Occurrence of Selected Minor Elements in the Waters of California

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1535–L

Prepared in cooperation with the State of California, Department of Water Resources

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By WILLIAM D. SILVEY

GEOCHEMISTRY OF WATER

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A study of the presence of 17 minor elements in 5 types of natural water in California

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1967

UNITED STATES DEPARTMENT OF THE INTERIOR

STEWART L. UDALL, *Secretary*

GEOLOGICAL SURVEY

William T. Pecora, *Director*

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price 15 cents (paper cover)

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OCCURRENCE OF SELECTED MINOR ELEMENTS IN THE WATERS OF CALIFORNIA

By WILLIAM D. SILVEY

ABSTRACT

This study determined the occurrence of 17 minor elements in the waters of California. Waters studied included: Water from springs, water from wells 25 to 500 feet deep, oil-field brine, water from streams, and sea water from the Pacific Ocean adjacent to the coast of California. The data obtained indicated that the occurrence of minor elements in these waters was strongly influenced by the vertical position of the water relative to the earth's surface. Spring water of deep-seated origin was substantially different chemically from stream water and sea water. Water from wells 25 to 500 feet deep and oil-field brine occupy an intermediate position between spring water of deep-seated origin and stream water and contain minor elements found in both deep-seated spring water and stream water. Although the lithosphere is the ultimate source of minor elements in water, the data indicate that the occurrence and concentration of minor elements are strongly affected by the biota in the hydrologic environment. Where biologic activity is at a minimum, as in deep-seated spring water, the concentration and number of elements found reached a maximum. Where biologic activity is at a maximum, as in sea water, the concentration and number of the minor elements were found to be at a minimum level.

The minor elements which had the highest frequency of occurrence in the various waters studied were iron, nickel, vanadium, aluminum, molybdenum, copper, manganese, and germanium. The elements that had a low frequency of occurrence in all water types were lead, titanium, zinc, cobalt, bismuth, chromium, cadmium, and gallium. Beryllium was not found in any of the waters studied.

INTRODUCTION

A study of the occurrence of minor elements in the waters of California began in 1959 by the Water Resources Division, U.S. Geological Survey, in cooperation with the California Department of Water Resources.

The major purposes of the study were to determine the differences in the occurrence of minor elements in the several types of water in and near California and to explore the reasons for these differences.

The study was divided into three phases. During the first phase a spectrochemical technique (Silvey and Brennan, 1962, p. 784) was developed specifically to detect the minor elements in microgram concentrations in the various water types found in California. The second phase of the study was the collecting and analyzing of water samples taken from springs, from water wells, from oil-field brine, from streams, and from the sea. The third and final phase was the study of the data obtained and preparation of a report.

The author extends his appreciation and thanks to Eugene Brown, former district chemist, and Robert Brennan, former assistant district chemist, Quality of Water Branch, U.S. Geological Survey, Sacramento, Calif., and to Marvin Skougstad, Quality of Water Branch, Denver, Colo., for their noteworthy assistance in this study.

METHODS

SAMPLE COLLECTION

Water samples for analysis were collected from springs, from water and oil wells of various depths, from streams, and from the sea. The bottles were always thoroughly rinsed at the sampling site prior to taking the actual sample. These samples should reflect any major differences in the occurrence of minor elements in these water types.

In this report, spring water is natural ground-water discharge at land surface and may or may not be of deep-seated origin (13,000 ft or more below land surface). Spring water was collected from points as near as possible to the issuing orifice.

Well water is water collected from wells 25 to 500 feet deep which are usually located in the San Joaquin Valley of California.

Oil-field brine is water collected from oil-producing zones at depths of 1,500 to 13,000 feet below land surface. This water was collected in southern California, where most of the oil pools in the State occur. Both oil-field brine and well water were collected from wells that either were pumping or had been pumping for a minimum of 5 minutes before the taking of the sample.

Stream water is water collected from rivers and most of the major streams in California at points where the drainage-basin outflow was well mixed and, where possible, flowing swiftly.

Sea water is water collected from the Pacific Ocean along the entire California coast, at points 50 miles apart and where no large quantity of surface water flows into the ocean. It was collected offshore at a depth of about 1 foot below the surface.

SAMPLE TREATMENT

During the early sample-collection and analytical phase of this study, it became apparent that some drastic changes were taking place in the sea-water samples between the time of collection and the time of analysis. Samples that were clear and odorless at the time of collections became turbid and when opened gave off a strong odor. These samples received no field treatment, such as immediate filtration and acidification at the point of collection. The subsequent analysis of these samples indicated that the concentrations of the minor elements were much greater than expected. Further studies of this problem showed that immediate filtration was necessary to eliminate the relatively high concentration of organisms found in sea water. If these organisms are not removed, they die, rapidly decompose, and in the process, release large amounts of minor elements into solution. These elements from decomposition cause errors in determining the minor elements actually in solution at the time of collection. In addition, the living sea-water organisms, under conditions favorable to growth, can also deplete the minor elements, this depletion resulting in very low values for the minor elements. Therefore, a procedure was adopted whereby the 3.5-liter water samples were immediately filtered at the time of collection and acidified with 5 milliliters of 6 *N* hydrochloric acid. A filter with a pore size of 0.45μ (micron) was used. Samples that could not be filtered at the sampling point were transported as soon as possible to the laboratory and immediately filtered and acidified.

ANALYTICAL TECHNIQUE

The samples, if not filtered in the field, were immediately filtered at the laboratory through a membrane filter having a pore size of 0.45μ. A sample volume of 3.5 l was evaporated on a hotplate to approximately 400 ml.

The following reagents were added to the samples:

15 ml of indium solution (1 ml contains 2 mg In),
5 ml of palladium solution (1 ml contains 0.2 mg Pd), and
10 ml of 5 percent 8-hydroxyquinoline in 2*N* acetic acid.

The pH was adjusted to 1.8 with concentrated ammonium hydroxide.

The following reagents were then added:

45 ml of 2*N* ammonium acetate,
2 ml of 10 percent tannic acid (in 2*N* ammonium acetate), and
2 ml of 1 percent thionalide (in acetic acid, specific gravity is 1.052).

The final pH was adjusted to 5.2 with concentrated ammonium hydroxide.

The samples were left overnight to insure quantitative precipitation. After 24 hours the precipitate, which consisted of the internal standard (palladium), the radiation buffer (indium), and the minor elements, was filtered to completely separate the minor elements from the major dissolved solids. The precipitate was then ignited overnight to convert the minor elements, internal standard, and radiation buffer to oxides prior to spectrographic analysis.

SPECTROGRAPHIC PROCEDURE

A 2.5-meter grating spectrograph with a Wadsworth mounting was used for all analytical determinations under the following conditions:

Amperage, direct current---amp--	6.0
Voltage, open circuit---v--	240
Slit width---μ--	40
Slit height---mm--	4
Preburn	None
Burn time	Complete
Arc gap---mm--	5

A two-step palladium filter was set as a step weakener to permit 40 percent transmission in the second step.

The ignited precipitate was mixed with spectrographically pure graphite and arced in duplicate.

Standard methods of film development and photometry were used.

The analytical element lines were selected on the basis that (1) they were never seen in the blanks, which were subjected to all reagents used in the chemical procedure, (2) no other element lines interfered in the concentration range used, and (3) the detectability range was found to be acceptable (tables 1 and 2).

TABLE 1.—*Analytical lines and range*

	Analytical lines (angstroms)	*Analytical range (mg in the electrode)*
Aluminum	2652.5	0.100–0.0025
Beryllium	3131.1	.010– .0005
Bismuth	3067.7	.010– .0005
Cadmium	2980.6	.250– .0025
Cobalt	3409.2	.050– .0010
Chromium	2780.7	.100– .0025
Copper	2824.4	.250– .010
Iron	2823.3	.250– .010
Iron	2966.9	.025– .001
Gallium	2450.1	.250– .010
Germanium	2651.6	.025– .0005
Manganese	2949.2	.100– .001
Molybdenum	3208.8	.010– .0005
Nickel	3414.8	.010– .001
Lead	2833.1	.025– .001
Titanium	3239.0	.050– .001
Vanadium	3110.7	.025– .001
Zinc	3345.0	.500– .050
Palladium	3287.2	Internal standard.

TABLE 2.—*Limit of detectability in analysis of 3.5–1 sample*

Element	Micrograms per liter	Element	Micrograms per liter
Aluminum	0.7	Germanium	0.3
Beryllium	.3	Manganese	.6
Bismuth	.3	Molybdenum	.1
Cadmium	.7	Nickel	.3
Cobalt	.6	Lead	.6
Chromium	.7	Titanium	.6
Copper	2.8	Vanadium	.6
Iron	.6	Zinc	14
Gallium	2.8		

ELEMENTS DETERMINED

The elements determined were aluminum, beryllium, bismuth, cadmium, cobalt, chromium, copper, iron, gallium, germanium, manganese, molybdenum, nickel, lead, titanium, vanadium, and zinc. The limits of quantitative detection shown in table 2 are based on a sample volume of 3.5 l. The 3.5-l volume was selected for this study because this amount can be obtained easily after filtration of a 1-gallon sample. Also, this volume permits determinations to less than 1μg (microgram) per l for most of the minor elements. The minor elements quantitatively determined by this analytical technique were selected for two reasons: (1) Thorough studies by many workers, principally Mitchell and Scott (1948, p. 367), have indicated that the three reagents used quantitatively precipitate all these 17 minor elements, (2) this group was thought to include those minor elements most likely to be detected in natural water by analysts using the methods developed.

OCCURRENCE OF MINOR ELEMENTS

GENERAL

As this study progressed, it became obvious that many unknown interacting factors have a direct control over the occurrence of minor elements in natural waters. For example, if the data obtained during this study were treated statistically to relate this data to various geologic environments from which the minor elements originally were derived, such a relation would ignore completely the effect that the biophase has on the occurrence of minor elements in natural water. This effect includes the control over which elements are found and, more importantly, which elements generally are not found in natural water as a result of uptake into the biophase. For this reason, the data are presented both in terms of average abundance (micrograms per liter) and as the percentage of samples in which the elements occurred.

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Those elements not detected may have been present, but were undetected because of technique limitations; that is, the actual concentration levels of the minor elements were below the concentrations that could be detected.

In addition to the results and discussion which follow, some of the previous findings by other workers also are reviewed.

SPRING WATER

PREVIOUS WORK

The literature contains numerous reports of minor-element content of spring water. Calker (1936, p. 396), detected copper, gallium, cobalt, lead, and nickel in eight samples of Swedish mineral water. Novokhalskii and Kalinin (1939, p. 323) reported the occurrence of aluminum, iron, molybdenum, copper, zinc, lead, germanium, and manganese variously distributed in residues of 16 samples of water from radioactive warm and hot springs of Tyan-Shan. Lourenco (1940, p. 41) found iron, aluminum, manganese, vanadium, nickel, molybdenum, and lead in 27 samples of mineral water in the United States. Posokhov and Kalinin (1943, p. 98) detected considerable quantities of molybdenum and traces of copper, lead, germanium, gallium, and nickel in water from hot springs in eastern Kazakhstan, U.S.S.R. Lopez de Azcona (1947, p. 3) detected aluminum, beryllium, cobalt, chromium, copper, iron, gallium, germanium, manganese, molybdenum, nickel, lead, titanium, and vanadium distributed in 187 water residues from medicinal springs on the Spanish peninsula. Ubain (1947, p. 1) reported iron, aluminum, manganese, chromium, copper, gallium, germanium, beryllium, molybdenum, nickel, lead, titanium, and vanadium in three groups of springs in the Pyrenees Mountains in southern France. Kent and Russell (1949, p. 161) found traces of aluminum, lead, manganese, molybdenum. and iron in warm springs in the Transvaal area of Africa. Babinets and Rad'ko (1956, p. 21) studied the occurrence of minor elements in springs on the southern slopes of the Soviet Carpathians. Their results indicated that nickel was present in most samples. Copper and lead occurred frequently, cobalt and zinc were found less frequently, and vanadium and beryllium were found very infrequently.

This brief review of the literature indicates that, although spring water in many areas throughout the world has been analyzed for minor-element content, little effort has been made to relate this content to water source or depth of origin. Whereas previous investigations were concerned with the occurrence of minor elements in water, this study attempts to relate the presence of minor elements to environmental fac-

tors; for example, the presence of germanium appears to be significant in relating chemical quality to depth of origin.

RESULTS

The results of the analysis of water from 72 springs in California are as follows:

Aluminum: Aluminum was found in 79 percent of the samples studied (fig. 1). The concentration rarely exceeded 100μg per l, although one sample (Sulfur Spring, Lake County) contained 243μg per l. The average concentration was 30μg per l.

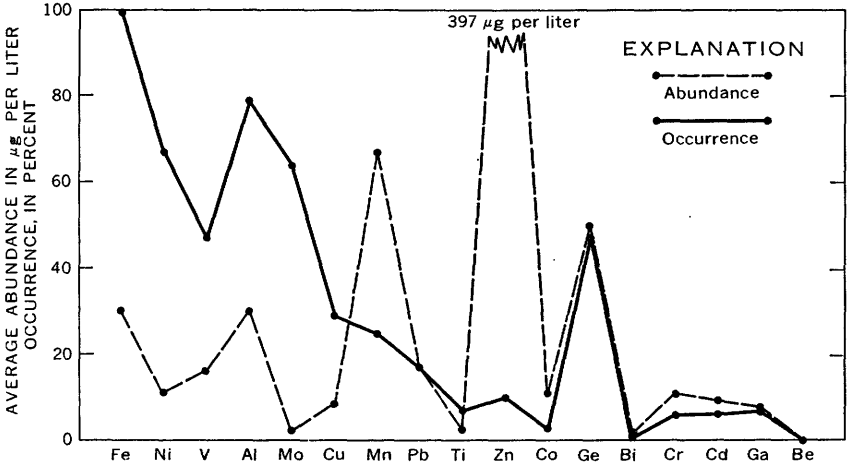

FIGURE 1.—Abundance and occurrence of minor elements in 72 samples of selected spring water.

Beryllium: Beryllium was not detected in any of the samples, even though as little as 0.30μg per l could have been detected.

Bismuth: Bismuth was found in only one sample (Lake City Hot Springs, Modoc County); its concentration was 0.7μg per l.

Cadmium: Cadmium was found in four samples. The greatest concentration was 20μg per l and the average was 8.2μg per l.

Cobalt: Cobalt was found in two samples that contained 0.71 and 22μg per l.

Chromium: Chromium was found in four samples; the concentrations were 6.0, 8.9, 11, and 21μg per l.

Copper: Copper was found in 29 percent of the samples studied. The maximum concentration was 89μg per l and the average was 8.6μg per l.

Iron: Iron was found in 99 percent of the samples studied. The concentration of iron in spring water varies widely. Many samples

contained more than 200μg per l which is the upper limit of determination, and it is quite possible that the actual concentration in these samples was as much as 1,000μg per l. Most (56) of the samples contained 50μg per l or less. The average concentration was more than 30μg per l.

Gallium: Gallium was found in five samples, all from the same general area in the San Jacinto Mountains, Riverside County. The concentrations in the samples were 4.9, 5.4, 7.4, 7.7 and 13 μg per l.

Germanium: Germanium was found in 47 percent of the samples. The maximum concentration of germanium that could be determined quantitatively was 50μg per l. The concentrations in most of these samples were greater than 50μg per l. Only 7 of the 34 samples contained less than 10μg per l.

Manganese: Manganese was found in 25 percent of the samples. The average concentration was 67μg per l.

Molybdenum: Molybdenum was found in 64 percent of the samples. Although this element had a high frequency of occurrence, the concentration rarely exceeded 5.0μg per l. The average concentration in 46 samples was 2.2μg per l.

Nickel: Nickel was found in 67 percent of the samples. Three samples contained more than 100μg per l. The average concentration in 48 samples was 11μg per l.

Lead: Lead was detected in 17 percent of the samples. One sample contained 143μg per l. Eleven samples contained much less, and the average concentration in the 12 samples was 17μg per l.

Titanium: Titanium was found in six samples which contained 0.70, 0.70, 0.70, 0.71, 11, and 12μg per l.

Vanadium: Vanadium was found in 47 percent of the samples. Four samples contained more than 100μg per l. The average concentration for 34 samples was 16μg per l.

Zinc: Zinc was found in 10 percent of the samples. The concentrations found were high; perhaps the samples were contaminated by galvanized pipes at the spring sites. The concentrations ranged from 63 to 1,000μg per l. The average concentration for the seven samples was 397μg per l.

DISCUSSION

The data indicate that detectable quantities of aluminum, iron, germanium, molybdenum, nickel, and vanadium occurred in approximately 50 to 99 percent of the spring-water samples. Copper, manganese, lead, and zinc were found in 10 to 40 percent of the samples; bismuth, cadmium, cobalt, chromium, gallium, and titanium were found in less than 10 percent of the samples; beryllium was not detected in any of the samples.

Consideration of the group including aluminum, iron, germanium, molybdenum, nickel, and vanadium suggests some geochemical anomalies. A high frequency of occurrence of iron and aluminum in spring water and in other types of natural water is quite common. Even molybdenum, nickel and vanadium occur frequently in various types of water, but the presence of germanium is exceptional. Germanium was not found in any of 24 sea-water samples. It was found in 2 of 65 samples of stream water, but these samples were taken from places where germanium-bearing spring water flowed into the stream above the sampling site. It was not found in 63 samples of well water but was found in 15 of 19 samples of oil-field brine. These results suggest that germanium is nearly absent in water at or near the earth's surface and increases both in abundance and frequency of occurrence in water influenced by conditions deep below the surface. Accordingly, the data were tabulated in terms of germanium spring water and nongermanium spring water (table 3). The data also include the average concentrations of chloride, fluoride, and boron. These elements may be indicators of deep-seated water associated with late stages of magmatic activity (Bateman, 1951, p. 47). Also included are the average specific conductance of the spring water and the predominant cations and anions.

Examination of the data in table 3 shows that the germanium spring water has higher specific conductances and higher concentrations of halogens and boron than does the nongermanium spring water.

The water containing germanium was predominantly of the sodium chloride sulfate type, whereas the nongermanium spring water was primarily of the sodium calcium bicarbonate type.

TABLE 3.—*A comparison of some chemical characteristics of germanium spring water with those of nongermanium spring water*

	Chloride	Fluoride	Boron	Specific conductance (micromhos at 25°C)	Predominant water type
	Milligrams per liter				
Germanium spring water (average of 30 samples).	471	3. 6	39	2, 680	Sodium chloride sulfate.
Nongermanium spring water (average of 35 samples).	53	1. 4	. 62	766	Sodium calcium magnesium bicarbonate.

The nongermanium spring water probably reflects recharge of meteoric origin, whereas the germanium spring water has a deep-seated and perhaps a magmatic origin.

Plots of the occurrence, in percentage, of minor elements in surface water of California versus their occurrence in both the nongermanium and the germanium spring water are shown in figures 2 and 3, respectively. There is little apparent difference between the occurrence of minor elements in stream water and in the nongermanium spring water (fig. 2) but substantial difference between the occurrence of minor elements in stream water and in the germanium spring water (fig. 3).

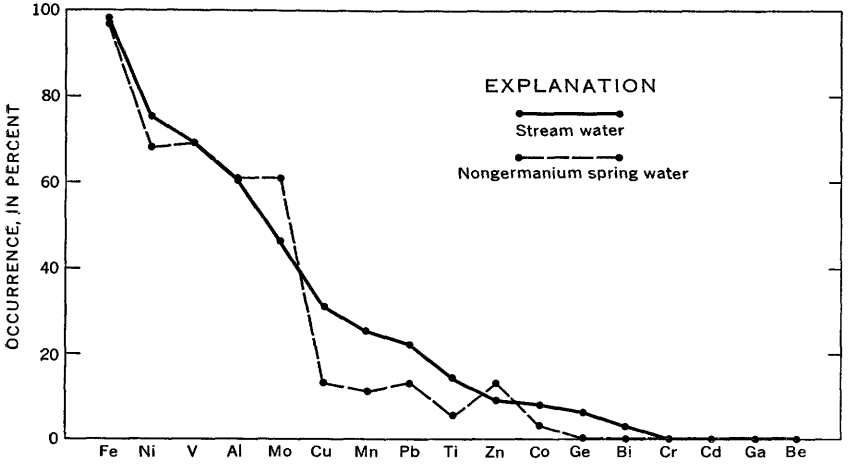

FIGURE 2.—A comparison of the occurrence of minor elements in stream water with that in nongermanium spring water.

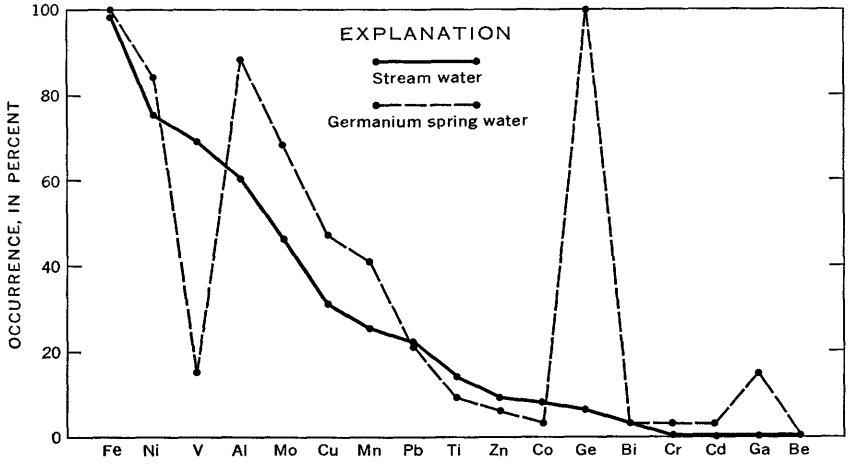

FIGURE 3.—A comparison of the occurrence of minor elements in stream water with that in germanium spring water.

First, vanadium occurs rather infrequently in the germanium spring water, whereas the occurrence of vanadium in the nongermanium springs is similar to that in the stream water. Also, nickel, aluminum, molybdenum, manganese, copper, and lead occur more frequently in the springs that contain germanium, than in nongermanium springs. Finally, bismuth, chromium, cadmium, and gallium are not found in the nongermanium springs, whereas these elements are present in the germanium spring water; however, the frequency of occurrence is low—10 percent or less.

Many workers have reported the occurrence of germanium in spring water throughout the world but have not offered an explanation as to the source of the element. The author believes that the source of the germanium found in spring water of California and other parts of the world is deep seated and that the water carrying it to the surface may even be partly juvenile. Water emerging from great depths within the earth is not likely to reach the surface without mixing to some extent with connate and meteoric water.

Rankama and Sahama (1950, p. 594) predicted, on the basis of their studies of meteorites, that germanium is strongly siderophile and increases in abundance toward the earth's nickel-iron core by a factor of perhaps 100 to 1. The data from the present investigation certainly tend to support their thesis. In this study, analyzed waters at or near the surface, including sea, stream, and well waters, were generally low in germanium. Oil-field brine, some collected from a depth of 13,000 feet, contained small amounts of germanium. Spring water of the sodium chloride sulfate type, on the other hand, contained relatively large amounts of germanium.

Rankama and Sahama (1950, p. 729) stated that, whereas germanium abundance increases from the silicate crust toward the metallic core, the reverse is true of vanadium. Vanadium is strongly lithophile and, accordingly, is more abundant near the earth's surface but is deficient toward the core. The thesis of Rankama and Sahama is somewhat substantiated by the data of the present report which shows the occurrence of vanadium is relatively high in both nongermanium spring water and in stream water.

These high concentrations of germanium in spring water may be indicative of a deep-seated, or perhaps even juvenile, origin. Water that contains little or no germanium, but has a high vanadium content, can be considered as spring water of meteoric origin or as stream water that enters the crustal surface at a given altitude and emerges as springs at some lower altitude. Other criteria that should also be considered include the chemistry of the major dissolved solids, the abundance of halogens in the water, and the presence or absence of boron (White, 1957, p. 1661).

WELL WATER AND OIL-FIELD BRINE

PREVIOUS WORK

A search of the literature shows little information pertinent to the findings of the present study.

RESULTS

The results of 82 analyses of water from 63 water wells and brine from 19 oil wells in California are as follows:

Aluminum: Aluminum was found in 64 percent of the 82 samples (fig. 4). The concentration rarely exceeded 100μg per l. The average concentration was 38μg per l.

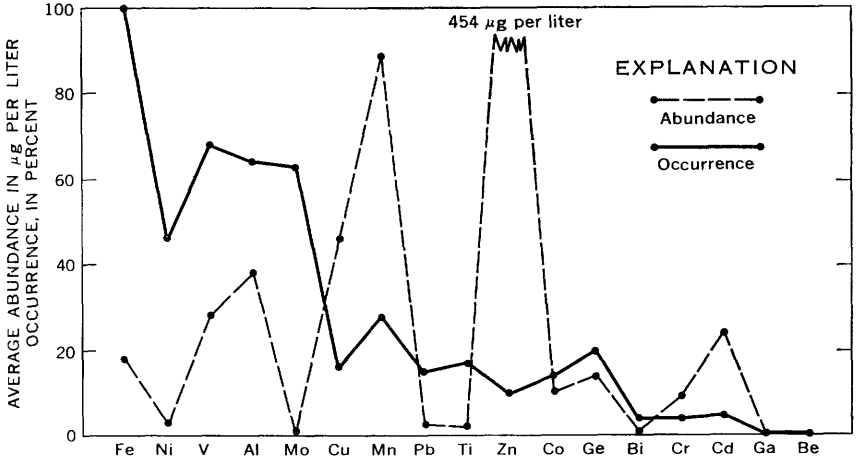

FIGURE 4.—Abundance and occurrence of minor elements in 82 samples of selected well water and oil-field brine.

Beryllium: Beryllium was not detected in any of the samples studied.

Bismuth: Bismuth was found in three samples, which contained 2.7, 0.85, and 0.80μg per l.

Cadmium: Cadmium was found in five samples that contained 71, 5.1, 11, and 7.1μg per l.

Cobalt: Cobalt was found in 14 percent of the 82 samples. The average concentration was 9.7μg per l.

Chromium: Chromium was found in three samples. The concentrations were 6.6, 13, and 7.4μg per l.

Copper: Copper was detected in 16 percent of the samples studied. The average concentration was 46μg per l.

Iron: Iron was present in all the 82 samples. The average concentration was 18μg per l.

Gallium: Gallium was not detected in any of the samples.

Germanium: Germanium was detected in 20 percent of the samples and was present only in the oil-field brines. The average concentration was 14μg per l.

Manganese: Manganese was detected in 27 percent of the 82 samples. Many samples contained 100μg per l or more of manganese, particularly those taken from the oil-field brine. The average concentration was 89μg per l.

Molybdenum: Molybdenum was found in 63 percent of the 82 samples. While its frequency of occurrence was high, the average concentration was only 1.2 μg per l.

Nickel: Nickel was found in 46 percent of the samples. The average concentration was 2.6μg per l.

Lead: Lead was found in 15 percent of the samples. The average concentration was 2.8 μg per l.

Titanium: Titanium was found in 17 percent of the 82 samples. The average concentration was 2.1μg per l.

Vanadium: Vanadium was detected in 68 percent of the 82 samples. The average concentration was 28μg per l.

Zinc: Zinc was found in 10 percent of the 82 samples. The average concentration was 454μg per l. The zinc found in these eight samples probably represents contamination from either pipes or storage tanks or both and is not indicative of the natural concentration of zinc in ground water.

DISCUSSION

The elements iron, vanadium, aluminum, molybdenum, and nickel were those most frequently found in the analysis for the 17 elements in well water and oil-field brine. These same elements also had the highest frequency of occurrence in stream water. The range of concentration of the five elements varied considerably with source. For example, the concentration of iron in stream water averaged 33μg per l, while in well water and oil-field brine the average concentration was 18μg per l. Vanadium was concentrated particularly in well water and oil-field brine and averaged 28μg per l. In stream water the average amount of vanadium was 3.0μg per l. In both, the frequency of occurrence, in percentage, was the same. Aluminum also was found to be rather highly concentrated in the well water and oil-field brine, where the average concentration was 38μg per l. The stream water contained an average concentration of 15μg per l. However, the frequency of occurrence, in percentage, both in well water and oil-field brine and in stream water was nearly the same. The concentration of molybdenum in stream water was somewhat higher than that in well water and oil-field brine—3.9 versus 1.2μg per l, respectively. Molybdenum occurred

in 46 percent of the 65 samples of stream water and in 63 percent of the 82 samples of well water and oil-field brine. The concentration of nickel was generally similar both in well water and oil-field brine and in stream water. The amount found in well water and oil-field brine was 2.6μg per l; the average amount detected in stream water was 3.5μg per l. The frequency of occurrence, in percentage, was quite different. Of the 82 samples of well water and oil-field brine studied, 46 percent contained nickel; of the 65 samples of stream water studied, 75 percent contained nickel.

The data obtained from the analysis of oil-field brine were included in calculating the averages for the concentration and frequency of occurrence of minor elements in ground water. This was done mainly to differentiate between water that is of subsurface, but shallow origin, and water that is apparently of deep-seated origin.

As indicated in the first paragraph of the discussion, the occurrence of minor elements in shallow-zone ground water is similar to that in surface water. The concentration and frequency of occurrence of minor elements in ground water collected from oil-producing zones (fig. 5) indicate a relationship between oil-field connate water and spring water that may have a deep-seated origin. This relationship is suggested by a depletion of vanadium and a concentration of germanium in water from the deep springs and from the oil-producing zones (fig. 6). This relationship presents several possibilities concerning the origin or alteration of the waters.

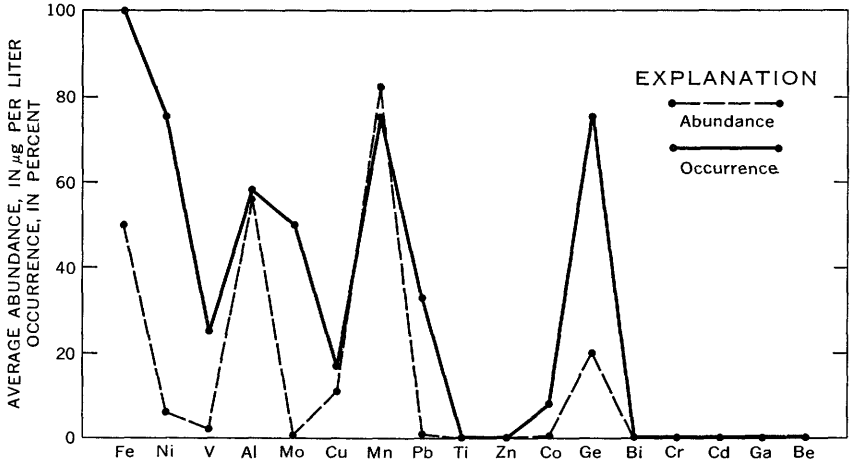

FIGURE 5.—Abundance and occurrence of minor elements in 19 samples of selected oil-field brine.

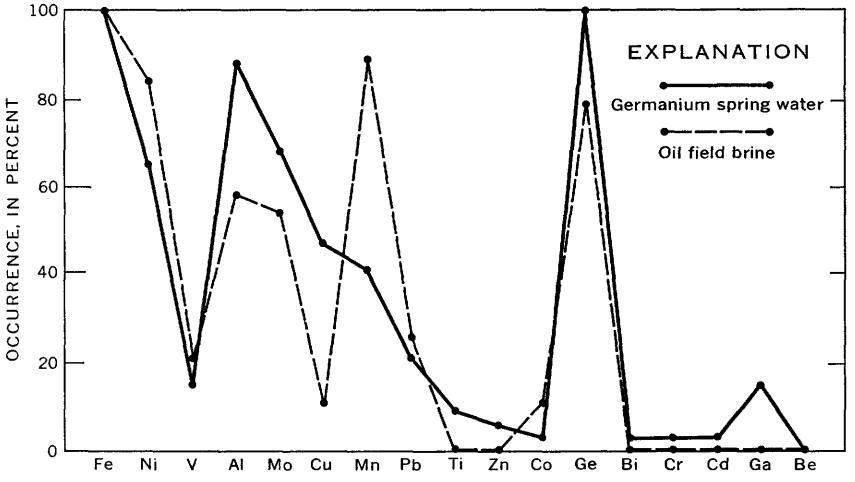

FIGURE 6.—A comparison of the occurrence of minor elements in germanium spring water with that in oil-field brine.

The germanium in oil-field brine may be an original constituent of the brine or may have migrated into the brine. The first possibility seems unlikely. If normal sea water is the source of the oil-field brine, then other minor elements commonly found in sea water should be highly concentrated in the oil-field brine; however, they are not. The second possibility, therefore, seems more plausible. Water migrating upward from deep-seated areas within the earth can issue unobstructedly at the surface, as either a liquid or vapor or both; it can migrate into the uppermost part of a ground-water body and mix with the shallow ground water tapped by wells; or it can migrate into a deeply confined water-bearing zone where it may be structurally or stratigraphically trapped with the oil-field brine. In this manner the water carrying germanium, as well as other elements, could be introduced into the confined water.

Oil-field brine varies from place to place, in gross concentration and in the proportions of both major and minor dissolved constituents. Some brine bears only incidental resemblance to the sea water in which the petroleum- and brine-bearing rocks presumably were deposited. The wide variations in brine composition from place to place may reflect in large degree the mixture of connate sea water with varying amounts and varieties of water of deep-seated origin.

STREAM WATER

PREVIOUS WORK

A study of the literature indicates that a small amount of data has been published concerning the occurrence of minor elements in stream water throughout the world. A few samples of the data follow. Recorder (1939, p. 16) detected iron, aluminum, manganese, zinc, and titanium in Rio Plata water in Argentina. Posokhov and Kalinin (1943, p. 98) reported that they did not detect germanium, gallium, or nickel in water from cold springs and rivers in eastern Kazakhstan. They also reported that, although they did find molybdenum, the amount found was much less than that in water from hot springs in the same area. Turekian and Kleinkepf (1956, p. 1129), in a study of 439 streams and lakes in Maine, detected copper, mangenese, lead, titanium, nickel, and chromium. They list the concentrations of the elements, in parts per billion, as follows: Copper, 1.16; molybdenum, 0.40; lead, 0.26; titanium, 0.20; chromium, 0.02; and nickel, 0.02. More recently, Durum, Heidel, and Tison (1960, p. 618), in a progress report on the worldwide runoff of dissolved solids from most of the major streams of the world, noted that aluminum, iron, and titanium were found in all the samples analyzed and chromium, copper, nickel, and lead were found in most of them.

RESULTS

Following are the results of the analysis of water from 65 streams in California:

Aluminum: Aluminum was found in 60 percent of the samples studied (fig. 7). The concentration rarely exceeded 30μg per l, and the average was 15μg per l.

Beryllium: Beryllium was not detected in any surface-water samples.

Bismuth: Bismuth was found in 2 of 65 samples. One sample contained 0.80μg per l, and the other sample contained approximately 0.60μg per l.

Cadmium: Cadmium was not detected in any of the 65 samples.

Cobalt: Cobalt was found in five samples. The highest value obtained was 15μg per l. Four other samples contained 2.9, 1.8, 1.0, and 0.74μg per l.

Chromium: Chromium was not detected in any of the 65 samples.

Germanium: Germanium was found in two samples which contained 3.7 and 0.41μg per l.

Manganese: Manganese was found in 25 percent of the 65 samples. The average concentration was 7.1μg per l.

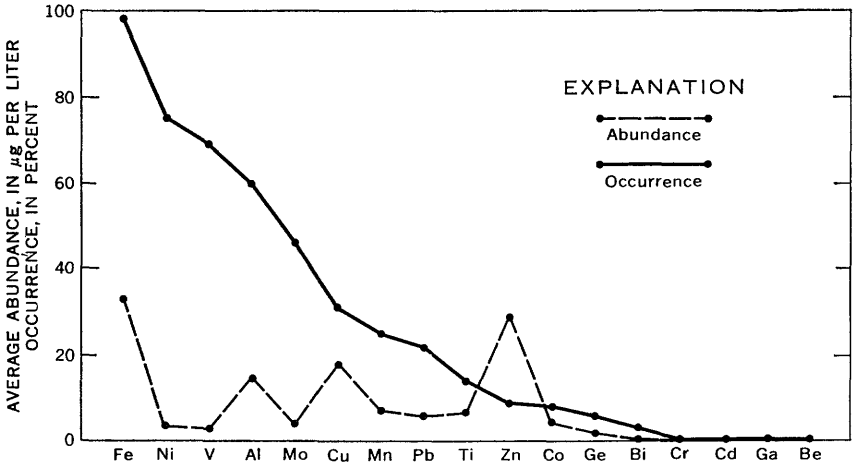

FIGURE 7.—Abundance and occurrence of minor elements in 65 stream samples of selected water.

Molybdenum: Molybdenum was found in 45 percent of the 65 samples. Concentrations ranged from 1.0 to 5.0μg per l. The average concentration was 4.0μg per l.

Copper: Copper was found in 31 percent of the 65 samples. The average concentration was 18μg per l.

Iron: Iron was found in 98 percent of the 65 samples, the highest frequency of occurrence of all the elements. The concentration rarely exceeded 100μg per l and averaged 33μg per l.

Gallium: Gallium was not detected in any of the samples studied.

Nickel: Nickel was found in 75 percent of the 65 samples, about the same abundance as molybdenum. The concentrations ranged from 1.0 to 5.0μg per l, and averaged 3.5μg per l.

Lead: Lead was found in 22 percent of the 65 samples. The average concentration was 5.7μg per l.

Titanium: Titanium was found in 14 percent of the 65 samples. The average concentration was 6.5μg per l.

Vanadium: Vanadium was found in 69 percent of the 65 samples. The concentrations rarely exceeded 5μg per l, and averaged 3.0μg per l.

Zinc: Zinc was found in 9 percent of the 65 samples. The average concentration was 29μg per l.

DISCUSSION

One of the intriguing questions that arose during the early stages of this study was if lithologic environments could be differentiated by the variations in the occurrence of minor elements in the water of

the streams which drained areas of differing lithology. Apparently where the rock types varied in chemical composition, the minor elements released into solution should also vary. This idea was disproved as the data became available from the study of stream water. For example, a large surface stream draining a granitic terrane contained the same minor elements as a stream draining a sedimentary terrane. The lithologic environment had little detectable effect on the occurrence of minor elements in stream waters.

Two possible explanations may account for this finding. First, the frequency of occurrence and the concentrations of the elements studied are considerably higher in the lithosphere than in stream water. For this reason, almost all types of lithologic environments contain more than sufficient amounts of the elements to account for their presence in the associated hydrologic environment; however, the rate of release of individual elements is probably not uniform from rock to rock and from various mineral species. This nonuniform rate of release would explain the variation in abundance of the elements in stream water.

The second explanation as to why the occurrence of minor elements in stream water appears to be independent of the lithologic environment is the biologic activity which exists in the hydrologic environment. Organisms that live in natural water have a great capacity for concentrating minor elements, but only a small amount of work has been done to show the magnitude of this effect or to identify the organisms involved, particularly in fresh water. For the purpose of illustrating this effect, a floating aquatic plant (*Lemna minor* L.) was collected from the American River near Folsom, Calif. The data obtained from an analysis of this plant were compared with the data on the minor elements in the American River water at the same point of collection (table 4).

TABLE 4.—*A comparison of the concentration of minor elements in American River water with that in* Lemna minor *L., collected from the American River, and the resulting concentration factors*

	Water from American River near Folsom, Calif. (parts per million)	*Lemna minor* L. collected from American River near Folsom, Calif. (parts per million [1])	Concentration factor
Aluminum	0. 003	1, 980	660, 000
Cobalt	<. 001	26	>26, 000
Copper	<. 0008	79	>79, 000
Manganese	<. 002	922	>461, 000
Iron	. 0057	1, 840	307, 000
Nickel	<. 001	26	>26, 000
Titanium	<. 0006	61	>102, 000
Vanadium	. 0034	4. 2	1, 240

[1] Based on dry weight at 105°C.

Table 4 shows that American River water contained detectable amounts of aluminum, iron, and vanadium—a total weight of 0.012 mg per kilogram of water for the three elements. The *Lemna minor* L. contained not only aluminum, iron, and vanadium, but also cobalt, copper, manganese, nickel, and titanium, none of which were detected in the American River water. The total weight of the minor elements found in the aquatic plant was 4,940 mg per kg. A further example of this biologic activity is illustrated in table 4 by the concentration factors which show that 1 kg of *Lemna minor* L. contains as much aluminum as 660,000 l of American River water. These data pose an interesting question. The decomposition of *Lemna minor* L., as well as that of many other aquatic organisms, is continuous, and during decomposition, high concentrations of minor elements presumably are released in one form or another and returned to the aqueous environment. Yet why are we seldom able to detect large increases or decreases in minor-elements concentrations in surface water during periods of drastic change, such as dieoffs and plankton blooms, within the associated biologic cycle? The most likely answer is that some of the decomposition products are rapidly taken up in some other part of the cycle; thus, a balance is quickly restored between the growing organisms and those that have died and undergone decomposition. Replicate samples taken at frequent intervals during critical times in cycles of bloom and decay might show temporary increases or decreases in minor-element concentrations. In general, such studies have not been made, nor have dilution effects coincident with increased runoff been adequately evaluated.

Other biologic materials that are not readily decomposed become part of the bottom deposits of the streams or lakes and are at least temporarily withdrawn from the cycle, as shown in table 5 by comparing the concentration of manganese with that of organic matter of a core sample from Castle Lake, Calif. During the early life of Castle Lake there was little or no organic matter or manganese in the lake-bottom deposits. As the lake's biologic system began to develop, the concentration of both organic matter and manganese increased. This deposition of organic material apparently reached a maximum during deposition of material now 1 m below the lake-bottom surface, and the rate of deposition has been constant to the present time. If the manganese is assumed to be unrelated to the organic matter present in the core sample, the implication is that the manganese was rendered soluble, transported in solution, and inorganically precipitated to become part of the lake-bottom deposits. This assumption would seem completely invalid because the rate of solution of the lithologic materials is constant within a fixed set of environmental

conditions; yet the data indicate that the rate of solution and deposition of manganese in the Castle Lake area has increased from zero to more than 190,000μg per kg since the formation of the lake.

TABLE 5.—*A comparison of the concentration of manganese with that of organic matter in a core sample taken from Castle Lake, Calif.*

Location of core sample, Castle Lake, Calif.	Manganese (μg per kg of core material [1])	Organic matter (g per kg of core material [2])
Lake-bottom surface	>189, 000	300
1 m below surface	>189, 000	300
1.5 m below surface	123, 000	265
2.0 m below surface	51, 600	205
3.0 m below surface	Absent	54
Bedrock, volcanic	Absent	1. 3

[1] Based on dry weight at 105°C.
[2] Ignited at 450°C for 24 hours.

Thus, the data strongly indicate that aquatic plants, such as *Lemna minor* L., and perhaps all fresh-water biota, concentrate minor elements in organic or inorganic form and may be the most important controlling factors in the occurrence of minor elements in surface water. Of course, the lithologic environments are the ultimate source of most of the minor elements found in the hydrologic environment.

SEA WATER

PREVIOUS WORK

The chemistry of sea water has been studied exhaustively for many years. Sea water has received perhaps more attention by more workers than any other simple water type. Discussion of the extent of the work that has been done is beyond the scope of this report. However, excellent discussions and bibliographies on the chemistry of sea water are given by Sverdrup, Johnson, and Fleming (1949, p. 165) and by Goldberg (1963, p. 3).

RESULTS

For this study, data were obtained from the analysis of 24 samples collected from the Pacific Ocean, at 50-mile intervals along the entire coast of California.

Aluminum: Aluminum was found in all the samples collected. The maximum concentration was 166μg per l; the minimum, 3.7μg per l; and the average, 9.8μg per l (fig. 8).

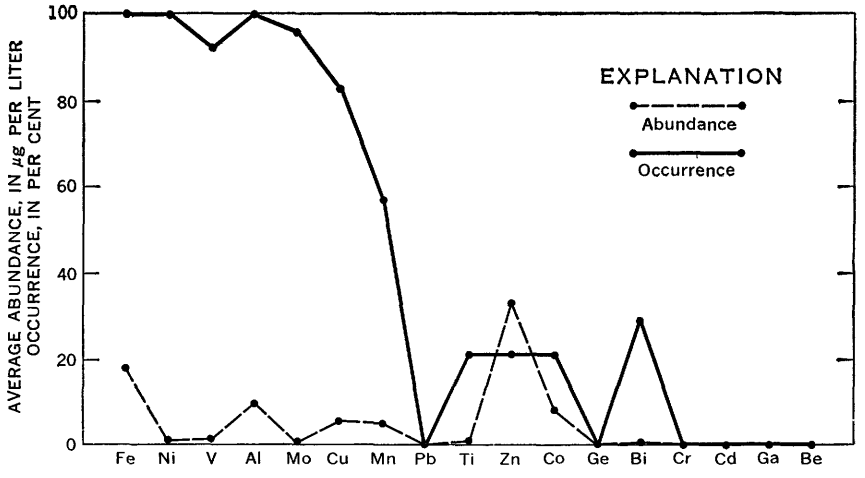

FIGURE 8.—Abundance and occurrence of minor elements in 24 samples of sea water along the coast of California.

Beryllium: Beryllium was not detected in any of the samples.

Bismuth: Bismuth was found in 29 percent of the samples. Measurable amounts were found in three samples. The maximum concentration was 1.4μg per l, and the minimum 0.4μg per l. Traces of bismuth (<0.4μg per l) were noted in four other samples.

Cadmium: Cadmium was not detected in any of the samples.

Cobalt: Cobalt was found in 21 percent of the samples. One sample contained 29μg per l, three contained 8.3, 1.5, and 0.7μg per l. Traces of cobalt (<0.6μg per l) were noted in two other samples.

Chromium: Chromium was not detected in any of the samples.

Copper: Copper was found in 83 percent of the samples. The concentration of copper was rather constant along the entire California coastline. The maximum was 12μg per l, and the minimum was 2.9μg per l. The average concentration was 5.7μg per l.

Iron: Iron was found in all the samples. The maximum concentration was 50μg per l; the minimum, 3.7μg per l; and the average, 18μg per l.

Gallium: Gallium was not detected in any of the samples.

Germanium: Germanium was not detected in any of the samples.

Manganese: Manganese was found in 57 percent of the samples. The maximum concentration was 81μg per l, and the minimum was 1.4μg per l. The average concentration for 9 samples was 5μg per l. Traces of manganese (<0.6μg per l) were noted in four other samples.

Molybdenum: Molybdenum was found in 96 percent of the samples. The concentration of molybdenum was remarkably constant along the entire coast of California. The maximum concentration was

1.3μg per l; the minimum, 0.3μg per l; and the average, 0.8μg per l.

Nickel: Like molybdenum, nickel had an almost constant concentration and was found in all the samples. The maximum concentration was 3.4μg per l; the minimum, 0.5μg per l; and the average, 1.2μg per l.

Lead: Traces of lead (<0.6μg per l) were noted in two samples.

Titanium: Titanium was found in 21 percent of the samples. Concentrations of 0.9 and 0.7μg per l were noted in two samples. Four samples contained trace amounts of titanium (<0.6μg per l).

Vanadium: Vanadium was found in 92 percent of the samples. Like molybdenum and nickel, vanadium had an extremely constant concentration along the coast of California. The maximum concentration was 4.0μg per l; the minimum, 0.6μg per l; and the average, 1.4μg per l.

Zinc: Zinc was found in 21 percent of the samples. The maximum concentration was 500μg per l, and the minimum was 15μg per l. The average concentration was 33μg per l.

DISCUSSION

Data presented in this report indicate that as water passes from a hydrologic environment low in biologic activity into environments of gradually increasing biologic activity, the concentrations of the minor elements gradually decrease. Finally, in sea water, where biologic activity is at a maximum, the concentrations of minor elements are at a minimum. This presents some interesting possibilities. It was shown in the discussion of stream water that biology rather than lithology is probably the controlling factor in the occurrence of minor elements in this water. This same possibility arises with respect to sea water. Do the biota control the concentrations of minor elements in sea water on a day-to-day or season-to-season basis? Aside from the minor elements contained in the sea water and the sea-water biota, the only other significant source of the minor elements is the stream water flowing into the sea. How significant is the amount of minor elements being transported to the oceans compared with the total amount present in both sea water and sea-water biota on a weight basis? The average stream in California carries 132 μg per kg of the 17 minor elements to the Pacific Ocean. Sea water contains an average of 84 μg per kg of the 17 minor elements. A common brown alga (*Fucus*) collected from sea water at Bolinas Beach, Calif., contained 209,000 μg per kg (table 6).

TABLE 6.—*Minor elements found and not found in common brown alga* (Fucus) *and concentration factor of the elements found in an equivalent weight of sea water*

Elements found	*μg per kg*	*Concentration factor*
Aluminum	14, 300	1, 500
Copper	35, 000	6, 700
Iron	68, 900	7, 000
Nickel	3, 000	2, 500
Titanium	2, 360	----------
Vanadium	1, 110	790
Zinc	83, 900	----------

Elements not found	*Less than indicated μg per kg*	*Elements not found*	*Less than indicated μg per kg*
Beryllium	0. 5	Gallium	1. 0
Bismuth	. 5	Germanium	. 5
Cadmium	2. 5	Manganese	1. 0
Cobalt	1. 0	Molybdenum	. 5
Chromium	2. 5	Lead	1. 0

The concentration of minor elements in either stream water or sea water is insignificant in comparison with the amount found in *Fucus*. Other workers have made similar findings concerning the concentration of minor elements in sea-water fauna and flora. For example, Mero (1960, p. 64) has shown that simple tunicates contain 50,000 times more vanadium than does an equal weight of sea water and that oysters effect a 200-fold greater concentration of copper than the amount that exists in sea water. Arrhenius (in Mero, 1960, p. 64) found that the skeletal remains of fish contain appreciable amounts of zinc, copper, tin, and rare earths. He also indicated that nickel and silver tend to concentrate in the bones of fish. Black and Mitchell (1952, p. 575) have shown that common Laminariaceae and Fucaceae concentrate as much as 10,000 times as much titanium as an equal weight of sea water contains. The amount of minor elements carried to the sea by stream water can increase only slightly the productivity potential of the biologic cycles, and minor elements in sea water apparently are in equilibrium with the biologic cycles. Thus, biota in sea water can concentrate minor elements from the sea water, and in this manner the concentration of minor elements in sea water is reduced to a minimum (equilibrium), beyond which no further depletion can occur. The biota then must depend on each other as a source of minor elements, or micronutrients.

SUMMARY

During the early phases of this study the presence of minor elements in the hydrologic environment was thought to be related directly to the associated geologic environment. To some degree this was found to be true. For instance, water emanating from unknown depths within the earth's crust contains germanium, while water at or near

the surface is characterized by the absence of germanium. The literature indicates that germanium should be enriched in the lithologic materials that are more corelike than crustlike. The spring-water data obtained during this study tend to substantiate this observation. Although little or nothing can be said about the actual depths involved, the minor elements in spring water probably reflect the geologic environment where the water originates.

Water, such as oil-field brine obtained from zones as much as 13,000 feet below land surface, contains minor elements that were found in spring water thought to be of deep-seated origin as well as elements characteristic of water that occurs near the surface. It is inferred that the deep-seated water has migrated into the oil-field brine and altered the original water chemistry of the brine. For example, the concentration of germanium in oil-field brine is intermediate between the concentration in spring water from great depth and the concentration found in near-surface water, where germanium is characteristically below limits of detection. Well water and oil-field brine contain elements similar to those found in surface water and sea water, but the amounts of the elements are somewhat different. In well water and oil-field brine, for example, the minor elements were found to be concentrated. In stream water the concentration of the minor elements was somewhat lower than that in well water and oil-field brine. In sea water, the concentration of the minor elements was at a minimum. The basic difference between these three water types, aside from the physical-chemical differences, appears to be the degree of biologic activity in each. In well water and oil-field brine, there is a very small amount of biologic activity. In stream water, the number of fauna and flora is much larger, a condition resulting in greatly increased biologic activity. In sea water this activity reaches a maximum. These observations and the presence of large amounts of minor elements in the aquatic plants collected from sea water and from stream water show that the concentrations of minor elements are closely related to the biologic cycle and its degree of development. In the absence of biologic activity, the occurrence of minor elements is controlled by purely physical-chemical relationships between the water and the lithologic environment.

LITERATURE CITED

Babinets, A. E., and Rad'ko, 1956, Microelements in the mineral waters of the southern slopes of the Soviet Carpathians: Akad. Nauk, Ukrain, S.S.R., Geol. Zhur., v. 16, p. 21–29.

Bateman, A. M., 1951, Economic mineral deposits: New York, John Wiley & Sons, 916 p.

Black, W. A. P., and Mitchell, R. L., 1952, Trace elements in the common brown algae and in sea water: Marine Biol. Assoc. United Kingdom Jour., v. 30, p. 575–584.

Calker, J. Van, 1936, New spectrographic studies: Jour. Anal. Chem., v. 105, p. 396–406.

Durum, W. H., Heidel, S. G., and Tison, L. J., 1960, World-wide runoff of dissolved solids: Internat. Assoc. Sci. Hydrology, Internat. Union Geodesy and Geophysics Pub. 51, p. 618–628.

Goldberg, E. D., 1963, The oceans as a chemical system *in* The sea: New York, John Wiley & Sons, v. 2, p. 3–23.

Kent, L. E., and Russell, H. D., 1949, Warm Spring on Buffelshock near Thabazimbi, Transvaal: Royal Soc. South Africa Trans., v. 32, p. 161–175.

Lopez de Azcona, J. M., 1947, A spectographic study of the elemental composition of medicinal waters of the Spanish Peninsula: Inst. geol. minero España Notas y comun., no. 17, p. 3–8.

Lourenco, O. B., 1940, Spectrographic analysis of mineral waters: Inst. Tech. Research [São Paulo, Brazil] Bull. 26, p. 41–45.

Mason, Brian, 1958, Principles of geochemistry: New York, John Wiley & Sons, 310 p.

Mero, J. L., 1960, Minerals on the ocean floor: Sci. American, December, p. 64–72.

Mitchell, R. L., and Scott, R. O., 1948, Applications of chemical concentration by organic reagents to spectrographic analysis: Spectrochim. Acta, v. 3, p. 367–378.

Novokhalskii, I. P., and Kalinin, S. K., 1939, Spectroscopic character of the thermae of the Transilian Alatau (Tyan-Shan): Acad. Sci. U.R.S.S. Comptes rendus, 22, p. 323–324.

Posokhov, E. V., and Kalinin, S. K., 1943, Spectroscopic characteristics of thermal and cold springs and mountain rivers in Eastern Kazakhstan: Acad. Sci. U.S.S.R. Bull., Geology Ser. No. 6, p. 98–103.

Rankama, K., and Sahama, Th. G., 1950, Geochemistry: Chicago Univ Press, 912 p.

Recorder, R. F., 1939, Spectrochemical analysis of Rio Plata River water and of tap water in Buenos Aires: Obras sanitarias nación [Buenos Aires], Bol., v. 3, p. 16–22.

Silvey, W. D., and Brennan, Robert, 1962, Concentration method for the spectrochemical determination of seventeen minor elements in natural waters: Jour. Anal. Chem., 1. 34, p. 784–786.

Sverdrup, H. U., Johnson, M. W., and Fleming, R. H., 1949, The Oceans: New York, Prentice-Hall, 1,087 p.

Turekian, K. K., and Kleinkopf, M. D., 1956, Estimates of the average abundance of copper, manganese, lead, titanium, nickel, and chromium in surface waters of Maine: Geol. Soc. America Bull., v. 67, p. 1129–1132.

Ubain, P., 1947, Analysis of mineral waters of Axles-Thermes Ariege: Inst. hydrologie et climatologie Annales. 18, p. 1–64.

White, D. E., 1957, Magmatic, connate, and metamorphic waters: Geol. Soc. America Bull., v. 68, p. 1659–1682.

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