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MINOR ELEMENTS IN OIL-FIELD WATERS*

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SUMMARY

The minor element composition of 823 oil-field water samples from the United States and Canada has been determined spectrochemically. In these samples the determined concentrations have a wide range but commonly are: K and Sr, 100 + p.p.m.; Al, B, Ba, Fe, Li, and Si, 1 - 100 p.p.m.; Cr, Cu, Mn, Ni, Sn, Ti, and Zr, p.p.b. (most waters); and Be, Co, Pb, V, W, and Zn, p.p.b. (some waters). When differences in total dissolved solid contents are eliminated (by calculation), Cr, Li, Mn, Si, and Sr are commonly more than twice as abundant as in present sea water; Cu, K, Ni, and Sn are commonly less than half as abundant.

Si content appears to vary between areas, between formations in the same area, and inversely with total solids content in the same formation. Relationships in the variation of other minor elements is more difficult to establish, partly because the minor elements, if actually present, were below our detection limits and partly because our spectrochemical method was not of high precision.

Extensive changes in pH of many waters occurred between collection and analysis. Because of this and changes that may occur between subsurface and surface, quantitative interpretation of geochemical relationships between water and rock composition will be difficult.

INTRODUCTION

The main objective of this paper will be to report on the minor element composition of 823 oil-field waters from the United States and Canada. After a description of how the samples were collected and analyzed, the variations that occur in total dissolved solid content and selected constituents will be presented and compared with sea water. Information on the variations in content of Sr, K, and Si will be presented in greater detail. A secondary

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objective will be to discuss some factors that may influence the analytical results and their interpretation.

The investigation was undertaken as a cooperative program in which Shell Development Company had primary responsibility for collection of oil-field water samples and Du Pont Company for their spectrochemical analysis. Some spectrochemical and other types of analyses of duplicate samples were made in the Shell Development Company laboratories.

THE SAMPLING PROGRAM

The sampling program was aimed at collecting up to 1,000 samples from the United States and Canada that would yield the maximum information on minor element composition of waters produced from oil and gas fields. Interest was not only in possible commercial recovery but also in obtaining an understanding of the origin and history of the waters and in the ways that they had contributed to rock diagenesis.

A tripartite approach was adopted:

(1) A relatively large number of samples were collected from the major producing horizons in different parts of five selected basins. These basins and the number of samples analyzed from each were: Williston Basin of United States and Canada (80); Anadarko Basin (including Oklahoma Platform, central Kansas uplift, and Ardmore Basin)(118); east Texas embayment (88); Permian Basin of west Texas and New Mexico (148); and San Joaquin Basin of California (82). Selection of sampling localities was guided by the variation in total dissolved solids (and in some cases sulphate content) shown by maps prepared from published[1] and unpublished water analyses for producing horizons or groups of horizons. In this way it was hoped that variation in minor element composition might be related to variations in water salinity or major element composition.

(2) In the Louisiana and Texas Gulf Coast areas, sampling was done mostly along five sections roughly perpendicular to the coast. The purpose was to obtain waters from various aged rocks in updip and downdip positions.

(3) In other parts of the United States samples were collected from major hydrocarbon producing horizons, usually either from fields producing large quantities of water or those that were at great distances from other producing areas.

In our sampling, fields or parts of fields where secondary recovery by water injection was underway were avoided. Also avoided, when known, were wells that had had such recent remedial treatment as acidizing or introduction of fresh water to dissolve salt precipitated near the well bore, or that were being treated with emulsion breakers or corrosion inhibitors.

Whenever possible, samples were collected at the wellhead of pumping or flowing wells, otherwise from heat treaters, water knockouts, wash tanks, gun barrels or, where there was danger from abnormal amounts of hydrogen sulphide gas, from dehydrating and recycling plants. Samples were bled into a two-gallon polyethylene bottle, using a length of Tygon tubing. After the

[1]Major sources of water data from United States oil fields published subsequent to Case et al. (1942) are listed as supplementary references.

water separated from the oil, it was bled through a valve at the bottom into new, one-quart polyethylene bottles, capped and sealed with electrical tape When an oil-water emulsion persisted, either samples were treated in the field with a small amount of R-24 or R-25 (Tretolite) emulsion breaker[1] or larger samples were collected. The two-gallon polyethylene bottle was washed with a solvent (mineral spirits, white gasoline, or kerosene) after each sample was collected and washed out with wellhead fluid before taking the next sample. The water temperature, pH, and resistivity were measured immediately, when possible. For some samples, however, measurement of pH had to be deferred for several hours due to extreme cold or failure of the pH meter. Samples were shipped to the laboratory by rail each week or two weeks.

All samples were collected by Mr. G.C. Flanagan, an oil scout of many years' experience. He was advised as to the general localities and horizons from which samples were desired, but selection of the specific wells sampled was based on accessibility, information obtained from the operators, and Mr. Flanagan's good judgment.

SPECTROCHEMICAL ANALYSIS OF BRINES

Spectrochemical methods are readily adaptable to the determination of major, minor, and trace metals in almost any type sample with reasonable accuracy and minimum sample manipulation. The methods are rapid and detection limits were usually lower than those obtainable by other sensitive procedures then available. Maximum accuracy in spectrochemical analysis requires that the samples and standards should have nearly the same general chemical composition and physical properties to avoid errors caused by variation in excitation temperature. The large difference in major element composition of brines precludes meeting this requirement without use of many reference standards. A spectrochemical buffer was not used to compensate for the matrix effects because dilution of the sample and subsequent detection limit alteration was not desired.

Two separate procedures were used for the analysis of brines described in this report because the number of elements and broad concentration ranges encountered preclude the use of a single method. Fifty metalic constituents were determined, and some of these are present in the parts per billion range.

The detection limits of the metals determined by direct excitation of an aliquot of the reference brine solution are indicated in Table I.[2] Concentration values of these metals in the brines were determined by comparison

[1]Analysis of several commonly used emulsion breakers indicated that they would not significantly alter the trace element composition.

[2]Because oil-field waters vary widely in concentration and composition, the detection limits in Tables I and II will not apply to many and, for some elements, most oil-field waters. Most of the detection limits given in Table III, based on eighteen artificial brines of varying composition and concentration, differ from those in Tables I and II.

TABLE I

Metals determined in untreated brine solution

Element	Detection limit (P.P.M.)	Element	Detection limit (P.P.M.)
Antimony	20	Mercury	50
Arsenic	20	Osmium	20
Barium	1	Palladium	1
Boron	1	Potassium	50
Bismuth	10	Platinum	5
Cadmium	10	Rhenium	5
Calcium	10	Rhodium	5
Cerium	20	Ruthenium	1
Germanium	5	Silicon	1
Indium	1	Silver	1
Iridium	20	Sodium	50
Iron	5	Strontium	10
Lead	1	Tellurium	10
Lithium	20	Thallium	1
Magnesium	1	Zinc	10

of selected spectrum lines on the sample spectrogram with a previously prepared reference spectrogram. This comparison procedure is rapid and is adequate for the purposes of this study but accuracy and precision do not compare favorably with methods in which the spectrum line intensity is measured instrumentally and calibration curves prepared.

The trace metals in the brines were determined after separation by precipitation from a 400 ml sample portion. Oxine, tannic acid, and thionalide were used as precipitating agents, and germanium was added to serve as a carrier element. The use of this combination of organic reagents has been suggested by Mitchell and Scott (1948) and is widely used for the determination of trace elements in waters. After ignition of the separated metal-organic precipitate to reduce it to an inorganic ash, a portion is subjected to direct current arc excitation. Selected spectrum lines are compared with corresponding calibration lines on a reference spectrogram and concentration values estimated. The detection limits and trace metals determined are indicated in Table II. It should be noted that the concentration values are in the parts per billion range.

When it was found that duplicate samples analyzed in the Du Pont and Shell Development laboratories showed some differences, eighteen synthetic brines having a wide range in eighteen major and minor components[1] were prepared and analyzed "blind" in each laboratory. Lines were fitted to these data by a least squares method. Results obtained by both laboratories on duplicate samples of the natural brines were also plotted in the sequence in which they had been analyzed.

[1]B, Be, Ca, Cr, Cu, Ga, Ge, K, Li, Mg, Mn, Mo, Na, Ni, Sr, V, W, Zn.

TABLE II

Metals determined after separation by precipitation

Element	Detection limit (P.P.B.)	Element	Detection limit (P.P.B.)
Aluminum	0.2	Nickel	0.5
Beryllium	0.05	Niobium	20
Chromium	2	Tantalum	30
Cobalt	2	Thorium	50
Copper	0.1	Tin	1
Gallium	0.2	Titanium	0.5
Hafnium	50	Tungsten	20
Gold	2	Vanadium	0.5
Manganese	0.3	Uranium	50
Molybdenum	20	Zirconium	2

In most cases, the differences between laboratories for the artificial and natural brines seemed consistent with correction by the least squares lines, and the results were corrected accordingly. The Sr least squares line, however, did not appear to give a good fit, and this was confirmed by the duplicate sample plot. Therefore, an "eyeball" fitted curve was used to correct the Sr values. For Ca, K, and Mg, the Shell analyses of artificial brines, made by titrimetric or flame photometric methods, gave excellent correspondence. Since the duplicate natural brines had also been analyzed by these methods, it was possible to make additional correction curves for some series of samples that had been analyzed spectrochemically.

AVERAGE COMPOSITION

The median concentrations and number of samples analyzed for various areas or parts of areas are presented in Table III. Also included are the concentrations in seawater and our estimated detection limits. Most median concentrations were estimated from histograms of the distribution of concentrations (Fig.1). Because of the wide range of values, their non-normal distribution, and the non-detection of some elements in some samples, the median is considered a better average value than the arithmetic mean.

The median total dissolved solids content ranges from 5 to 222 g/l in different areas and, as shown for west Texas and New Mexico in Table III, may also range widely in rocks of different ages within the same area. Further, as previously shown by Dott and Ginter in 1930 and by other investigations including our own since then, the total dissolved solids within the same formation tends to increase toward the central parts of structural basins. This may be due wholly or in part to dilution of the brines with meteoric waters near the basin margins. Variation in total dissolved solids between and in basins may also result from: (1) solution of salt deposits or salt domes (Rittenhouse, 1967); (2) original composition (fresh, brackish, normal marine, or bitterns from salt deposition); (3) variation in composi-

TABLE III

Median concentration (equaled or exceeded by 50% of the samples) in each area[1]

	Number of samples	Total solids (median) (g/l)	Co	Cr	Cu	K	Li	Mg
Illinois Basin	22	98	ND	2p	10p ?	300	15	6,000
Louisiana and Texas Gulf Coast	79	69	ND	<1p	< 25p	300	ND	250
East Texas	88	66	ND[2]	ND	< 1	< 50	ND	250
North Texas	24	222	ND	<1p	150p	300	ND	5,000
West Texas and New Mexico	148	111	ND	2p	1p	350	15	1,000
Permian only	74	143	ND	2p	2p	400	10	1,000
Pennsylvanian only	34	115	ND	3p	< 1p	300	10	1,000
Silurian–Devonian only	15	55	ND	2p	4p	300	10	400
Ordovician–Cambrian only	21	67	ND	<2p	4p	400	15	800
Anadarko Basin[3]	118	137	ND	10p	10p	250	10	1,550
Williston Basin, post-Paleozoic	25	59	<5p	<2p	< 25p	300	ND	250
Williston Basin, Paleozoic	55	173	ND	3p	3p ?	800	35	600
Powder River Basin	22	5	<5p	<2p	< 25p	300	ND	40
Other Wyoming	28	5	ND	ND	ND	300	ND	100
Colorado	18	5	<5p	ND	< 25p	300	ND	30
California	116	18	ND	5p	5p	45	ND	90
Sea water[4]	-	35	0.27p	0.04p–0.07p	1p–15p	380	0.1	1,272
Estimated Detection Limit	-	-	1p	1p	1p	50	2	10

TABLE III (continued)

	Mn	Ni	Sn	Sr	Ti	V	Zr
Illinois Basin	175p	ND	< 1p	300	<10p	ND	<10p
Louisiana and Texas Gulf Coast	3.5	< 1p	< 1p	85	<10p	ND	<10p
East Texas	3.3	< 1p	3p	350	ND[2]	ND[2]	ND
North Texas	45	15p	12p	450	7p.?	ND	<10p
West Texas and New Mexico	1.8	< 1p	< 1p	200	<10p	ND	ND
Permian only	1.7	< 1p	< 1p	90	<10p	<1p	ND
Pennsylvanian only	2.8	< 1p	< 1p	300	<10p	<1p	ND
Silurian–Devonian only	300p	< 1p	1p	90	<10p	ND	ND
Ordovician–Cambrian only	400p	< 1p	1p	250	<10p	ND	ND
Anadarko Basin[3]	5.6	6p	2p	300	<10p	<1p	<10p
Williston Basin, post-Paleozoic	300p	< 3p	< 1p	100	ND	<1p	ND
Williston Basin, Paleozoic	660p	ND	< 1p	95	<10p	<1p	ND
Powder River Basin	450p	< 3p	< 1p	25	<10p	<1p	<10p
Other Wyoming	300p	ND	< 1p	20	<10p	<1p	ND
Colorado	300p	< 3p	<10p	20	<10p	<1p	<10p
California	950p	10p	2.5p	10	<10p	<1p	ND
Seawater[4]	1p–10p	5.4p	3p	13	Present	0.3p	ND
Estimated Detection Limit	1p	1p	1p	16	10p	1p	10p

[1]ND = below detection limits; p = concentration in parts per billion, otherwise parts per million.
[2]No data; less sensitive methods of analysis used.
[3]Includes Oklahoma Platform and Ardmore Basin.
[4]Data for Cr and Cu from Krauskopf (1956); data for Co, Ni, and Zn from K.K. Turekian (personal communication, 1963); data for other elements from Sverdrup et al. (1946).

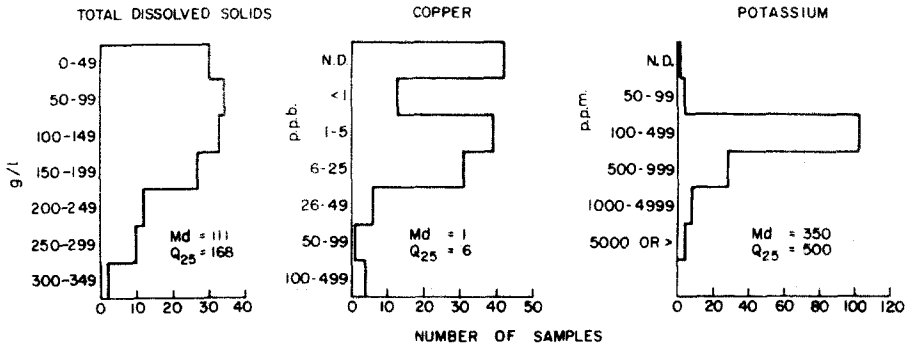

Fig.1. Distribution of total dissolved solids, copper and potassium in west Texas and New Mexico oil-field waters.

tion of compaction waters at different stages in the compaction process (Degens and Chilingar, 1967, p.489), or (4) concentration by the semipermeable membrane action of clays (De Sitter, 1947; White, 1965).

In oil-field waters, elements are commonly present in concentrations as follows:

%	Na, Cl
% or p.p.m.	Ca, SO_4
100+ p.p.m.	K, Sr
1-100 p.p.m.	Al, B, Ba, Fe, Li
p.p.b. (most waters)	Cr, Cu, Mn, Ni, Sn, Ti, Zr
p.p.b. (some waters)	Be, Co, Ga, Ge, Pb, V, W, Zn

The median content of various components of oil-field waters varies between areas, in rocks of different ages in the same area, and in different parts of the same formation in a single area (Table III and Fig.1).

That the median content of different elements is not directly related to change in the median total dissolved solids content is shown in Table III, but it is easier to see in Fig.2 where the data for strontium and magnesium from Table III have been plotted. The values scatter widely. For comparison, the strontium and magnesium content in sea water is shown and indicates how those contents would change with evaporation of the sea water (assuming no precipitation). The strontium content of oil-field waters is commonly much greater than sea water; the magnesium content is much lower. In addition to the causes outlined above for variation in total dissolved solids, major variation in element composition may occur through deposition of cements, solution of the rock framework, or exchange with other elements. Our data show no clear relationship between water composition and lithology or age of the containing rock, but do suggest that less saline waters may have a relatively larger proportion of some minor elements than do more saline waters.

COMPARISON WITH SEA WATER

To obtain a better comparison with sea water, the minor element medians were computed to a common base of 35 g/l total dissolved solids.

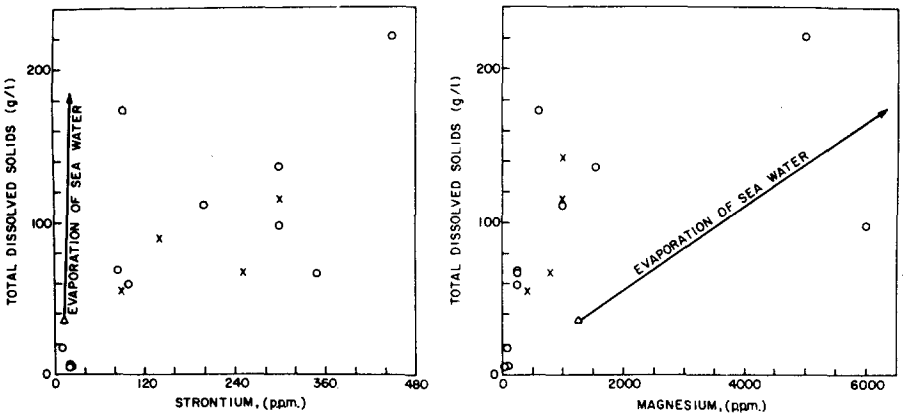

Fig.2. Median total dissolved solids versus median magnesium and strontium contents for areas listed in Table III (*o*) and for rocks of different ages (*x*) in west Texas and New Mexico.

The results are summarized in Table IV. Mn, Li, Cr, and usually Sr are present in amounts more than five times their concentration in sea water. In contrast, Sn, Ni, Mg, and K are commonly present in amounts less than half and, in some areas or rocks, less than one-fifth that in sea water.

A similar computation to a common base of 35 g/l total dissolved solids was also made using the content exceeded by 25% of the samples (Table V). In most area and rock subdivisions Mn, Cr, and Li in this 25% of the samples exceeded their concentration in seawater by more than 25 times. Sr commonly is between 5 - 25 times as much. Co, Cr, Ni, K, Ti, Sn, and V exceed their concentration in sea water by at least two times in at least one rock or area subdivision.

These differences cannot be explained by simple dilution of sea water with fresh water or by concentration of seawater by evaporation.

INDIVIDUAL ELEMENTS

Strontium

The median concentration of strontium versus total dissolved solids for the different areas and ages of rock in Table I are presented in Fig.2. A similar plot for individual samples from Pennsylvania (mostly from sands) and from both carbonates and sands from various places in the United States is presented in Fig.3. Shown for comparison in both figures is the concentration of strontium that would result from evaporation of sea water, assuming no precipitation.

For the medians and nearly all of the individual samples, the strontium content is much greater than that to be expected from evaporation of sea water. The difference appears to increase as salinity increases. No difference is apparent between samples from carbonate and sand reservoirs.

TABLE IV

Median composition oil-field water relative to sea water

Area	Very large (>5 times)	Large (2–5 times)	About same (2–1/2 times)	Small (1/2–1/5 times)	Very small (<1/5 times)
Illinois Basin	Mn, Sr, Li, Cr	-	Mg, Cu (?)	K	Sn, Ni
Louisiana and Texas Gulf Coast	Mn	Sr	-	K	Sn, Mg, Ni
East Texas	Mn, Sr	-	Sn	-	K, Mg, Ni
North Texas	Mn, Sr	Cu (?)	Sn, Mg	Ni	K
West Texas and New Mexico	Mn, Li, Cr	Sr	-	K, Mg, Cu (?)	Sn
Permian only	Mn, Li, Cr	-	Sr	K, Mg, Cu (?)	Sn, Ni
Pennsylvanian only	Mn, Sr, Li, Cr	-	-	K, Mg	Sn, Cu (?), Ni
Silurian–Devonian only	Mn, Li, Cr	Sr	K, Cu (?)	Mg, Sn	Ni
Ordivician–Cambrian only	Mn, Sr, Li	-	K, Cu (?)	Mg	Sn, Ni
Anadarko Basin	Mn, Sr, Li, Cr	-	Cu (?)	Mg, Ni	Sn, K
Williston Basin, post-Paleozoic	Mn	Sr	-	K	Sn, Mg
Williston Basin, Paleozoic	Mn, Li, Cr	-	Sr	Cu (?), K	Sn, Mg, Ni
Powder River Basin	Mn, Sr, K	-	-	Mg	-
Other Wyoming	Mn, Sr, K	-	Mg	-	Cu (?)
Colorado	Mn, Sr, K	-	-	-	Mg
California	Mn, Cr	Ni	Sn, Sr, Cu (?)	K	Mg

TABLE V

Concentrations of certain elements (relative to sea water) in 25% of the oil-field waters

Area	>25 times	25–5 times	5–2 times
Illinois Basin	Mn, Li	Sr, Cr	-
Louisiana and Texas Gulf Coast	Mn	Sr, Li	-
East Texas	Mn	Sr, Cr	Sn
North Texas	Mn, Cr, Li	Sr	Ti, Cu, Ni
West Texas and New Mexico	Mn, Li	Sr, Cr	-
Permian only	Mn, Li	Sr, Cr	-
Pennsylvanian only	Mn, Li	Sr, Cr	-
Silurian–Devonian only	Mn, Cr, Li	Sr	-
Ordovician–Cambrian only	Mn, Cr, Li	Sr	-
Anadarko Basin	Mn, Cr, Li	Sr	Ni
Williston Basin, post-Paleozoic	Mn, Li	Sr	-
Williston Basin, Paleozoic	Cr, Li	Mn, Sr, Ti, K	-
Powder River Basin	Mn, Sr, Cu, Li	K	-
Other Wyoming	Mn, Cr, Li	Sr, K	Ni
Colorado	Mn, Sr	K	-
California	Mn, Co, Cr	Ti, V, Ni	Sn, Sr, Cu

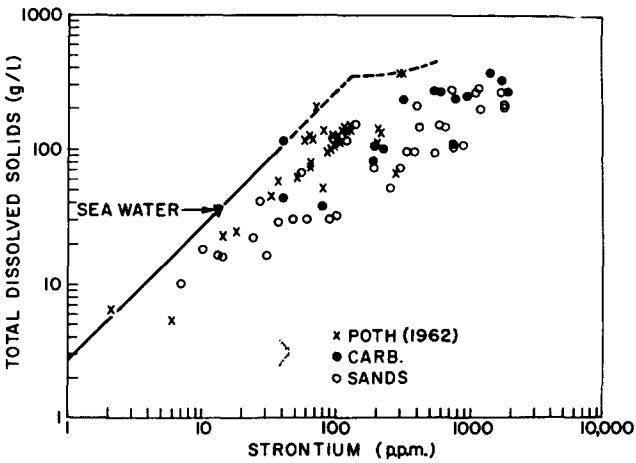

Fig.3. Total dissolved solids versus strontium content for individual oil-field water samples. Strontium determined by wet chemical methods (Poth, 1962) and spectrochemically (this study).

In waters from carbonate beds, concentrations of strontium greater than in seawater might be explained by release of strontium during alteration of aragonite to calcite or dolomite. Calculations suggest that it may also be an adequate mechanism in sandstone reservoirs as well, if as much as 1% of aragonite was present as grains or cement. Because much of the water now in sandstone reservoirs may have been squeezed from shales during their compaction, conversion of aragonite in the shales might be the source.

Actually, the problem may not be in finding an adequate source of the strontium in oil-field waters, but in understanding why the concentration is not greater, particularly in waters from limestones or calcareous shales. Control by sulfate, i.e., precipitation as strontium sulfate, may afford an explanation for some, but not all waters. For about half of the samples for which data are available, a fairly good inverse relationship between Sr and SO_4 exists, but on the half of the samples in which sulfate is below our detection limit (about 16 p.p.m.), the strontium content varies widely. Plots of Sr versus HCO_3 and Sr versus SO_4 and HCO_3 together show a wide scatter and suggest no obvious control by bicarbonate.

Potassium

In contrast to strontium, potassium is commonly less abundant in oil-field waters than might be expected from evaporation of sea water. Data from the Bocana de Virrila, Peru (Morris and Dickey, 1957), an estuary in which evaporation exceeds precipitation plus runoff, are plotted in Fig.4A. Four of the six observations fit the expected evaporation concentrations closely; two that have relatively high potassium content may result from dilution of highly concentrated water with less saline water.

Fig.4B is a plot of potassium content (flame photometric method only) versus total dissolved solids for oil-field waters - mostly from California,

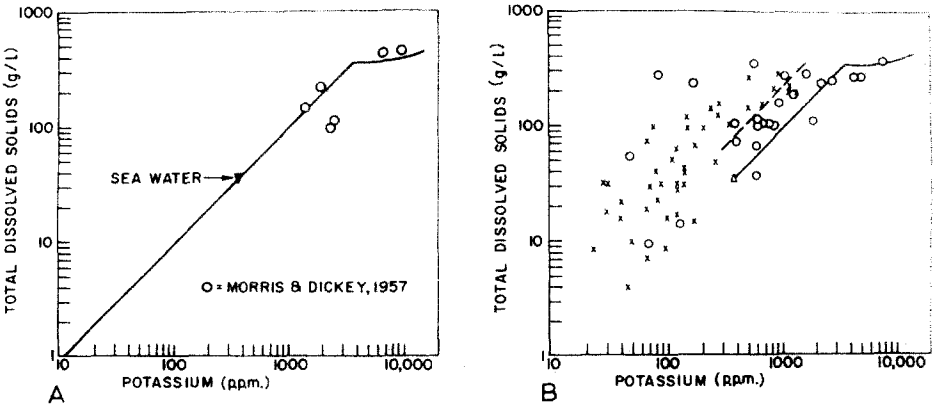

Fig.4. Total dissolved solids versus potassium content. A. Bocana de Virrila, Peru (Morris and Dickey, 1957). B. Oil-field waters from sandstone (*x*) and carbonate (*o*) reservoirs.

east Texas, and west Texas. Except for a few waters of high salinity from carbonate reservoirs and of low salinity from sandstone and carbonate reser voirs, the potassium content is less than would result from evaporation of sea water. For waters having total dissolved solids greater than 60 g/l, the dashed line separates those from most carbonate and most sandstone reservoirs - the waters in sandstone reservoirs generally being more deficient in potassium.

We suggest that the waters in the sandstones have been in contact with clays and that the greater deficiency in potassium results from base exchange or incorporation of potassium in the clay lattice. The apparent discrepancies, i.e., too much potassium from some sandstones and too little potassium from some carbonates, appear to be explainable under this hypothesis. The three sandstone waters having too much potassium are all from the Oil Creek Sandstone which occurs in the predominantly carbonate Paleozoic sequence in Oklahoma, and, consequently, may have had their sandstone-like water displaced by water from the limestones.

Of the six waters having too little potassium, five are from the Pettet and Rodessa in east Texas. Four of these waters have from 1,260 to 2,900 p.p.m. bromine and are interpreted to be slightly diluted bitterns from Jurassic salt deposition (Rittenhouse, 1967). Loss of potassium could have occurred as these waters migrated through shales to their present position in Cretaceous carbonate reservoirs. The less distinctive bromine content of the other much less saline water may result from more extensive dilution, either during the cross-formational migration or after entering the present reservoirs. The more extensive loss of potassium from Pettet and Rodessa waters than from Paluxy and Woodbine waters in the same area may by due to higher initial salinity of the bitterns, which caused greater uptake of potassium by the clays.

The sixth anomalous carbonate reservoir water (about 108 g/l T.D.S. and 380 p.p.m. K) is from the San Andres Formation in west Texas. Bromine is deficient in this water, suggesting that its high salinity results from solution of NaCl. Little addition of potassium would accompany this solution of NaCl.

It is hoped that laboratory experiments with natural waters and clays, and accurate K, Br, and T.D.S. analyses of a larger and more representative group of waters will be made to test these suggestions.

Silicon

As shown in Fig.5, the Si content of 783 oil-field waters ranges from less than 1 to more than 500 p.p.m. The median is 7.8 p.p.m. For Oklahoma and Kansas and for California, the Si content ranges widely within a single area and differs markedly between areas.

In west Texas and New Mexico the median Si content differs in rocks of different ages and, in rocks of all ages, decreases as the total dissolved solids increases (Fig.6). The low salinity waters of Wyoming, California, and parts of Montana also have higher median Si contents than do more saline waters in other areas.

The reasons for this inverse relationship of Si to total dissolved solids content is not understood and may be difficult to determine. Rock composi-

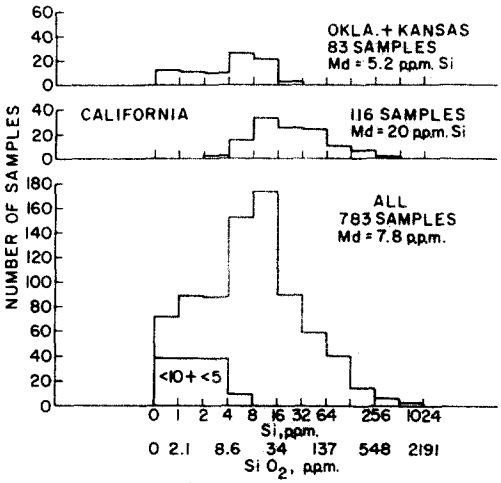

Fig.5. Distribution of silicon in oil-field waters.

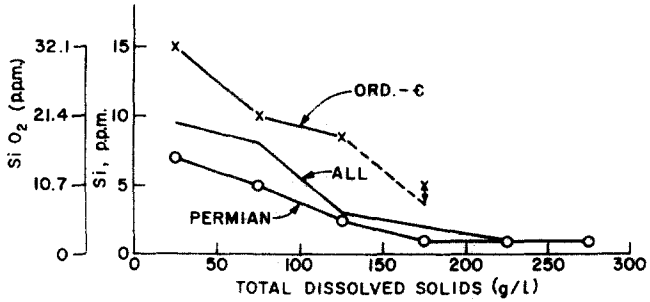

Fig.6. Total dissolved solids versus silicon content in oil-field waters from west Texas and New Mexico.

tion does not appear to be a major control, since high or low salinities and Si contents may occur in both carbonates and sandstone reservoirs. High Si contents occur in some rocks having an abundance of volcanic amorphous or cryptocrystalline silica, but also in rocks having little or no amorphous silica.

Salinities commonly are low near margins of structural basins and increase toward their centers where, because of greater depth, temperatures and pressures also are greater. It may prove difficult to separate the effects on Si content of such increases in temperature and pressure from the effects of mixing of meteoric water flowing into the basins with higher salinity waters already there.

In trying to understand how subsurface waters have been changed and how much of this change may have resulted from interaction with the enclosing rocks, we must work largely with samples. It becomes critical, therefore, to have a clear understanding of how well these samples represent the waters as they actually occur underground. It is with the waters as they occur there that we are concerned. We believe it would be useful to summarize some factors that bear on this important problem and will attempt to do so in the pages that follow.

Although it is possible, by use of a bomb, to collect a water sample at formation pressure and temperature, the cost is so high in deep wells as to be prohibitive except in special circumstances. Even then, pressure, temperature, and water composition may only approach that originally in the formation. Pressure, for example, may have been reduced by nearby production of oil, gas, or water or, in some places, by production many miles away from the well being sampled (Levorsen, 1954, pp.447–448). Therefore, with few exceptions, past and future water samples will be those collected at the surface and will require extrapolation back to subsurface conditions.

Pressure and temperature

In most places, virgin formation pressure approximates hydrostatic, that is, the weight of a column of water extending to the surface or the water table. For fresh water this is 0.433 p.s.i./ft. of depth and increases as the salinity increases. The approximate pressure-depth relationship for the Gulf Coast is shown by Fig.7A. Thus, water from 10,000 ft. in the Gulf Coast would have been at a pressure approximating 4,650 p.s.i. in the formation, and might be expected to have lost a large proportion of carbon dioxide or other gases as it moved to the surface. The loss of carbon dioxide particularly might change the pH of the water and perhaps cause precipitation of some salts.

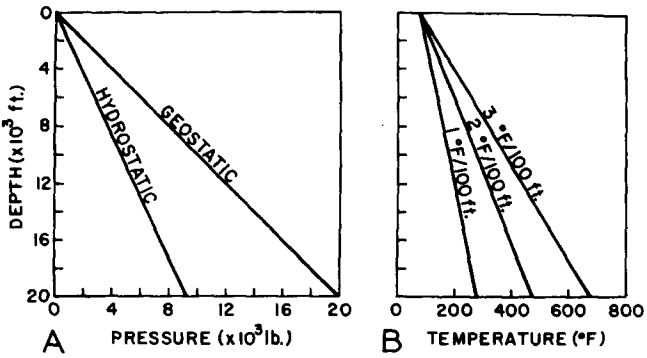

Fig.7. A. Approximate pressure-depth relationship for Gulf Coast. B. Variation in temperature–depth relationships for different average temperature gradients.

With production of water or hydrocarbons, the pressure decrease extends into the formation away from the well. Consequently, release of gas or precipitation of salts may occur in the formation before the water reaches the well.

Pressures greater or less than hydrostatic occur in some places. Abnormally high pressures are not uncommon in the Gulf Coast, exceeding 9,000 p.s.i. at 10,000 ft. in a few places. Loss of dissolved gases between formation and surface would be even greater in waters from these formations with abnormally high pressure.

Temperature also increases with depth, the average rate of increase varying in different areas from less than 1°F/100 ft. to more than 3°F/100 ft. of depth. Fig.7B shows temperatures that exist at various depths for constant gradients of 1°, 2° and 3°/100 ft. Thus at 10,000 ft., the temperatures might be 174°F, 274°F, or 374°F for 1°, 2°, or 3°/100 ft. temperature gradients, respectively. The temperature gradients are not necessarily uniform with depth, commonly being higher near salt domes and in beds with abnormally high pressure and lower where the proportion of sand is high.

Measurement of true formation temperatures is not easy. During drilling of a well, the rocks near the well are cooled by the mud circulated to lubricate the bit, remove cuttings, and seal porous formations. Expansion of carbon dioxide or other gases may also reduce the temperature in a well and the surrounding formation. Unless the well has been shut in for a sufficient time to permit temperature equilibrium to be re-established (days or weeks), the measured temperatures will be too low, sometimes by 30°F or more. Temperatures measured after casing has been cemented in place may be too high because of the heat generated as the cement cures.

In attempting to extrapolate surface samples to subsurface conditions, one is thus faced with two difficulties, i.e.: (1) of knowing or determining the precise temperature to which extrapolation is needed, and (2) of knowing what effect the lowering of temperature in the formation or as the water moves from the formation to the surface has on the dissolved constituents in the water. In some waters, precipitation occurs as shown by the deposition of $BaSO_4$, $CaSO_4$, or other scales in the well tubing or casing, or by the reduction in permeability caused by deposition of NaCl or other salts in the formation adjacent to the well. In some places, fresh water is introduced into such wells to dissolve NaCl, and the total dissolved solids and the proportions of Na, Cl, and other elements measured in samples collected at different times may vary accordingly.

Other downhole changes

At present, most wells are drilled with rotary tools, and many are treated initially or at later times in one or more ways to stimulate the flow of fluids to the well bore. As a result, the water composition may be modified.

In rotary drilling, the weight of the column of mud circulated down the drill pipe exceeds the pressure in the formation. When a porous and permeable bed is penetrated, this excess pressure results in a mud cake forming on the rock surface and filtrate penetrating into the formation around the hole. If a fluid sample is collected with a formation tester (bomb) or a drill

stem test is made, the first water to enter the tester or hole will be this filtrate or a mixture of filtrate and formation water. On drill stem tests, this difficulty can be overcome by testing water samples for chloride ion content until a constant value is obtained (Buckley et al., 1958, pp.852–854).

To increase the flow of fluids to the well bore, "mud acid" may be introduced to remove the mud cake, hydrochloric acid may be forced into carbonate formations, or fracturing of the bed may be accomplished by: (1) explosives or (2) applying enough excess pressure to fracture the rock and to force fluid containing sand or other materials into the fractures to hold them open when the pressure is reduced. Due to these and other types of treatments to stimulate production or prevent friable sands from entering the hole, non-representative water compositions may be obtained until the contaminated water has been produced.

Another common source of contamination is leakage of water from one formation to another because of inadequate cementing, leaking packers, or holes in the casing. Some samples are obtained for the specific purpose of determining whether such leakage is occurring, and the possibility that the samples are contaminated may not always be indicated on the analytical data sheets.

Corrosion of casing and tubing in the wells or in gathering lines or separators above ground is another source of contamination in some places. As shown by Carpenter and Miller (1969), such corrosion may affect especially the content of certain trace metals which are present in steel alloys.

Secondary recovery methods, particularly water flooding, may modify extensively the composition of subsurface waters, the extent of such modification being dependent on the amount and composition of the introduced water. Even when produced water is returned to the same formation, its exposure at the surface may result in precipitation of some elements, particularly Fe. When produced water is injected into other formations, these will also be contaminated.

Another problem about which little is now known is whether water produced with oil is representative of waters in the same bed away from the fields. Zargaryan (1959) found that in the Karachukur-Zykh field: (1) the salinity and composition vary areally, marginal waters being less saline than water in contact with the oil, and (2) a systematic change in chemical composition occurred as exploitation proceeded. It has also been noted that the amount of sulphate in salt brines often is in direct ratio to the distance from oil fields (Rogers, 1917) and that in West Virginia, areas most productive of oil and gas also produce the brines that contain the largest percentages of barium (Heck, 1940). Reactions between hydrocarbons and the waters in contact with them are suggested. Water produced from gas or condensate wells may be, in part, water that is condensed from the gas phase as the pressure is reduced and, consequently, may not be representative of the formation water in total dissolved solids or element content.

Changes at the surface

After water reaches the surface, its temperature may continue to be reduced, and it is exposed to the oxygen in air and to bacteria. Even in sam-

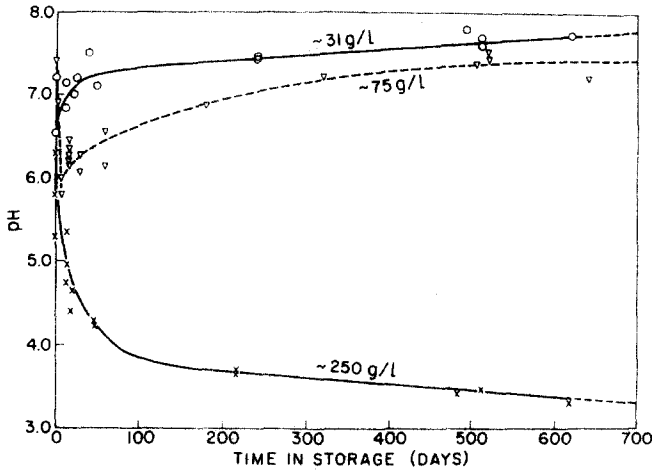

Fig.8. Changes in pH with time of typical oil-field waters stored in polyethylene bottles.

ples collected at the well head, we were unable to exclude all air from the samples, even though attempts were made to do so for a few samples.

For samples collected at the well head, gases may be lost, but the mineral content is preserved, even though precipitation may occur in the sample bottle later. For samples that are collected from separators, gathering lines, or plants, however, there may be an opportunity for precipitates to be removed from the water before the sample is collected and, thus, modify its composition.

We have found that extensive changes may occur, particularly in pH, between the time of collection and analysis. Typical changes in pH with time of storage in polyethylene bottles are shown in Fig.8. In general, the pH of high salinity waters is reduced, that of low salinity waters increased, and that of waters of intermediate salinity first decreases and then increases.

Extensive tests were made to obtain an understanding of these changes. Sixty-four duplicate samples were obtained from each of several wells. Half were placed in polyethylene and half in glass bottles. To half of each of these an organic bacterial inhibitor (Duomen C-50) was added, and half of each was kept refrigerated. The pH of samples of each type was measured after varying times of storage. The change in pH was more extensive in polyethylene than in glass bottles, and less extensive and less rapid in the refrigerated samples. No effect due to bacteria was noted. Samples exposed to air in the laboratory for less than 24 h attained the same pH as those stored in polyethylene bottles for about 600 days.

Analysis of precipitates and acid washings of the bottles, together with the differences in pH change with type of bottle and temperature during storage, suggests oxidation reactions that are temperature dependent. The polyethylene bottles appear to "breathe," and the changes within the glass bottles appear to be due to air included in the samples at the time of collection. H.F. Young (personal communication, 1961) interpreted the pH change

in samples that become more acid as due to oxidation of ferrous to ferric iron and hydrolysis of the ferric iron, and in those that become more basic to oxidation of sulphides to free sulphur. The precipitates and acid washings contained no concentration of minor elements.

Our results indicate that unless pH measurements are made immediately at the well site, they will be of little value. Even good measurements there may not be representative of formation conditions because of prior loss of gases and of salts from precipitation. This and the other factors discussed above will make interpretation of the geochemistry of subsurface waters and their relationships to the associated rocks exceedingly difficult.

CONCLUSIONS

(1) In oil-field water, elements are commonly present in concentrations as follows:

%	Na, Cl
% or p.p.m.	Ca, SO_4
100+ p.p.m.	K, Sr
1-100 p.p.m.	Al, B, Ba, Fe, Li
p.p.b. (most waters)	Cr, Cu, Mn, Ni, Sn, Ti, Zr
p.p.b. (some waters)	Be, Co, Ga, Ge, Pb, V, W

(2) The median content of total dissolved solids and of various elements varies between areas, in rocks of different ages in the same area, and in different parts of the same formation in a single area.

(3) Except for potassium, our data show no clear relationship between water composition and lithology or age of the enclosing rock. They suggest a relationship between composition and salinity of the water.

(4) When computed to the common base of 35 g/l total dissolved solids, Mn, Li, Cr, and usually Sr are present in amounts more than five times their content in seawater; in contrast, Sn, Ni, Mg, and K are commonly present in amounts less than half and, in some areas or rocks, less than one-fifth that in sea water.

(5) In a single area or age of rocks, Si content appears to vary inversely with the content of total dissolved solids.

(6) Many factors make the composition of samples collected at the surface non-representative of virgin waters in the subsurface. Consequently, the interpretation of the geochemistry of these waters and of the water-rock relationships will be difficult.

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REFERENCES

Buckley, S.E., Hocott, C.R. and Taggart Jr., M.S., 1958. Distribution of dissolved hydrocarbons in subsurface waters. In: L.G. Weeks (Editor), Habitat of Oil - A Symposium. Am. Assoc. Petrol. Geologists, Tulsa, pp. 850–882.

Carpenter, A.B. and Miller, J.C., 1969. Geochemistry of saline subsurface water, Saline County, Missouri. Chem. Geol., 4: 135–167.

Case, L.C., Heck, E.T., Fash, R.H., Minor, H.E., Crawford, J.G., Jessen, F.W., Foster, M.D. and Ginter, R.L., 1942. Selected annotated bibliography on oil-field waters. Bull. Am. Assoc. Petrol.Geologists, 26: 865–881.

Degens, E.T. and Chilingar, G.V., 1967. Diagenesis of subsurface waters. In: G. Larson and G.V. Chilingar (Editors), Diagenesis in Sediments. Elsevier, Amsterdam, pp. 477–502.

De Sitter, L.V., 1947. Diagenesis of oil-field brines. Bull. Am. Assoc. Petrol. Geologists, 31: 2030–2040.

Dott, R.H. and Ginter, R.L., 1930. Iso-con map for Ordovician waters. Bull. Am. Assoc. Petrol. Geologists, 14: 1215–1219.

ck, E.T., 1940. Barium in Appalachian salt brines. Bull. Am. Assoc. Petrol. Geologists, 24: 486–493.

Krauskopf, K.B., 1956. Factors controlling the concentrations of thirteen rare elements in sea water. Geochim. Cosmochim. Acta, 9: 1–32a.

Levorsen, A.I., 1954. Geology of Petroleum. Freeman, San Francisco, Calif., 703 pp.

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

Morris, R.C. and Dickey, P.A., 1957. Modern evaporite deposition in Peru. Bull. Am. Assoc. Petrol.Geologists, 41: 2467–2474.

Poth, C.W., 1962. The occurrence of brine in western Pennsylvania. Penna. Topogr. Geol. Surv., Bull., M 47: 53 pp.

Rittenhouse, G., 1967. Bromine in oil-field waters and its use in determining possibilities of origin of these waters. Bull. Am. Assoc. Petrol. Geologists, 51: 2430–2440.

Rogers, G.S., 1917. Chemical relations of oil-field waters in San Joaquin Valley, California. U.S., Geol. Surv., Bull., 653: 1–119.

Sverdrup, H.V., Johnson, M.W. and Fleming, R.H., 1946. The oceans. Prentice Hall, New York, N.Y., 1087 pp.

White, D.E., 1965. Saline waters of sedimentary rocks. In: A. Young and J.E. Galley (Editors), Fluids Subsurface Environments: a Symposium - Am. Assoc. Petrol. Geologists, Mem., 4: 342–866.

Zargaryan, E.L., 1959. Formation waters of the Karachukur-Zykh field. Petrol. Geol. (U.S.S.R.) (English Transl.), 3: 717–722.

SUPPLEMENTARY REFERENCES

Collins, A.G., Zelinsky, W.P. and Pearson, C.A., 1967. Bromide and iodide in oil-field brines in some Tertiary and Cretaceous formations in Mississippi and Alabama. U.S.,Bur. Mines, Rept. Invest., 6959: 27 pp.

Gullikson, D.M., Caraway, W.H. and Gates, G.L., 1961. Chemical analysis and electrical resistivity of selected California oil field waters. U.S., Bur. Mines, Rept. Invest., 5736: 20 pp. (43 analyses).

Hawkins, M.E., Jones, O.W. and Pearson, C., 1963a. Analyses of brines from oil-productive formations in Mississippi and Alabama. U.S., Bur. Mines, Rept. Invest., 6167: 22 pp. (324 analyses).

Hawkins, M.E., Dietzman, W.D. and Seward, J.M., 1963b. Analyses of brines from oil-productive formations in south Arkansas and north Louisiana. U.S. Bur. Mines, Rept. Invest., 6282: 28 pp. (199 analyses).

Hawkins, M.E., Dietzman, W.D. and Pearson, C.A., 1964. Chemical analyses and

electrical resistivities of oilfield brines from fields in east Texas. U.S., Bur. Mines, Rept. Invest., 6422: 20 pp. (422 analyses).
Hoskins, H.A., 1947. Analyses of West Virginia brines. West Va. Geol. Surv., Rept. Invest., 1: 22 pp.
Jessen, F.W. and Rolshausen, F.W., 1944. Waters from the Frio Formation, Texas Gulf Coast. Petrol. Technol., Am. Inst. Mining Met. Engrs., 7: 1–16; Tech. Publ., 1729, Class G, Petrol. Div., 213.
Lamborn, R.E., 1952. Analyses of brines from Ohio. Ohio Geol. Surv., Rept. Invest. 11: 56 pp.
McGrain, P. 1953. Analyses of oil field brines in Kentucky. Producers Monthly, 18: 30–33.
Meents, W.F., Bell, A.H., Rees, O.W. and Tilbury, W.G., 1952. Illinois oilfield brines, their geologic occurrence and chemical composition. Ill. Geol. Surv., Ill. Petrol., 66: 38 pp. (Isicon maps by formation).
Poth, C.W., 1962. The occurrence of brine in western Pennsylvania. Penna. Geol. Surv., Bull. M, 47, p.53.
Rall, C.G. and Wright, J., 1953. Analyses of formation brines in Kansas. U.S., Bur. Mines, Rept. Invest., 4974: 40 pp. (600 analyses).
Walker, F.H., 1959. Natural brines of Indiana and adjoining parts of Illinois and Kentucky. Indiana Dept. Conserv., Geol. Surv., Rept. Prog., 13, p.58.
White, D.E., Hem, J.D. and Waring, G.A., 1963. Data of geochemistry. U.S. Geol. Surv., Profess. Papers, 440-F, 6th Ed., Chapter F: Chemical composition of subsurface waters.
Wright, J., Pearson, C., Kurt, E.T. and Watkins, J.W., 1957. Analyses of brines from oil-productive formations in Oklahoma. U.S., Bur. Mines, Rept. Invest., 5326: 71 pp. (923 analyses).