Waves and surface actions provide a good supply of oxygen to 50 meters, but beyond this depth the oxygen rapidly decreases until it completely disappears at a depth of 150 to 200 meters. Toxic H_2S begins to appear, and as a result, the entire Black Sea basin is stagnant, quiet and uniform. The H_2S is derived principally from organic matter by sulfate reducing bacteria.

So uniform is the Black Sea bottom that distinct sedimentary units can be recognized in all cores taken during the Atlantis II cruise of Woods Hole.

In July-August 1965, during a cruise of the R/V JOHN PILLSBURY, organized by the late Dr. F. F. Koczy of the Institute of Marine Sciences, several cores have been taken. One of these cores has been analyzed for uranium, thorium isotopes, minor and trace elements by the principal investigator. The core is P6507-15 (42°54'N, 32°35'E).

Three cores from the cruise of Atlantis II, April-May 1969, of the Woods Hole Oceanographic Institution have also been studied. The three cores are: 1474 (42°23'N, 37°36'E), 1462 (43°01'N, 33°03'E), 1445 (43°08'N, 31°27'E). See Fig. 2.

The results are given in Tables 4 and 5.

In the three cores of Woods Hole three units could be distinguished by micropaleonthogic analysis. In the upper layer, Unit I, present salinity is already established; in Unit II some freshwater starts to enter the basin; in the lowest layer, Unit III, fresh water conditions are established. These three units can also be correlated by their uranium content. Unit I has a very high uranium content, high carbonate, relatively low organic matter; in Unit II the uranium content is lower but organic carbon is the highest of that of the three units. In all the cores the U-234/U-238 ratio is oceanic (1.15). In Unit III, at depth from 160 cm., the uranium content is lower, fresh water conditions are fully established at 9000 to 10,000 years ago. Only old coccoliths have been found (Ross, 1970) transported by rivers from land or turbidity currents; organic matter is low. In this unit uranium concentration is low, that of pelagic clay and the isotopic U-234/U-238 ratio is near to one. In core 1462 a clay layer at 60-80 cm. is a turbidite interposed in Unit II (Rona and Joensuu, 1972).

Similar units can be recognized in core P6507-15. The uppermost

30 cm. have not been analyzed. The sediment from 30 to 79 cm. is obviously equivalent of Unit II of the Woods Hole cores. The uranium contents and the U-234/U-238 isotopic ratios (oceanic) are very nearly the same. Below the depth of 121 cm., where fresh water conditions are established, and down to 609 cm., this core is similar to Unit III of the Woods Hole cores.

For more information thorium has been determined in the Woods Hole cores and thorium and protactinium in the Miami core. However, since the age of the cores, which we analyzed does not reach beyond 10,000 years, too recent for Th-230 and Pa-231 to have grown from their uranium parents, dating using the Th-230/Pa-231 isotopic ratio is not feasible.

The minor and trace elements of the Woods Hole cores are presented in Table 6. Unit II is rich in organic matter and molybdenum, copper and barium are also enriched in the sediment, which is rich in organic matter (sapropel). In core P6507-15 these three elements and organic matter are correlated with uranium. See Fig. 3.

The continuity of the sediment layers evidenced by micropaleontological observations (Ross, 1970), was further documented by the correlation of uranium concentrations in the four cores analyzed by us. They testified to the uniform sedimentation in most of the Black Sea.

Mediterranean Sea:

Whereas the Black Sea is a quiet sea with negligible vertical circulation, high productivity and a great amount of organic matter on the bottom, the Mediterranean has a high circulation, rapid water exchange and low productivity. The maximum salinity of the Black Sea is 22 °/oo, that of the Mediterranean Sea is 38 °/oo. The chemistry reflects the differences of these two basins.

A core taken from the Mediterranean Sea, P6510-4, at 32°50'N, 32°00'E, was analyzed for uranium-thorium isotopes and protactinium. The results are presented in Table 8.

This core was dated by the use of C-14 method: 41-49 cm., 5255±170 B.P., giving sedimentation rate of 8.5 cm. in 1000 years.

Table

33°54'N 28°29'E Depth: 2,664 m.

Depth m	Uranium μg/1000 g.
11	3.6
319	3.6
2244	3.6

The sea water was analyzed for uranium. The analysis was made using unfiltered sea water; therefore, the uranium content is somewhat higher than the average value of 3.2 for the world oceans. Sea water for the Black Sea water was analyzed for uranium at only one depth, seven meters at 44°12'N, 33°46'E, and found to be 3.6μg per 1000g.

Geochemistry of Lakes with Trapped Sea Water:

During and after the last glaciation large areas in the northern hemisphere were flooded with sea water. When the water retreated, lake basins which had been flooded were left filled with sea water. When communication with the sea was restricted due to isostatic elevation of the land, the saline water, filling the bottom of the basin was overlaid by fresh water. While there are many landlocked basins with trapped sea water, which still have communications with the sea from above or with inflowing sea water through narrow channels, there are a few which contain salt water in the bottom, isolated for hundreds of years. The general features of such lakes are: fresh water is a few meters below sill, oxygen diminishes and disappears at a certain depth, used up for the decomposition of the large amount of organic matter which accumulate at the bottom. Sulfate ions are reduced by anaerobic bacteria to H_2S and sulfides. All the cores from the lakes are rich in methane. A low rate of sedimentation prevents a dilution of authigenic minerals by terrigenous detritus, thus playing a special role in preservation and accumulation of minerals. The basins are isolated from the outside water because of the restriction of the sill and a sharp pycnocline, prevent vertical mixing.

Characteristic features of these lakes are complete disappearance of sulfates (normal sea water contains 0.23%) and the appearance of H_2S and sulfides. Methane is present in great amounts and there is also some ammonia. The bottoms of the lakes are catchments for organic matters. It is not known whether there are basins which still have salt water which have never been renewed. Basins which have still relict water in in the bottom are: Rohrholtfjord*, Botnvatn, Rørhopvatn, Framvarn in Norway, and Powell Lake in British Columbia.

The lakes which we studied were discovered by K. M. Strøm (1936, 1948, 1958, 1961) and Williams (1961).

The sediment material and the water samples we owe to the generosity of Dr. John Reitzel.

The lakes which we analyzed are: Rohfoltfjord, part of Lake Tokke, in Southern Norway; Framvarn, the most inland of a series of three fjords being connected with the ocean south of the town of Farsund; Botnvatn and Rørhopvatn, Nordland, uplifted fjords but smaller and younger than Lake Tokke; Blankvatn, a small meromictic lake; Powell Lake, in Mesozoic British Columbia.

<u>Description of the cores</u>, (by Dr. Reitzel):

All the cores are gravity cores. Most of the cores have thin watery tops, so that the top of the sediments were unavoidably lost in recovering the corer. It is thus hard to estimate the distance of any sample under the bottom, which is ill defined in these lakes in any case**. Each sample was wrapped in aluminum foil and sealed in

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*The term fjord is used in Norway not only for arms of the sea, but also for fresh water lakes.

** For this reason we adopted the notation of Reitzel with alphabetic letters, the first letter A denotes the deepest sediment layers; decreasing depths are designed with letters increasing in the alphabet. The layers of the highest letter is the nearest to the top. Each letter represents approximately 17 cm of the depth.

glass jars, each of which contained 17 cm., (except for top and nose). These lakes have been chosen by Dr. Reitzel for the measurements of heat conductivity of the bottom sediments, because the bottoms have a likelihood of being free of seasonal temperature changes imposed from above.

The results of Dr. Reitzel's heat conductivity measurements, which are also of interest to us, are: Powell Lake and Botnvatn show no important lateral variations, the average bottom gradients in the deep parts of these lakes are well determined and that seems to be the case for Rorhopvatn. The scattered values in Framvarn result from a recent invasion by the sea. The scattered results in Blankvatn may well be due to varying thickness in a small basin with irregular bottom. One important feature to be seen from the gradients themselves is that, in the lakes studied, there is no significant change of gradients with depths in the upper 2 1/2 meters of sediments. No error due to yearly temperature changes or chemical generated of heat in the sediments.

In Table 9 are presented the description of the lakes, and Figs. (4 to 7) give the location of the lakes.

Experimental

Lake water and sediments were investigated. Water samples were taken with Ruttner bottles. The sediments were gravity cores.

Microscopic Inspection

The cores are gray, clay-rich sediments. Under the microscope most of the mineral grains appear to be smaller than 30 microns (mainly clay minerals); among the large grains, pyroxene crystals appear to be abundant, along with feldspars, chlorites, volcanic glass, some quartz and apatites. Those sections nearer to the top have more biogenous tests.

Analytical

Chlorinities were determined by electric conductivity. The chlorinities of the interstitial water have been analyzed by Volhard titration, after the water has been acidified with HNO_3 and H_2S evaporated by heating.

The analytical procedure for the uranium-throrium isotopes and protactinium and the counting technique to determine these concentrations were described before in this report. The major and trace elements and $CaCO_3$ were determined by Atomic Absorption with an estimated 2-3% accuracy. Titanium and SiO_2 were determined by emission spectroscopy with an accuracy about 10-15%.

Rorholtfjord (Lake Tokke):

This lake is narrow, deep, and its surface is 60 meters above the present sea level. No rivers are entering it. The water from surface down to 80 meters is fresh water subject to normal circulation in spring and autumn; from 80 to 134 meters the water is not subject to normal circulation, because it has a slight salt content, the partial renewal being through turbulence. This layer very effectively protects the bottom layer from any direct contact with fresh water and from any disturbance from turbulence. Interchange between the second and third layer is only through diffusion, which is very slow. This is the most stagnant of the meromictic lakes (Strøm, 1957). The cores which we analyzed smelled of H_2S and were under pressure of methane, which was obvious when the bottles were opened.

Salinities are given in Table 10 together with the salinities given by Strøm (1957).

Table 10

Depth meters	Salinities °/oo	(Strøm) Salinities °/oo
132	0	4.62
134	0	-
136	0.95	10.28
138	9.61	13.06
141	12.86	15.01
143	15.75	16.28
144	N.D.	16.81

Because it is difficult to explain that sea water was left in the bottom of the fjords several meters above present sea level for a long time, the major elements in the deep waters have been compared with those in sea water, normalized to the same chlorinity.

As can be seen from Tables 11, 13, 14, 16, the concentrations are nearly the same in lake and sea water.

Table 11

	I Present paper	Strøm	II Sea water	I/II
Na	5148	5000	5145	1.00
Mg	759	781	616	1.23
Ca	309	245	198	1.56
K	140	0	188	0.74

Framvarn:

This lake is separated from Ytre Lyngadsfjord by a 4.3 meter threshold which leads to a chain of three fjords. Coastal water has access to the outermost. Communication with Framvarn is through a narrow canal, two meters deep. It lies near the center of a distinct intrusion of farsundite, a rock that ranges from monzonite to alkali granite. Analysis of farsundite is taken from Holtedahl (1960).

	%
Quartz	20.0
Microcline perthite	35.0
Oligoclase	36.0
Hornblende	5.0
Biotite	2.0
Accessories	2.0

In Framvarn, 61 cm. of putrid mud abruptly rest on hard, stiff inorganic clay. The clay is probably not intact glacial clay, but reworked or redeposited. The black mud represents present sedimentation and the clay sediments of the last exchange of the fjord with salt water.

Salt water at the top is zero; at a depth of 160 meters, we determined it to be 24.1 °/oo.

Rorhopvatn:

A lake in northern Norway, Lofoten, lies at only 3 meters of altitude. Table 12 presents our analysis of the salt content from 40 to 60 meters. We found an abrupt change from zero to 12.8 °/oo in 6 meters.

Our maximum salinity is much higher than that determined by Strøm, 20 °/oo from a depth of 44 to 90 meters.

TABLE 12

Depth in meters	Salinity in °/oo
40	0
43	0
46	12.77
50	26.26
60	28.03

In Table 13 the concentration of the major elements are presented and compared to those of sea water (Sverdrup, 1942), based on chloride concentration of 15,600 mg/1000 ml. of sea water.

TABLE 13

	I Rorhopvatn Water	II Sea Water	I/II
Na	8500	8621	0.99
Mg	1000	1038	0.96
Ca	305	326	0.93
K	280	310	0.90

Botnvatn:

Botnvatn, in the district of Salten, Northern Norway at 67°N lies at an altitude of the 12 meters; the salinity at the top is 2.25 ^{o}/oo and at a depth of 111 meters 13.14 ^{o}/oo (Strøm, 1961). The concentration of the major elements and those in normal sea water, calculated to the chlorinity of the lake of 7260 mg chloride ions per 1 liter, are presented in Table 14.

TABLE 14

	I Botnvatn Water	II Sea Water	I/II
Na	4300	4045	1.06
Mg	445	487	0.91
Ca	173	153	1.13
K	123	145	0.85

Powell Lake:

Powell Lake is a fjord in British Columbia. The oxygen depletion bottom water measured by Williams in situ has a pH of 6.7-6.9 and a very high total sulfide concentration of about 89 mg per liter (Williams, 1961).

The salinity of this lake was measured from 130 meters to 334 meters. The results are given in Table 15.

TABLE 15

Depth meters	Salinity ^{o}/oo
130	0
280	3.0
300	11.0
330	16.6

The concentration of the major elements and those in normal sea water, calculated to the chlorinity of the lake for 9196 mg chloride ions per liter, are presented in Table 16.

TABLE 16

	I Powell Lake Water	II Sea Water	I/II
Na	5550	5111	1.08
Mg	735	616	1.19
Ca	101	194	0.52
K	189	184	1.03

The organic matter, zero to thirty cm. below surface of Powell Lake, was dated by C-14 method. The age has been found to be 7,680 ±120 years B.P. by Ostlund.

Mathews (personal communication) estimated the age of freshly deposited organic matter in Powell Lake to 10,000 years B.P.

Blankvatn:

Blankvatn is a lake with 20 m of fresh water superposed upon stagnant waters. The total depth of the lake is 55 m and covers an area of only 0.008 Km^2. Strøm (1948) explains these unusual proportions as being a crater lake, a basin plucked by the effect of of ice on an area of extremely shattered rocks, possibly aided by dissolution of limestone. The lake receives detritus and a very large amount of organic matter, produced in the fresh water above. This lake is meromictic on what is called on a biological basis.

It was difficult to secure sediment samples, because the lake is narrow and has straight and rocky walls. The short core which we analyzed smelled strongly of H_2S and contained methane. Salt content of the water is zero. The U-234/U-238 activity ratios are unusually high, Table 18. High activity ratios were observed by Kaufman et al. (1969) for rivers and fresh water lakes.

Results and Discussion

Uranium concentrations of cores from the Black Sea and Norwegian Fjords and Powell Lake of British Columbia are presented in Tables 4,5,17,18,19,20,21 and 22. Data from Caribbean cores and from the Cariaco Trench are given for comparison. A striking difference is apparent between the uranium in sediments taken from anoxic basins, from that in sediments taken from the open sea, with free circulation.

In sediments taken from reducing environments such as the Black Sea and the Norwegian Fjords, which are rich in organic matter, the uranium concentration is high and activity ratio of $\frac{\text{U-234}}{\text{U-238}}$ is 1.15, i.e., oceanic. In sediments taken from the open ocean the activity ratio is one or less and the uranium concentration is typical of that of pelagic clay (2-4 ppm.) (Core P6304-1; Table 23).

It is suggested that in reducing environments with H_2S present and pH 7 or less, uranium is removed from the water as U^{+4}. Latimer (1964) gives for the reduction of UO_2^{+2} to U^{+4} an Eh value of -0.33.

Piper (1971) measured an Eh value of the water of Framvarn at a depth of 180 cm (almost the water sediment interface) of -.02. However, the redox potential in unconsolidated organic matter is probably lower. If ferrous ions are present (as they almost always are) pH reduction of uranium from the six to the four valence state is favored, as suggested by Adams <u>et al</u>. (1959). The redox potential of UO^{+2} U^{+4} -0.3 reaction is close to the potential necessary to reduce ferric to ferrous ion, -0.2 (Pourbaix, 1963) at a pH of 8. Correlation of uranium with organic matter can also be seen in cores from the Cariaco Trench (Dorta, 1971). Agamirov (1963) suggests similar mechanisms for the high concentration of uranium in Black Sea mud.

Manheim (1961) dismisses the path for the removal of uranium from the water which was mentioned above. In samples from the Baltic Sea he found that high uranium concentrations are in the transitional zone, at the periphery of the basin and not in the center, where organic matter accumulates. He explains this behavior by the erosion of uranium-rich sediments from the mainland during previous glacial periods and redeposition at the land sea interface at the present time. The Black Sea cores give a different picture, as discussed above. Samples taken from the same depth and organic matter of similar concentration taken from the east, west, and middle of the basin (Fig. 2) have about the same uranium concentration. The explanation of Manheim is probably valid for the Baltic Sea where uranium-rich deposits are nearby. For instance, his sample S-32 is near the uranium-rich Latvian deposits. There are no especially uranium-rich sediments near the Black Sea, Cariaco Trench or the Fjords. The conditions in a geological setting are so complex that each situation has to be explained on its own merit.

Minor and trace element concentrations are presented in Tables 6, 7, and 24 through 32. The concentrations of most elements in sea water are only a fraction of that of rivers pouring into it. The balance is in the sediments. The problem, which has been discussed for a long time, concerns the mechanism of removal of the elements from sea water, a mechanism which is more effective for one element than for another. The removal of elements, under the same environmental conditions, depends, among other things, on their solubility. The solubility or stability depends on pH and Eh. In the open sea, which has free circulation and is oxidizing, pH changes little and Eh values vary from highly positive to less positive values. In anaerobic stagnant waters, with negative Eh, pH varies between 8 and 6.9. In any environment chemical changes might take place during the travel of an ion to its final burial place, or they might be diluted by detrital material, a "mixing effect". In this report only solubilities of oxides and of sulfides, produced under reducing conditions high in organic matter, are considered; compounds of metals with other anions (phosphates, sulfates, carbonates) are not discussed. Solubilities are published in the literature usually for an ionic strength of 0.1 for infinite dilution and an ionic strength of one-one valence state.

Even if they are corrected for ionic strength proper to the prevailing conditions, the result is only a rough approximation because of the complex geochemical situation in the sediments. The best way to avoid the influence of the adjacent environment is to compare two elements under the same environmental conditions. This is done by constructing stability fields, Eh-pH diagrams. Only the ferrides are considered in this report. Stability fields for the elements Fe, Ni, Co and Mn can be found in the literature (Garrels, 1965; Latimer, 1964). The discussions in this paper are based on the stability fields, taken from a paper of Carvajal and Landergren (1968) (Figs. 7 to 10). Oxides and hydroxides of manganese are more soluble than the corresponding compounds of iron, and consequently, the oxides of iron are more readily deposited on near shore sediments; manganese in sea water is present as Mn^{+2} state (Rona et al., 1962). Under anaerobic conditions, iron as FeS is insoluble whereas manganese sulfide is soluble. The stability fields for cobalt sulfide and nickel sulfide are almost identical. No stable oxides exist for cobalt or nickel. The ratio of the two sulfides in sea water is 0.17. In authigenic sediments the ratio should approach that of sea water; in detrital material this ratio should approach that of the Earth's crust, 0.31. Co/Ni have usually a value between 0.17 and 0.31, the changes between the ratios being brought about by environmental conditions. The ratios of Co/Ni, Fe/Mn and Co/Mn are given in Tables 33-41, for the sediments of which have been studied.

The average values of the cores which have been investigated are given in Table 42 and are compared with average values for pelagic clays, igneous rocks and sediments from the Pacific Sea. The latter values are taken from the literature (Carvajal, 1968). Co/Ni ratios are very nearly the same for samples taken from such different environments as cores from the Caribbean Sea, Mediterranean and most of the Norwegian Fjords. The similarity of the Co/Ni ratios are expected because cf the similarity of the stability fields of the two elements. All the ratios are nearer to those of igneous rocks than to those of pelagic clays. During weathering of igneous rocks, more cobalt than nickel is dissolved and transported to the oceans. The ratio of Powell Lake is almost identical to those cores which were taken from the open Pacific Ocean.

More information can be obtained by calculating the correlation of any of two ferrides. The interrelationship is calculated by the equation:

$$\text{Correlation coefficient} = \frac{\sum_{1}^{n} Xi\ Yi}{\sqrt{\sum_{1}^{n} X_j^2 \sum_{1}^{n} Y_j^2}}$$

(Wiener, 1966), where X_1 ....X_n are the numbers of one set and Y_1 ....Y_n that of another set, the numbers must fall between -1 and +1. The values were computed by the I.B.M. 360 computer of the University of Miami. Correlation coefficients are given in Tables (43-47).

It is interesting to note that Co-Ni are strongly correlated in all the samples, and the correlation coefficients are approximately of the same order except for a lower value for Botnvatn). Obviously the Co-Ni correlation is not affected by environmental factors nor by manganese or iron which are present in overwhelmingly higher concentrations. Fe-Mn correlation is positive and high in all the inland waters, because the concentrations of these two ferrides are of the same order of magnitude in these sediments. Co-Fe, Ni-Fe, Co-Mn, Ni-Mn are weakly correlated or not at all (Black Sea sediment P6507-15), probably because affected by iron and manganese. The repression of a correlation by manganese, and possibly by iron might be due to the adsorption effects. It was noted before that manganese is a scavenger for many elements (Goldsmith, 1937; Krauskopf, 1957). Colloid of manganese in sea water is negatively charged and adsorb positive ions.

Enrivonmental factors, such as reducing or oxidizing environments and mixing or dilution of authigenic with detrital material, are the main factors influencing the concentrations, ratios, and correlations of trace elements in marine sediments as reported here.

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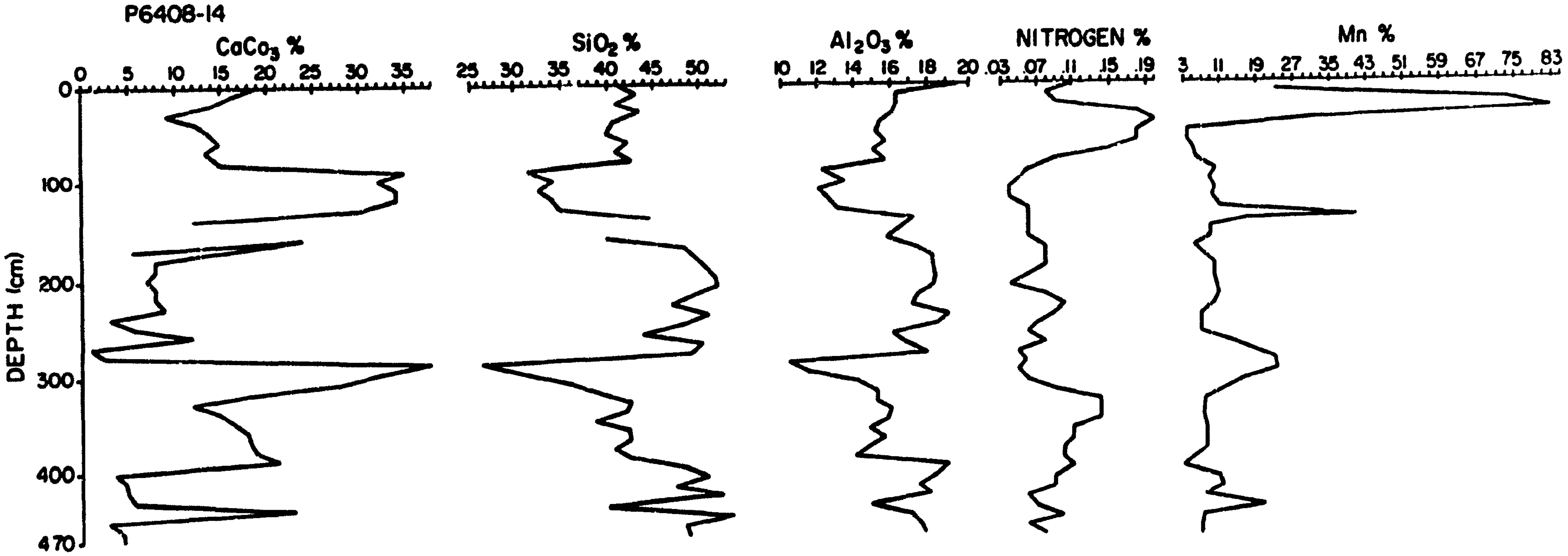

P6408-14
$CaCo_3$ %
0 5 10 15 20 25 30 35
SiO_2 %
25 30 35 40 45 50
Al_2O_3 %
10 12 14 16 18 20
NITROGEN %
.03 .07 .11 .15 .19
Mn %
3 11 19 27 35 43 51 59 67 75 83
DEPTH (cm)
0
100
200
300
400
470

Figure 1

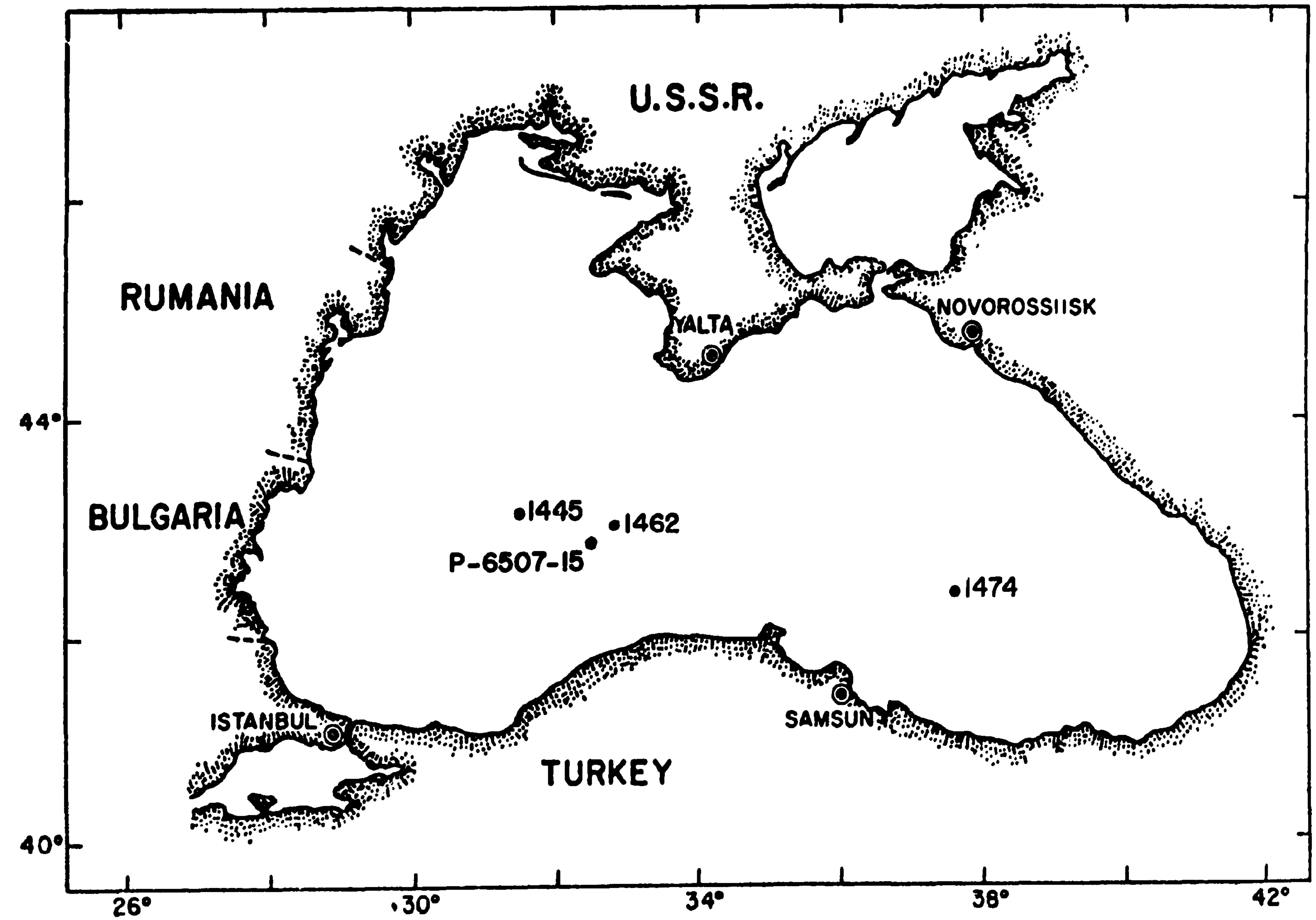

U.S.S.R.
RUMANIA
BULGARIA
TURKEY
YALTA
NOVOROSSIISK
ISTANBUL
SAMSUN
1445
1462
P-6507-15
1474
44°
40°
26°
30°
34°
38°
42°

Figure 2

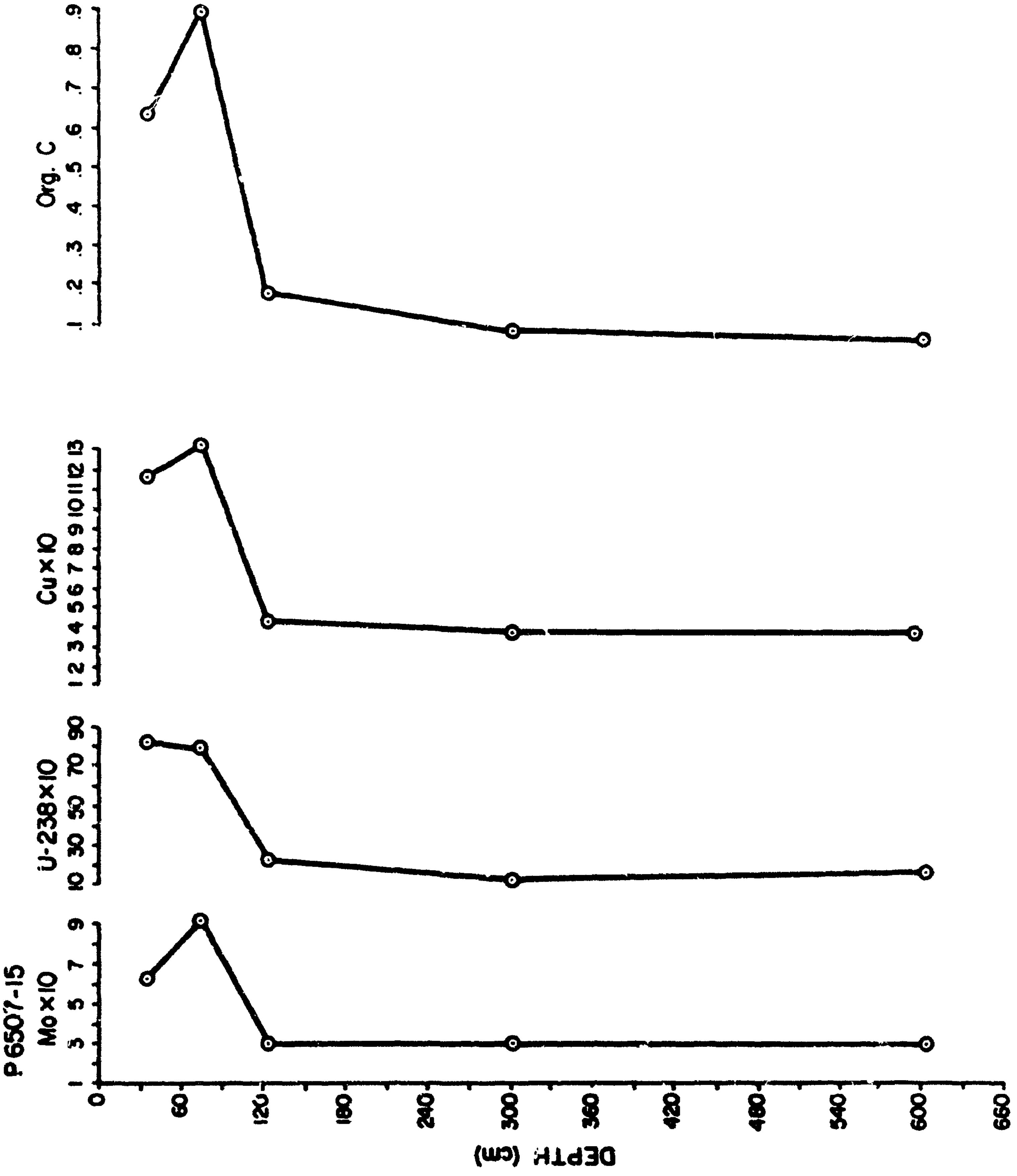

P6507-15
Mo×10
1 3 5 7 9
U-238×10
10 30 50 70 90
Cu×10
1 2 3 4 5 6 7 8 9 10 11 12 13
Org. C
.1 .2 .3 .4 .5 .6 .7 .8 .9
0 60 120 180 240 300 360 420 480 540 600 660
DEPTH (cm)

Figure 3

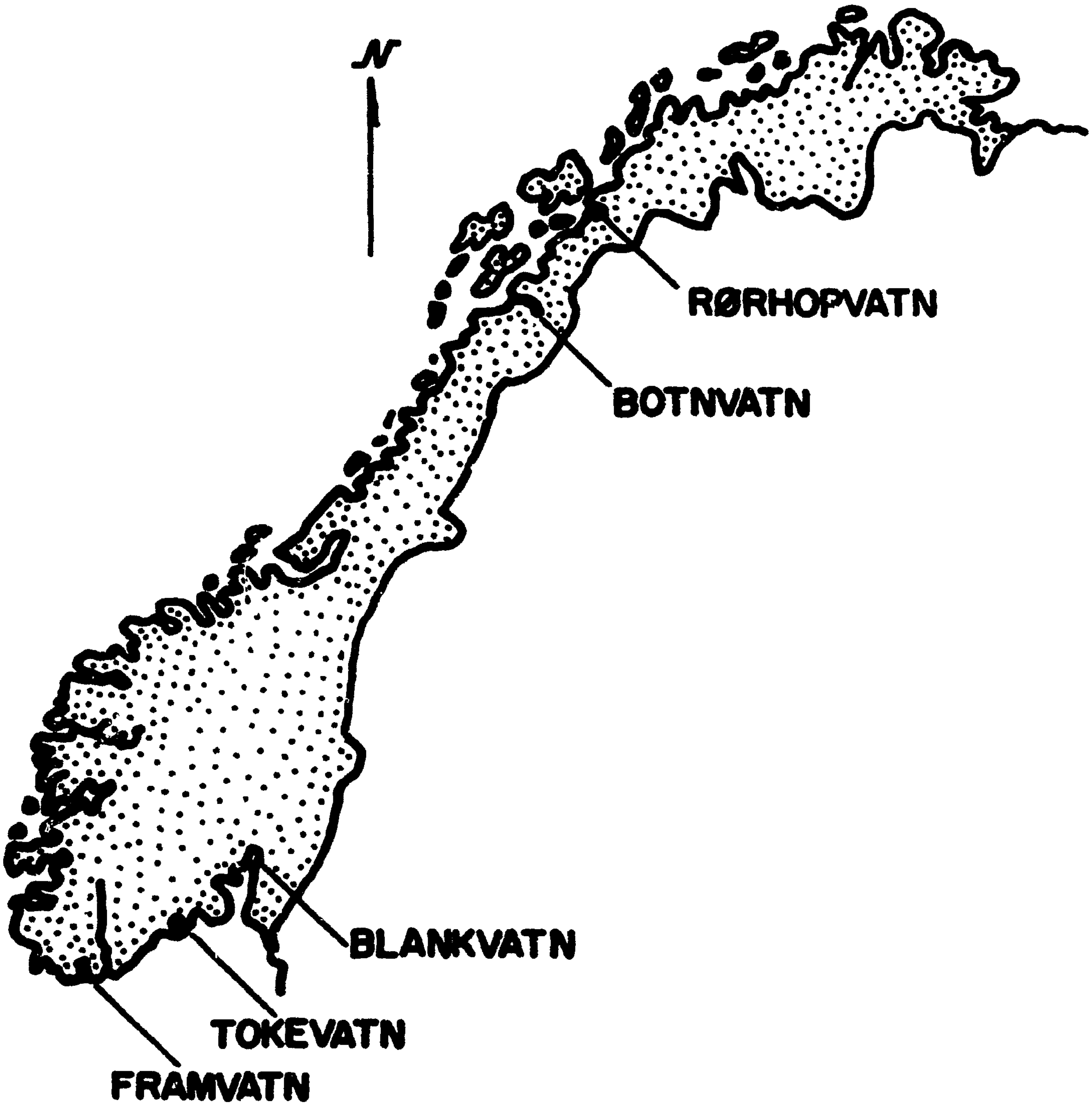


Figure 4 Geographical Location of Norwegian Lakes

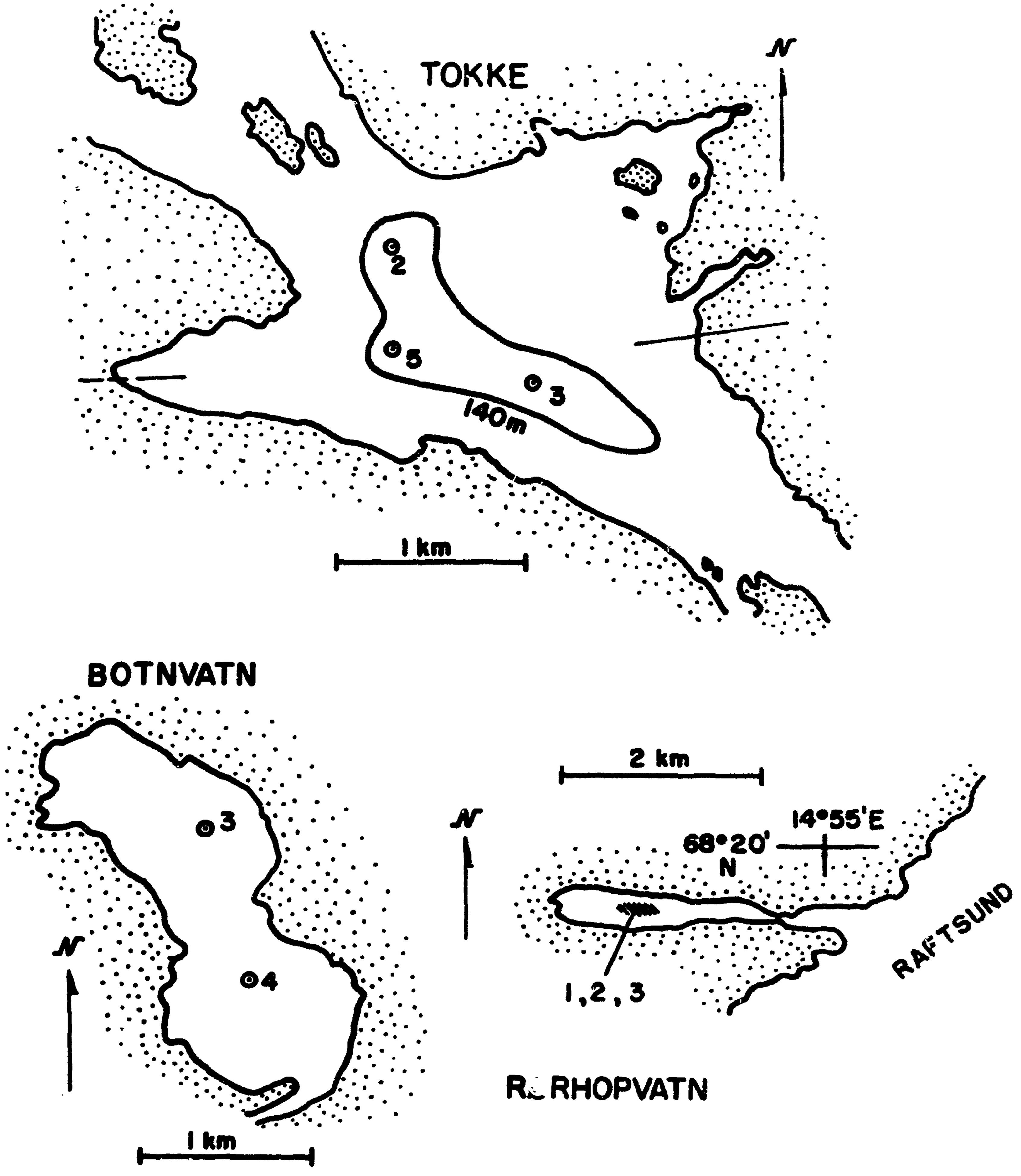
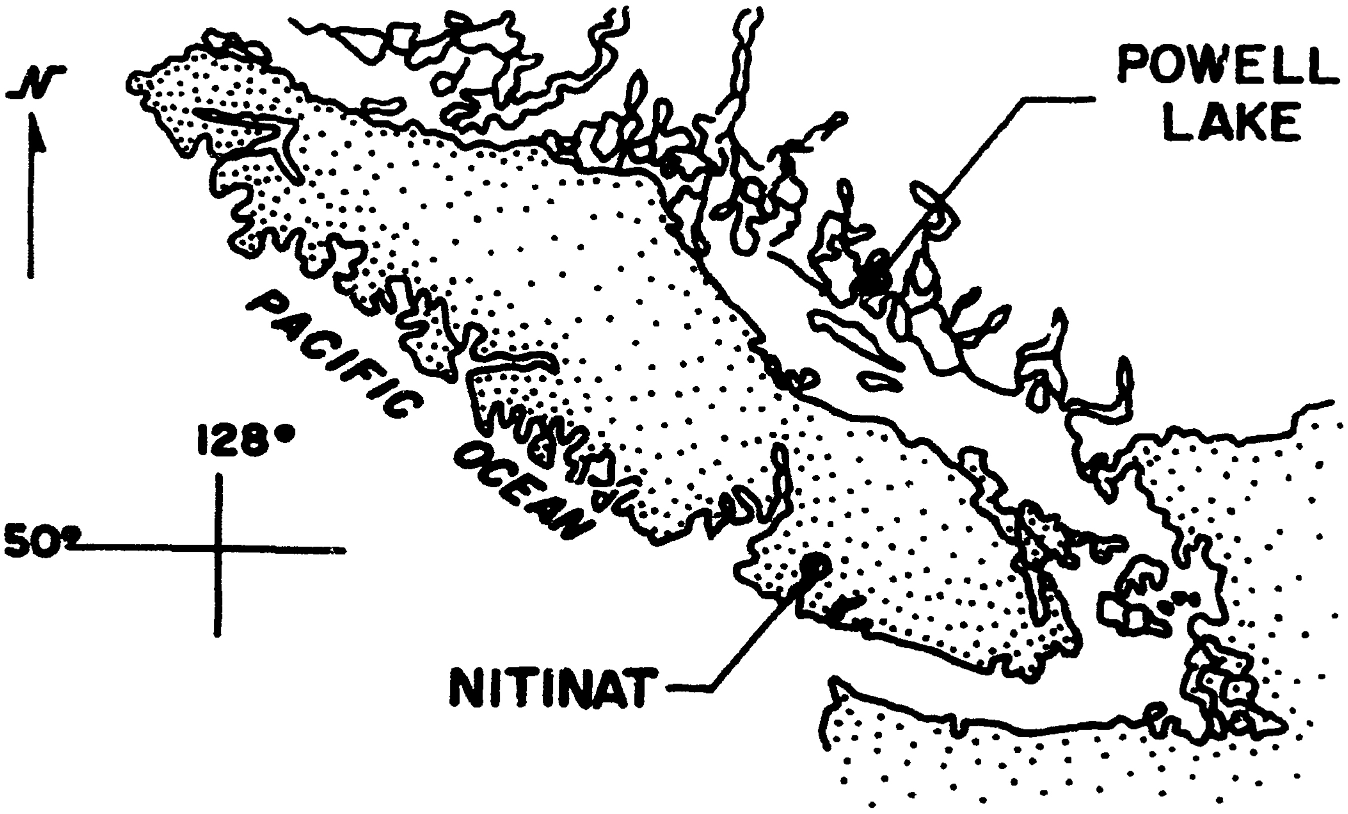


Figure 5 Sample Locations in Lake Tokke, Botnvatn and Rorhapvatn



Geographical Location of Lakes of British Columbia

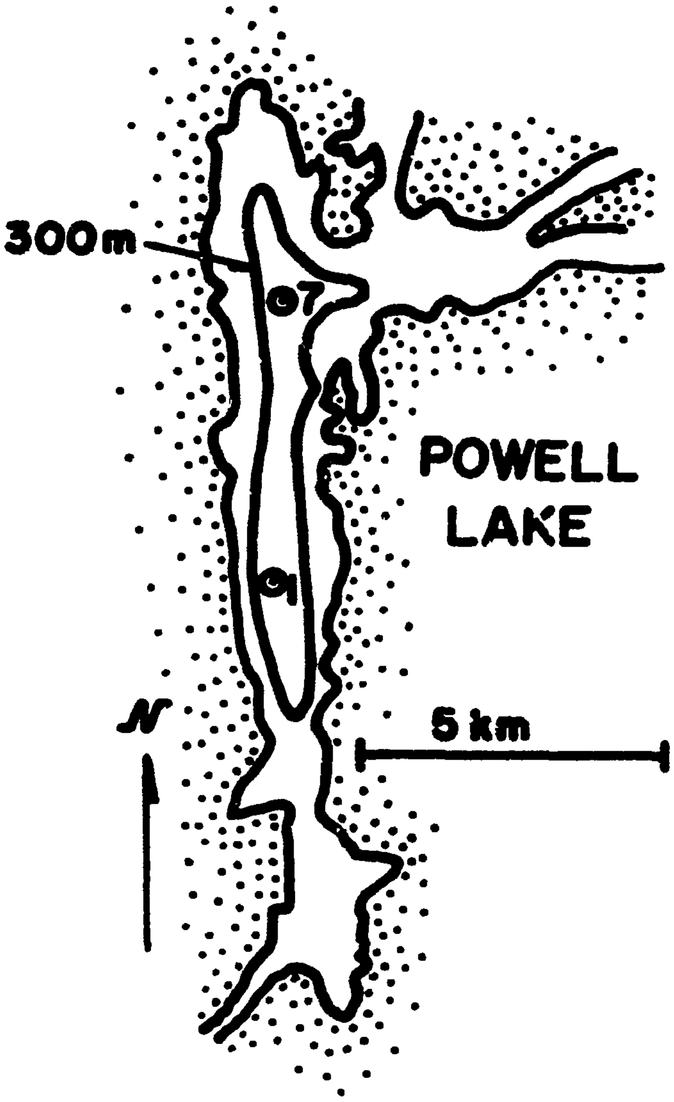
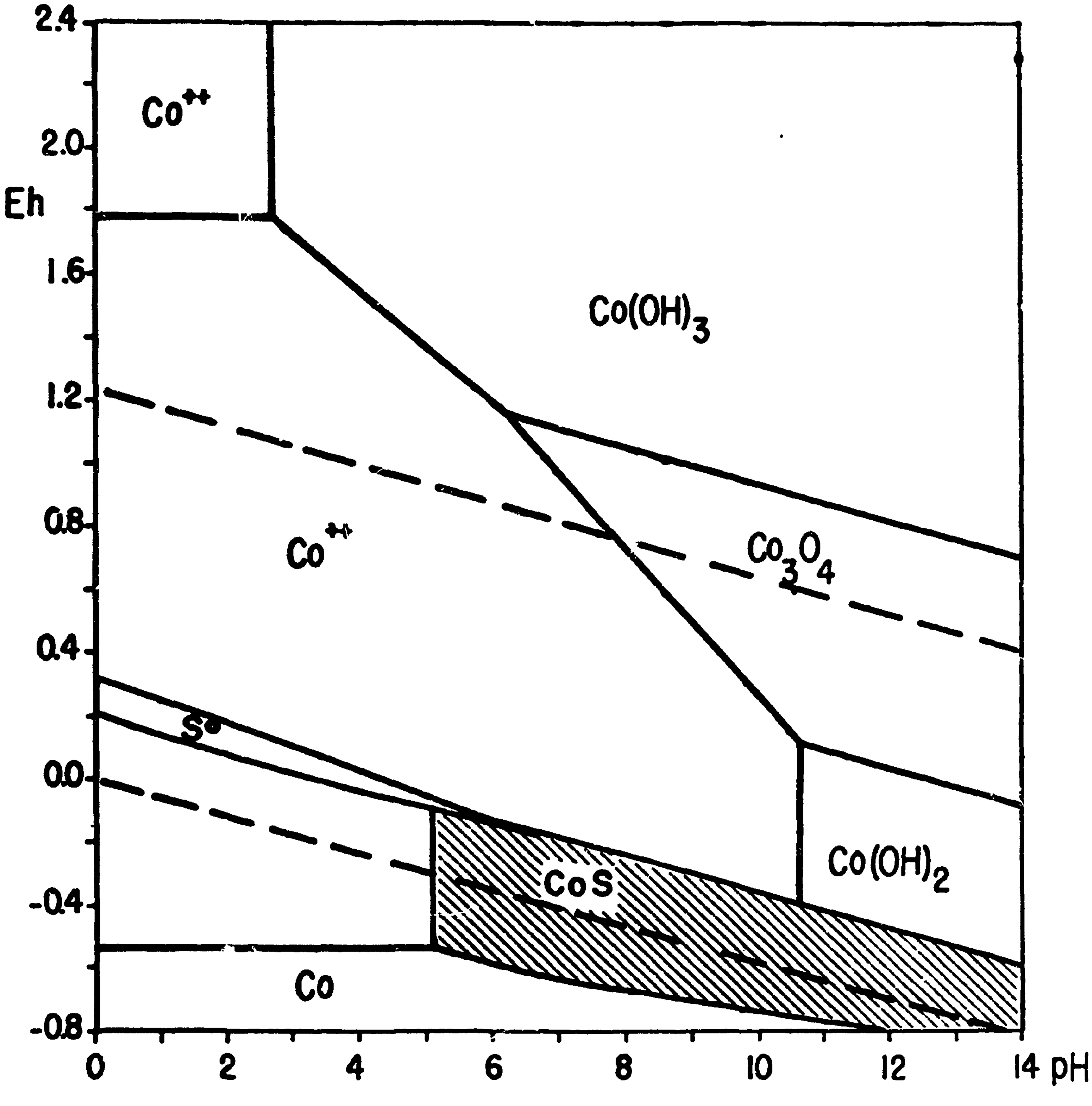


Figure 6 Sample Location in Powell Lake



Eh
2.4
2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
0
2
4
6
8
10
12
14 pH
Co⁺⁺⁺
Co(OH)₃
Co⁺⁺
Co₃O₄
S°
CoS
Co(OH)₂
Co

Figure 7

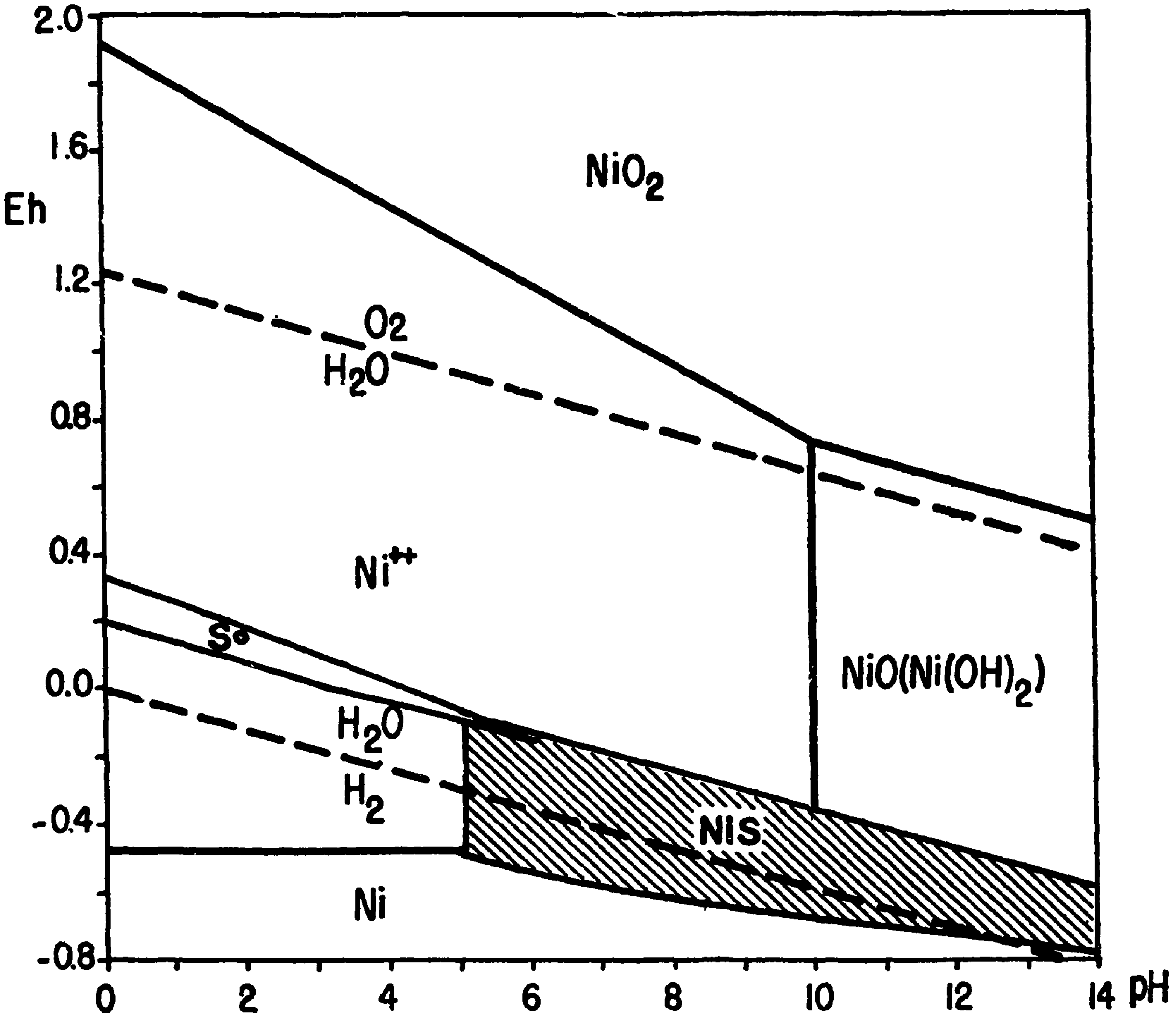

2.0
1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
Eh
0
2
4
6
8
10
12
14
pH
NiO_2
O_2
H_2O
Ni^{++}
S^o
H_2O
H_2
Ni
NIS
$NiO(Ni(OH)_2)$

Figure 8

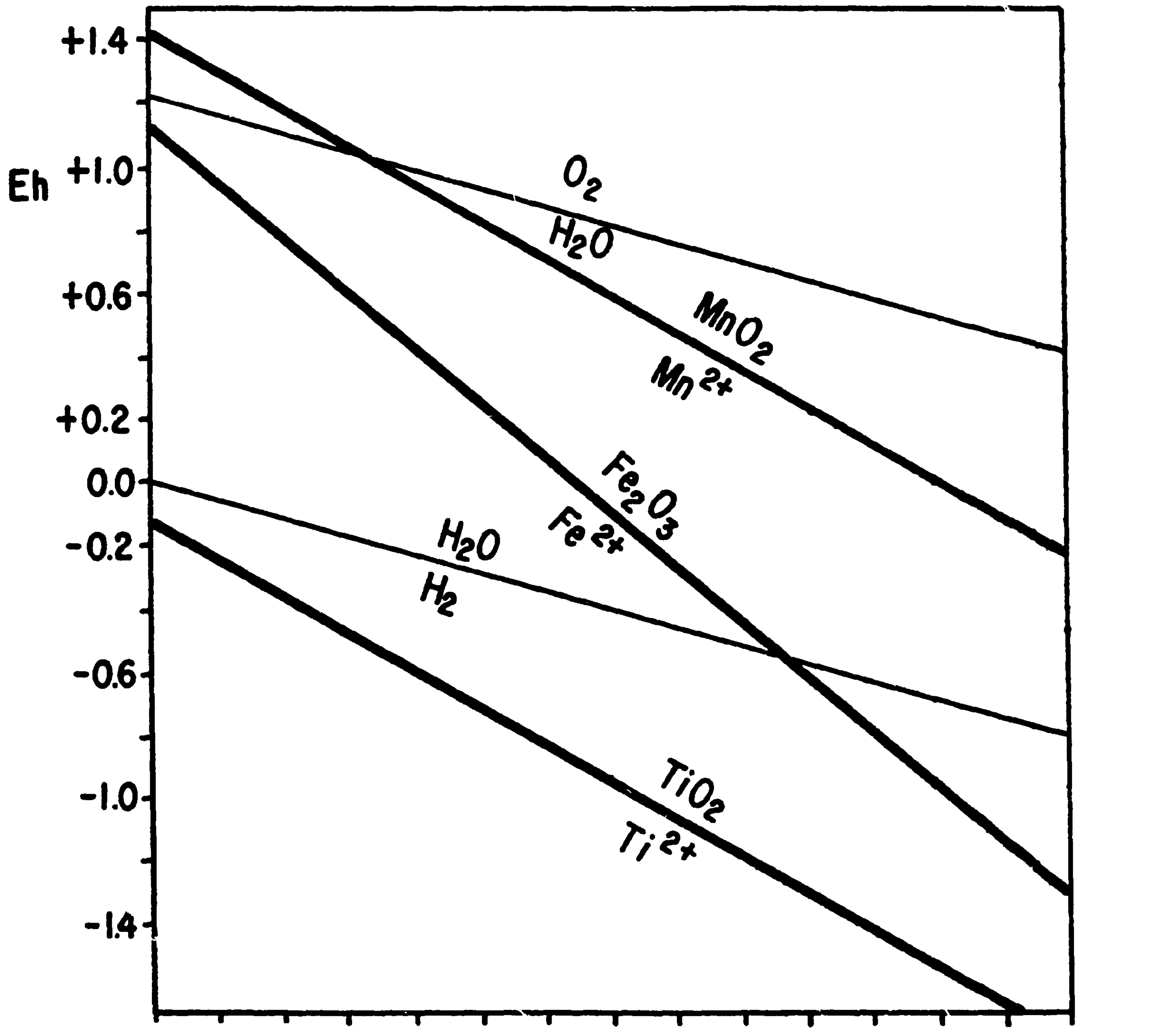
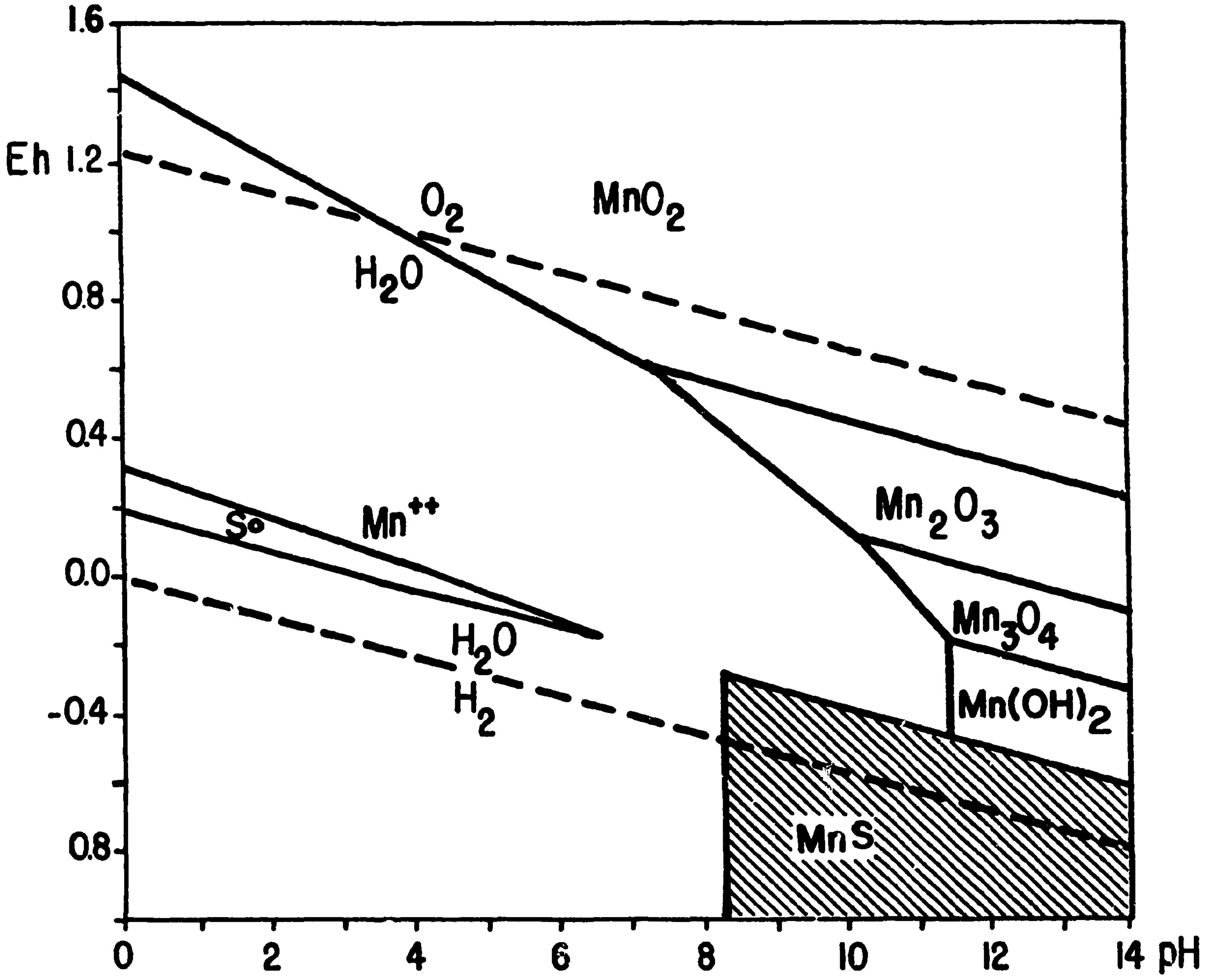

Eh
+1.4
+1.0
+0.6
+0.2
0.0
-0.2
-0.6
-1.0
-1.4
0
2
4
6
8
10
12
14
pH
O_2
H_2O
MnO_2
Mn^{2+}
Fe_2O_3
Fe^{2+}
H_2O
H_2
TiO_2
Ti^{2+}

Figure 9



Eh
1.6
1.2
0.8
0.4
0.0
-0.4
0.8
0
2
4
6
8
10
12
14
pH
O_2
H_2O
MnO_2
S^o
Mn^{++}
H_2O
H_2
Mn_2O_3
Mn_3O_4
$Mn(OH)_2$
MnS

Figure 10

Refer to the text for the following tables:

Table 10, see page 15

Table 11, see page 15a

Table 12, see page 17

Table 13, see page 17

Table 14, see page 18

Table 15, see page 18

Table 16, see page 19

TABLE I

P6408-14

Depth cm	U-238† DPG	U-238 PPM	U-234† DPM	U-234/U-238	Th-232† DPM	Th-230†* DPM	Pa-231†* DPM	Th-230/Pa-231	$CaCO_3$ %	Age years
Top	36.31±4.33	0.82±0.10	40.22±4.55	1.11±0.18	108.65±7.49	352.88±21.14	40.14±1.28	8.79±0.59	17.5±6.7	
91-99	91.91±8.74	2.09±0.20	106.62±9.41	1.16±0.15	92.92±9.98	312.06±37.89	30.09±6.24	10.37±2.48	34.0±23.9	
110-120	41.51±6.00	0.94±0.14	47.17±6.39	1.14±0.22	142.20±29.32	464.22±30.89	33.82±1.45	13.73±1.07	34.0±7.8	26,152±2040
171-179	114.37±3.03	2.60±0.07	133.75±3.28	1.17±0.04	155.78±6.45	15.75±7.12	9.76±0.37	9.89±4.48	7.0±45.3	
291-299	80.10±6.00	1.82±0.14	87.26±3.94	1.09±0.09	152.63±17.75	326.16±29.47	20.07±2.74	16.25±2.65	35.0±16.3	44,741±7290
451-456	108.73±5.26	2.47±0.12	112.20±5.34	1.03±0.07	117.15±6.61	28.23±8.99	5.73±0.71	4.93±1.68	3.4±34.0	

* corrected for uranium

† carbonate free basis

TABLE 2

P6304-7

15°06'N 69°38'W 3929m

Depth cm.	U238* d/h/g	U-238* ppm	U-234* d/h/g	U-234/U-238	Th-232* d/h/g	Th-230* d/h/g	Pa-231* d/h/g	Th-230/Pa-231	$CaCO_3$ %
4-9	2433.0	55.3	875.0	0.40	131.0†	385.0†	47.8	8.10	60.5
10-20	232.0	5.3	101.0	0.44	105.0	644.0	57.4	11.22	63.0
60-70	171.0	3.9	110.0	0.64	116.0	489.0	23.3	20.99	NM
120-130	91.0	2.1	80.0	0.87	94.0	379.0	21.2	17.90	60.5

* on carbonate free basis

† not corrected for uranium

Depth cm	U^{238+} d/h/g	U^{234+} d/h/g	Th^{230*+} d/h/g	Pa^{231+*} d/h/g	$\frac{Th^{230}}{Pa^{231}}$	$\frac{Th^{230}\ age}{Pa^{231}\ age}$ (Y.B.P.)	C^{14} age (Y.B.P.)	$CaCO_3$ (%)
11-14	117.0	117.0	406.2	38.56	10.5	modern	3275±90	68.0
75-79	117.4±10.6	117.2±10.6	284.3±6.2	24.5±4.9	11.60±2.4	17,300±3640	21,480±9.5	54.8
231-239	114.1±9.1	119.1±7.7	266.3±6.1	11.11±1.7	23.97±2.9	77,000±8700	-	55.2
401.5-409.5	117.7±12.4	125.7±12.7	172.0±6.7	6.1±0.6	28.2±3.0	88,225±9400	-	68.0
451-459	99.0±9.6	99.0±9.8	136.0±5.4	4.12±0.4	33.03±3.5	103,750±11200	-	58.3

* corrected for uranium
\+ calculated on carbonate free basis

Table 2b

Core P6304-1: absolute ages of selected core layers.

The U, Th, and Pa data are on a carbonate-free basis.

The Th and Pa data are corrected for the concentration of U.

TABLE 3

M S N - 96

Depth cm.	U-238[*] d/h/g	U-234[*] d/h/g	U-234/U-238	Th-232[*+] d/h/g	Th-230[*+] d/h/g	Th-230/Th-232	Pa-231[*+] d/h/g	Th-230/Pa-231	$CaCO_3$ %
0-8	33.0	35.5	1.08	100.0	2580.0	25.8	354.0	7.29	6.2
18-22	-	-	-	84.6	1138.0	13.4	173.0	6.58	1.4
28-32	78.9	82.5	1.04	92.3	1274.0	13.8	109.8	11.60	2.4
36-44	38.6	38.6	1.00	91.0	1201.0	13.2	130.2	9.22	3.0
40-44	-	-	-	84.6	964.0	11.4	72.7	13.26	2.8
56-64	-	-	-	106.5	1289.0	12.1	157.0	8.21	1.65
72-80	20.5	30.1	1.50	73.2	1250.0	17.1	118.0	10.59	2.3
88-96	43.0	36.0	0.84	90.0	1382.0	15.3	-	-	2.3
Opal	125.0	229.6	1.84	59.6	1182.0	19.8	85.7	13.79	-

[*] on carbonate free-basis

[+] corrected for

TABLE 4

P6507-15

42° 54' N, 32° 35' E

Depth cm.	U-238* Error d/h/g	U-238 ppm	U-234* Error d/h/g	$\frac{U-234}{U-238}$	Th-232* Error d/h/g	Th-230* Error d/h/g	Pa-231* d/h/g	$CaCO_3$ %
31-39	808.7±15.2	18.4	911.3±16.2	1.13	111.5±5.1	152.9±5.8	12.20	19.0
71-79	776.8±11.6	17.6	881.0±12.4	1.13	107.3±3.8	169.8±4.7	12.75	6.7
121-129	220.2±7.6	5.0	217.2±7.6	0.91	152.4±4.6	118.0±4.1	8.50	2.1
301-309	133.0±3.3	3.0	124.0±3.2	0.93	140.0±4.4	131.2±4.3	9.74	4.5
601-609	162.0±3.9	3.7	158.4±3.8	0.98	163.2±4.0	147.8±3.8	-	17.6

* corrected for carbonate free basis.

TABLE 5

BLACK SEA CORES

1474	42°23'N,	37°36'E
1462	43°01'N,	33°03'E
1445	43°08'N,	31°27'E

	Depth cm.	U-238* Error d/h/g	U-238* Error ppm	U-234* Error d/h/g	U-234 / U-238 Error	Th-232* Error d/h/g	Th-230* Error d/h/g	Th-230 / Th-232 Error	CaCO %	Org. C %	Age y. C-14
Unit I											
1445 P	0- 30	2202.3±88.09	50.05±2.00	2496.9±93.80	1.13±0.06	91.1±16.94	171.1±23.22	1.88±0.43	58.0	6	~1,500
1462	10- 30	1948.8±139.43	44.29±3.17	2171.4±147.17	1.11±0.11	100.4±9.71	211.1±14.07	2.10±0.25	63.0	6	~1,500
Unit II											
1474	40- 50	1015.0±11.12	23.07±0.25	1170.1±11.94	1.15±0.02	123.9±4.77	250.7±6.79	2.02±0.09	8.42	17	~5,000
1445	40- 60	874.3±10.34	19.87±0.23	995.4±11.04	1.14±0.02	86.5±6.62	153.0±8.93	1.77±0.17	8.42	16	~5,000
Unit III											
1445	70- 90	564.6±13.01	12.83±0.30	650.3±13.96	1.15±0.04	157.7±5.59	186.5±6.08	1.18±0.06	46.0	2	~8,000
1462	100-120	565.9±20.56	12.86±0.47	637.5±21.82	1.13±0.06	148.8±3.29	194.9±3.77	1.31±0.04	27.0	~2	~8,000
1474	160-170	104.6±9.96	2.66±0.23	118.5±10.96	1.13±0.14	146.7±3.28	146.5±3.28	1.00±0.03	25.0	1	~10,000
1474	540-550	119.3±5.73	2.71±0.13	109.3±5.49	0.92±0.06	259.5±10.92	262.1±10.97	1.01±0.06	17.0	0.5	~16,000
Clay 1462 (turbidite)	60- 80	265.7±10.37	6.04±0.24	252.6±10.11	0.95±0.05	185.3±5.50	157.6±5.07	0.85±0.04	18.0	~3	

* on carbonate-free basis.

TABLE 6

MINOR AND TRACE ELEMENTS

	percent						ppm											
	SiO_2	TiO_2	Fe	Al_2O_3	MnO	P_2O_5	B	Ba	Co	Cr	Cu	La	Mo	Ni	Sc	V	Y	Zr
Unit I																		
1445 P 0-30	15.0	0.16	1.8	3.0	0.05	-	80.0	450.0	25.0	25.0	25.0	14.0	95.0	55.0	6.0	80.0	19.0	35
1462 10-30	15.0	0.18	1.5	4.0	0.05	-	190.0	520.0	55.0	220.0	32.0	12.0	32.0	50.0	5.0	67.0	16.0	27.0
Unit II																		
1474 40-50	30.0	0.45	3.4	9.0	0.047	-	200.0	1000.0	27.0	102.0	150	30.0	182.0	167.0	13.0	275.0	25.0	77.0
1445 40-60	-	-	3.7	9.7	0.09	-	250.0	1200.0	25.0	85.0	145.0	17.0	105.0	150.0	15.0	300.0	200.0	100.
Unit III																		
1445 70-90	30.0	0.40	24.0	9.0	0.08	-	90.0	350.0	11.0	50.0	30.0	18.0	<30	45.0	8.0	70.0	18.0	65.
1462 100-120	40.0	0.47	3.3	12.0	0.06	-	125.0	105.0	20.0	67.0	43.0	27.0	32.0	75.0	9.0	110.0	20.0	122.
1474 160-170	40.0	0.65	4.7	11.0	0.13	-	75.0	350.0	18.0	140.0	50.0	25.0	<30	150.0	15.0	120.0	20.0	90
540-550	55.0	0.75	4.8	14.0	0.12	-	70.0	400.0	19.0	200.0	35.0	35.0	<30	130.0	16.0	130.0	30.0	125.

TABLE 7

P6507-15

Depth	ppm													%					
	B	Ba	Co	Cr	Cu	La	Mo	Ni	Sc	V	Y	Zr	Zn	SiO_2	TiO_2	Fe	Al_2O_3	MnO	P_2O_5
31-39	160	1725	27.5	72	105	25	52	112	12	177	25	85	120	35	.47	3.95	10	.06	.15
71-79	187	425	17.5	87	122	19	87	117	12	200	17	77	95	35	.47	3.35	11	.04	.13
121-129	141	525	17.0	130	50	35	<30	80	16	130	25	100	-	50	.75	5.40	15	.15	.14
301-309	122	500	12.5	115	35	52	<30	60	17	110	37	222	90	47	.95	4.35	17	.06	.15
601-605	90	500	13.0	110	27	40	<30	62	14	107	30	132	120	50	.82	4.00	13	.08	.10

TABLE 8
Mediterranean Sea
32° 50' N, 32° 00' E

Depth cm.	U-238* Error d/h/g	U-238 ppm	U-234* Error d/h/g	$\frac{U\text{-}234}{U\text{-}238}$	Th-232* Error d/h/g	Th-230* Error d/h/g	$CaCO_3$ %	Org. C
3-10	110.6±8.2	2.5	118.0±8.5	1.07	108.7±12.1	236.4±17.8	48.0	0.36
71-79	154.5±4.8	3.5	145.8±4.7	0.94	93.4±4.0	135.6±4.8	14.0	0.57
161-169	105.7±6.7	2.4	106.2±6.7	1.00	130.0±7.9	203.3±9.9	37.0	0.29
201-209	77.5±3.0	1.8	80.3±3.1	1.04	93.0±4.2	121.0±4.8	11.5	0.39
381-388	169.0±4.6	3.8	183.7±4.8	1.09	93.3±4.1	118.8±4.6	13.5	0.47
701-709	1302.6±8.5	29.6	1424.1±8.9	1.09	234.5±4.4	710.1±7.7	8.0	2.60

* corrected for carbonate free basis.

TABLE 9

DESCRIPTION OF LAKES

Lake	Position	Max. depth (m)	Area (Km^2)	Surface elev. (m)
Powell Lake, B.C. (south basin (Williams et. al., 1961)	49°55'N 124°30'W	358	23	46
Tokkevatn, South Norway (Rorholt Fjord) (Strøm, 1957)	59°01'N 13°20'E	150	8	60
Botnvatn, North Norway (Strøm, 1961)	67°06'N 15°30'E	117	2	12
Rorhopvatn, North Norway (Strøm, 1961)	68°19'N 14°52'E	96	0.5	3
Framvaren, South Norway (Strøm, 1936, 1948)	58°09'N 6°45'E	180	6	0

TABLE 17

- BOTNVATN -

67° 06' N 15° 30' E

Sta.	U-238 Error d/h/g	U-234 Error d/h/g	U-238 Error ppm	$\frac{\text{U-234}}{\text{U-238}}$ Error	Th-232 Error d/h/g	Th-230 Error d/h/g	$\frac{\text{Th-230}}{\text{Th-232}}$ Error	Pa-231 Error d/h/g	Org. C %
E	261.9±5.6	288.3±5.9	5.95±0.13	1.10±0.03	212.6±6.9	205.6±6.8	0.97±0.04	11.68 0.59	2.33
D	252.6±7.6	280.1±8.0	5.74±0.17	1.11±0.05	241.7±7.2	218.2±6.9	0.90±0.04		2.82
C	152.0±5.1	163.5±5.3	3.45±0.12	1.08±0.05	153.0±6.0	132.6±5.6	0.87±0.05		0.92
B	731.4±15.7	748.6±15.9	16.62±0.36	1.02±0.03	301.4±6.9	295.4±6.8	0.98±0.03		1.47
Nose	253.4±6.2	233.4±6.1	5.35±0.14	0.99±0.04	399.1±11.5	375.7±11.2	0.94±0.04		1.20

TABLE 18

Blankvatn

Depth	U-238 d/h/g	U-238 ppm	U-234 d/h/g	$\frac{U-234}{U-238}$	Th-232 d/h/g	Th-230 d/h/g	$\frac{Th-230}{Th-232}$	$CaCO_3$ %	Org. C %
B	313.0	7.11	495.7	1.58	44.0	62.0	1.41	-	-
A	529.0	12.02	980.0	1.85	48.0	96.0	2.00	7.2	19.71

TABLE 19

Framvarn

Depth	U-238 d/h/g	U-238 ppm	U-234 d/h/g	U-234 / U-238	Th-232 d/h/g	Th-230 d/h/g	Pa-231 d/h/g	Th-230 / Pa-231	$CaCO_3$ %	Org. C %
E	1079.7	24.5	1156.0	1.07	86.0	57.0	17.5	3.26	-	-
D	4872.0	110.7	5679.5	1.17	129.0	110.0	18.9	5.82	-	-
B	511.0	11.6	631.6	1.24	162.0	88.0	9.1	9.67	-	-
A	NM	-	NM	-	66.4	56.7	11.6	4.89	0.57	0.24

TABLE 20

Rorhopvatn

Depth	U-238 d/h/g	U-238 ppm	U-234 d/h/g	U-234/U-238	Th-232 d/h/g	Th-230 d/h/g	Th-230/Th-232	$CaCO_3$ %	Org. C %
C---D	132.0	3.00	160.0	1.21	19.37	16.30	0.84	-	-
B	282.0	6.40	320.0	1.13	20.80	22.60	1.09	10.49	4.41
A	295.0	6.70	331.3	1.12	25.30	27.28	1.08	-	-
Nose	218.6	4.97	253.6	1.16	56.30	56.00	0.99	3.44	5.91

TABLE 21

Rorholfjord

59°01'N 13°20'E

Sta. 2	U-238 Error d/h/g	U-234 Error d/h/g	U-238 Error ppm	U-234/U-238 Error	Th-232 Error d/h/g	Th-230 Error d/h/g	Th-230/Th-232 Error	Org. C %
G	744.7±10.8	788.9±11.1	16.92±0.25	1.06±0.02	530.5±15.7	620.7±17.0	1.17±0.05	0.89
E	654.7±10.9	621.3±10.6	14.88±0.25	0.95±0.02	466.0±14.9	544.6±16.1	1.17±0.05	
C	589.8± 9.8	608.6± 9.9	13.40±0.22	1.03±0.02	623.9±12.0	693.8±12.7	1.11±0.03	
A	601.1± 9.9	597.5± 9.9	13.66±0.23	0.99±0.02	469.0±12.4	546.1±13.4	1.16±0.04	

TABLE 22

Powell Lake

Depth	U-238 d/h/g	U-238 ppm	U-234 d/h/g	$\frac{U\text{-}234}{U\text{-}238}$	Th-232 d/h/g	Th-230 d/h/g	$\frac{Th\text{-}230}{Th\text{-}232}$	$CaCO_3$ %	Org. C %
L + M	1064	24.2	894.8	0.84	88.0	144.0	1.64	-	8.1
K	1036	23.5	954.0	0.92	58.0	69.6	1.20	-	-
J	362	8.2	354.0	0.98	38.0	83.0	2.18	0.86	6.9
C	1306	29.7	1238.0	0.95	241.0	244.0	1.01	-	2.4

TABLE 23

Depth cm.	Oak Ridge	Miami
75-79	2.39±0.03	2.67±0.24
231-239	2.38±0.03	2.59±0.21
401.5-409.5	2.31±0.03	2.67±0.28
451-459	2.10±0.03	2.25±0.21

Core P6304-1: Concentration (ppm) of U^{238} in selected samples by isotope dilution Oak Ridge and alpha spectrometry (Miami).

TABLE 24

P6304-8

15°59'N 69°20'W

Depth	ppm													%				
	B	Ba	Be	Co	Cr	Cu	La	Ni	Sc	Sr	V	Y	Zr	MnO	Fe	MgO	TiO_2	$CaCO_3$
21	50	200	0.7	9	30	45	9	45	6	1200	65	10	35	.15	2.1	1.5	.26	64.3
71	80	190	1.8	20	50	40	20	35	10	1150	85	25	45	.24	2.3	1.7	.38	-
151	60	260	0.8	25	45	130	20	70	9	780	80	20	40	.36	2.7	1.8	.32	67.8
331	75	350	1.1	20	45	50	20	45	1.0	830	90	20	45	.20	2.9	-	.38	-
571	75	400	0.9	20	40	100	15	70	8	830	90	15	40	.26	3.4	1.6	.38	-

TABLE 25

P6510-4

Depth	ppm													%					
	B	Ba	Co	Cr	Cu	La	Mo	Ni	Sc	V	Y	Zr	Zn	SiO_2	TiO_2	Fe	Al_2O_3	MnO	P_2O_5
3-10	77	197	13.5	57	30	22	<30	50	10	60	21	110	100	25	.60	3.35	7	.37	.12
71-79	105	250	27.5	95	42	37	<30	92	16	100	27	172	87	42	1.00	5.50	15	.16	-
161-169	87	225	15.5	65	25	27	<30	50	11	65	25	187	64	35	.77	3.55	10	.20	.12
201-204	92	250	25.0	92	35	40	<30	67	16	105	27	22	-	42	1.17	6.20	13	.19	.19
381-384	117	300	30.0	102	60	45	<30	82	16	115	30	195	90	42	1.15	4.35	14	.19	.17
701-709	164	1025	21.5	80	55	40	137	80	15	122	30	155	80	37	.77	5.35	13	.07	.10

TABLE 26

MSN-96

	ppm													%							
Depth	B	Ba	Be	Co	Cr	Cu	La	Ni	Sc	Sr	V	Y	Zr	SiO_2	TiO_2	Al_2O_3	Fe	CaO	K_2O	Mn	P_2O_5
0 - 4	110	2200	2	33	60	125	17	120	15	250	105	17	95	53.3	0.87	10.1	4.4	6.1	1.9	.32	.15
4 - 8	85	1950	2	30	55	100	12	110	12	350	90	15	80	50.0	0.67	9.2	3.9	8.3	1.8	.35	.14
8 - 12	100	2500	2	30	60	100	17	98	15	300	100	17	100	52.7	0.76	10.1	4.2	5.9	1.9	.35	.15
12 - 16	110	2300	2	22	55	75	16	87	14	200	90	15	92	53.8	0.65	10.4	4.1	2.2	1.9	.28	.15
16 - 20	115	2500	2	27	50	75	17	63	15	210	110	16	100	57.9	0.74	10.3	4.2	1.9	1.9	.25	.14
20 - 24	115	1950	2	36	55	75	17	80	13	200	95	15	95	58.0	0.64	10.3	4.1	2.0	1.8	.38	.15
24 - 28	105	2100	2	33	65	130	13	110	13	240	120	13	100	59.0	0.71	9.4	3.8	1.9	1.8	High	.20
28 - 32	100	2300	2	26	70	90	14	60	12	240	105	12	110	63.0	0.55	10.2	4.0	2.1	1.9	.36	.15
32 - 36	105	2400	2	27	60	70	11	55	10	200	100	13	105	62.3	0.69	9.7	3.9	2.0	1.8	.30	.10
36 - 40	100	2500	2	32	60	[illegible]	10	60	11	210	105	13	100	55.5	0.61	9.7	3.7	1.7	1.7	High	.15
40 - 44	105	2300	2	23	65	80	12	55	12	210	100	12	95	60.2	0.64	9.0	3.6	1.7	1.7	.33	.10
44 - 48	120	2400	1.5	15	50	90	<5	55	10	160	95	10	90	61.7	0,53	8,7	3.6	1.5	1.6	.40	.15
48 - 52	105	2100	2	8	65	65	<5	40	13	130	85	8	85	64,2	0,61	8,8	3.4	1.5	1.7	.06	.09
52 - 56	150	1750	2	14	64	73	11	44	14	170	90	13	95	62,7	0,53	9,8	3.4	1.5	1.7	.10	.11
56 - 60	105	2300	2	15	75	85	<5	50	13	180	95	9	85	64.2	0,52	9.3	3.5	1.6	1.7	.18	.11
60 - 64	100	2000	2	23	65	80	<5	50	12	170	85	9	80	64.5	0,58	7.9	3.2	1.3	1.47	.29	.12
64 - 68	95	1900	2.5	23	75	80	<5	55	14	190	90	11	90	65.3	0,55	8.3	3.4	1.4	1.57	.29	.13
68 - 72	95	1950	1.5	22	50	80	<5	55	11	145	80	8	75	64.7	0,53	8.0	3.6	1.5	1.61	.29	.12
72 - 76	110	1800	2	20	60	75	<5	49	12	170	80	27	78	65.3	0,57	8.3	3.4	1.3	1.6	.31	.14
76 - 80	110	1900	3	16	75	82	<5	53	14	200	93	28	88	64.7	0,52	8.7	3.6	1.3	1.6	.33	.14
80 - 84	100	1750	2	9	60	57	<5	37	12	170	80	35	78	66.5	0.60	8.3	3.3	1.3	1.5	.16	.10
84 - 88	120	1600	2	9	60	54	<5	49	12	135	78	24	80	62.6	0.48	7.3	3.1	1.3	1.5	.16	.11
88 - 92	115	1900	2	8	62	82	<5	54	13	160	82	23	84	63.0	0.57	7.5	3.4	1.4	1.5	.19	.12

TABLE 27

Rorhopvatn

Depth	ppm													%			
	B	Ba	Be	Co	Cr	Cu	La	Ni	Sc	Sr	V	Y	Zr	MnO	Fe	MgO	TiO_2
C	67	1300	.87	5.0	30	15	38	14	14	320	37	23	115	.10	5.7	1.8	.73
B	82	1550	1.1	9.0	35	24	54	19	20	140	58	27	73	.14	5.4	2.3	1.1
A	100	1950	1.0	6.0	42	12	37	16	22	350	50	23	100	.15	5.4	1.9	1.3
Nose	47	2400	1.0	<5	16	24	18	14	13	320	26	16	17	.09	4.0	0.65	.55

TABLE 28

Rorholtfjorden

Depth	ppm													%			
	B	Ba	Be	Co	Cr	Cu	La	Ni	Sc	Sr	V	Y	Zr	MnO	Fe	MgO	TiO_2
G	35	530	4.5	15	50	35	100	35	13	165	70	85	190	.10	4.8	2.3	.83
F	25	550	4.5	15	55	35	100	30	12	115	70	85	200	.10	5.1	2.5	.85
E	30	600	4	15	45	25	98	30	12	140	65	83	165	.095	4.5	2.0	.83
D	32	600	4	14	50	20	95	25	12	150	70	83	170	.10	4.4	2.2	.83
C	37	580	4.5	16	45	25	105	35	12	135	70	85	210	.092	4.6	2.1	.84
B	30	600	4	16	45	20	93	30	12	135	70	85	200	.097	4.4	2.2	.88
A	35	600	4	16	55	25	100	30	13	130	70	85	220	.10	4.4	2.2	.88
Nose	37	540	4	12	40	45	87	30	11	115	60	75	200	.092	4.1	2.2	.49

TABLE 29

Framvarn

Depth	ppm													%			
	B	Ba	Be	Co	Cr	Cu	La	Ni	Sc	Sr	V	Y	Zr	MnO	Fe	MgO	TiO_2
B	60	870	3	17	85	45	75	57	15	180	100	55	190	.068	5.6	3.1	1.0
A	110	890	3	18	70	55	80	50	17	185	80	65	220	.058	5.5	2.6	.91
Nose	55	1100	3	17	70	50	80	33	17	200	100	70	240	.095	5.6	2.7	.93

TABLE 30

Botnvatn

Depth	ppm													%			
	B	Ba	Be	Co	Cr	Cu	La	Ni	Sc	Sr	V	Y	Zr	MnO	Fe	MgO	TiO_2
E	62	660	2.6	20	110	49	48	51	16	230	130	41	296	.08	5.0	2.8	1.1
B	71	690	3.0	15	100	38	59	49	14	210	120	40	300	.11	4.4	2.6	.90
A	30	350	2.5	5	15	45	30	45	18	150	20	25	42	.05	1.4	.55	-
Nose	110	1050	3.5	15	100	40	75	40	15	290	140	42	180	.11	4.0	3.1	-

TABLE 31

Powell Lake

Depth	ppm													%			
	B	Ba	Be	Co	Cr	Cu	La	Ni	Sc	Sr	V	Y	Zr	MnO	Fe	MgO	TiO_2
H	110	550	1.2	23	38	84	26	22	13	300	110	28	80	0.12	5.4	2.6	.48
F	90	350	1.5	17	25	110	20	15	6	330	85	16	20	0.075	4.5	3.2	.30
E	90	550	1.5	17	25	110	20	15	6	330	85	16	20	0.075	4.4	1.3	.80
C	65	500	1.5	17	30	100	21	17	7	200	100	15	20	0.086	4.6	.086	.42
A	110	610	1.3	20	35	36	24	20	10	320	90	21	90	0.11	5.2	3.2	.40

TABLE 32

Blankvatn

Depth	ppm														%			
	B	Ba	Be	Co	Cr	Cu	La	Mo	Ni	Sc	Sr	V	Y	Zr	TiO_2	Fe	MnO	MgO
B	32	200	2.25	< 5	30	32	50	14	23	3.5	165	25	27	40	0.27	1.3	0.10	0.87
A	28	290	2.33	< 5	18	33	38	30	18	2.7	167	19	26	40	0.12	1.3	0.05	0.55
Nose	32	440	3.75	9	38	65	52	195	35	7.0	310	46	41	140	1.02	3.1	0.10	1.20

TABLE 33

P-6304-9

Depth	Co/Ni	Fe/Mn	Co/Mn
22-36	0.20	62.50	0.012
62-76	0.18	31.25	0.019
82-86	0.67	13.16	0.010
231-234	0.43	13.04	0.006
532-536	0.67	11.11	0.007
608	0.50	7.14	0.004
861-869	0.40	16.67	0.007

TABLE 34

P-6304-8

Depth	Co/Ni	Fe/Mn	Co/Mn
21	0.20	19.09	0.008
71	0.57	12.78	0.011
151	0.36	9.64	0.009
331	0.44	19.33	0.013
571	0.28	17.00	0.010

TABLE 35

P-6507-15

Depth	Co/Ni	Fe/Mn	Co/Mn
31-39	0.24	79.00	0.055
71-79	0.15	111.67	0.058
121-129	0.21	49.09	0.015
3[illegible]-309	0.21	87.00	0.025
6[illegible]	0.21	66.67	0.022

TABLE 36

MSN - 96

	Depth	Co/Ni	Fe/Mn	Co/Mn
	0-8	0.27	12.4	0.009
	16-28	0.38	<4.0	<0.003
	28-36	0.46	11.8	0.008
(High in OPAL)	36-44	0.47	<3.6	<0.003
	48-56	0.26	34.0	0.014
	56-64	0.38	30.0	0.079
	64-72	0.40	29.2	0.079
(High in OPAL)	72-80	0.35	10.9	0.006
	80-92	0.19	19.4	0.005

TABLE 37

Powell Lake

Depth	Co/Ni	Fe/Mn	Co/Mn
H	1.04	60.00	0.025
F	1.13	75.00	0.028
E	1.13	73.33	0.028
C	1.00	65.71	0.024
A	1.00	65.00	0.025

TABLE 38

Botnvatn

Depth	Co/Ni	Fe/Mn	Co/Mn
E	0.39	83.33	0.033
B	0.31	55.00	0.019
A	0.11	35.00	0.012
Nose	0.37	50.00	0.019

TABLE 39

Rorhopvatn

Depth	Co/Ni	Fe/Mn	Co/Mn
C	0.36	71.25	0.006
B	0.47	49.09	0.008
A	0.37	49.09	0.005
Nose	<0.36	57.14	<0.007

TABLE 40

Rørholtfjorden

Depth	Co/Ni	Fe/Mn	Co/Mn
G	0.43	60.00	0.019
F	0.50	63.75	0.019
E	0.50	64.28	0.021
D	0.56	55.00	0.017
C	0.46	65.71	0.023
B	0.53	62.86	0.023
A	0.53	55.00	0.020
Nose	0.40	58.57	0.017

TABLE 41

Blankvatn

Depth	Co/Ni	Fe/Mn	Co/Mn
B	<0.22	16.25	<0.006
A	<0.28	32.50	<0.012
Nose	0.26	38.75	0.011

TABLE 42

	Co/Ni	Fe/Mn	Co/Mn	Ni/Mn
Powell Lake	1.06	67.81	0.026	0.026
Botnvatn	0.27	57.78	0.021	0.080
Rorhopvatn	0.40	56.48	0.006	0.016
Framvarn	0.33	124.75	0.039	0.106
Rørholtfjorden	0.50	60.94	0.020	0.044
P6304-8 (Caribbean)	0.37	15.57	0.010	0.029
P6510-4 (Mediterranean)	0.31	26.9	0.015	0.040
MSN-96 (Pacific)	0.35	16.0	0.013	NM
P6507-15 (Black Sea)	0.20	78.69	0.035	0.087
Clays*	0.21	-	0.030	0.14
Igneous rocks*	0.31	-	0.018	0.058
Pacific*	0.94	-	0.013	0.019
Mediterranean*	0.31	-	0.017	0.054
Black Sea*	0.24	-	0.021	0.087
Caribbean*	0.28	-	0.014	0.049

* taken from Carvajal (1968).

TABLE 43

Correlation Coefficients: P6507-15

Fe - MnO	+0.957
Co - Fe	-0.072
Ni - Fe	-0.406
Co - MnO	-0.102
Ni - MnO	-0.360
Co - Ni	+0.759

TABLE 44

Correlation Coefficients: P-6510-4

Fe - MnO	+0.679
Co - Fe	+0.780
Ni - Fe	+0.785
Co - MnO	+0.949
Ni - MnO	+0.795
Co - Ni	+0.930

TABLE 45

Correlation Coefficients:	Rorhopvatn
Fe - MnO	+0.534
Co - Fe	+0.317
Ni - Fe	+0.356
Co - MnO	+0.658
Ni - MnO	+0.767
Co - Ni	+0.987

TABLE 46

Correlation Coefficients: Rorholtfjord (Tokke)

Fe - MnO	+ 0.574
Co - Fe	-0.063
Ni - Fe	-0.019
Co - MnO	+0.431
Ni - MnO	+0.341
Co - Ni	+0.678

TABLE 47

Correlation Coefficients: Botnvatn

Fe - MnO	+0.724
Co - Fe	+0.395
Ni - Fe	+0.393
Co - MnO	+0.622
Ni - MnO	- 0.161
Co - Ni	+0.395

Geochemistry of Uranium and Trace Elements in the Sediments of the Norwegian Fjords and the Black Sea*

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Abstract

Concentrations of the ferride metals Co, Ni, Fe, Mn and U, have been determined in fjords of Norway and British Columbia, which have trapped sea water on the bottom. The concentrations of these elements have also been determined in cores taken from the Black Sea. The ratios of pairs of the ferride elements, Co/Ni, Ni/Fe, Co/Mn, were determined, and also their correlations. The most important factors responsible for the distribution and concentration of these elements are the stability of their sulfides, dilution and "mixing effects" with inorganic and organic matter.

Introduction

During and after the last glaciation, large areas in the northern hemisphere were flooded with sea water. When the water retreated, lake basins which had been flooded were left filled with sea water. When communication with the sea was restricted due to isostatic elevation of the land, the saline water filling the bottom was overlane with fresh water. There are a few lakes which contain "trapped sea water" on the bottom.

The characteristic features of these lakes are complete disappearance of sulfates, and the appearance of H_2S and sulfides. Methane is present in great amounts and there is also some ammonia. The bottom of the lakes are catchments for organic matter.

This paper reports the environmental influence on the ferride elements and uranium in lakes with trapped sea water at the bottom and on the uranium concentration and distribution in these lakes and in cores taken from the Black Sea.

Material and Analytical Methods

Rorholtfjord[1] (part of Lake Tokke): The surface is 60 m above the present level; no rivers enter it. Water from surface down to 80 m is fresh water, subject to normal circulation in spring and autumn; water from 80 to 134 m is slightly saline, the partial renewal being through turbulence. This layer effectively protects the bottom layer from any direct contact with fresh water and from disturbance from turbulence. Interchange between the second and third layer is by diffusion only, which is a slow process. This lake is the most stagnant of the lakes investigated by Strøm (1957, 1961). Maximum salinity is 16.8 °/oo.

Framvarn: This lake is separated from Ytre Lyngadsfjord by a 4.3 m threshold leading to a chain of three fjords. Coastal water has access to the outermost. Communication with Framvarn is through a narrow canal, 2 m deep. It lies near the center of a distinct intrusion of farsundite, a rock that ranges from monzonite to alkali granite. In Framvarn, 61 cm of putrid mud rest on hard, stiff clay. The clay is probably not intact glacial clay, but reworked or redeposited. The black mud represents present sedimentation, while the clay represents sediments of the last exchange of the fjord with sea water (Strøm, 1936). This fjord is occasionally flooded with sea water. The salinity at 160 m has been found to be 24.1 °/oo.

Rorhopvatn, Lofoten and Botnvatn, Salten, Northern Norway, are uplifted fjords, both smaller and younger than Rorholtfjord. Salinities in the bottom are 28.0 °/oo and 13.4 °/oo, respectively.

Powell Lake is a fjord lake in Mesozoic British Columbia. The oxygen depleted bottom water has a pH of 6.7-6.9, and a very high total sulfide concentration of about 89 mg per liter, measured in situ by Williams (1961). Salinity is zero from surface to a depth of 280 m and increased to 16.6 °/oo at the depth of 330 m. The organic matter, from surface to about 30 cm, has been dated by the C-14 method by Östlund (1965) and found to be 7,680±120 years B.P. Mathews (personal communication) estimated the age of freshly deposited organic matter in Powell Lake to 10,000 B.P. Location of the lakes are in Figs. 1, 2, and 3.

All the cores from the fjords are gravity cores. Each sample was sealed in glass jars, each of which contained 17 cm of core material. The top of the sediments were unavoidably lost in recovering the corer. For this reason the notation of Dr. Reitzel was adopted; this notation is with alphabetic letters, the first letter A denotes the deepest sediment layers, and the layers of the highest letter is the nearest to the top. Each letter represents approximately 17 cm of the depth. These lakes have been chosen by Dr. Reitzel for the measurement of heat conductivity of the bottom sediments, because the bottom is free from seasonal temperature changes imposed from above.

The results of Dr. Reitzel's heat conductivity measurements (personal communication) are: there is no important lateral variation, the average bottom gradients in the deep part of the lakes are well determined, there is no significant change of gradients with depths in the upper 2 1/2 m of sediments. All samples smelled of H_2S. Methane was obvious from the pressure when the jars were opened. Chlorinities were determined by electric conductivity, and salinities calculated by the equation 0.03+1.805 x Chlorinity (Sverdrup, 1964). Trace elements and $CaCO_3$ were determined by Atomic Absorption with an accuracy of 2-5%. Organic carbon was determined by dry combustion. The method to determine uranium was given in Technical Report No. 69070, Institute of Marine Sciences, University of Miami, 1969.

The Black Sea

The Black Sea is the largest anoxic basin containing salt water in the bottom; the only connection with the Mediterranean Sea is long, narrow and shallow through the Bosporus.

Stratification of the water preserves the anoxic water from mixing with fresh water. The influx of fresh water is small in proportion to the total volume of the Black Sea so that complete renewal of the water below 30 m would take about 2500 years. This is in good agreement with Östlund's (1965) dating of the deep Black Sea water at 2230 to 2260 years B.P.

In July-August 1965, during a cruise of the R/V JOHN PILLSBURY of the Institute of Marine Science, University of Miami, several cores have been taken. Core P6507-15 (42°54'N, 32°35'E) has been analyzed for uranium and trace elements.

Three cores from the cruise of Atlantis II, April-May 1969 of the Woods Hole Oceanographic Institution have also been studied. The three cores are numbered 1474 (42°23'N, 37°36'E), 1462 (43°01'N, 33°03'E) and 1445 (43°08'N, 31°27'E). Location of the cores is given in Fig. 4.

Results and Discussion

Uranium: The uranium contents of the fjords and of the Black Sea cores are presented in Tables 1 through 6. The uranium concentrations of the fjords are high, the activity ratio of U-234/U-238 is higher than one.[2] In the narrow lake Botnvatn uranium is lower, probably due to dilution with lithogenic matter.

It was indicated (Dorta and Rona, 1971) that uranium is a useful marker for geological events. In the four Black Sea cores, uranium concentration and activity ratios of U-234/U-238 follow the sedimentation pattern set by micropaleontology and mineral features (Ross and Degens, 1970). Three distinct sedimentary units can be correlated in all four cores, which are several hundred kilometers apart.

In Unit I, present salinity is already established; in Unit II salinity is lower; in Unit III full fresh water conditions prevail around 9,000 to 10,000 years B.P. where only old coccolith have been found transported from land by rivers or turbidity currents.

These three units can also be correlated by their uranium content. In Unit I the uranium concentration is high; in Unit II, it is somewhat lower and the activity ratio U-234/U-238 is higher than one, i.e. oceanic; in Unit III the uranium concentration is low, similar to that of pelagic clay (Table 6), with an activity ratio of U-234/U-238 less than one and a low concentration of organic matter (Rona and Joensuu, 1972).

Similar units can be recognized in core P6507-15, the uppermost 30 cm have not been analyzed, but sediments from 30 to 70 cm are obviously equivalent to Unit II and sediments below 120 cm to 600 cm are equivalent to Unit III in the four Woods Hole cores. The correlation of uranium concentrations in four cores taken hundreds of kilometers apart testify to the uniform sedimentation in most of the Black Sea (Fig. 4).

The uranium concentration and U-234/U-238 activity ratios are strikingly different in sediments taken from the open sea, which has free circulation, from that in sediments of anoxic basin (Table 7). The uranium concentration is 2-3 ppm in all the layers and the activity ratio U-234/U-238 is one or less than one (Table 8).

It is suggested that in reducing environments with H_2S present and rich in organic matter, low Eh and a pH of 7 or lower, uranium is removed from the water as U^{+4}. Latimer (1964) gives a value of -0.33 for the reduction potential necessary for the reaction $UO_2^{++} \rightarrow U^{+4}$. Piper (1971) measured an Eh value of the water in Framvarn at 160 m (almost the water sediment interface) of -0.2. However, the redox potential is probably lower in the presence of organic matter. If ferrous ions are present, reduction of uranium from the six to the four valence state is favored as suggested by Adams et al. (1959). The redox potential -0.3 necessary for the reaction $UO_2^{++} \rightarrow U^{+4}$ is close to the redox potential necessary to reduce ferric to ferrous ions (Pourbaix, 1949). Agamirov (1963) suggested this same mechanism. It is obvious from the data that in these anaerobic basins uranium is removed from the water.

Manheim (1961) suggests a different mechanism for the high uranium concentration of the Baltic Sea. Uranium concentration is higher in the transition zone at the periphery of the basin than in the center where organic matter is high. He can explain this situation partly, at least, by the erosion of uranium rich sediment from the shelf during glacial periods and continued redeposition to the present time.

The uranium concentrations in the Black Sea samples (Tables 5 and 6) are the same for corresponding depths in sediments taken from the East -- and from the West, where large rivers enter the Black Sea (Fig. 4).

Trace Elements: In the fjords only the ferrides, Co, Ni, Mn, and Fe are considered in this paper, but molybdenum and copper have also been determined in the Black Sea sediments (Tables 9 through 13).

In anoxic basins with a high amount of H_2S and rich in organic matter, and relatively low Eh, multivalent metallic ions are highly Eh-pH dependent. The equilibrium constant K of the reaction: $H_2S = S + 2H^+ + 2e^-$ and $H_2S_{(Aqu)} = H^+ + HS^-$ is calculated to be 10^{-7} (thermodynamic constant from Latimer, 1964, at a low pH of 7 or less).

All the concentrations of the sulfides also depend on their environment, i.e. on dilution by detrital lithogenic material. The best way to avoid the influence of adjacent environments is to compare two elements taken from the same environment and to consider their stability fields. Eh-pH diagrams are to be found in the literature (Garrels and Christ, 1965; Latimer, 1964). The following discussion in this paper is based on stability fields, taken from a paper by Carvajal and Landergren (1968). Stability fields for Co, Ni, Mn and Fe are given in Figs. 5, 6, 7 and 8.

The CoS and NiS stability fields are almost identical, therefore, the ratios are nearly the same in different environments (Table 14). In sea water this ratio has been found to be 0.17, authigenic minerals should approach that ratio; in the earth crust is 0.31. The Co/Ni ratio of the anoxic sediments of the fjords is around 0.31 or larger, depending on the contribution of detrital material. The Co/Ni ratio in Powell Lake is near to the value of the sediments taken from the Pacific Ocean. The Fe/Mn ratios are different in all the sediments. The sedimentary behavior of manganese is similar to that of iron, but MnS is more soluble than FeS. During weathering MnS goes into solution, and the Fe/Mn ratio is highly dependent on environmental conditions. The Co/Mn and Ni/Mn ratios in the Black Sea core P6507-15 are similar to those of the earth crust: 0.23 and 0.080, respectively (Barth, 1962). The ratios of Co to Mn and of Ni to Mn in Powell Lake are similar to those in sediments taken from the Pacific Ocean; the absolute values for Ni and Co are somewhat higher, which is easily understood bearing in mind the contribution of detrital material in the sediments of the lakes. Molybdenum copper and barium are enriched in organic matter in the Black Sea core

P6507-15. The strong correlation of these elements and uranium with organic matter is presented in Fig. 9.

More information can be obtained by calculating the correlation of any of two ferrides. The interrelationship is calculated by the equation:

$$\text{Correlation coefficient} = \frac{\sum_{1}^{n} X_i \; Y_i}{\sqrt{\sum_{1}^{n} Xj^2 \; \sum_{1}^{n} Yj^2}}$$

(Wiener, 1966), here $X_i \cdots\cdots X_n$ are the numbers of one set and $Y_i \cdots\cdots Y_n$ those of another set.

The numbers must fall between -1 and +1. The values were computed by IBM 360 computer. Correlation coefficients are given in Tables 15 through 18.

It is interesting to note that Co-Ni are strongly correlated in all the samples, and the correlation coefficients are approximately of the same order, except for a lower value for Botnvatn. Obviously the Co-Ni correlation is not affected by environmental factors nor by manganese or iron which are present in overwhelmingly higher concentrations. Fe-Mn correlation is positive and high in all the inland waters. Co-Fe, Ni-Fe, Co-Mn, Ni-Mn are weakly correlated or not at all (Black Sea sediment P6507-15), probably because affected by iron and manganese. The repression of a correlation with manganese, and possibly with iron might be due to the adsorption effects. It was noted before that manganese is a scavenger for many elements (Goldsmith, 1937; Krauskopf, 1957). Colloids of manganese in sea water are negatively charged and adsorb positive ions.

Environmental factors, such as reducing or oxidizing environments and mixing or diluting of authigenic with detrital material, are the main factors influencing the concentrations, ratios and correlations of trace elements in marine sediments as reported here.

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Footnotes

[1] The term fjord is used in Norway not only for arms of the sea but also for fresh water lakes with some salt water in the bottom.

[2] Thurber (1962) found that the activity ratios of U-234/U-238 is about 1.15. In this paper we refer to an activity ratio around this value as oceanic.

Figure Legend

Fig. 1. Geographic location of the Norwegian Fjords.

Fig. 2. Locations of samples taken from Rorholtfjord (Lake Tokke) Botnvatn, Rorhopvatn.

Fig. 3. Geographic location of lakes from British Columbia.

Fig. 4. Location of Black Sea cores.

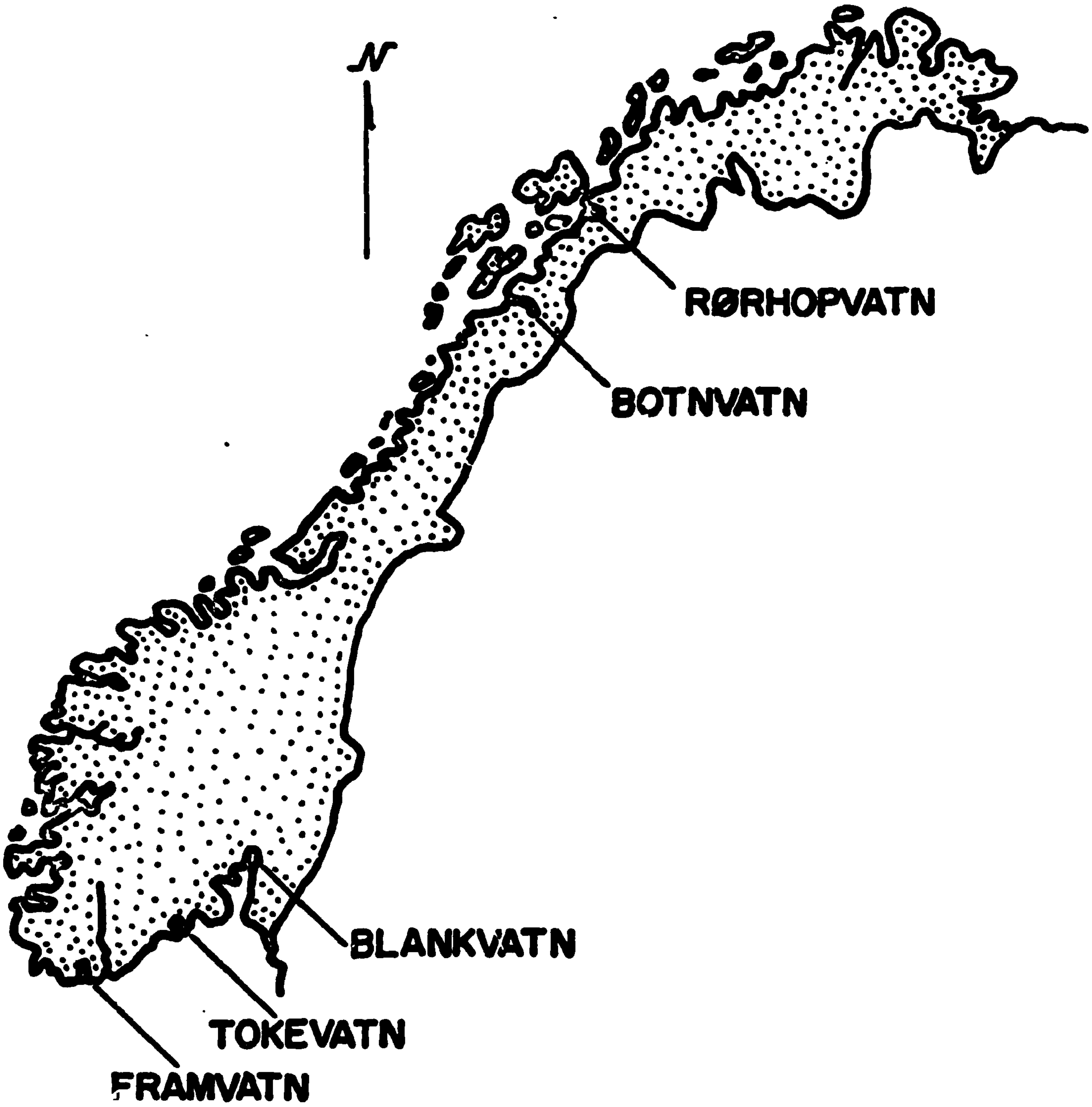
Fig. 5. Eh-pH diagram Cobalt.

Fig. 6. Eh-pH diagram Nickel.

Fig. 7. Eh-pH diagram Manganese.

Fig. 8. Eh-pH diagram Iron.

Fig. 9. Correlations, Molybdenum, Uranium, Copper and Organic Carbon.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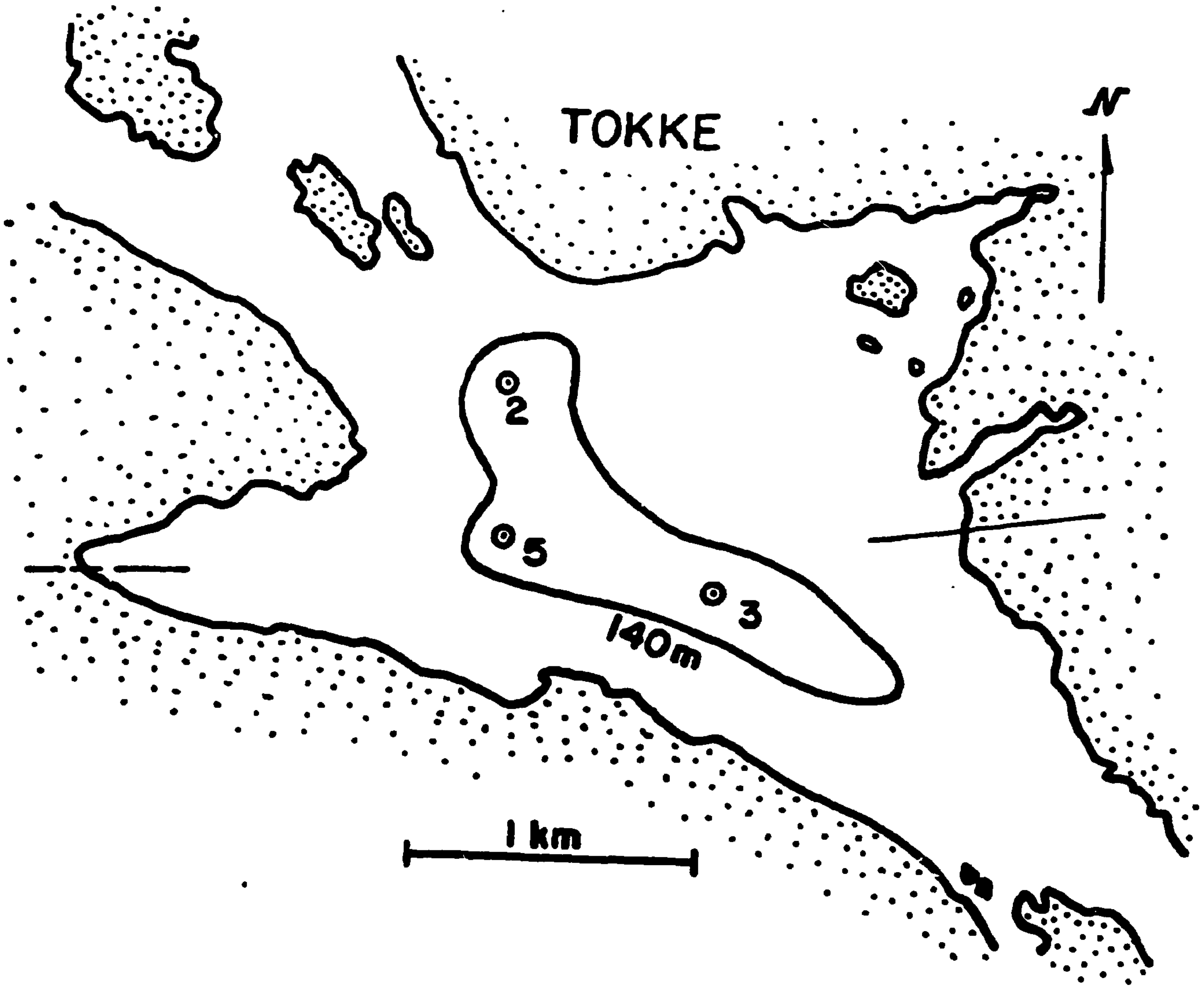

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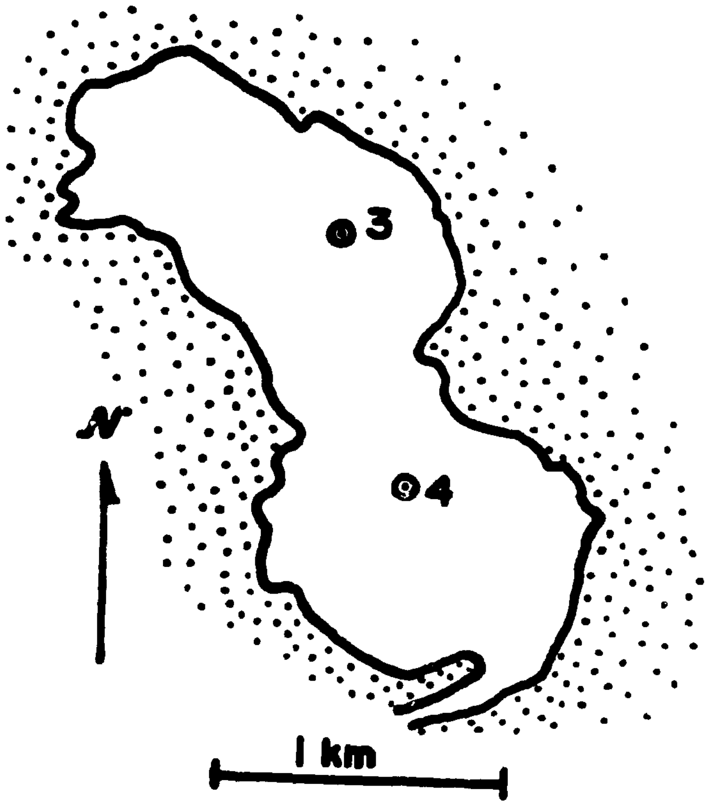

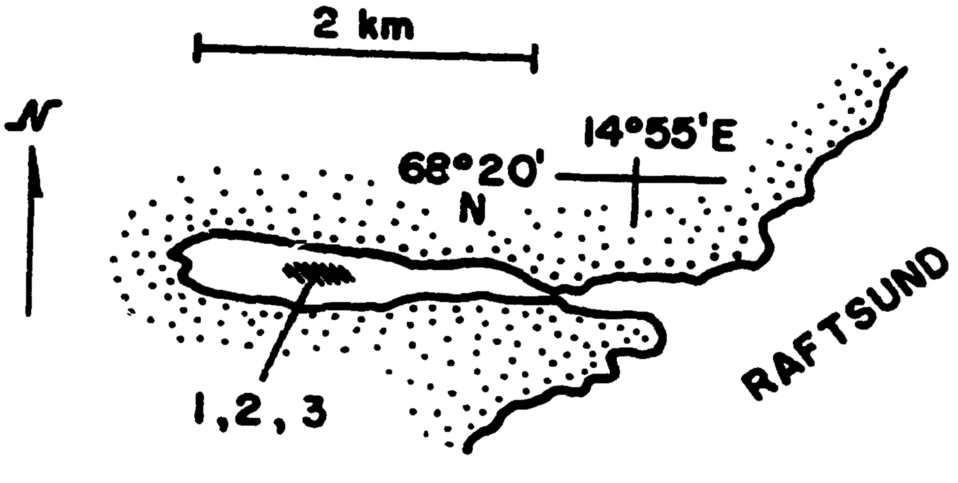

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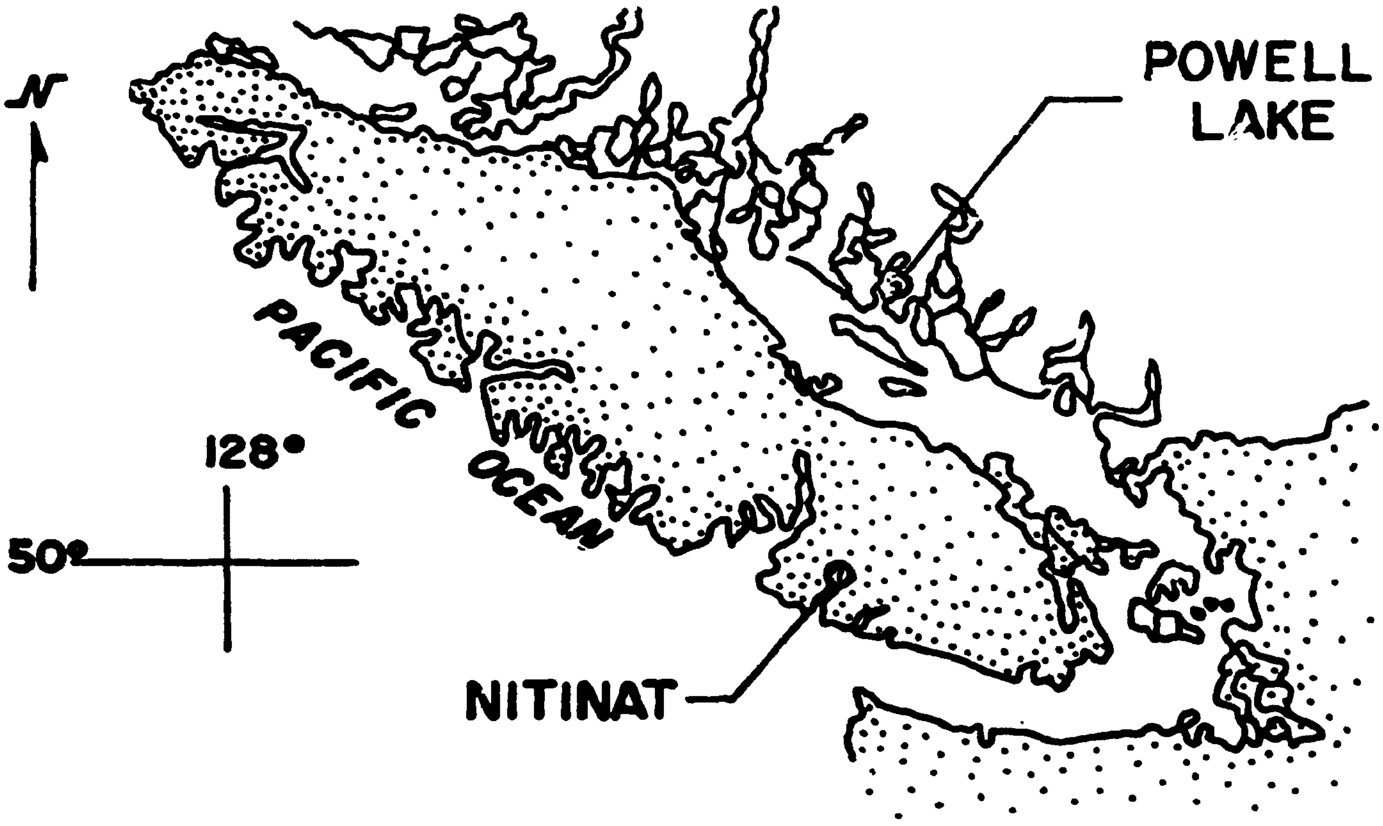
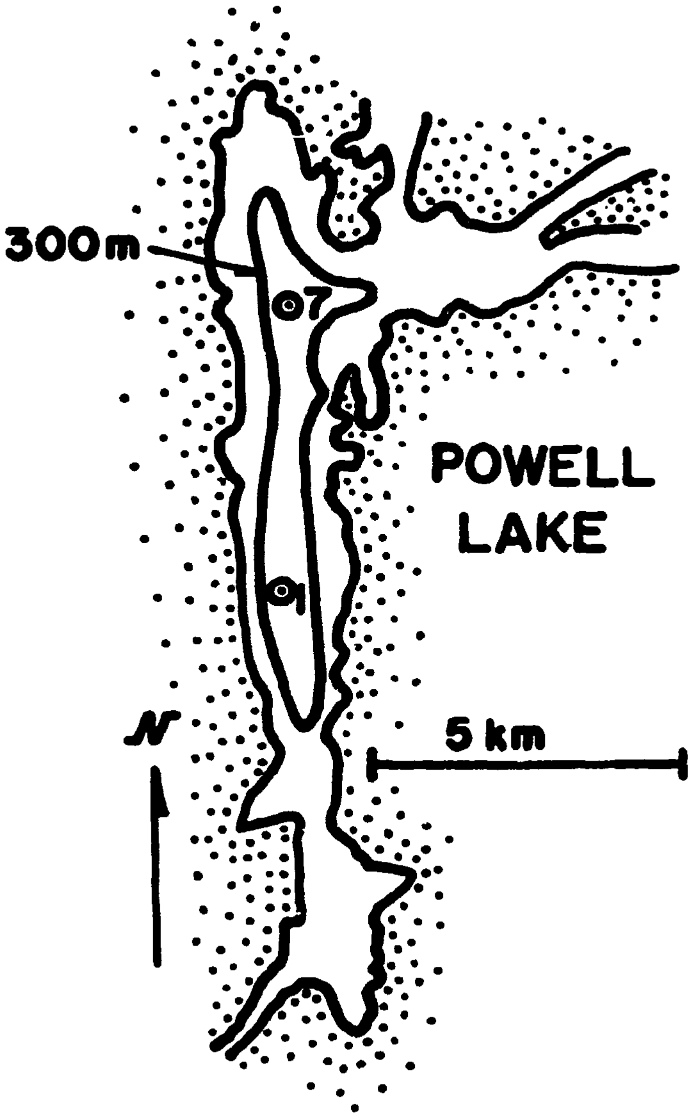
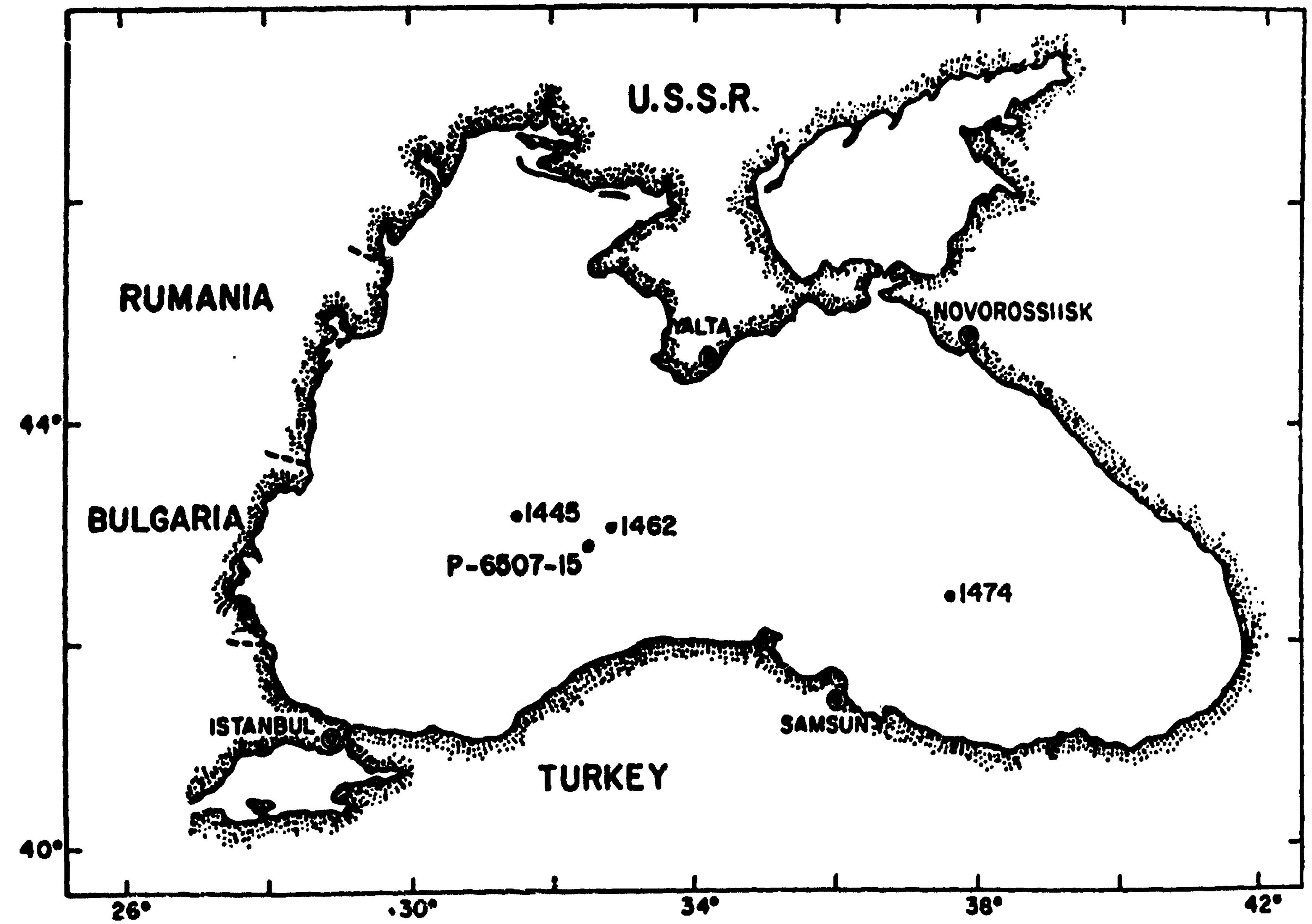


Geographical Location of Lakes of British Columbia




U.S.S.R.
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NOVOROSSIISK
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BULGARIA
•1445
•1462
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•1474
ISTANBUL
SAMSUN
TURKEY
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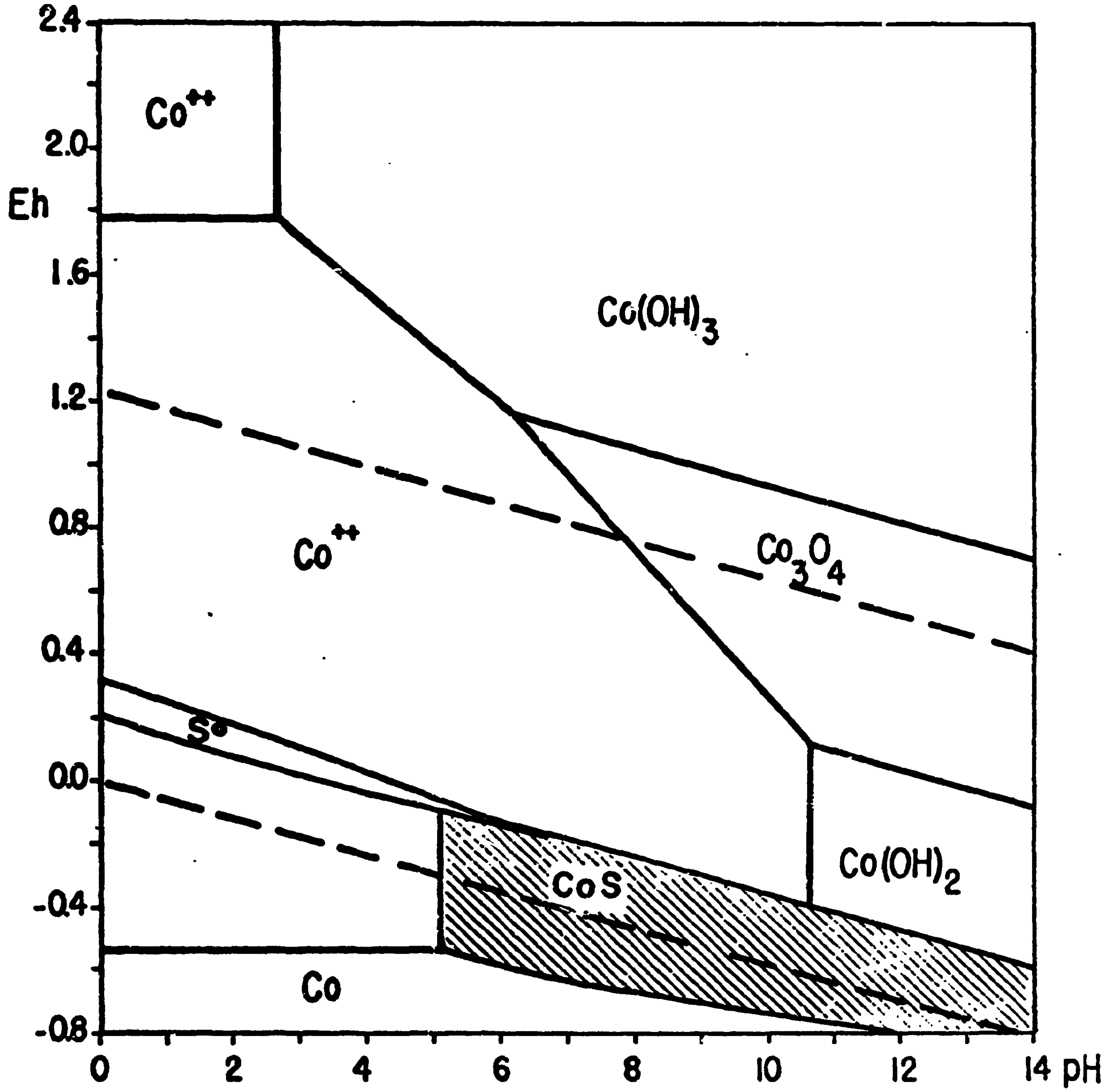
26°
30°
34°
38°
42°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1.6
1.2
0.8
0.4
0.0
-0.4
-0.8
Eh
0
2
4
6
8
10
12
14 pH
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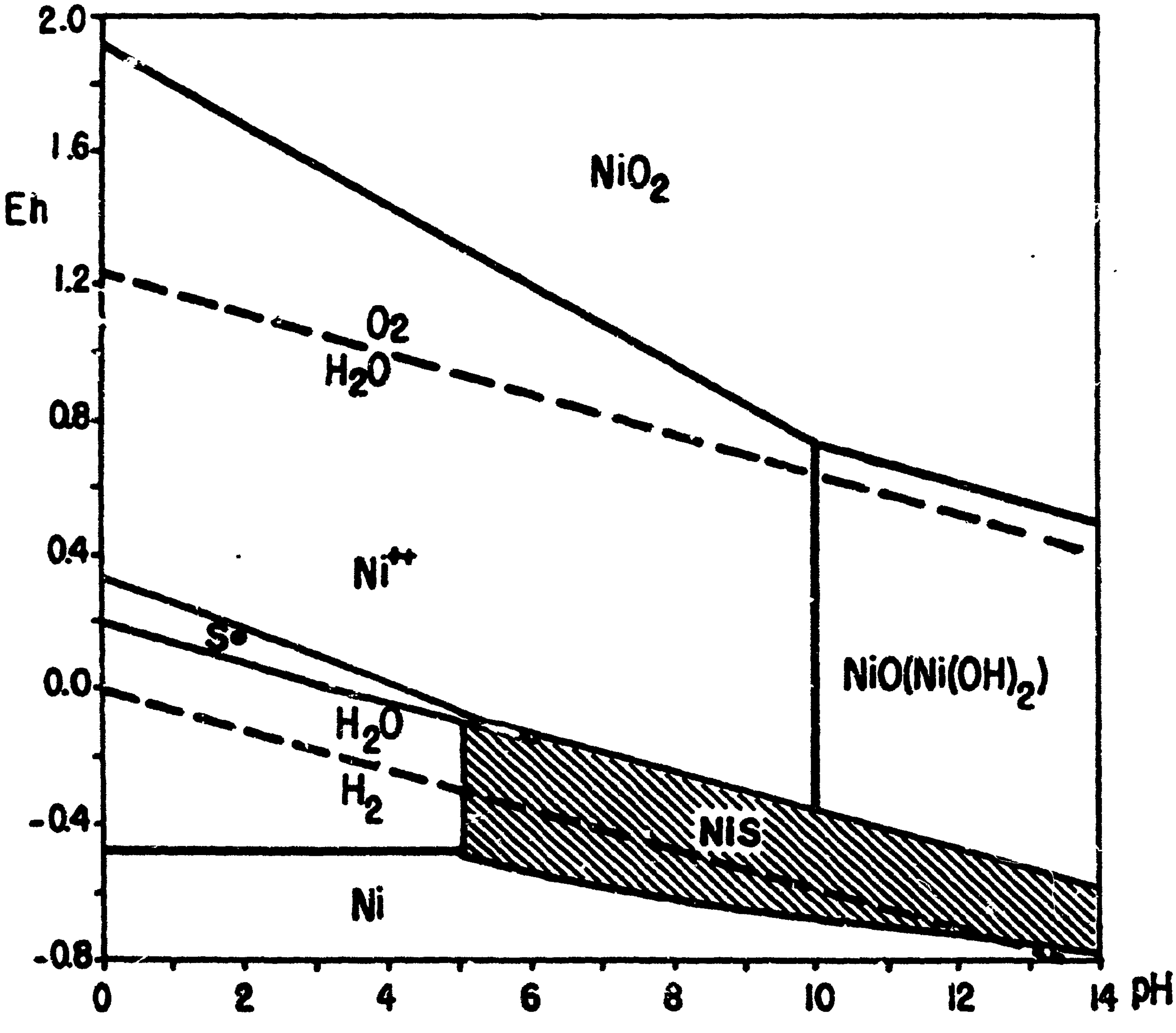
Co⁺⁺
Co(OH)₃
Co₃O₄
S°
CoS
Co(OH)₂
Co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Eh
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12
14
pH
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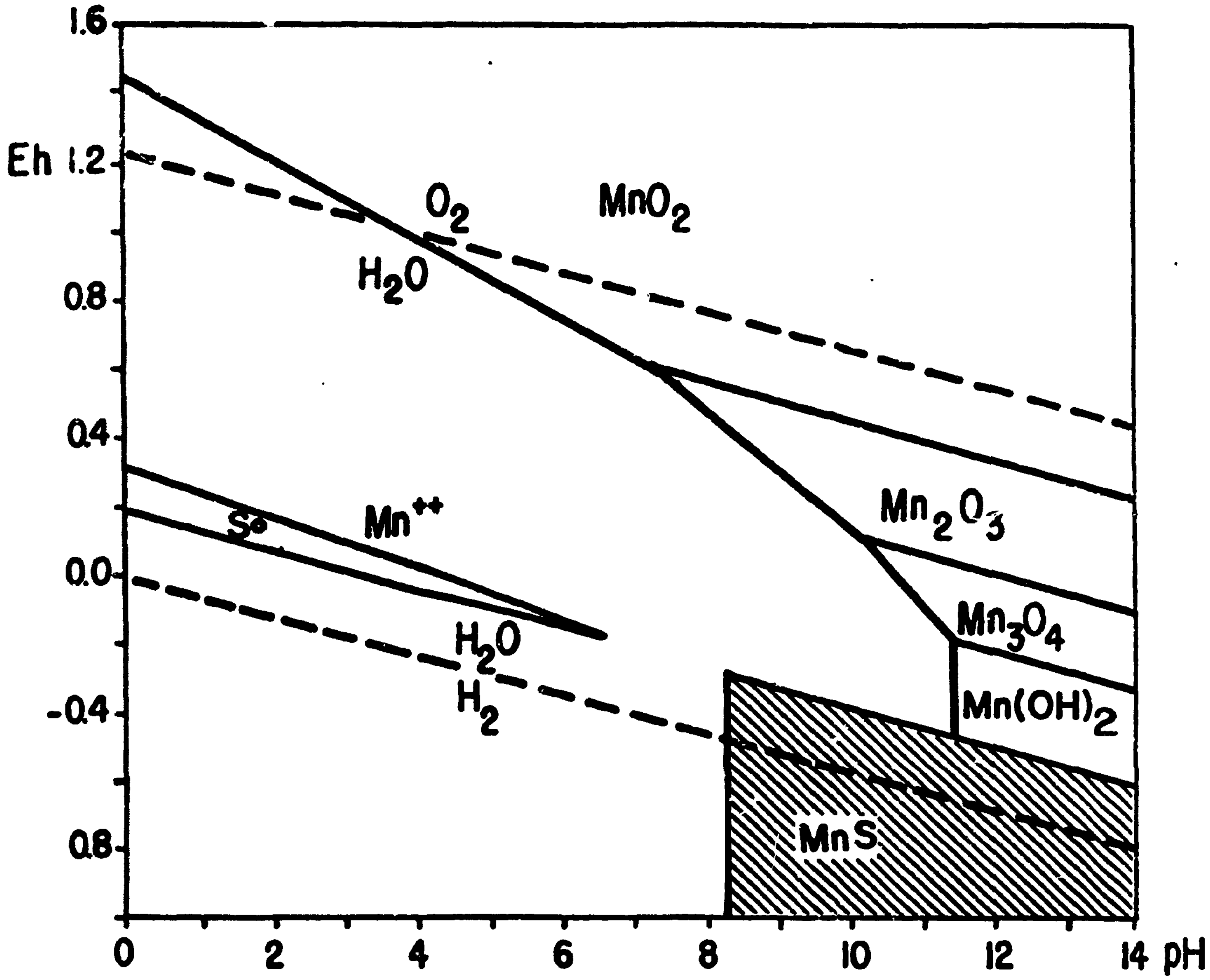
O2
H2O
Ni++
S°
H2O
H2
NiO(Ni(OH)2)
NiS
Ni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0.4
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-0.4
0.8
0
2
4
6
8
10
12
14 pH
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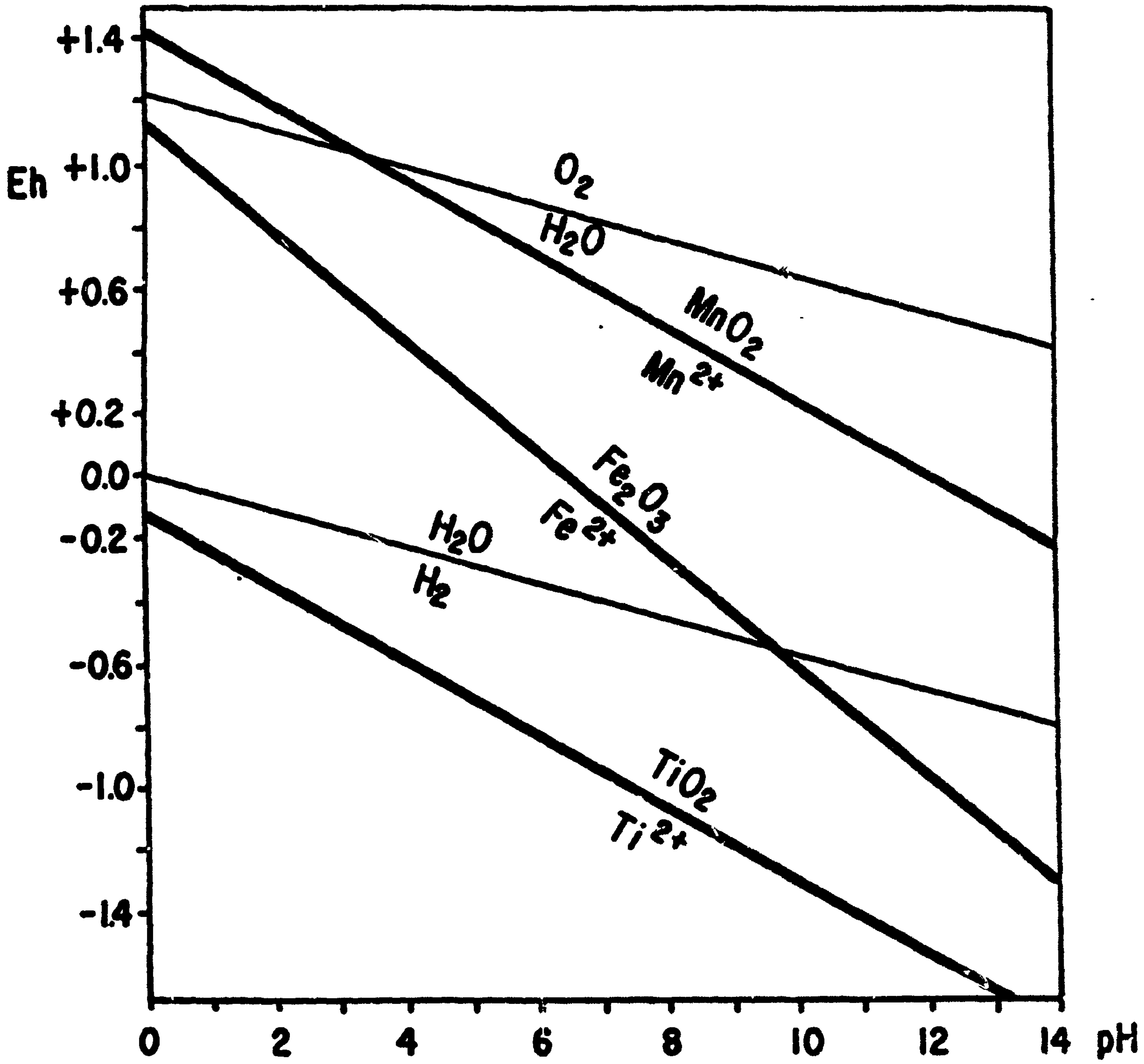
H2O
MnO2
S°
Mn++
H2O
H2
Mn2O3
Mn3O4
Mn(OH)2
MnS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2
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6
8
10
12
14
pH
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H_2O
MnO_2
Mn^{2+}
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H_2
TiO_2
Ti^{2+}

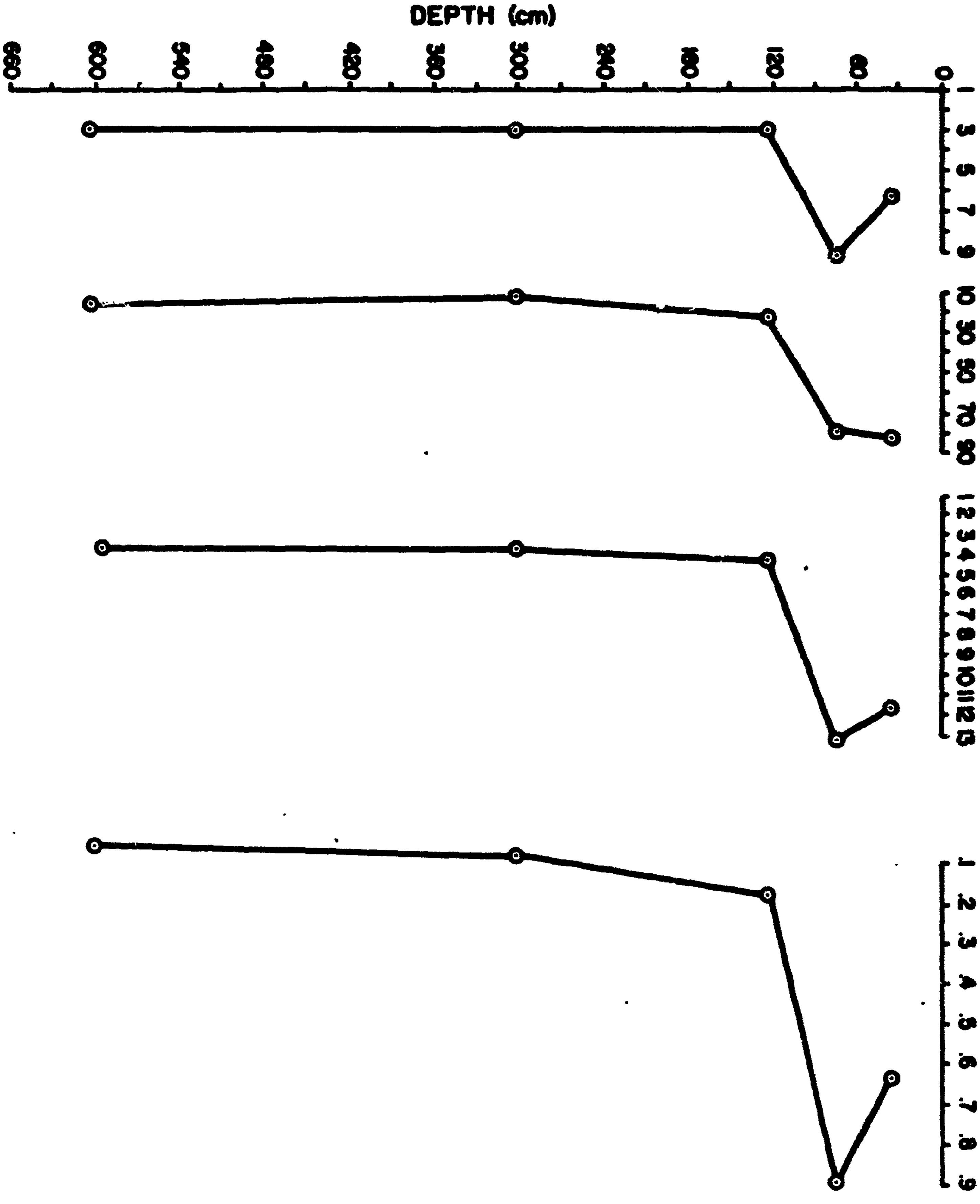
P6507-15
DEPTH (cm)
0
60
120
180
240
300
360
420
480
540
600
660
Mo×10
1 3 5 7 9
U-238×10
10 30 50 70 90
Cu×10
1 2 3 4 5 6 7 8 9 10 11 12 13
Org. C
.1 .2 .3 .4 .5 .6 .7 .8 .9

Table 1

Botnvatn

67°06'N, 15°30'E

Sta.	U-238 Error d/h/g	U-234 Error d/h/g	U-238 Error ppm	$\frac{U\text{-}234}{U\text{-}238}$ Error	Org. C %
E	261.9±5.6	288.3±5.8	5.95±0.13	1.10±0.03	2.33
D	252.6±7.6	280.1±8.0	5.74±0.17	1.11±0.05	2.82
C	152.0±5.1	163.5±5.3	3.45±0.12	1.08±0.05	0.92
B	731.4±15.7	748.6±15.9	16.62±0.36	1.02±0.03	1.47

Table 2

Rorhopvatn

Depth	U-238 d/h/g	U-238 ppm	U-234 d/h/g	$\frac{U\text{-}234}{U\text{-}238}$	Org. C %
C—D	132.0	3.00	160.0	1.21	-
B	282.0	6.40	320.0	1.13	4.41
A	295.0	6.70	331.3	1.12	-

Table 3

Rorholtfjord

Sta. 2	U-238 Error d/h/g	U-234 Error d/h/g	U-238 Error ppm	$\frac{\text{U-234}}{\text{U-238}}$ Error	Org. C %
G	744.7±10.8	788.9±11.1	16.92±0.25	1.06±0.02	0.89
E	654.7±10.9	621.3±10.6	14.88±0.25	0.95±0.02	-
C	589.8±9.8	608.6±9.9	13.40±0.22	1.03±0.02	-
A	601.1±9.9	597.5±9.9	13.66±0.23	0.99±0.02	-

Table 4

Powell Lake

Depth	U-238 d/h/g	U-238 ppm	U-234 d/h/g	$\frac{\text{U-234}}{\text{U-238}}$	Org. C %
L + M	1064	24.2	894.8	0.84	8.1
K	1036	23.5	954.0	0.92	-
C	1306	29.7	1238.0	0.95	2.4

Table 5

P6507-15

42°54'N, 32°35'E

Depth cm.	U-238* Error d/h/g	U-238 ppm	U-234* Error d/h/g	$\frac{U\text{-}234}{U\text{-}238}$	$CaCO_3$ %
31-39	808.7±15.2	18.4	911.3±16.2	1.13	19.0
71-79	776.8±11.6	17.6	881.0±12.4	1.13	6.7
121-129	220.2±7.6	5.0	217.2±7.6	0.91	2.1
301-309	133.0±3.3	3.0	124.0±3.2	0.93	4.5
601-609	162.0±3.9	3.7	158.4±3.8	0.98	17.6

* corrected for carbonate free basis

Table 6

Black Sea Cores

1474: 42°23'N, 37°36'E
1462: 43°01'N, 33°03'E
1445: 43°08'N, 31°27'E

	Depth cm.	U-238* Error d/h/g	U-238* Error d/h/g	U-234* Error d/h/g	$\frac{\text{U-234}}{\text{U-238}}$ Error	$CaCO_3$	Org. C %
Unit I							
1445 P	0-30	2202.3±88.09	50.05±2.00	2496.9±93.80	1.13±0.06	58.0	6
1462	10-30	1948.8±139.43	44.29±3.17	2171.4±147.17	1.11±0.11	63.0	6
Unit II							
1474	40-50	1015.0±11.12	23.07±0.25	1170.1±11.94	1.15±0.02	8.42	17
1445	40-60	874.3±10.34	19.87±0.23	995.4±11.04	1.14±0.02	8.42	16
Unit III							
1445	70-90	564.6±13.01	12.83±0.30	650.3±13.96	1.15±0.04	46.0	2
1462	100-120	565.9±20.56	12.86±0.47	637.5±21.82	1.13±0.06	27.0	~ 2
1474	160-170	104.6±9.96	2.66±0.23	118.5±10.96	1.13±0.14	25.0	1
1474	540-550	119.3±5.73	2.71±0.13	109.3±5.49	0.92±0.06	17.0	0.5
Clay							
1462 (turbidite)	60-80	265.7±10.37	6.04±0.24	252.6±10.11	0.95±0.05	18.0	~ 3

Table 7

P6304-1

16°37'N, 74°54'W

Depth cm.	U-238* Error d/h/g	U-234* Error d/h/g	$\frac{U-234}{U-238}$	$CaCO_3$ %
11-14	117.0	117.0	1.00	68.0
75-79	117.4±10.6	117.2±10.6	1.00	54.8
401.5-409.5	117.7±12.4	125.7±12.7	0.94	68.0
451-459	99.0±9.6	99.0±9.8	1.00	58.3

Table 8

P6304-1

16°37'N, 74°54'W

Depth cm.	Oak Ridge	Miami
75-79	2.39±0.03	2.67±0.24
231-239	2.38±0.03	2.59±0.21
401.5-409.5	2.31±0.03	2.67±0.28
451-459	2.10±0.03	2.25±0.21

<u>Core P6304-1</u>: Concentration (ppm) of U^{238} in selected samples by isotope dilution (carried out by R. Walker, Oak Ridge National Laboratory and alpha spectrometry (Miami).

Table 9

Rorholtfjord

	ppm		%	
Depth	**Co**	**Ni**	**Fe**	**Mn**
G	15	35	4.8	0.08
F	15	30	5.1	0.08
E	15	30	4.5	0.07
D	14	25	4.4	0.08
C	16	35	4.6	0.07
B	16	30	4.4	0.07
A	16	30	4.4	0.08
Nose	12	30	4.1	0.07

Table 10

Powell Lake

	ppm		%	
Depth	**Co**	**Ni**	**Fe**	**Mn**
H	23	22	5.4	0.09
F	17	15	4.5	0.06
E	17	15	4.4	0.06
C	17	17	4.6	0.07
A	20	20	5.2	0.08

Table 11

Framvarn

Depth	ppm		%	
	Co	Ni	Fe	Mn
B	17	57	5.6	0.05
A	18	50	5.5	0.04
Nose	17	33	5.6	0.07

Table 12

P6507-15

Depth cm.	ppm					%	
	Ba	Co	Cu	Mo	Ni	Fe	Mn
31-39	1725	27.5	105	52	112	3.95	0.05
71-79	425	17.5	122	87	117	3.35	0.03
121-129	525	17.0	50	<30	80	5.40	0.11
301-309	500	12.5	35	<30	60	4.35	0.05
601-605	500	13.0	27	<30	62	4.00	0.06

Table 13

Minor and Trace Elements

	%		ppm				
	Fe	Mn	Ba	Co	Cu	Mo	Ni
Unit I							
1445 P 0-30	1.8	.038	450.0	25.0	25.0	9.5	55.0
1462 10-30	1.5	.038	520.0	55.0	32.0	32.0	50.0
Unit II							
1474 40-50	3.4	.036	1000.0	27.0	150	182.0	167.0
1445 40-60	3.7	.069	1200.0	25.0	145.0	105.0	150.0
Unit III							
1445 70-90	24.0	.062	350.0	11.0	30.0	30	45.0
1462 100-120	3.3	.046	105.0	20.0	43.0	32.0	75.0
1474 160-170	4.7	.100	350.0	18.0	50.0	30	150.0
540-550	4.8	.092	400.0	19.0	35.0	30	130.0

Table 14

	Co/Ni	Fe/Mn	Co/Mn	Ni/Mn
Powell Lake	1.06	67.81	0.026	0.026
Botnvatn	0.27	57.78	0.021	0.080
Rorhopvatn	0.40	56.48	0.006	0.016
Framvarn	0.33	124.75	0.039	0.106
Rorholtfjord	0.50	60.94	0.020	0.044
P6304-8 (Caribbean)	0.37	15.57	0.010	0.029
P6507-15 (Black Sea)	0.20	78.69	0.035	0.087
*Clays	0.21	-	0.030	0.14
*Igneous Rocks	0.31	-	0.018	0.058
*Pacific	0.94	-	0.013	0.019
*Mediterranean	0.31	-	0.017	0.054
*Black Sea	0.24	-	0.021	0.087
*Caribbean	0.28	-	0.014	0.049

*Taken from Carvajal (1968).

Table 15

Correlation Coefficients:	Rorhopvatn
Fe - MnO	+0.534
Co - Fe	+0.317
Ni - Fe	+0.356
Co - MnO	+0.658
Ni - MnO	+0.767
Co - Ni	+0.987

Table 16

Correlation Coefficients:	Rorholtfjord (Tokke)
Fe - MnO	+0.574
Co - Fe	-0.063
Ni - Fe	-0.019
Co - MnO	+0.431
Ni - MnO	+0.341
Co - Ni	+0.678

Table 17

Correlation Coefficients: Botnvatn

Fe - MnO	+0.724
Co - Fe	+0.395
Ni - Fe	+0.393
Co - MnO	+0.622
Ni - MnO	-0.161
Co - Ni	+0.395

Table 18

Correlation coefficients: P6507-15

Fe - MnO	+0.957
Co - Fe	-0.072
Ni - Fe	-0.406
Co - MnO	-0.102
Ni - MnO	-0.360
Co - Ni	+0.759