MOBILIZATION OF SELECTED TRACE ELEMENTS FROM SHALES

by

DAVID TIMOTHY LONG

MAY, 1977

LAWRENCE, KANSAS

Kansas Geological Survey
Open-file Report

Disclaimer

The Kansas Geological Survey does not guarantee this document to be free from errors or inaccuracies and disclaims any responsibility or liability for interpretations based on data used in the production of this document or decisions based thereon. This report is intended to make results of research available at the earliest possible date, but is not intended to constitute final or formal publication.

MOBILIZATION OF SELECTED TRACE

ELEMENTS FROM SHALES

by

David T. Long

B. A., Monmouth College, Illinois, 1969

M. S., University of Illinois, Chicago, 1973

Submitted to the Department of Geology and the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Dissertation Committee:

Ernest E. Angino
Chairman

Lawrence R. Hathaway

Roger L. Kaesler

W. R. Van Schmus

[illegible]

Jacob Kleinberg

MOBILIZATION OF SELECTED TRACE ELEMENTS FROM SHALES

DAVID TIMOTHY LONG

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

Let's face it, if it were not for the encouragement and help of my wife, I wouldn't be writing this. Thanks, Jean. To Dr. Ernest E. Angino goes my deepest appreciation. His constant encouragement and prodding allowed me to grow and develop intellectually during my apprenticeship. Thanks, Ernie. And next time check the labels on the wires before hooking them up.

One thing that made the task of getting this degree more rewarding was having a good dissertation committee. I would like to thank the members of my committee for their encouragement and advice: Doctors Lawrence R. Hathaway, W. R. Van Schmus, Roger L. Kaesler, Louis A. Dellwig, Jacob Kleinberg and Richard Middaugh. Sorry about the water bath, Larry.

My appreciation goes to Mr. George Ochoa for allowing me to take samples of the Heumader shale from the underground storage area at Page Airways, Atcheson, Kansas. I also thank Mr. Jack Davis for allowing me access to a core of the Davis shale from the new Lead-Zinc belt, southeastern Missouri.

Finally I would like to thank Doctors R. M. Garrels, F. T. MacKenzie, H. L. Barnes, and A. L. Carpenter for helping me in the early stages of this study by reviewing my proposal for research.

This research was in part supported by grants from the Geological Society of America, the American Association of Petroleum Geologists, Sigma Xi, the General Research Fund at the University of Kansas, and Mobil Oil Corporation.

MOBILIZATION OF SELECTED TRACE ELEMENTS FROM SHALES

David T. Long, Ph.D.
University of Kansas, 1977

The intent of this research was to investigate the conditions and mechanisms of trace element mobilization from shales by brine solutions. The trace elements investigated were Pb, Zn, Cu, Co, Ni, and Fe. Both theoretical and experimental techniques were used.

Observations in this study were based on the working hypothesis that two reactions comprise the mobilization process, base exchange reactions and extraction reactions. Chloride complexing might be the mechanism for the extraction reaction. The results suggest that both extraction and exchange reactions contribute to the mobilizing process.

The theoretical approach showed the distribution of the chemical species of the trace elements in various aqueous solutions. Three aspects were studied: (1) speciation changes as a result of mixing solutions, (2) speciation changes as a result of changing the complexing ligand, and (3) speciation changes as a result of changing the temperature of the solution.

An ion association model was used for the evaluation of the chemical species. Results show that the major controls on the amount and type of inorganic complexing that takes place in various natural water solutions are the absolute and relative concentrations of the competing inorganic ligands. At freshwater concentrations most of

the elements (Pb, Cd, Ca, Zn) existed as the free ion unless the pH was high (greater than about 7), when hydroxide complexing becomes important. The chemical speciation of Zn and Cu was very similar. At brine concentration (a Ca, Na-Cl solution was used at an ionic strength of 4) the chemical speciation of Zn, Cd, and Pb was very much alike, all highly complexed by chloride. Copper speciation differed by remaining complexed to a variety of different ligands. A significant amount of Cu remained as the free ion even in the pure brine. Different ligands effect different species distributions. For Pb, a ranking was suggested in the ability of a halogen ligand to dominate hydroxide speciation. In descending order, the ranking was I>F>Cl>Br.

Increasing the temperature (25°C to 90°C) tended to decrease the amount of free ion in solution, but the general distribution of the species changed little.

Four aspects were studied experimentally: (1) the ability of certain fractions of the shales (oxidizing and reducing fractions) to release trace metals, (2) how changes in temperature (25°C, 50°C, 90°C) affect mobilization, (3) how changes in the ionic strength (0I, 0.7I, 2I, 4I) of the solution affect mobilization, and (4) how changes in the composition of the solution affect mobilization (leaching solutions used were KI, KBr, KCl, NaCl, $CaCl_2$, $MgCl_2$, and a Ca, Na-Cl brine which was similar to the composition of liquids found in fluid inclusions).

The fractions of the shales were defined by the trace metals released by leaching with a 1N solution of hydroxylamine hydrochloride in 25% acetic acid (acid-reducing) and those metals released by leaching with 30% H_2O_2 (oxidizing). The metals mobilized by the aqueous solutions came mostly from the acid-reducing fraction.

An increase in either temperature or ionic strength increased the amount of mobilization, but these trends are not linear or simple. A brine of ionic strength 10 at 120°C might not be any more effective in leaching trace elements than a 5I brine at 90°C.

Changing the composition of the brine changes mobilization. In this study Ca^{2+} was found to be an efficient mobilizer of Zn and Pb, while K^{+} was found to be effective in mobilizing Cu.

The results of this study support the hypothesis of a low-temperature origin for some strata-bound ores with shales as the source for ore metals and basin brines as the mobilizing solution. An example might be the Pine Point ores of the Northwest Territories.

The results of this study also demonstrate that mobilization is a selective process which could be caused by (1) the fraction of the shale that contains the metal, (2) the composition of the brine, and (3) the nature of the metal itself.

INTRODUCTION

The basic concern of aqueous geochemistry is the nature of the chemical interactions between the various solutions and sediments in terms of both the effect of the solutions on the sediments and vice versa. As part of this, there is increased interest in the chemical behavior of certain trace elements such as copper, lead and mercury in sediments during the diagenesis of the sediments. During the diagenetic process, the sediment may be exposed to solutions of various concentrations and compositions ranging from freshwater to heavy brine. Information on trace-element behavior while being subjected to the processes described above is needed if we are to understand properly the geochemical cycling of elements (Garrels and McKenzie, 1971) and the pathways of trace elements in the environment. Of particular interest is the potential for application of the data from these studies to the origin of stratiform metal deposits.

One hypothesis for the development of stratiform ore deposits suggests a low-temperature (<200°C) and low-pressure (<400 bars) origin with no associated igneous activity. Examples of this type of sedimentary ore deposit are the Mississippi Valley and Tennessee lead and zinc deposits of the United States and the deposits of Pine Point in the Northwest Territory of Canada.

A general summary of the process of sedimentary ore formation encompasses a four-phase process of preconcentra-

tion of the ore elements into the source rock, mobilization of these elements from the source rock by the transporting fluid, transportation of the elements to the depositional area and deposition. These phases are not rigidly defined and are therefore subject to various interpretations by different investigators, particularly as regards the subject of the origin of the elements of the ore deposits.

One source rock proposed is shale. It is known to contain base metals. Subsurface brines are suggested as the mobilizing agent that removes the metals from the shale (Jackson and Beales, 1967).

A question is necessarily raised: Can shales act as a source for ore-forming fluids? To begin to answer this we must know something about the trace-element content of shales and how selected trace elements are mobilized from the shale.

The intent of this research was to investigate the conditions and mechanisms of trace-element mobilization from shales by brine solutions. The trace elements investigated were Pb, Zn, Cu, Co, Ni and Fe. These are included in the term "trace elements" when used in this study. Information from this study should provide insight as to the ability of any shale to act as a source of metal for base-metal deposits and possibly as to why certain metals, such as Pb and Zn, tend to associate in deposits.

DEVELOPMENT OF PROBLEM

This section reviews the nature of the problem and is comprised of three parts. The first discusses the characteristics of low-temperature ore deposits. The second summarizes the chemical nature of brines and their possible role in the formation of low-temperature ore deposits. In the third part possible sources for the metals in an ore deposit are discussed and the trace-element content of shales is summarized.

CHARACTERISTICS OF MISSISSIPPI VALLEY-TYPE DEPOSITS

Mississippi Valley-type mineral deposits are typified by the strata-bound deposits found in the middle and upper Mississippi Valley area. Galena and sphalerite are the common ore minerals. They are commonly contained in a carbonate host, which is usually a magnesium-rich calcite or dolomite. This investigation will refer to these deposits as Mississippi Valley-type (MVT), which includes the various synonyms for these ores, such as the "Tri-state" type and the "Alpin" type. Deposits of this type occur world wide and are usually younger than Precambrian.

Table 1 summarizes the major characteristics of the MVT deposits. In general, the presence of igneous rocks is rare, and if they are present, there is no apparent association between the rocks and the deposit (White, 1968). The mineralogy of the deposits is simple (Heyl, 1969). Galena, sphalerite and chalcopyrite are the most common ore minerals

Table 1. Some characteristics of strata-bound ore deposits.

1. Igneous rocks are rare (White, 1968).
2. The mineralogy of the deposits is simple (Heyl, 1968).
3. Radiogenic leads are normally present (Stanton, 1972).
4. Mineralization is usually not genetically related to any episodes of structural deformation (Hoagland, 1971).
5. The depth of ore emplacement is usually less than 3,000 feet and not more than 5,000 feet (White, 1968).
6. Many deposits occur on structurally positive areas (Noble, 1963).
7. The deposits are epigenetic (Snyder, 1967).
8. The temperature of the depositing ore solution was usually in the range of 70°C to 180°C and no more than 200°C (Roedder, 1968).
9. The total salinity of the depositing solution was four to ten times that of seawater (Roedder, 1968).
10. The solution was a Ca, Na-Cl brine, low in K, Mg and S and high in trace elements, and similar to present "oil field" brines (Roedder, 1968).

with barite, fluorite and dolomite being the most common gangue minerals. Cadmium concentration is usually high and that of silver, low. This differs from stratiform deposits in which silver concentration is high. Radiogenic leads (Joplin or "J" type) are usually present and are usually not isotopically uniform (Stanton, 1972). If there is any structural deformation of the deposits, the mineralization is not genetically related to the deformation event (White, 1968), although mineralization fluids may have followed the fault lines. The depth of ore emplacement is usually less than 3,000 feet and not more than 5,000 feet (White, 1968). Deposits often occur on structurally positive areas and are rare in basins (Noble, 1963; Heyl, 1969). The deposits are not considered to be syngenetic (White, 1968).

From fluid inclusion evidence the temperature of the depositing ore solution was found to be in the range of 70°C to 180°C and no more than 200°C (Roedder, 1967, 1968 and 1971). The low-temperature origin is supported by the heterogeneous nature of the lead crystals, in which the temperature of homogenization (>200°C) was not reached (Stanton, 1972). Total salinity of this solution was four to ten times that of seawater. Commonly, the fluid was a Ca, Na-Cl brine, low in K, Mg and S (as S^{2-} and SO_4^{2-}) and high in base metals. These fluid-inclusion brines are similar in composition to present oil-field brines.

The common genetic features of the MVT deposits are: (1) they occur as cratonic platform deposits; (2) they were

deposited by a low-temperature, concentrated brine; (3) they were epigenetic; and (4) they rarely occur in basins. Any hypothesis for the origin of these ores must also consider the differences among them. These differences have been discussed by Heyl (1969) and are: (1) their lead-isotope ratios, (2) their mineralogy, (3) their trace-element content, and (4) their zonation and geologic setting.

BRINES AND SEDIMENTARY ORE FORMATION

Fluid-inclusion studies on minerals from Mississippi Valley-type ores suggest the mineralizing solution to be a brine (Roedder, 1968). Brines are concentrated aqueous solutions of up to 735,000 mg/l total dissolved solids (TDS). Some of the synonyms that appear in the literature are formation brines, formation water, oil-field waters or brines and petroleum brines. Table 2 presents the composition of a variety of different brines compared to the composition of selected fluid inclusions and seawater.

Brines vary in composition, concentration and origin (Collins, 1975). The types of brines that are believed to have formed in ore deposits are thought to be similar to present-day brines associated with petroleum (Table 2, columns 3, 4, 5, 6 and 11). These brines are high in Na, Ca and Cl and low in K, Mg and S. Column 2 summarizes the concentration levels of the various components of oil-field brines. These values compare favorably with the compositions of fluid inclusions (column 12) except for K and SO_4.

Table 2. The chemistries of various natural brines.

(Data: 1--seawater, Berner, 1971; 2--general concentrations of elements commonly present in oilfield waters, Rittenhouse, 1969; 3--brine from Saline Co., Mo., Carpenter and Miller, 1969; 4--connate Na-Ca-Cl brine from Saline Co., Ill., White, 1965; 5--connate NaCl brine from Texas, White, 1968; 6--brine from western Canada sedimentary basin, Hitchon et al., 1971; 7--membrane concentrated brine from Kettleman North Dome oilfield, Calif., Kharaka and Berry, 1974; 8--Salton Sea brine, Tooms, 1970; 9--Red Sea brine, Tooms, 1970; 10--Cheleken Peninsula brine, Tooms, 1970; 11--oilfield brine, central Mississippi, Carpenter et al., 1974; 12--fluid inclusion brine, Roedder, 1971; 13--sabkha brine, Bush, 1970)

Table 2. The chemistries of various natural brines. (See explanation on opposite page.)

ION	BRINE 1	2	3	4	5	6	7	8	9	10	11	12	13
Ca^{2+}	400	% or ppm	1077	10100	587	26300	9290	28000	5150	19380	28800	18000	20700
Mg^{2+}	1272	---*	405	1920	722	2710	9.3	54	760	---	1830	2400	14400
Na^{+}	10560	%	5904	42000	9450	74300	51700	50400	926000	69740	61100	57100	58900
K^{+}	380	>100	114	323	63	7400	856	17500	1870	---	854	2700	3800
Cl^{-}	18980	%	11450	90300	17300	172000	93300	155000	156030	145020	150700	124600	168800
SO_4^{2+}	2649	% or ppm	1306	990	1.5	269	833	5.4	840	280	80	3300	200
HCO_3^{-}	140	---	263	72	415	412	2130	150	140	22	<30	---	---
Cu^{2+}	0.003	ppb	<0.002	0.2	0.06	0.05	---	8	0.3	0.83	---	---	---
Pb^{2+}	0.003	ppb	0.0016	---	---	---	---	100	0.6	3.58	44	---	---
Zn^{2+}	0.01	ppb	0.094	---	---	0.4	---	540	5	3.83	217	---	---
Co^{2+}	0.0005	ppb	---	---	---	0.014	---	---	---	---	---	---	---
Ni^{2+}	0.0005	ppb	---	---	---	0.035	---	---	---	---	---	---	---
Fe^{2+}	0.02	1-100 ppm	0.03	5.6	9.0	9.0	12.7	2290	80	12.0	338	---	---
TDS**			20440	146440	28703	111778	159301	258970	257760	235620	246700	---	---

*--- not presented in original work

** Total dissolved solids

Brines are known to be capable of containing high concentrations of trace elements. Columns 8, 9 and 10 of Table 2 list the concentrations of Cu, Pb, Zn and Fe in brines from the Salton Sea, the Red Sea and the Cheleken Peninsula, respectively. Recently Carpenter et al. (1974) have reported on the occurrence of Pb and Zn in brines from the oil fields of central Mississippi. Column 11 shows the concentrations of elements in one of these brines.

Four mechanisms are proposed for brine formation (Collins, 1975): (1) evaporation of seawater, (2) dissolution of evaporites, (3) reactions with minerals in sediments and rocks, and (4) shale membrane filtration.

Brines that have been formed by the evaporation of seawater or dissolution of evaporites can usually be identified by their Br, Mg and K concentrations and δO^{18} values (Collins, 1975; Rittenhouse, 1967; Carpenter et al., 1974). In many brines, however, δO^{18} values suggest that there has been no association with an evaporite sequence (Rieke and Chilingarian, 1974). Also in many instances evaporite sequences are not regionally associated with the brine (Chilingarian, 1968).

Another major mechanism for the formation of a brine from seawater could be the action of geological membranes during the compaction of argillaceous sediments. A review of past literature on filtration of aqueous solutions by membranes was given by Berry (1969), and White (1965) explained the general theory of the filtration process.

Excellent experimental data on the effectiveness of some of the geological membranes and the specific behavior of some major cations and anions during compaction were given by Kharaka and Berry (1973).

In addition to compaction, hyperfiltration of meteoric waters moving through shales can cause increased ion concentration in the water, resulting in the formation of a brine solution (Kharaka and Berry, 1973 and 1974). Column 7 of Table 2 could be a brine formed in this manner. Although these brines of meteoric origin are of a different major element composition than that of the connate brines formed by the entrapped seawater in sediments, they are still capable of leaching trace elements from shales. The membrane theory is gaining popularity; but some still view it with caution, urging care in its use due to certain hydrodynamic difficulties that need to be solved (Carpenter et al., 1974).

The formation of a brine from seawater is a complex process involving influences from chemical interactions with the sediment, membrane filtration, and possible solution of evaporites (Collins, 1975). The association of brines with petroleum is well established and might suggest a common origin. This common origin is probably a result of the diagenesis and compaction of sediments in developing basins (Degens and Chilingar, 1967). Brines could be formed as a result of the chemical alteration of seawater trapped as

interstitial fluids during compaction (Rieke and Chilingarian, 1974).

Burst (1966), Perry (1970), and Hower et al. (1976) have described the chemical alterations that take place in sediments during burial and during diagenesis. As depth of burial increases, temperature increases and porosity decreases. Generally diagenesis works to increase the illite content and to decrease that of mixed layer illite-smectites. Engelhardt and Gaida (1963) discussed some of the chemical changes that take place in the pore water as compaction of the sediments continues.

Various studies have demonstrated that interstitial waters change in composition with depth (Schmidt, 1971; Bischoff, 1970 and 1971; Nissenbaum et al., 1971; and Presley et al., 1972). The general effects of diagenesis on interstitial waters have been summarized by Manheim (1974). In general Cl^- varies only to a minor degree in the interstitial waters; SO_4^{2-} is often depleted; Mg, K and some of the Na are depleted; and Ca is enriched. Many previous investigations found K to increase with depth. Sayles et al. (1973), however, using a new technique to analyze interstitial waters, found K to be greatly depleted with depth. This was an important breakthrough in the understanding of the development of a brine from seawater. Comparing the ideal brine (column 2) to seawater, it is clearly seen that the result of the diagenesis of interstitial water is to change the relative concentrations of the chemical species

in seawater to a brine-like composition. Further diagenesis of the interstitial water by influences from membrane filtration or dissolution of evaporites would chemically alter the solution and increase its concentration to that of a brine (Collins, 1975).

The behavior of trace elements during the diagenesis of sediments is largely unknown (Van Everdingen, 1968). Recent studies show variability of the trace-element content of the interstitial waters with depth and at higher concentrations than in the overlying water (e.g. Brooks et al., 1967). The general behavior has been summarized by Duchart et al. (1973). Metals will accumulate at the interface between sediment and water. In oxidizing waters the metals are distributed between iron and manganese oxides and organic material. The oxides, however, are the major scavengers of trace metals. Upon burial the oxides are reduced and release the trace elements, increasing the trace-element content of the interstitial water. In marine sediments organic scavenging and adsorption onto clay particles would be the concentrators of the trace elements.

During diagenesis some trace elements also have a tendency to change solid phases (Presley et al., 1972). Based on selective chemical attacks on sediment, Presley et al. (1972) found the tendency was for the trace elements to go into an H_2O_2 soluble phase which could represent an organic phase. Organic complexing was suggested as the

mechanism by which the trace elements change between solid phases.

The previous discussion has focused on the development of the subsurface brines commonly associated with petroleum. Another type of brine is found associated with sabkhas (Bush, 1970). A sabkha is an evaporite flat with a subaerial depositional interface, differing from an evaporite pan which has a subaqueous depositional interface (Renfro, 1974). In the sabkha environment evaporation greatly exceeds rainfall, thereby causing pore waters to become concentrated. These concentrated pore waters form the sabkha brine.

The chemistry of a sabkha brine is summarized in column 13 of Table 2. It is characterized by a higher K^+ and SO_4^{2-} content than brines associated with petroleum. A sabkha brine has been suggested as forming the ore solution for some strata-bound copper deposits (Renfro, 1974; Smith, 1975).

SOURCE OF ORE MINERALS

One question that needs to be answered is what is the source of the base metals in the deposits. There are a variety of possible sources, which could be summarized as: (1) hydrothermal solutions generated within magmas, (2) solutions leaching igneous rocks, (3) direct precipitation from seawater, (4) solutions leaching arkosic sediments, (5) solutions leaching carbonates, and (6) solutions leaching shales.

Hydrothermal waters are formed from igneous activity at depth and are assumed by some workers to be derived from the vapor phase (Holland, 1972). Checking δS^{34} values for the strata-bound ores, one finds they are usually negative and quite variable. If the hydrothermal solutions were of igneous association, the δS^{34} values would be close to zero and homogeneous (Stanton, 1972). Another objection is that the vapor phase can contain only 5 percent NaCl, which is too dilute to account for the concentrations found in the inclusions (White, 1968). The strongest objection, however, is that igneous rocks are usually not associated with the ore deposits (Noble, 1963).

Leaching of igneous rocks by brines as a source for trace elements is subject to the same difficulty; i.e., igneous rocks are not commonly associated with the deposits. However, this does not eliminate the possibility of leaching deep basement rock as suggested by Heyl (1969). In any hypothesis about the source rock for the trace elements, account must be taken of the source of the heterogeneous "J" type leads because leads from an igneous source would be of ordinary type and homogeneous. A small contribution to the chemistry of a brine by an igneous source is not eliminated by this, however.

Direct precipitation from seawater implies a syngenetic origin for the ores, and most investigators are agreed that the MVT deposits are epigenetic (Snyder, 1967).

Leaching of carbonates is a possibility since they are known to coprecipitate some trace elements, such as Pb and Zn (Krauskopf, 1965; Weiss and Amstutz, 1966). To release the metals from the carbonate, a solution would have to be capable of dissolving the rock. Calcite has been demonstrated to be a stable phase in most depositing brine solutions of MVT deposits by both field observation and theory (Beales, 1975; Anderson, 1975). Dissolution would therefore not take place. However, there is the possibility of release of metals during the recrystallization of calcite to dolomite. In addition, when the ore solutions originated they could have been capable of dissolving limestone. How great a contribution this would make to the metal content of the brine is not known (Weiss and Amstutz, 1966). More work is needed on the diagenesis of carbonates and the release of trace elements.

Arkosic sediments have the potential of being a source, as some leaching studies have shown that base metals can be removed from these sediments by brines (Ellis, 1968). The question arises as to whether a sufficient volume of these sediments occurs in the vicinity of the ore deposits, or better in the ore solution generating areas, and whether sufficient metals could have been released from these arkosic sediments to form a deposit. More work is needed in this area.

Shales are ubiquitous and are known to contain and concentrate trace elements (Vine and Tourtelot, 1970).

Table 3 summarizes the concentrations of Fe, Pb, Cu, Zn, Co and Ni in a variety of earth materials. The trace-element concentrations in the shales, although taken from different sources and having different absolute values, demonstrate the ability of shales to concentrate trace elements. This is seen by comparing the concentrations of the elements in shales versus the concentrations in soils. The soil data are averages of all the data for the A, B and C soil horizons presented by Conner and Shaklith (1975).

In general, the soils have a lower trace-element content than shales. Although the values presented are only gross averages, the magnitude of the difference in concentration between soils and shales suggests that clays, during the process of erosion, transportation and deposition in the ocean, concentrate trace elements.

A likely source of the trace elements is seawater. Krauskopf (1955) demonstrated that the undersaturation of seawater with respect to most of these trace elements could be accounted for by adsorption processes onto such media as clay. The extent to which trace elements can be adsorbed onto clays is a function of the pH of the solution and the nature of the ligand present, as shown for Cu by Payne and Pickering (1975). Tiller and Hodgson (1962), in a test with Co and Zn sorption onto various layered silicates, suggested that although the dominant form of sorption probably involves base exchange, a nonexchangeable form also exists

Table 3. The concentrations of Fe, Pb, Cu, Zn, Co and Ni in selected sediments and rock. Unless otherwise indicated, concentrations are in ppm of rock.

	Seawater[1] ppm	Shales[2]	Deep sea clay[2]	Carbonates[2]	% Shales[3]	% Limestone[3]	Coal[4]	Shale[4]	Black Shale[4]	A Soil[4]	B Soil[4]	C Soil[4]	Soil[4]
Fe		47200	65000	9000	3.1	1.13	1.92%	3.56%	33%	1.73	2.16	3.56	2.4
Pb	.003-.008	20	80	9	.014	.0026	34.78	15.33	23	14.36	14.2	9.8	21.3
Cu	.001-.015	45	250	30	.009	.0018	15.16	14.25	130	14.74	18.56	21.0	16.3
Zn	.005-.021	95	165	35	.016	.004	272.29	327.4	<500	29.5	34.5	33.7	48.7
Co	.0001	19	74	7			9.57	9.9	8.1	7.5	7.2	9.3	10.4
Ni	.0001-.0005	68	225	30	.011	.0015	21.07	32.8	110	11.2	16.5	15.3	17.5

1. Krauskopf (1955)
2. Turekian and Wedepohl (1961)
3. Ostrom (1957)
4. Conner and Shaklith (1975)

that is characterized by penetration of the lattice by the trace elements.

Stability on clay minerals follows the order Pb>Fe>Cu>Zn (Leland et al., 1973). Trace-element adsorption on clays usually decreases in the order vermiculite>montmorillonite>kaolinite (Cody, 1971).

Besides clays, shales comprise various other fractions that can contribute to the total trace-element content by the sorption process (Krauskopf, 1955). Particularly effective scavengers of certain trace elements are the iron and manganese oxides (Jenne, 1968; Chao and Anderson, 1974; Laganathan and Burau, 1973). Copper, cobalt, nickel and lead are frequently found associated with the oxides (Bostrom, 1972). The coprecipitation on the oxides is probably an important mechanism for removing cobalt and nickel from seawater, since their removal cannot all be accounted for by clay sorption (Krauskopf, 1955; Spencer et al., 1972). The oxides may also be an important transport mechanism for trace elements in streams (Steele and Wagner, 1975; Angino and Schneider, 1975; Gibbs, 1972). Stability on the iron-manganese oxides follows the order Cu>Co>Mn>Zn>Ni>Pb (Steele and Wagner, 1975).

Organic matter is also known to be a highly effective scavenger of trace elements (Duce et al., 1972). De Groot and Allersma (1973) found organo-metallic complexes to be highly successful in mobilizing Cu, Zn and Pb from oxide coatings in stream sediments. The fulvic acid fraction was

mainly responsible for the mobilization. The effectiveness of fulvic acid in removing trace elements from shales was demonstrated by Kodama and Schnitzer (1974) for copper on montmorillonite. The major mechanism for removal was attributed to complexation of the fulvic acid to the copper. Generally the stability follows the order Pb>Cu>Ni>Co>Zn>Cd>Fe>Mn>Mg for fulvic acid (Schnitzer and Skinner, 1968).

Rashid (1974) studied humic acid adsorption of various trace elements. Selectivity followed the order Cu>>Zn>Ni>Co>Mn. Copper also formed a very strong bond with the humic material compared to the others tested. Adsorption of trace elements to the humic acid was through chelation, cation exchange, and surface adsorption. The effectiveness of humic acid in peat moss in adsorbing trace elements was reduced in seawater, however, due to the preferential adsorption of alkali and alkaline earths.

Five mechanisms of trace-element concentration with particulate organic matter were listed by Ferguson and Bubda (1974, p. 164):

> (1) direct incorporation into the sediments of metals concentrated by living organisms, (2) the sorption of metal ions from solution onto particulate organic or organic-inorganic matter, (3) the sorption of soluble metal organic complexes from solution onto particulate inorganic or organic matter, (4) the sorption of metals from pore waters by organic materials in sediments, and (5) the solubilitization, as metal-organic complexes, of metals dispersed in sediments and their subsequent transport and concentration in veins and fissures.

Metal sorption by particulate organic matter was found to be the main reaction. Stability of the metals with the

organic matter followed the order Pb> Cu> Cd> Zn. The presence of other cations in the solution reacting with the organic matter reduced Zn sorption to near zero. The results suggested that for organic matter to accumulate enough metal to form an ore deposit, the initial concentration of the reacting solutions would have to be at least two orders of magnitude above that of normal seawater.

McLerran and Holmes (1974) show that bacteria can remove about 70 to 80 percent of the zinc and cadmium in solution. About 10 to 20 percent of the trace metals removed were associated with the bacteria, either assimilated or bound to the surface. The other 80 to 90 percent were removed by direct precipitation as sulfides (or coprecipitated with FeS) by the H_2S generated by the bacteria. Venogradov (1953) and Boyle and Lynch (1968) also demonstrated the ability of marine organisms to concentrate trace elements (TE) by assimilation. The final major mechanism in building the trace-element concentration of the shales is additions from the detrital minerals (Gibbs, 1973).

In summary, shales comprise various fractions such as clay, oxides and organics, each of which acts individually to increase the total trace-element content of the shale.

Studies using selective chemical attacks on shales and sediment indicate that different metals may prefer different fractions (Hirst and Nicholls, 1958; Watney, 1972; Nissenbaum, 1974).

The present state of the art shows enough variability in the data to warrant caution in the interpretation of the data from selective chemical attacks (Angino and Schneider, 1975). If trace metals do prefer different fractions, the ability of the shale to act as a source for trace elements will depend on the ability of the individual fractions to release the metals.

Leaching of shale and the mobilization of the trace elements by brines has been proposed as a mechanism for concentrating metal in the Pine Point ores in the Northwest Territory of Canada (Billings et al., 1972), for copper in some strata-bound copper deposits (Davidson, 1965), for base metals in Mississippi Valley-type deposits in general (Boyle, 1968), for base metals in the Red Sea brines (Bischoff, 1969), and for the metals in present brines in southern Mississippi (Carpenter et al., 1974). A few experimental studies have shown that trace elements can be leached from shale (Hathaway et al., 1972; Williams, 1971).

In this study the mobilization process was investigated theoretically and experimentally. A theoretical approach was used in order to gain insights into the chemical behavior of the trace elements during the mobilization process. The theoretical distribution of the chemical species of selected trace elements was determined in various brine compositions. From this type of approach predictions might be made as to what are the mechanisms of the mobilization process. Experimentally, various shales were leached with

solutions of different concentrations and the amounts of trace elements mobilized were measured.

THEORETICAL CONSIDERATIONS

In this section the theoretical distribution of the chemical species of selected trace elements (Cd, Cu, Pb and Zn) is examined. These metals were chosen because of the relative completeness of the list of the needed stability constants and because of their known selective nature in ore deposits. For example, zinc deposits are relatively high in cadmium concentration and low in copper, while copper deposits are relatively low in lead, zinc and cadmium. Three aspects were studied: (1) speciation changes as a result of mixing solutions, (2) speciation changes as a result of changing the complexing ligand, and (3) speciation changes as a result of changing the temperature of the solution.

Information from a theoretical study such as this could provide insights as to why the ore deposits tend to have certain metals concentrated (for example, a lead-zinc deposit with very little copper). This selective nature might be a function of the way the metals exist in solution and this, in turn, might affect the mobilization process. This type of approach is also useful in determining how chemical changes in the composition of the brine change the manner in which the metals exist in solution. Information from the study of these chemical changes might be used to suggest the changes that might occur in the mobilization process as the chemistry of the brine is varied.

COMPUTATIONS

Various theoretical approaches have been proposed for determining the speciation of specific trace elements in different natural water systems. For details one can refer to the works of White et al. (1958), Garrels and Thompson (1962), Morel and Morgan (1972), Elder (1975), Whitfield (1975) and Wood (1975). Several proposed models show the changes in chemical speciation that accompany changes in ionic strength or in the concentrations of the individual ions. Evaluation of these models usually involves simultaneous solution of several mass balance and complexing equilibria using data on stability constants.

The calculations used to determine the chemical speciation of Cd, Cu, Pb and Zn in the various aqueous solutions are similar to those of Zirino and Yamamoto (1972). Complexes between the divalent metals and the ligands Br^-, F^-, I^-, Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^- and OH^- of the type MeL_n were considered. Me and L represent the metal and the ligand, and n equals 1 to 4. Generally, third and fourth order associations of the cation with the ligand were limited to the halides and hydroxo complexes. Since the metals were assumed to be in low concentrations (<10 ppm), polynuclear complexes were not considered (Helgeson, 1969). As in all models of this type, thermodynamic equilibrium was assumed to exist.

Since (1) many trace elements are normally quite undersaturated in natural aqueous solutions with respect to the

(2) the mean salt method (Garrels and Christ, 1965). This is based on the MacInnes assumption, which is

$$\gamma_{K^+} = \gamma_{Cl^-} = \pm\gamma_{KCl}$$

(3) Davies' (1962) modification of the Debye-Huckel equation, which is

$$-\log \gamma_i = 0.5 Z_i^2 \left[\frac{I^{1/2}}{\beta I^{1/2}} - .3I \right]$$

where the equation parameters are the same as in the Debye-Huckel equation.

(4) Helgeson's (1969) trace activity coefficient equation (modified from the Stokes-Robinson equation). This equation for 25°C is

$$-\log \gamma_j^x = \frac{A \cdot Z_i^2 \cdot I^{1/2}}{1 + \mathring{a} \cdot B \cdot I^{1/2}} + B' \cdot I$$

where the equation parameters are the same as in the Debye-Huckel equation plus B', which is the deviation function.

As an example of how the different methods compare, Figure 1a shows how the value of the activity coefficient of Mg varies as a function of ionic strength as determined by the different methods.

At ionic strengths of less than about 0.1, all four methods agree fairly well. At higher ionic strengths the results differ remarkably. Davies' equation is not considered to be valid when the ionic strength is greater than 0.1 since it does not have an adjustable parameter. For the calculations presented here the mean salt method was

(c) for percent complex $ML(i)_n$,

$$\% \left(mL(i)_n\right) = \frac{100\,\beta(i)_n \left(L(i)\right)^n \cdot \frac{\gamma_m \gamma_{L(i)}^n}{\gamma_{mL(i)_n}}}{1 + \sum_{n=1}^{4} \sum_{i=1}^{j} \beta(i)_n \left(L(i)\right)^n \cdot \frac{\gamma_m \gamma_{L(i)}^n}{\gamma_{mL(i)_n}}}$$

where:

(m) = concentration of free cation in moles;
j = number of ligand associations;
n = order of association;
$\beta(i)_n$ = stability constant of i^{th} associations, n^{th} order;
$L(i)^n$ = concentration of i^{th} ligand in moles for n^{th} order association;
γm = activity coefficient of cation;
$\gamma L(i)$ = activity coefficient of i^{th} ligand; and
$\gamma mL(i)_n$ = activity coefficient of complex.

Similar equations were used to calculate the distribution of the major anions. Individual activity coefficients were used to calculate the activities of the chemical species and were determined in accordance with the ionic strength of the mixture. Activity coefficients of ions in concentrated solutions are difficult to determine theoretically. Furthermore, no method is generally accepted (Truesdale and Jones, 1969). Four approximations can be considered:

(1) the extended Debye-Huckel equation,

$$-\log \gamma_i = \frac{Az_i^2 \cdot I^{1/2}}{1 + B\mathring{a} \cdot I^{1/2}}$$

where:

A = constant relating to solvent;
B = constant relating to solvent;
I = true ionic strength;
$\mathring{a}$ = distance of closest approach of i^{th} ion; and
z_i = charge of the i^{th} ion.

precipitation of minerals and (2) precipitated metal would be unavailable for any sorption reactions, the trace-element speciation is computed on the basis of the percentage of the metal concentration that would be complexed and uncomplexed. In this way the absolute trace-element concentrations are not needed, and the systems studied would be unaffected by precipitation reactions. The models presented and discussed are strictly inorganic systems; competition for the trace elements by other ligands such as clays or organic matter is not considered.

Two steps were used to calculate the distribution of the chemical species in each aqueous mixture. Step one involved the computation of the species distribution of the major ions by the ion association model of Garrels and Thompson (1962). In step two the chemical speciation of the trace elements was determined.

The mass action equations used in calculating both major cations and trace-element distributions are:

(A) for total concentration of metals,

$$(m)_{TOTAL} = (m) + \sum_{n=1}^{4} \sum_{i=1}^{j} \beta(i)_n (m)(L(i))^n \cdot \frac{\gamma_m \gamma_{L(i)}^n}{\gamma_{mL(i)_n}}$$

(B) for percent uncomplexed elemental ion,

$$\%_0(m) = 100 \Big/ \left(1 + \sum_{n=1}^{4} \sum_{i=1}^{j} \beta(i)_n (L(i))^n \cdot \frac{\gamma_m \gamma_{L(i)}^n}{\gamma_{mL(i)_n}} \right)$$

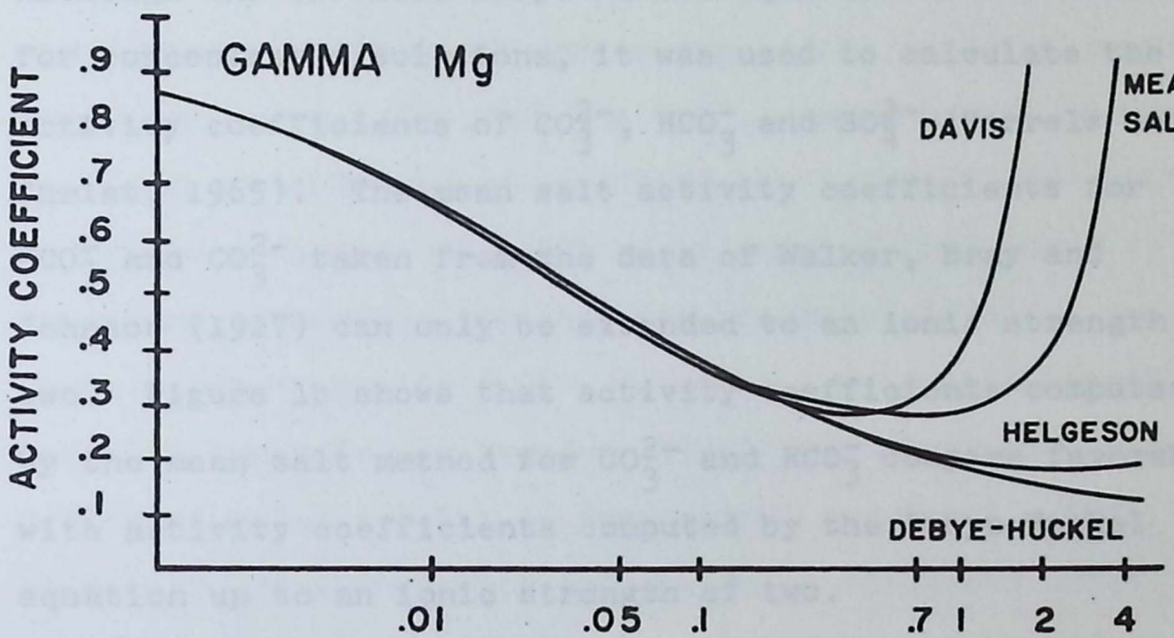


Figure 1a: Activity coefficients of Mg as a function of ionic strength as determined by various methods.

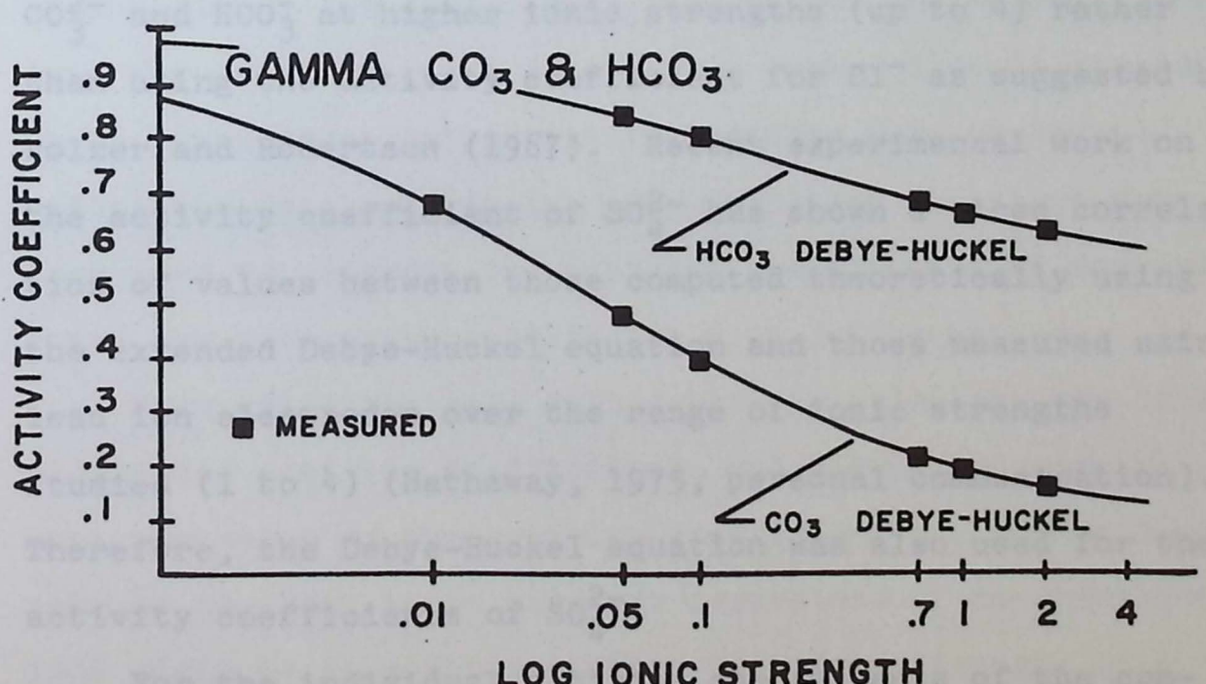


Figure 1b: Activity coefficients of CO_3^{2-} and HCO_3^- as a function of ionic strength for measured values and determinations using the extended Debye-Huckel equation.

used to calculate the activities of the major ions and the method proposed by Helgeson was used for the trace elements. Although the extended Debye-Huckel equation is not defined for concentrated solutions, it was used to calculate the activity coefficients of CO_3^{2-}, HCO_3^- and SO_4^{2-} (Garrels and Christ, 1965). The mean salt activity coefficients for HCO_3^- and CO_3^{2-} taken from the data of Walker, Bray and Johnson (1927) can only be extended to an ionic strength of two. Figure 1b shows that activity coefficients computed by the mean salt method for CO_3^{2-} and HCO_3^- compare favorably with activity coefficients computed by the Debye-Huckel equation up to an ionic strength of two.

Because of this close correlation, the Debye-Huckel equation was used to compute the activity coefficients of CO_3^{2-} and HCO_3^- at higher ionic strengths (up to 4) rather than using the activity coefficient for Cl^- as suggested by Polzer and Robertson (1967). Recent experimental work on the activity coefficient of SO_4^{2-} has shown a close correlation of values between those computed theoretically using the extended Debye-Huckel equation and those measured using lead ion electrodes over the range of ionic strengths studied (1 to 4) (Hathaway, 1975, personal communication). Therefore, the Debye-Huckel equation was also used for the activity coefficients of SO_4^{2-}.

For the individual activity coefficients of the complexes, the Debye-Hyckel equation was used for ionic strengths below 0.1 when the adjustable parameters in the

equation were defined for the complex. Above 0.1, or when the adjustable parameters were not defined, values were assigned depending on the charge of the complex. Complexes with charges of +1 or +2 were assigned the activity coefficients determined for HCO_3^- and CO_3^{2-}, respectively. Neutrally charged complexes were assigned the value of the activity coefficient (gamma) of $H_2CO_3^o$ as calculated from the Setchenow expression (Reardon and Langmuir, 1974):
Gamma $H_2CO_3^o$ = antilog 0.06 · I, where I = ionic strength. Recently Langmuir and Reardon (1976) have suggested using a different value (-0.5 · I) for neutral complexes. The effect of using their new value will be discussed later.

The data for the activity coefficients of the salts used in the mean salt method were taken from Robinson and Stokes (1959) for $CaCl_2$, $MgCl_2$, NaCl, KCl and Na_2SO_4. The data for each salt were examined in terms of ionic strength. Up to ninth order polynomial regressions were needed to define the data accurately. The resultant equations were then used to generate the activity coefficients of the salts which are necessary to solve the mean salt equations.

When using the mean salt method to calculate the individual ion activity coefficients, one assumption made is that the value of the activity coefficient for an ion is the same at constant ionic strength regardless of how many other ions might be in solution. When the ionic strength of a solution is less than 1.0 this assumption appears to be valid. When the ionic strength is greater, one needs to

correct the activity coefficient values to account for the presence of other ions. This is done using the empirical equation known as Harned's Rule (Berner, 1971), which is

$$\log \gamma_{\pm 1} = \log \gamma_{\pm 1(0)} = \alpha_{1,2} I_2$$

where:

$\gamma_{\pm 1}$ = mean activity coefficient of an electrolyte 1 in the presence of another electrolyte 2;
$\gamma_{\pm 1(0)}$ = mean activity coefficient in a solution of pure electrolyte 1 with an ionic strength the same as the total ionic strength ($I_1 + I_2$) of the electrolyte mixture;
I_2 = ionic strength contributed by electrolyte 2 (assuming complete dissociation); and
$\alpha_{1,2}$ = Harned's Rule coefficient referring to the effect of salt 2 upon salt 1 and not vice versa.

In the early calculations the activities of the ions were not adjusted for the effect of the various species on one another. Species diagrams calculated with activities corrected for salt interactions using Harned's Rule were compared to the same diagrams calculated using uncorrected salt activities. The results showed that for ionic strengths below 2.0 there was no significant difference between diagrams. Thus, in subsequent calculations, Harned's Rule was not used to correct salt activities. For the special studies involving ionic strengths greater than 2, Helgeson's equation was used instead of the mean salt method; therefore, Harned's Rule was not necessary.

STUDY ONE - MIXING SYSTEMS

Mixing systems were set up using the end-member concentrations of freshwater, seawater and brine shown in

Table 4. A variety of definitions exist for the term freshwater; consequently, its exact meaning is ambiguous. Usually freshwater implies an aqueous solution dilute with respect to the concentrations of the various ions (e.g. river water, ground water and rain water). In this study the term freshwater was defined as one in which the total dissolved solids content was less than 1,000 mg/l. Such solutions would correspond roughly to those with an ionic strength less than 0.5 mole kg^{-1}.

Major and trace-element speciation was calculated for the five mixtures defined as 100 percent seawater, 75-25 (seawater-freshwater, respectively), 50-50, 25-75 and 100 percent freshwater as a function of pH. The pH was varied from 3.5 to 11.0 at 25°C using 0.5 pH increments. Similar mixtures were studied for the freshwater-brine system.

Since the four trace elements considered in this study have different outer electron orbital structures as the divalent ions, different chemical speciation could be expected. Zinc (2+) and cadmium (2+) have complete 3d and 4d outer orbital structures, respectively. Copper (2+) has a $3d^9$ structure and lead (2+), a complete 6s structure with inner f orbitals. The stability constants for the chemical species give an idea of the relative importance of a particular complex (App. A), but it is not readily apparent from these constants at what concentrations or at what pH's a given complex is important.

Table 4. The molal concentrations of the chemical end members used in the theoretical calculations.

COMPONENT	FRESHWATER[3]	SEAWATER[4]	BRINE[5]
Calcium	0.000375	0.0104	0.0964
Magnesium	0.000168	0.054	0.0223
Sodium	0.000274	0.4752	1.6845
Potassium	0.000059	0.01	0.0079
Chloride	0.00022	0.554	2.0198
Ta[1]	0.000955	0.00234	0.0001
Sulfate	0.000955	0.0284	0.0029
I[2]	0.0021	0.661	2.099

(1) Total alkalinity
(2) Effective molal ionic strength (after computation of species distribution)
(3) Taken from Livingstone (1963)
(4) Taken from Berner (1963)
(5) Taken from Carpenter et al. (1974)

Freshwater-Seawater Mixing System

Figures 2 through 5 show the results for the mixing of seawater and freshwater in different proportions. The figures are arranged with 100 percent seawater at the bottom and 100 percent freshwater at the top; pH increases to the right on the abcissa and the percentage aqueous species or association is plotted on a log scale on the ordinate. Associations are shown for percentages between 0.1 and 100 percent.

Zinc

Zinc speciation (Figure 2) in aqueous solution can be characterized by three fields--one at pH's up to about 6.5 (designated the precrossover field), a second covering the pH range 6.5 to 9.5 (the crossover field), and a third at pH values greater than about 9.5 (the post crossover field). Similar fields can be recognized on the speciation diagrams of the other trace elements. The precrossover field of zinc is characterized in all the mixtures by the dominance of free zinc (Zn^{2+}) and by the invariance of the associations with change in pH.

Chloride becomes an important ligand soon after the addition of small amounts of seawater to the freshwater solution. As would be expected, with greater amounts of chloride in solution, higher order associations become important. Also as the Cl^{2-} concentration is increased, the difference in magnitude of the various orders of the chloride association becomes less. The relative importance

Figure 2: Zinc chemical speciation in seawater-freshwater mixtures.

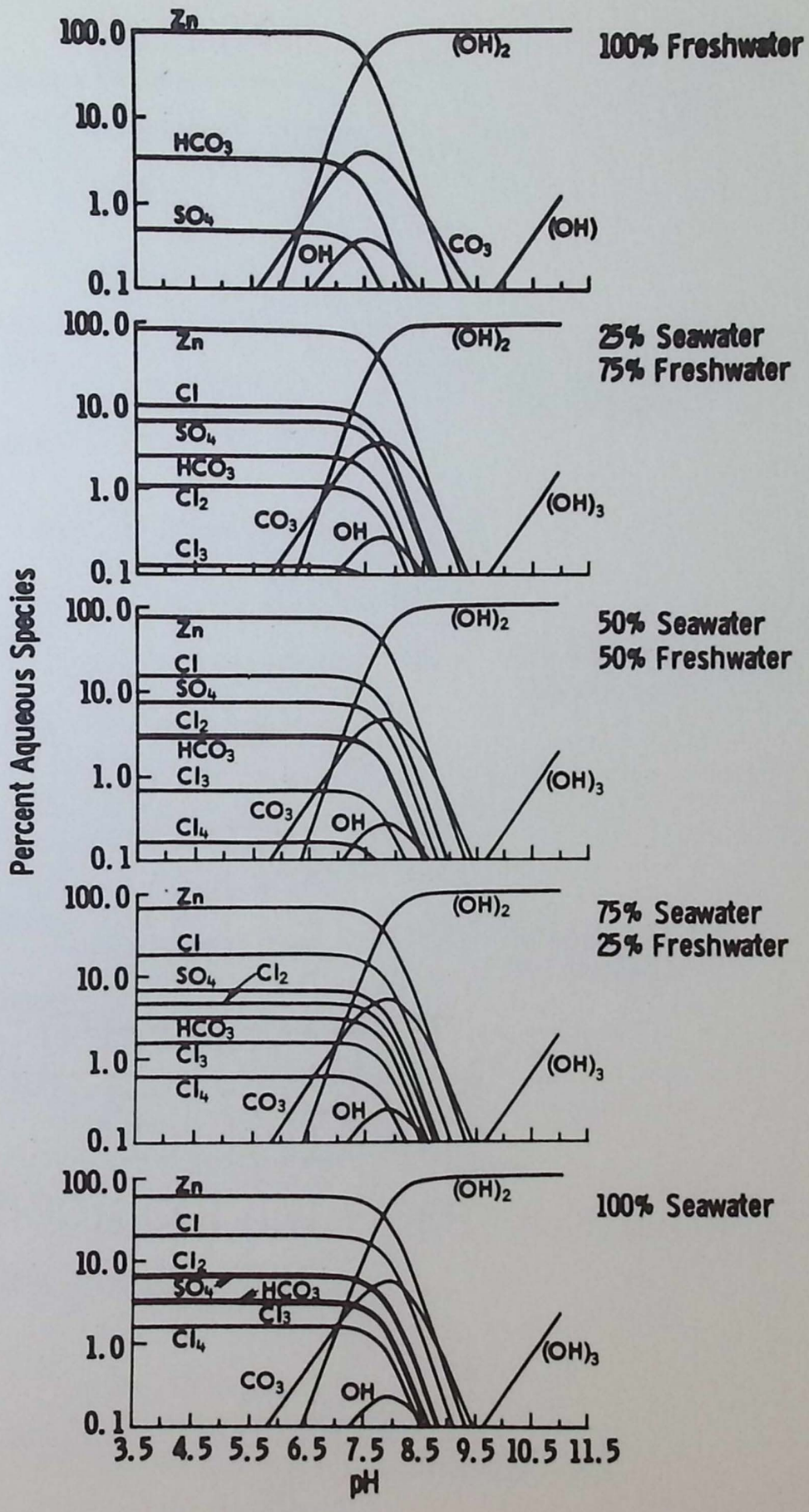

Percent Aqueous Species
100.0
10.0
1.0
0.1
Zn
(OH)2
HCO3
SO4
OH
CO3
(OH)
100% Freshwater
Cl
Cl2
Cl3
(OH)3
25% Seawater
75% Freshwater
50% Seawater
50% Freshwater
75% Seawater
25% Freshwater
100% Seawater
3.5 4.5 5.5 6.5 7.5 8.5 9.5 10.5 11.5
pH

Figure 3: Cadmium chemical speciation in seawater-freshwater mixtures.

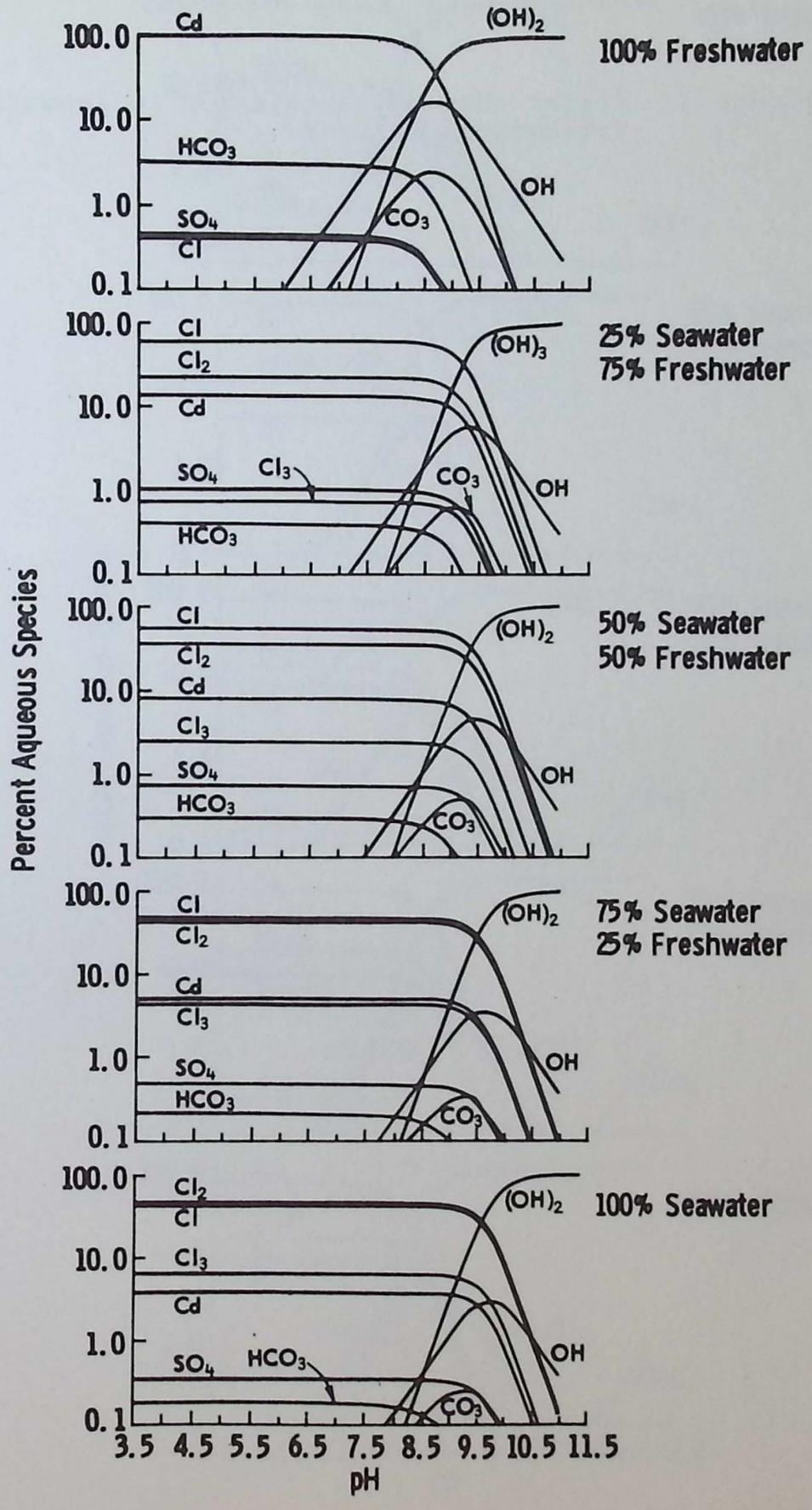

Percent Aqueous Species
100.0
10.0
1.0
0.1
Cd
(OH)2
HCO3
OH
SO4
CO3
Cl
100% Freshwater
Cl
Cl2
(OH)3
Cd
SO4
Cl3
CO3
OH
HCO3
25% Seawater
75% Freshwater
50% Seawater
50% Freshwater
75% Seawater
25% Freshwater
100% Seawater
3.5 4.5 5.5 6.5 7.5 8.5 9.5 10.5 11.5
pH

Figure 4: Copper chemical speciation in seawater-freshwater mixtures.

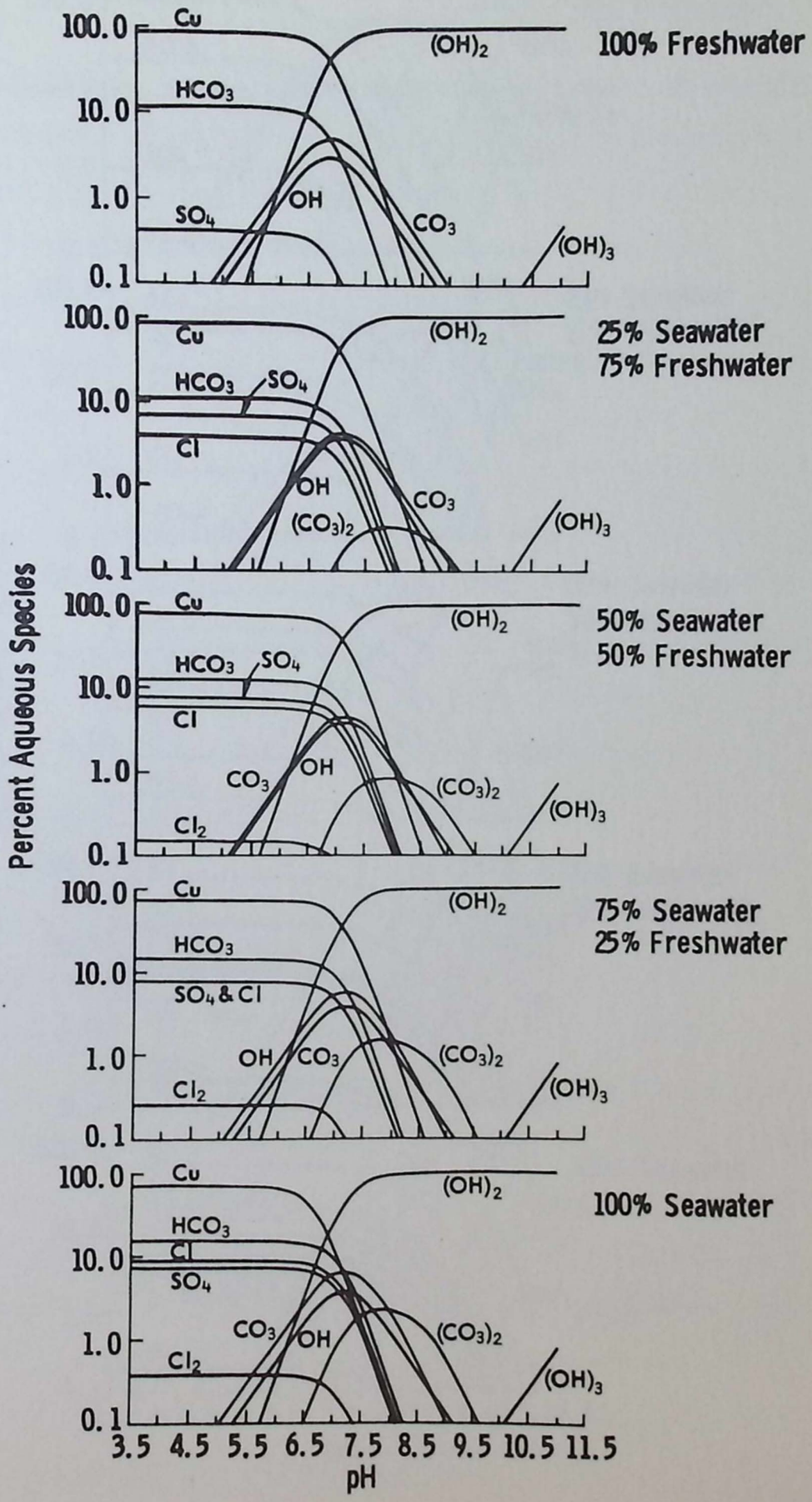
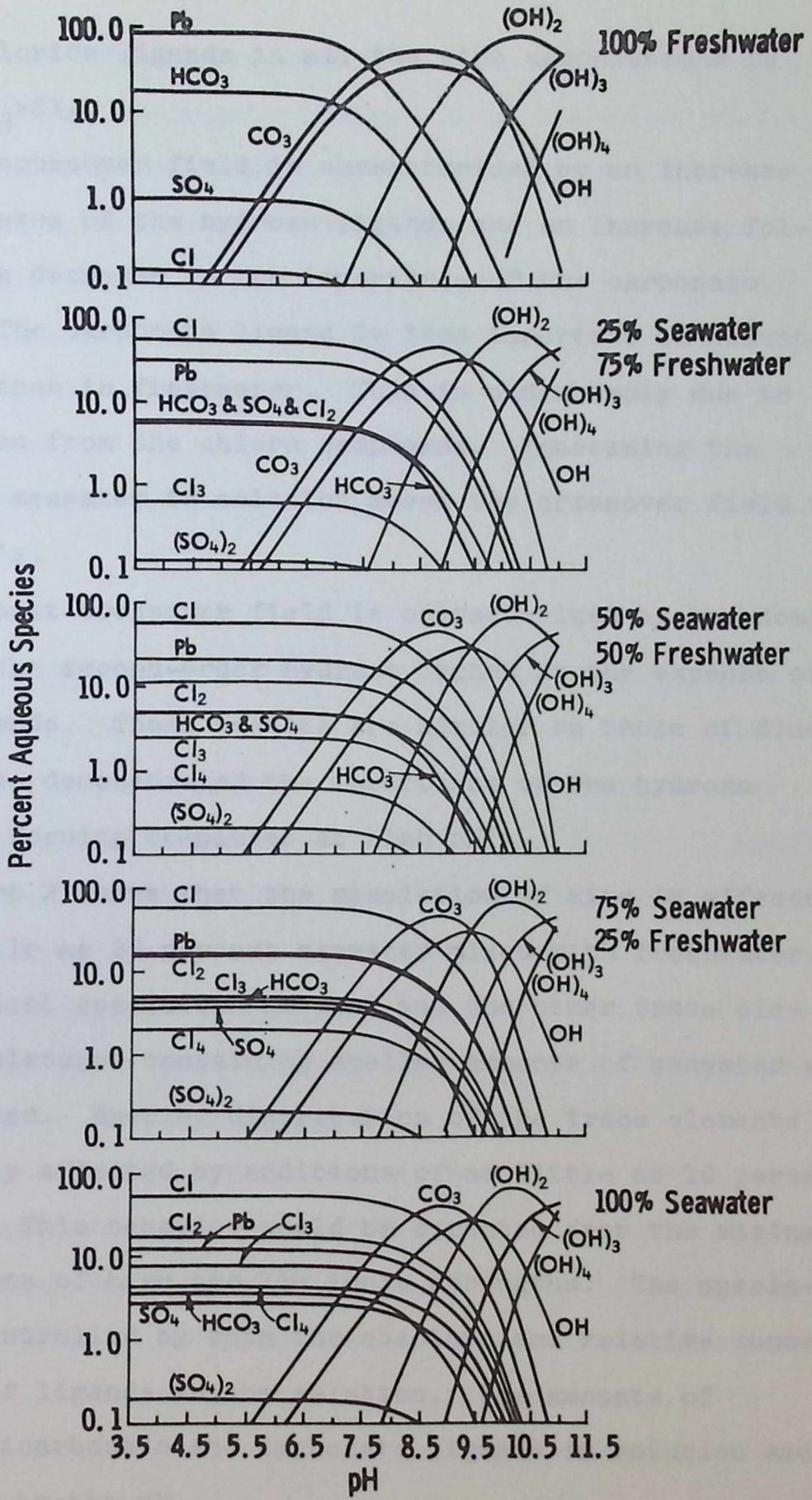

Percent Aqueous Species
100.0
10.0
1.0
0.1
Cu
(OH)2
HCO3
OH
SO4
CO3
(OH)3
100% Freshwater
Cl
(CO3)2
25% Seawater
75% Freshwater
50% Seawater
50% Freshwater
Cl2
75% Seawater
25% Freshwater
SO4 & Cl
100% Seawater
3.5 4.5 5.5 6.5 7.5 8.5 9.5 10.5 11.5
pH

Figure 5: Lead chemical speciation in seawater-freshwater mixtures.


100% Freshwater
25% Seawater
75% Freshwater
50% Seawater
50% Freshwater
75% Seawater
25% Freshwater
100% Seawater
Percent Aqueous Species
pH
100.0
10.0
1.0
0.1
3.5 4.5 5.5 6.5 7.5 8.5 9.5 10.5 11.5
Pb
HCO3
CO3
SO4
Cl
(OH)2
(OH)3
(OH)4
OH
Cl2
Cl3
Cl4
(SO4)2
HCO3 & SO4 & Cl2
HCO3 & SO4

of the chloride ligands in all the zinc associations is $Cl > Cl_2 > Cl_3 > Cl_4$.

The crossover field is characterized by an increase in the complexes of the hydroxo ligands and an increase followed by a decrease in the importance of the carbonato ligand. The carbonato ligand is less important in seawater mixtures than in freshwater. This is undoubtedly due to competition from the chloro complexes. Increasing the amount of seawater in solution moves the crossover field to higher pH's.

The post crossover field is characterized by the dominance of the second-order hydroxo ligand at the expense of other ligands. These results are similar to those of Elder (1975), who demonstrated the importance of the hydroxo ligand in forming complexes at high pH's.

Figure 2 shows that the speciation of zinc is affected by as little as 25 percent seawater mixed with freshwater.

Chemical speciation of zinc and the other trace elements in mixtures containing smaller amounts of seawater was also studied. Species distribution of the trace elements was clearly affected by additions of as little as 10 percent seawater. This behavior would be expected from the mixing of solutions of high and low ionic strengths. The speciation is controlled by both the absolute and relative concentrations of ligands in the solution. The amounts of hydroxo, bicarbonato and carbonato ligands in solution are controlled by the pH.

In a near-shore environment such as an estuary or delta front the pH values expected might be in the range of 7.5 to 8.5. The speciation of zinc to be expected in these environments is demonstrated by the crossover field. The dominant species would be the free zinc ion, second-order hydroxo complexes and first-order chloride complexes. Figure 2 shows that slight changes in the pH will affect the species distribution to a significant degree and therefore might affect the ability of the sediments to concentrate zinc.

Cadmium

Cadmium (2+) has an outer orbital structure similar to that of zinc. Figure 3 shows the speciation to be reasonably similar, as might be expected. Cadmium, however, is more highly complexed by Cl^{2-}. Because of the chloride associations, the effect of adding seawater in small amounts is readily apparent by the rapid increases in Cl complexes and the decrease in all other species. The crossover field narrows with increased additions of seawater. For Cd, the post crossover field is minor.

The complexation of cadmium with chloride further demonstrates the trends noted for zinc; i.e., the increase in complexing order and the decrease in the difference of magnitudes between the orders with increased chloride concentration. For cadmium this trend is continued to the point where a reversal in the relative importance of the complexes occurs. This reversal takes place at a mixture

of 25 percent freshwater and 75 percent seawater in which $CdCl_2^\circ > CdCl^+ > CdCl_3^-$

In a near-shore environment the speciation of cadmium should correspond to that shown in the precrossover and the crossover fields. Cadmium's species distribution would be much simpler than that of zinc. One would expect it to be dominated by chloride and relatively unaffected by small changes in pH.

The species of Cd would be more affected than those of Zn during the change from freshwater to seawater, such as a river entering the ocean. Many of the freshwater zinc species, including Zn^{2+}, retain a similar distribution in 100 percent seawater. For example, little change can be noted for the $ZnCO_3^\circ$ and $ZnHCO_3^-$ species during the mixing process. This type of chemical behavior may affect the manner in which Cd and Zn are concentrated in sediments.

Copper

Copper (2+) has a d^9 outer orbital structure and its complexes are characterized by Jahn-Teller distortion. Copper's crystal field stabilization energy and chemical speciation would be expected to differ from those of zinc and cadmium. Figure 4 shows that the crossover field embraces a wider pH range at all salinities than was found for either Zn or Cd. This reflects the increased importance of the chloride ligand relative to Cd and Zn. It seems likely that the increased association of the carbonato

ligand is due to the stabilizing influence of a bidentate bond.

The major species for all mixtures are free Cu^{2+}, the bicarbonato complex and the second-order hydroxo complex. There is only a minor shift of the crossover field toward higher pH's with increased amounts of seawater.

The relative importance of the copper complexes present in a near-shore environment will evidently be little affected by additions of seawater and will be largely a function of changes in pH.

Lead

Figure 5 shows that the complexation of lead is much more complicated than for the previous elements discussed. Clearly, the speciation of lead is distributed among many more ligands over the pH range studied. Association with the carbonato ligand is dominant in all systems studied. Increasing the amount of seawater in the mixtures shifts the large crossover field only slightly toward higher pH values (Figure 5). Complexing with Cl rapidly increases with minor additions of seawater. No reversal occurs, but at seawater concentrations the chloride complexes compete with the carbonato complexes in a pH range that might be expected in an estuarine environment.

In the near-shore systems Cl^- and CO_3^{2-} are by far the most important complexers of Pb. The percentage of CO_3^{2-} does not change appreciably with changes in the other ligand concentrations. The major speciation changes upon the

addition of seawater to freshwater are the disappearance of free Pb^{2+} and the appearance of the chloride complexes.

The models developed herein for the mixing of freshwater and seawater were compared with similar models based on the dilution of seawater with distilled water. The results of this comparison suggested that a major factor controlling the chemical speciation of Pb, Cu, Zn and Cd in the mixing environment of an estuary would be just the dilution of the seawater by freshwater.

Freshwater-Brine Mixing System

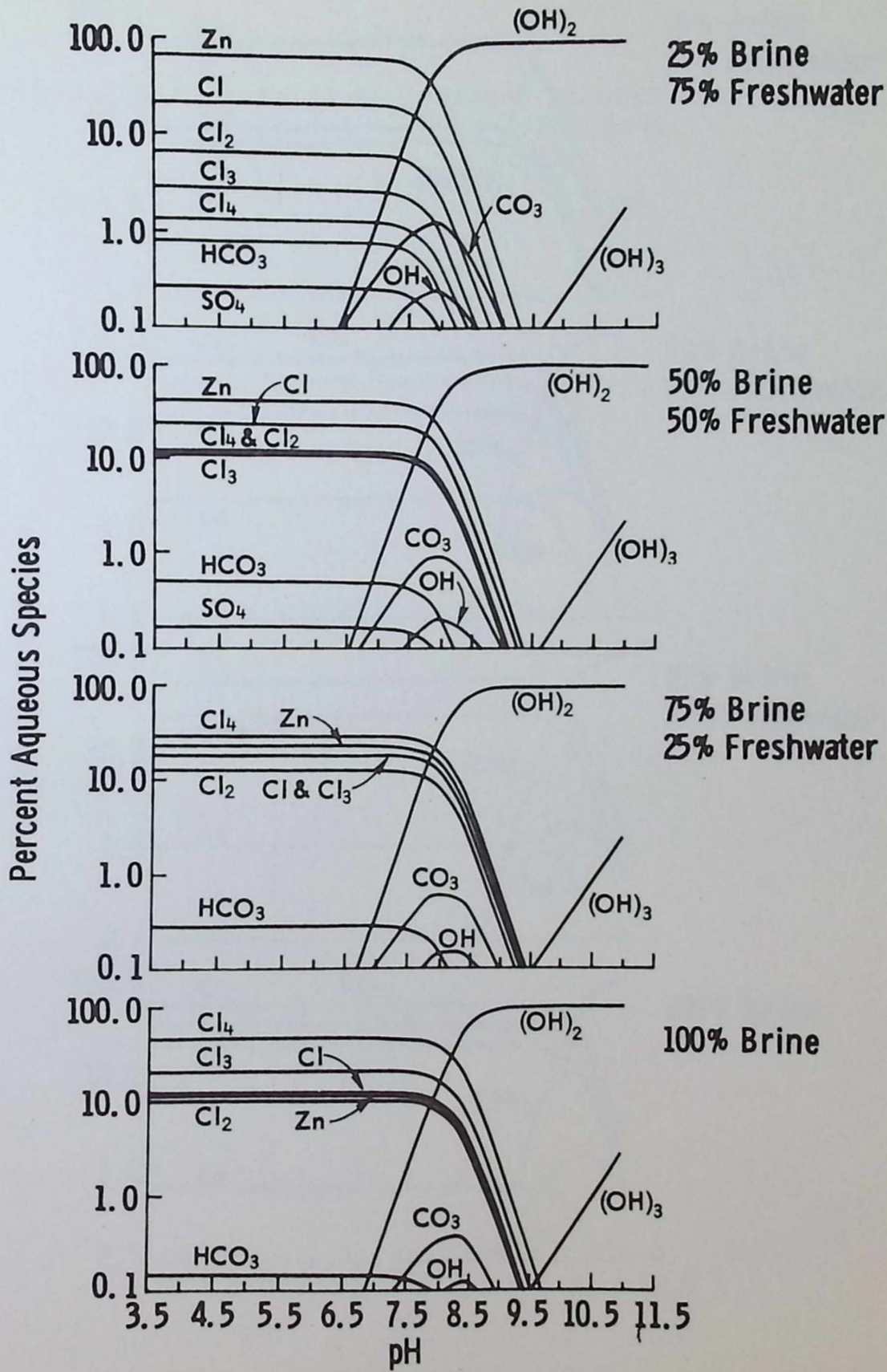
The next series of species distribution diagrams (Figures 6 through 9) summarize the results obtained for the changes in complexation resulting from the mixtures of freshwater and a Ca,Na-Cl brine. These figures are arranged similarly to those previously shown except that 100 percent freshwater is not included.

Zinc

Figure 6 shows the changes in speciation for zinc. Recalling from Table 4 that the ionic strength of the brine is 2, the mixture of 25 percent freshwater and 75 percent brine yields an ionic strength of about 0.7. Seawater has a similar ionic strength and as Figure 6 shows, the species distribution in this solution is quite similar to that of seawater.

The brine speciation of zinc is characteristically simple, the result of the dominance of the chloro ligand. A rather large shift of the crossover field to higher pH's

Figure 6: Zinc chemical speciation in brine-freshwater mixtures.


Percent Aqueous Species
100.0
10.0
1.0
0.1
Zn
Cl
Cl2
Cl3
Cl4
HCO3
SO4
(OH)2
CO3
OH
(OH)3
25% Brine
75% Freshwater
Zn
Cl
Cl4 & Cl2
Cl3
HCO3
SO4
(OH)2
CO3
OH
(OH)3
50% Brine
50% Freshwater
Cl4
Zn
Cl2
Cl & Cl3
HCO3
(OH)2
CO3
OH
(OH)3
75% Brine
25% Freshwater
Cl4
Cl3
Cl
Cl2
Zn
HCO3
(OH)2
CO3
OH
(OH)3
100% Brine
3.5 4.5 5.5 6.5 7.5 8.5 9.5 10.5 11.5
pH

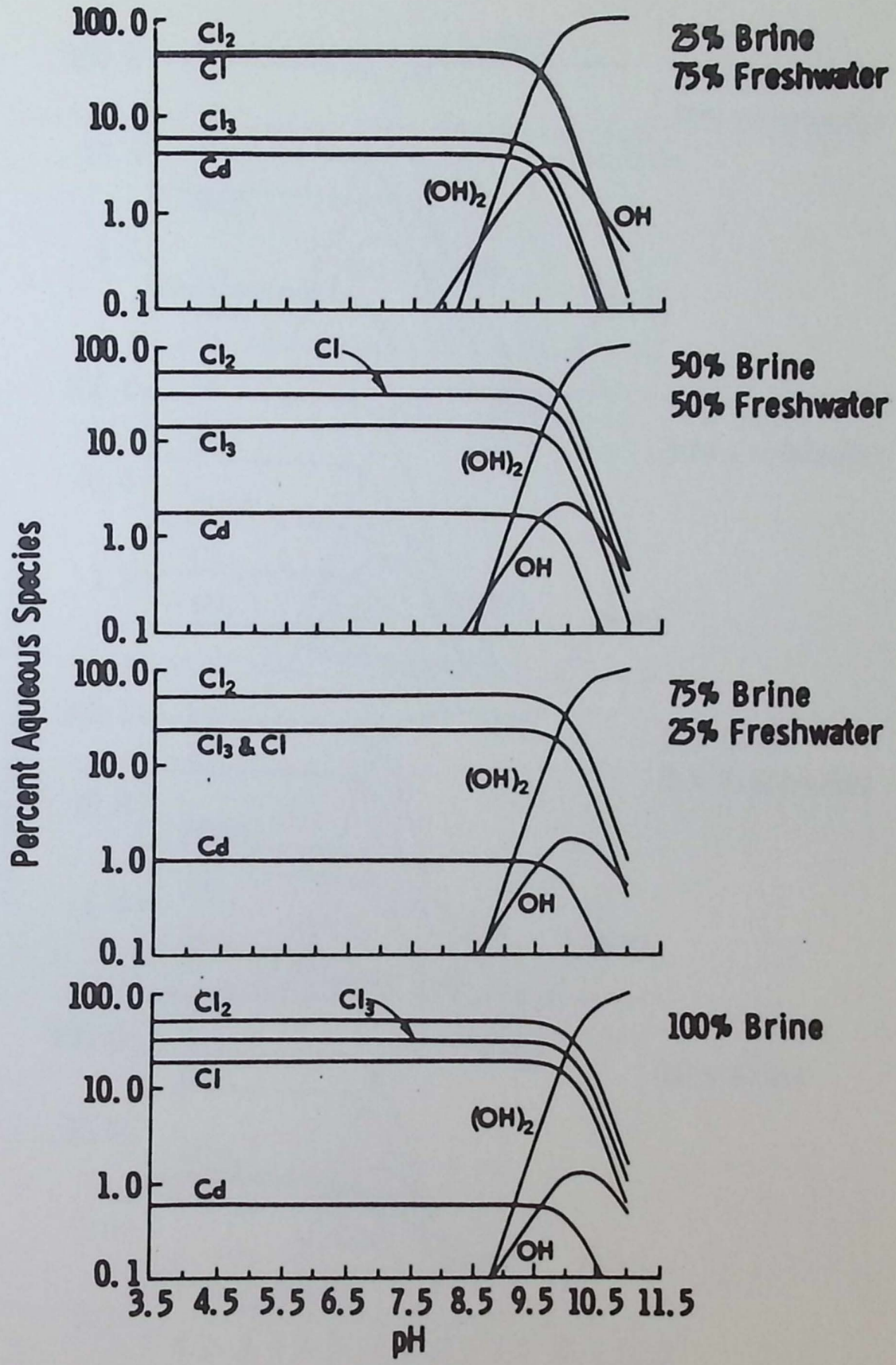

Percent Aqueous Species
100.0
10.0
1.0
0.1
Cl2
Cl
Cl3
Cd
(OH)2
OH
25% Brine
75% Freshwater
50% Brine
50% Freshwater
Cl3 & Cl
75% Brine
25% Freshwater
100% Brine
3.5 4.5 5.5 6.5 7.5 8.5 9.5 10.5 11.5
pH

Figure 8: Copper chemical speciation in brine-freshwater mixtures.

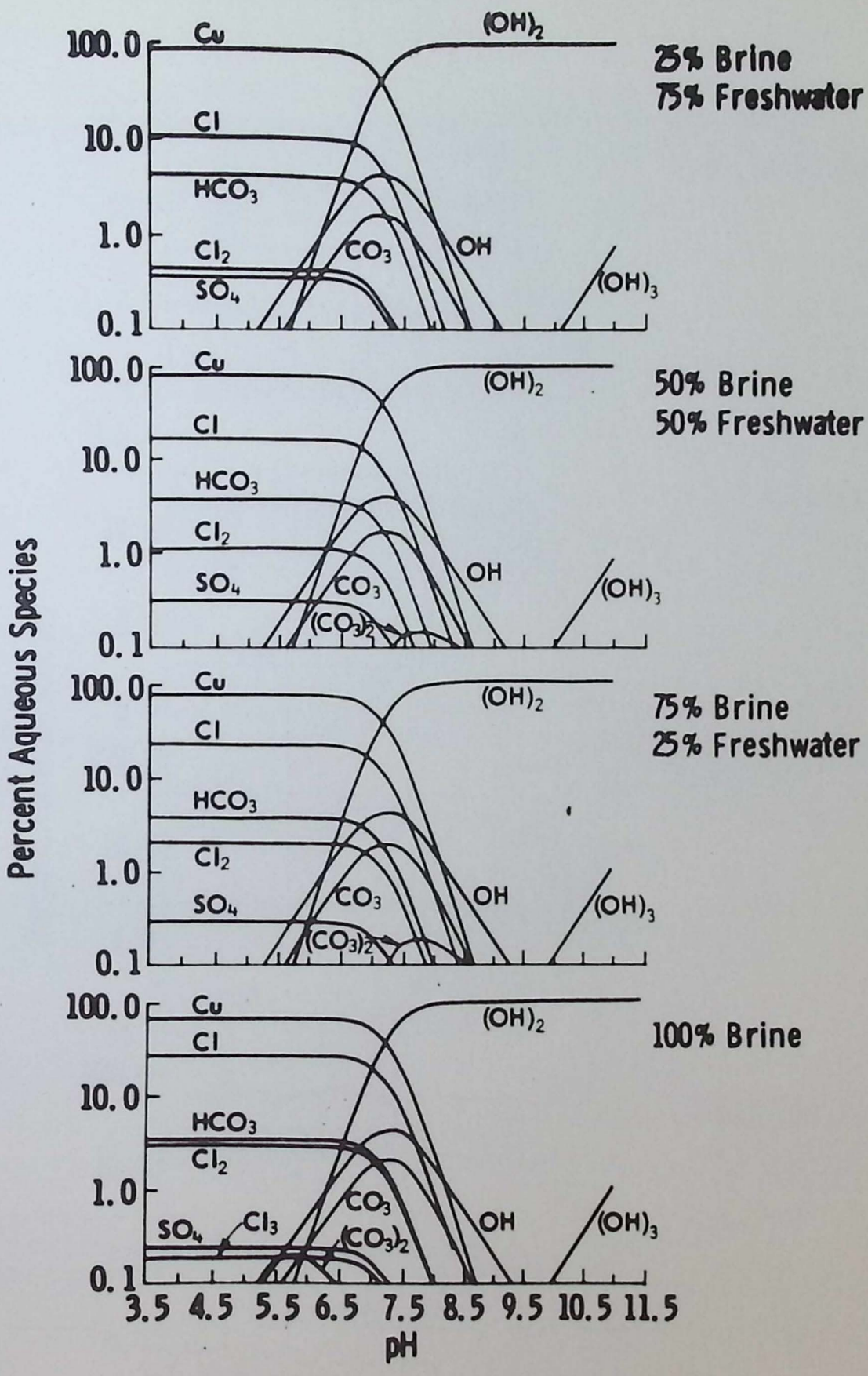
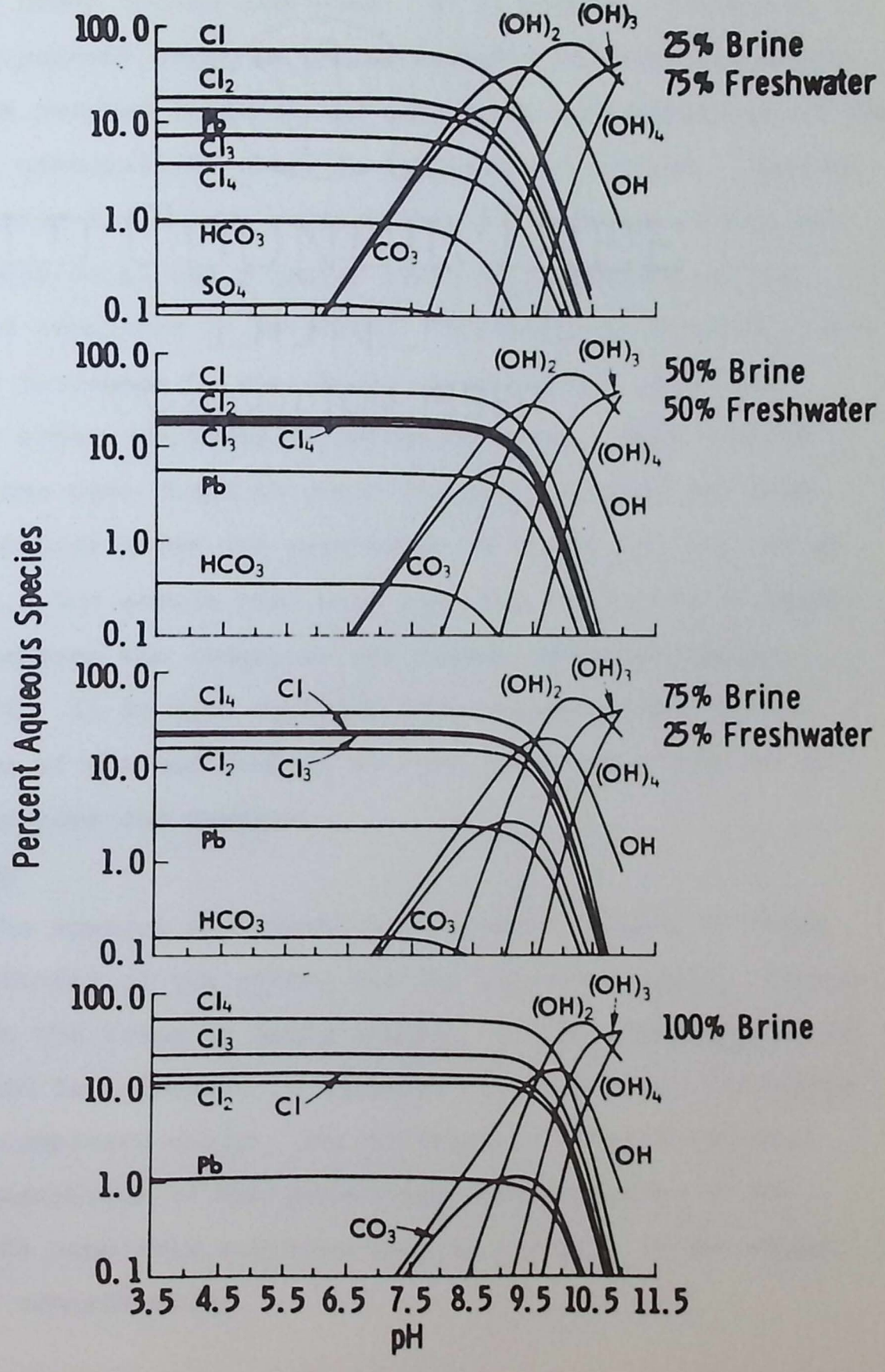

Percent Aqueous Species
100.0
10.0
1.0
0.1
Cu
Cl
HCO3
Cl2
SO4
Cl3
CO3
(CO3)2
OH
(OH)2
(OH)3
25% Brine
75% Freshwater
50% Brine
50% Freshwater
75% Brine
25% Freshwater
100% Brine
3.5 4.5 5.5 6.5 7.5 8.5 9.5 10.5 11.5
pH

Figure 9: Lead chemical speciation in brine-freshwater mixtures.


Percent Aqueous Species
100.0
10.0
1.0
0.1
Cl
Cl2
Pb
Cl3
Cl4
HCO3
SO4
CO3
(OH)2
(OH)3
(OH)4
OH
25% Brine
75% Freshwater
50% Brine
50% Freshwater
75% Brine
25% Freshwater
100% Brine
3.5 4.5 5.5 6.5 7.5 8.5 9.5 10.5 11.5
pH

is apparent. Zinc behaves similarly to cadmium in yielding higher order chloro complexes. At 50 percent freshwater and 50 percent brine in the Zn system a chloride concentration is reached in which the percentage concentrations of the chloro associations start to approach one another. Further increasing the chloro concentration, a reversal occurs and continues until the relative order of importance of the various complexes is reversed. Following the reversal, continued increases in the ligand concentration cause the higher order complexes to become dominant. This type of trend has been found to occur for zinc, cadmium and lead. The relative order for pure brine is $Cl_4 > Cl_3 > Cl > Cl_2$ for Zn and Pb. One should also note that the difference in magnitude between the orders of the chloro complexes has increased. It is also apparent that the speciation in the mixture of the end members is more complicated than it is for the pure end members.

Cadmium

The species distribution of cadmium (Figure 7) shows the affinity of the cation for the chloride ligand. Speciation in the brine is again simple. As the concentration of a ligand is increased in solution (in this case, Cl) higher order complexes occur. The differences between the absolute magnitudes of the percentage concentrations of the chloride complexes decrease with an increase in the chloro ligand concentration.

The second-order chloro complex remains relatively dominant, however, even in the 100 percent brine solution (ionic strength equals 2).

Copper

Figure 8 shows that the distribution of the copper species remains fairly complicated even at brine concentrations. Copper still complexes the carbonato ligand with the total alkalinity in the brine system at less than 50 mg/l. It is clear that for a reversal to occur with chloride and the chloro ligand to dominate the speciation, Cl would have to be present in much larger concentrations.

The percentage of free copper is still high even at brine concentrations. Competition from other complexing components like organic material or clays would have much free copper available.

Lead

Figure 9 shows the speciation for lead. It is immediately apparent that lead, like Cd and Zn, has a simple chemical species distribution in the brine solution. Lead complexes with CO_3^{2-} in a manner similar to copper and shows a reversal in the relative importance of the chloride complexes.

APPLICATION OF BRINE-FRESHWATER MODEL TO ORES

One concern in studies of the genesis of sedimentary ore deposits is the common occurrence of some base metals to the exclusion of others. For example, present observations show that copper is not commonly associated with lead and

zinc strata-bound ore deposits. Similarly, many copper deposits are found to be low in zinc and lead concentrations.

Why there is a selective occurrence of trace elements is open to speculation. One must, of course, consider source as a factor. If the various trace elements were transported as complexes to the site of deposition in a low-temperature (<200°C) brine and deposited as sulfides, two other factors should be considered. One is the chemical behavior of the trace elements with the various complexing ligands and the other is the behavior of the trace elements with S^{2-}.

Renfro (1974) demonstrated how the behavior of trace elements with sulfide in a sabkha could account for the formation of some strata-bound ore deposits. Results of this theoretical study demonstrate that the behavior of the base metals with the various ligands in the transporting medium is also a factor that must be considered in determining the base-metal distribution in sedimentary ore deposits.

Compare Figures 6, 7 and 9 for the 100 percent brine chemical speciation of zinc, copper and lead, respectively. Unfortunately, these diagrams are calculated for 25°C, whereas most strata-bound ores are deposited at higher temperatures. Nevertheless, the figures show the similarity in the chemical speciation of zinc and lead in the brine solution. Both metals are dominated by the chloro ligand; both show a reversal; and both are dominated (>90 percent) by

the fourth-order chloride. Significant contributions (>1 percent) of other ligands to the complexing do not occur until the pH is greater than about 9.5 for zinc and about 11.0 for lead. It might be speculated that fourth-order chloride complexes dominate the speciation of zinc and lead in ore-forming solutions.

Copper speciation in the brine, on the other hand, is complicated by the variety of speciation (Figure 8). The speciation is not dominated by one order of ligand as it is for zinc and lead. Free copper is a major species (>30 percent) up to a pH of about 7.5, and no reversal occurs. Thus, it might be anticipated that in an ore-forming solution copper would be distributed among more ligands and its chemical behavior at the depositional site would be different than that of zinc or lead.

COMMENT ON APPROACH

Recently Reardon and Langmuir (1976) demonstrated that the activity coefficients of $MgCO_3^\circ$ and $CaSO_4^\circ$ based on potentiometric data did not follow computed values based on the Setchenow expression. At 25°C the γ's for the ion pairs fit the equation, $\log \gamma_i = -BI$, where B equals about 0.63 and about 0.45 for $MgCO_3^\circ$ and $CaSO_4^\circ$, respectively. Assigning values to neutral ion pairs based on the Setchenow expression for the γ of $H_2CO_3^\circ$ may be invalid.

In order to examine the effect this new value has, the distribution of species of the elements Cd, Cu, Pb and Zn

was recalculated using the equation log γ_i = -0.5I for the γ of neutral species (Reardon and Langmuir, 1976).

Figure 10 shows the chemical species distribution for the four elements in the brine solution (2I) using the new calculations. The result in all cases was to increase the dominance of the neutral species at the expense of the charged species.

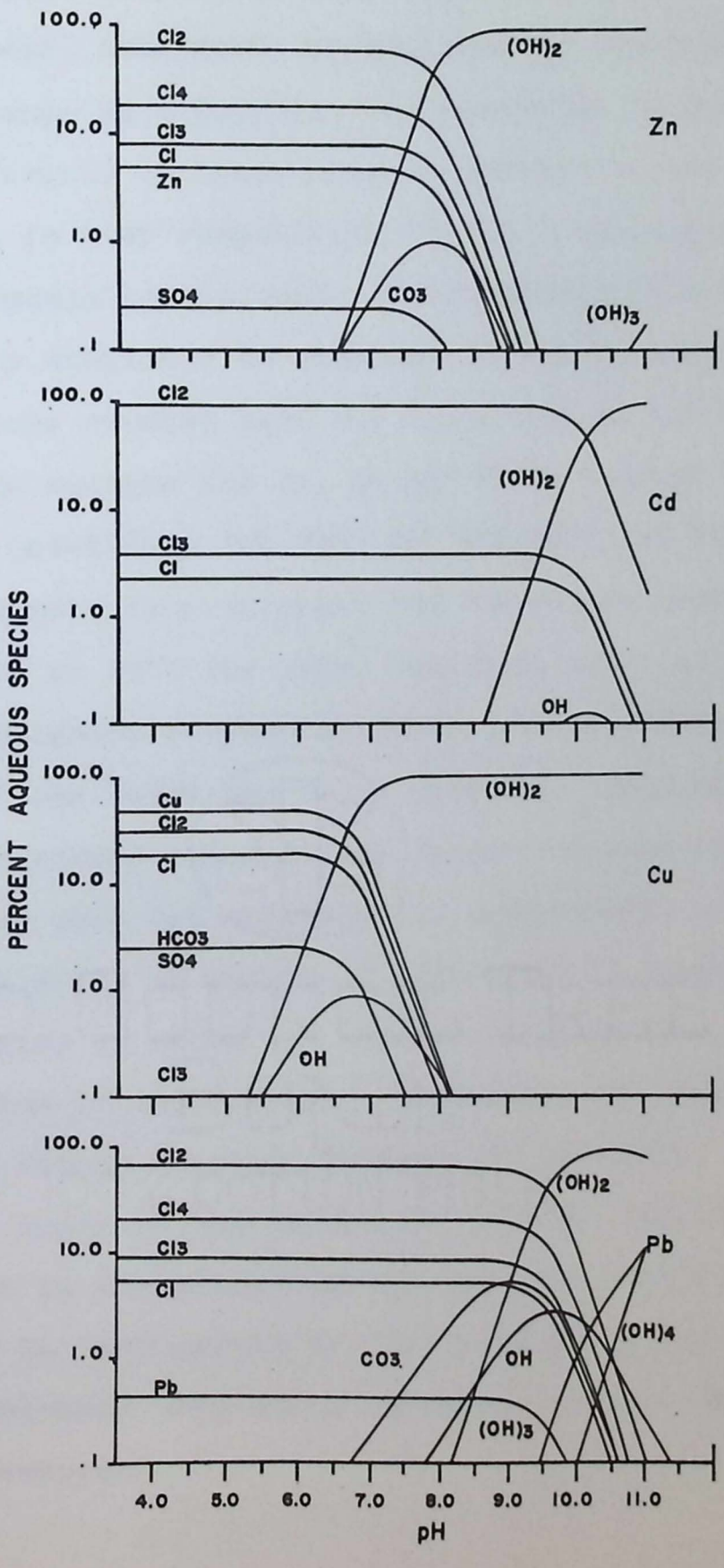
The order of importance of chloride for both lead and zinc changed from Cl_4>Cl_3>Cl>Cl_2 to Cl_2>Cl_4>Cl_3>Cl. Copper speciation, although changed by the increased dominance of Cl_2 and SO_4 complexes, remains fairly complicated and differs from both Zn and Pb. Speculations on the behavior of lead and zinc versus copper in sedimentary ore deposits based on chemical speciation differences are still valid.

Use of the expression log γ_i= -0.5I for the activity coefficients of neutral species clearly changes the species distribution. This suggests that past determinations and interpretations of the theoretical distribution of chemical species in aqueous solutions may need to be reinvestigated.

STUDY TWO - SPECIATION AND TEMPERATURE CHANGE

Helgeson (1969) demonstrated how the speciation changes for a few trace elements as a function of temperature. As temperature increased, the amount of trace elements complexed to higher order chloride increased. The changes in speciation were not necessarily similar among trace elements. In particular, zinc and lead were similar but differed from copper.

Figure 10: Chemical speciation of Zn, Cd, Cu and Pb determined using log $\gamma = -.5I$ for γ of neutral species suggested by Reardon and Langmuir (1976).


PERCENT AQUEOUS SPECIES
100.0
10.0
1.0
.1
Cl2
Cl4
Cl3
Cl
Zn
SO4
CO3
(OH)2
(OH)3
Zn
Cl2
(OH)2
Cd
Cl3
Cl
OH
Cu
Cl2
Cl
HCO3
SO4
Cl3
OH
(OH)2
Cu
Cl2
Cl4
Cl3
Cl
Pb
CO3
OH
(OH)2
(OH)4
(OH)3
Pb
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
pH

Part of this investigation involved the study of the mobilization process as a function of temperature. It is of interest, therefore, to know how the chemical speciation might change as a function of temperature in these systems. The difference in these systems compared to the studies of Helgeson is that competition for the trace elements from other ligands is included. Unfortunately, few data are presently available on complexes at higher temperatures. The systems studied were the trace element-chloride-hydroxide systems for Cu, Zn and Pb in 4 molal NaCl solutions. Speciation for 25°, 50° and 90°C was computed using the constants from Helgeson for the chloro complexes. The constants at 25°C for hydro complexes were used for 50° and 90°C. Helgeson's trace activity coefficients were used for the γ of the trace and major elements. Although the systems are simple and somewhat inexact because the hydro complexes were not adjusted for temperature, some information may still be gained on what might be expected.

Figure 11 shows the changes in speciation for Zn as a function of temperature. Generally, the distribution remains fairly constant between 25° and 90°C. Small increases occur in the amount of chloride complexes, and a decrease in the percentage of free zinc results. The changes in lead speciation are similar to zinc in Figure 12; i.e., chloride complexing increases and the amount of free ion decreases.

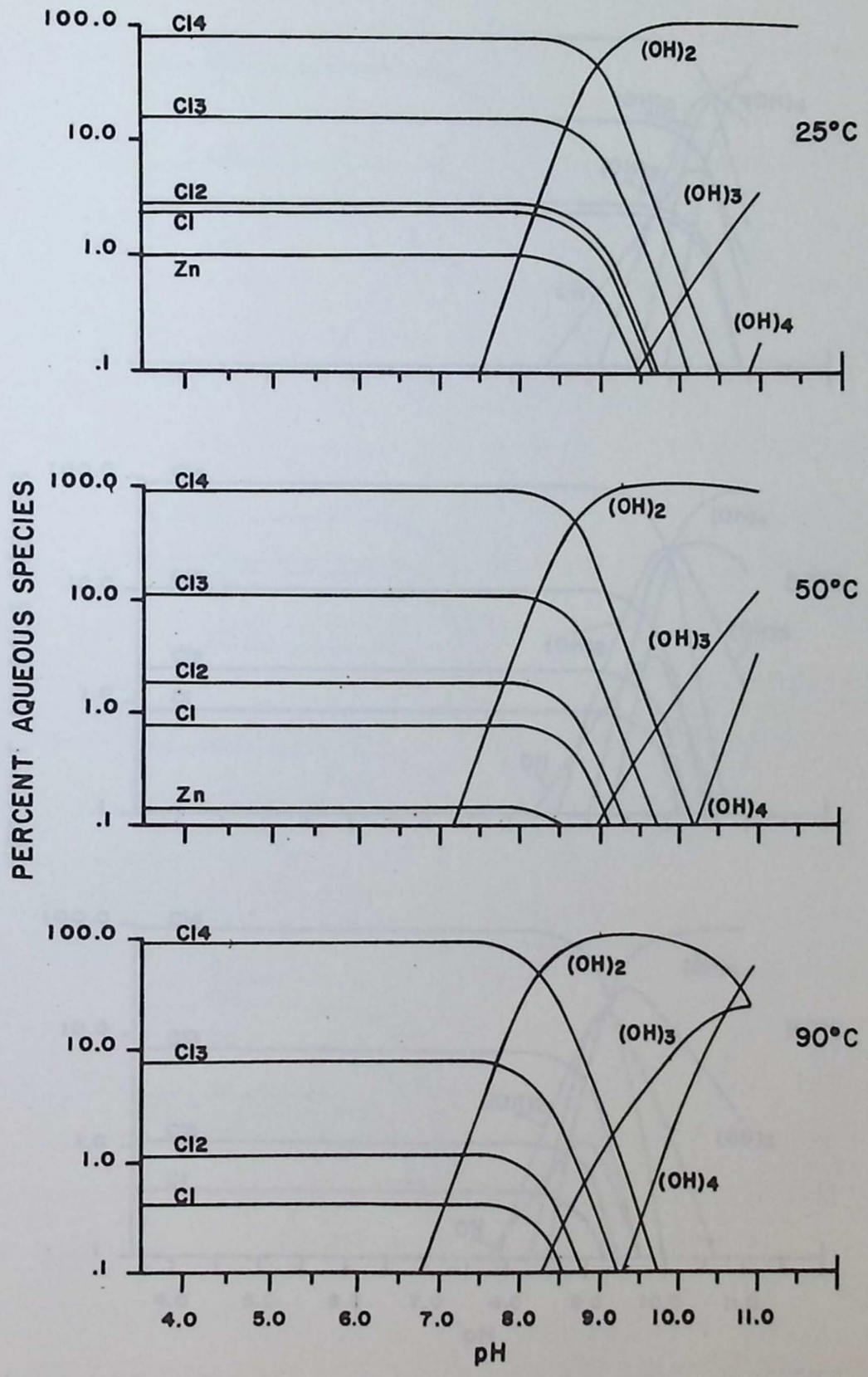


Figure 11: Zinc speciation as a function of temperature (25°C, 50°C and 90°C).

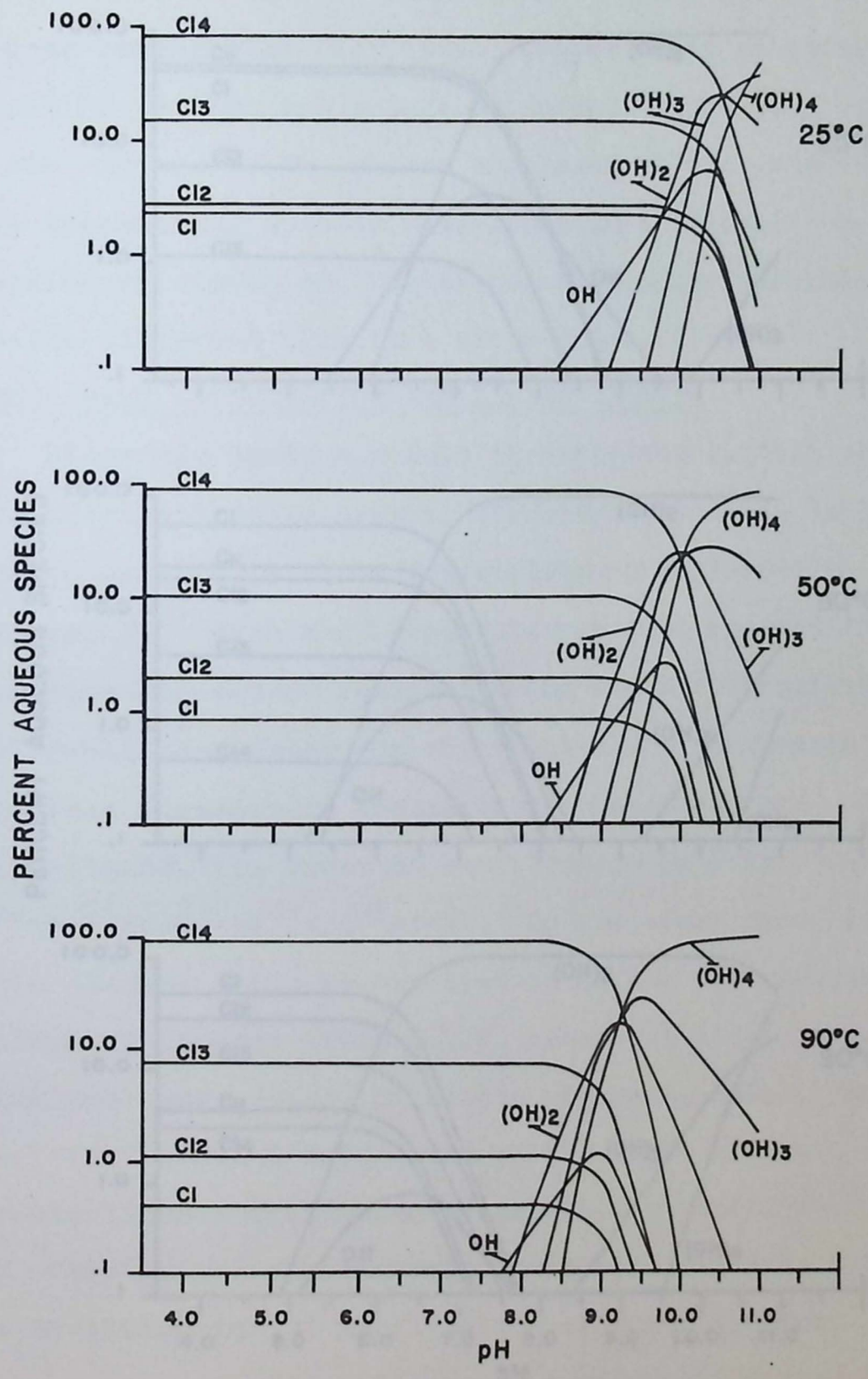


Figure 12: Lead speciation as a function of temperature (25°C, 50°C and 90°C).

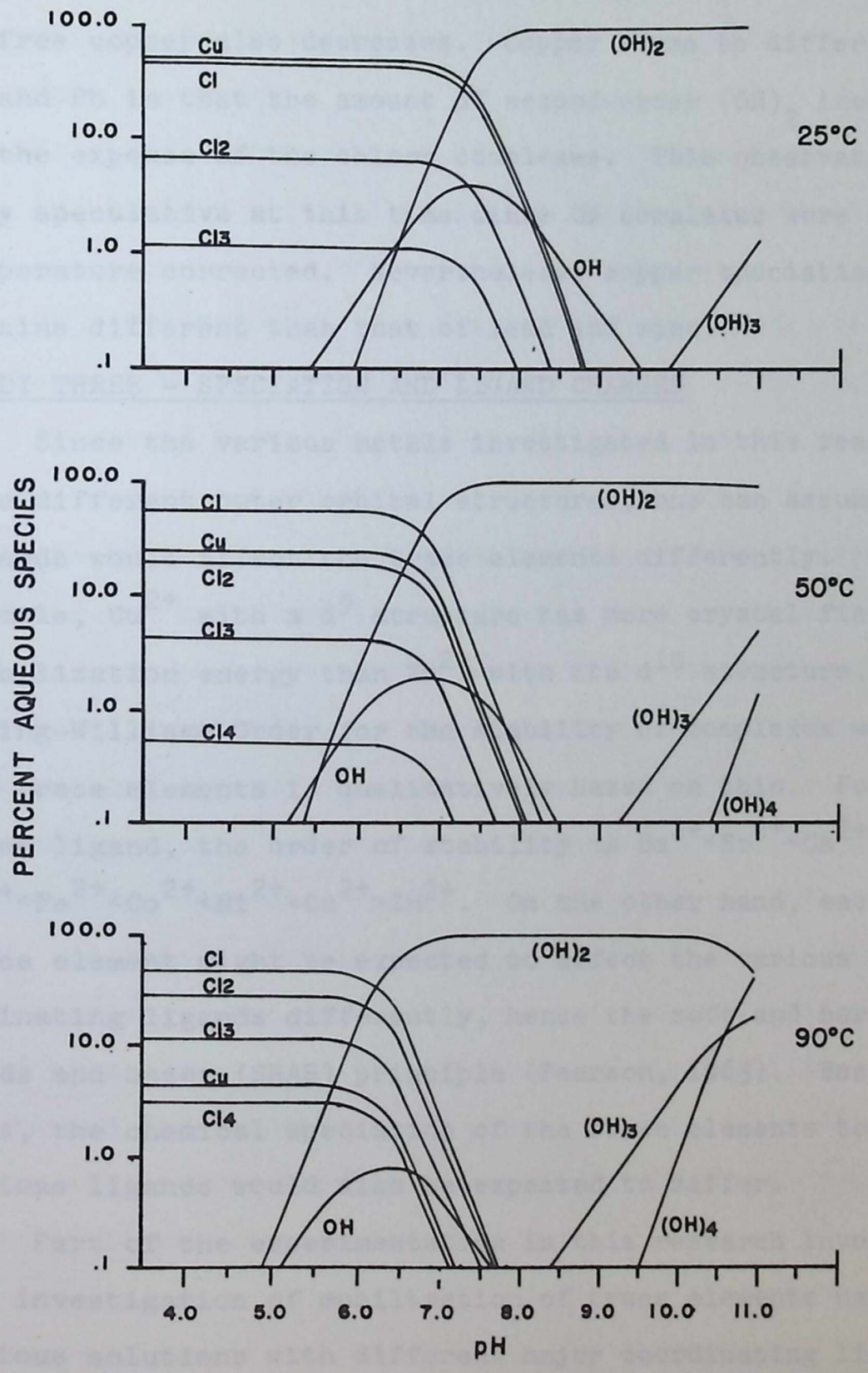


Figure 13: Copper speciation as a function of temperature (25°C, 50°C and 90°C).

The amount of higher order complexing of copper increases with changes in temperature (Figure 13). The amount of free copper also decreases. Copper seems to differ from Zn and Pb in that the amount of second-order $(OH)_2$ increases at the expense of the chloro complexes. This observation is only speculative at this time since OH complexes were not temperature corrected. Nevertheless, copper speciation remains different than that of lead and zinc.

STUDY THREE - SPECIATION AND LIGAND CHANGES

Since the various metals investigated in this research have different outer orbital structures, one can assume that ligands would affect the trace elements differently. For example, Cu^{2+} with a d^9 structure has more crystal field stabilization energy than Zn^{2+} with its d^{10} structure. The Irving-Williams Order for the stability of complexes with the trace elements is qualitatively based on this. For a given ligand, the order of stability is $Ba^{2+}<Sr^{2+}<Ca^{2+}<Mg^{2+}<Mn^{2+}<Fe^{2+}<Co^{2+}<Ni^{2+}<Cu^{2+}>Zn^{2+}$. On the other hand, each trace element might be expected to affect the various coordinating ligands differently, hence the soft and hard acids and bases (SHAB) principle (Pearson, 1963). Based on this, the chemical speciation of the trace elements to the various ligands would also be expected to differ.

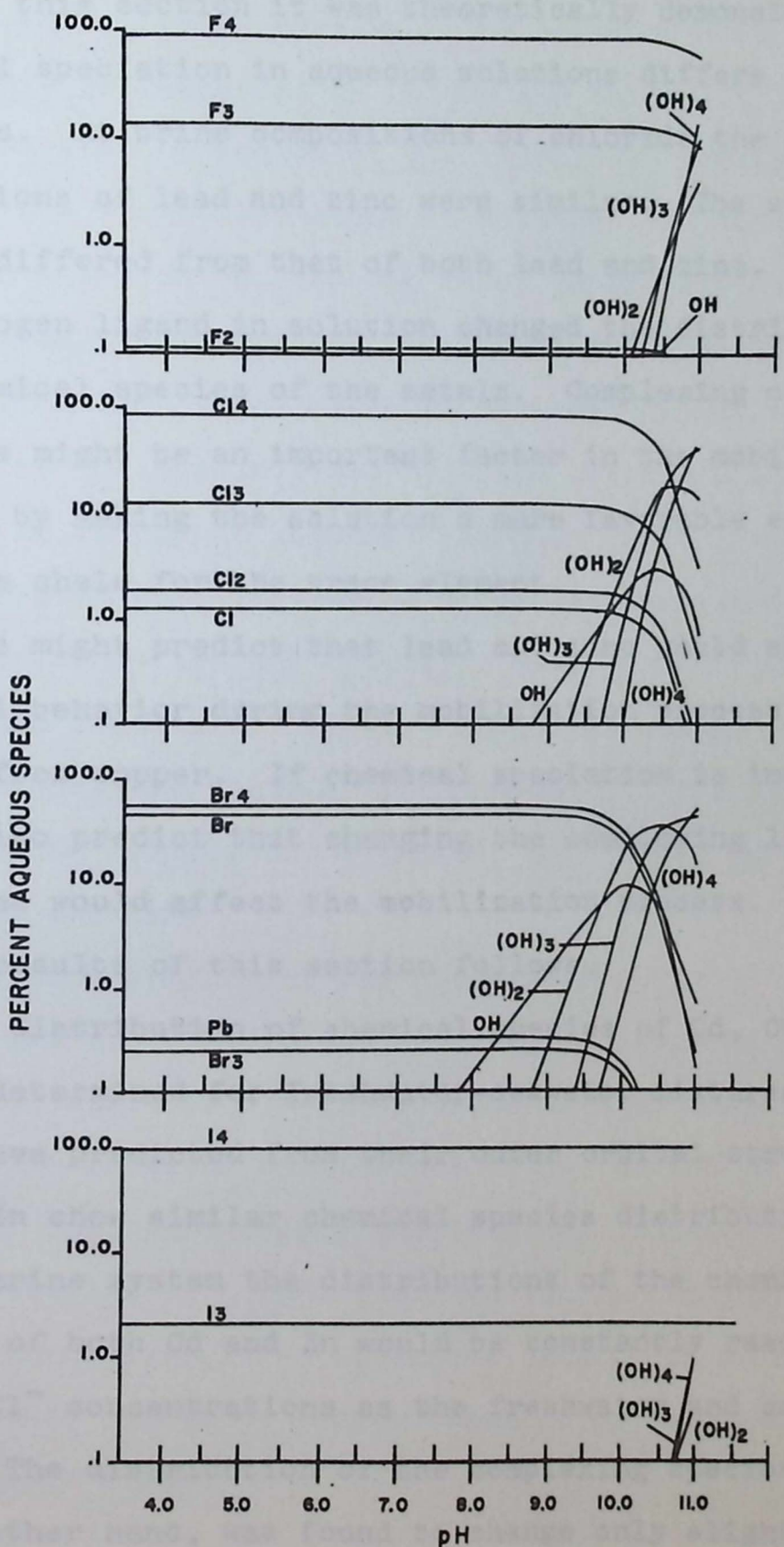
Part of the experimentation in this research involved the investigation of mobilization of trace elements using various solutions with different major coordinating ligands, such as KF and KBr. It is of interest to know how the

speciation would differ using the different ligands. Unfortunately, as in the case of speciation changes with changing temperature, few dissociation constants are available for the trace elements.

In order to get an idea of how speciation might differ with the various major ligands, the species distribution of lead was computed for the associations with four halogens (F^-, Cl^-, Br^- and I^-). The dissociation constants for these complexes were taken from Sillen and Martell (1964 and 1971).

Figure 14 shows the species distributions of lead in potassium salt solutions of the above halogens at an ionic strength of 4. In all solutions the fourth-order association was the most important, and only in the bromide solution was the sequence of complexing order not completely reversed from 1>2>3>4. A ranking is suggested in the ability of a halogen ligand to dominate hydroxide speciation. In descending order, the ranking is I>F>Cl>Br. This is similar to the order suggested by the SHAB principle of I>Br>Cl>F>OH. In this case lead would act as a soft acid. The differences between the SHAB order and the order found here could be a function of the selection of the stability constants and the concentrations used. However, each halogen ligand affects the chemical species distributions of the selected trace elements differently.

Figure 14: Lead speciation as a function of changes in ligands in solution (I, F, Cl and Br).



SUMMARY AND CONCLUSIONS OF THEORETICAL INVESTIGATION

In this section it was theoretically demonstrated that chemical speciation in aqueous solutions differs among the elements. At brine compositions of chloride the chemical speciations of lead and zinc were similar. The speciation of copper differed from that of both lead and zinc. Changing the halogen ligand in solution changed the distribution of the chemical species of the metals. Complexing of the trace elements might be an important factor in the mobilization process by making the solution a more favorable environment than the shale for the trace element.

One might predict that lead and zinc would show similar chemical behavior during the mobilization process but would differ from copper. If chemical speciation is important one might also predict that changing the complexing ligands of the brine would affect the mobilization process. A summary of the results of this section follows.

1. The distribution of chemical species of Cd, Cu, Zn and Pb was determined for freshwater-seawater mixtures. As one might have predicted from their outer orbital structures, Cd and Zn show similar chemical species distributions. In an estuarine system the distributions of the chemical species of both Cd and Zn would be constantly readjusting to new Cl^- concentrations as the freshwater and seawater mixed. The distribution of the complexing species of copper, on the other hand, was found to change only slightly in the mixtures from freshwater to seawater.

2. Lead was highly complexed to the carbonato ligand in the freshwater-seawater mixtures. This means that lead is likely to be highly available for sorption onto suspended materials as suggested by Leland and Shimp (1973) and as demonostrated by Angino et al. (1972) for freshwater.

3. In the freshwater-seawater mixtures the amount of free ions in solution follows the order Cu>Zn>>Pb>Cd.

4. The major controls on the amount and type of inorganic complexing that takes place in various natural water solutions are the absolute and relative concentrations of the competing inorganic ligands. Gardner (1974) theoretically demonstrated that free amino acids and hydrocarboxylic acids probably are not effective complexers of trace metals. Therefore conclusion number 4 would not change by incorporating organic ligands into the model. The effect of polymerized organic matter, humic and fulvic acids on the model is unknown.

5. The distribution of the chemical species of Cd, Cu, Zn and Pb was also determined for freshwater-brine mixtures. The brine was a Ca, Na-Cl solution with an ionic strength of 2. The chemical speciations of Zn, Cd and Pb were very similar. All were highly complexed by chloride. The chemical speciation of copper remained fairly complex (no ligand was dominant except for hydroxide at high pH's) and a significant amount of copper remained as the free ion even in the pure brine.

6. Changes in the distributions of the chemical species of Pb, Zn and Cu were studied as a function of changes in temperature at 25°C, 50°C and 90°C. The general distributions of the species changed little with the changes in temperature. As the temperature increased the amount of free ion in solution tended to decrease and the amount of complexing by chloride increased.

7. Changes in the distribution of the chemical species of Pb were studied as a function of changes in the major complexing ligand in solution. The four study solutions comprised the halogens F, Cl, Br and I at an ionic strength of 4. The fourth-order complex was dominant in all cases, but each diagram showed differences in the distribution of the chemical species. A ranking was suggested in the ability of a halogen ligand to dominate hydroxide speciation. In descending order, the ranking was I>F>Cl>Br.

Theoretical investigations such as this have limitations. Two of these are the methods used in the calculation of the activities of the ions and the choice of the stability constants. I chose to use individual ionic activity coefficients and feel that the interpretations at the ionic strengths considered in this paper would not be significantly different if another method were used. The stability constants used were values determined by experimentation. Values for the bicarbonato complexes were taken from Zirino and Yamamoto (1971) and probably overestimate the stability of HCO_3^- complexes (Langmuir, personal

communication, 1975). De-emphasizing the bicarbonato complexes by choosing another stability constant would change the distribution diagrams but would not change the conclusions of this paper.

EXPERIMENTAL APPROACH

The purpose of these experiments was to determine whether one could measure the conditions and mechanisms of selected trace-element removal from shales by concentrated aqueous solutions. Six metals were studied--Pb, Zn, Cu, Co, Ni and Fe. The mobilization process was investigated by (1) determining in what fraction or fractions of the shale the trace elements exist, (2) studying the ability of these shale fractions to release trace elements, and (3) studying how changes in the composition of the brine could affect mobilization. The prediction made in the previous section that changing the major complexing ligand could affect the mobilization process was also studied.

PREVIOUS LEACHING STUDIES

Weiss and Amstutz (1966) found that lead could be extracted from artificially lead-enriched clays and precipitated by solutions of 3 percent NaCl enriched in S^{2-} or CO_3^{2-}. Shale from the Fredericktown deposit of Missouri was used as a guide as to what might be a typical clay composition in a mineral deposit. The exchangeable ions in kaolinite and montmorillonite from the deposit were replaced by lead ions. Weiss and Amstutz (1966) suggested that the clays act as semipermeable membranes which anions could not enter but cations could. The cations go into the clay and exchange the lead while the anions, such as S^{2-}, wait on the outside. When lead comes to the surface of the clay, it is precipitated.

Ellis (1968) showed that increasing the temperature and salinity of the leaching solution increased the amount of trace element removed from shales. He used a dense, black, fine-grained, poorly sorted shale. Quartz, feldspar, micaceous material and minor chlorite and epidote were also present. Solutions of 0 molal (distilled water), 2 molal, and 4 molal NaCl at 1500 bars pressure and temperatures between 300°C and 500°C were used. Generally large amounts of Fe were extracted (up to 10^3 ppm) with minor extraction of lead and copper.

Using a 25 percent acetic acid leach, Hirst (1971) found the average percentage of trace elements to be removed decreased in the order Co (10.3 percent), Ni (9.9 percent), Cu (5.0 percent) and lead (0.16 percent). Powdered sands, silts, muds and shales were leached. More trace elements were leached from unconsolidated sediment than from consolidated sediment.

Williams (1967) concluded that shales have significant amounts of trace elements that can be leached even though the shales might be from an outcrop and therefore weathered. Shales from outcrops in Alberta, Canada, were treated with distilled water followed by leaching with a 1N solution of ammonium acetate at a pH of 8. The leachates were then analyzed for Zn, Cu, Fe and Mn. The percent of clay in the shale was a major factor determining the amount of trace elements present and therefore the amount of leachable metals.

Hathaway et al. (1972) demonstrated that increasing the duration of leaching and increasing the temperature or the ionic strength of the leaching solution increased the amount of trace-element mobilization. A black shale from an outcrop in Kansas was used. The approach was to leach the shale at either 24°C or 80°C with a brine solution of about 34,000 to 70,000 mg/l total ionic concentration. Different compositions were used for the brine. The percentages of maximum leaching followed the order Mn (16 percent), Co (6.8 percent), Zn (5.7 percent), Ni (2.1 percent), Cu (0.7 percent) and Fe (0.05 percent). Chromium and lead were not leached, although they were present in the rock at 7 ppm/gm and 1 ppm/gm, respectively.

Belevtow (1973) found that more elements were mobilized by acid solutions. Three types of solutions were used: (1) an acid solution 0.1 molal NaCl and 0.1 molal HCl with a pH of 1 to 2; (2) a neutral solution of 0.1 molal NaCl at a pH of 6.9; and (3) a basic solution 0.1 molal $NaHCO_3$ and Na_2CO_3 at a pH of about 9.9. The material leached ranged from sedimentary and slightly metamorphosed rocks to highly metamorphosed rocks. Mobilization of the metals decreased with increasing amount of metamorphism. Since the brine solutions were of different compositions, chlorinity and salinity, only an approximate relationship was shown between leaching and salinity. It appears from this experiment that the composition of the brine may be just as much a factor as ionic strength in mobilizing metals. This is

similar to what was predicted earlier in this paper based on theoretical considerations.

Carpenter (personal communication, 1975) studied the ability of K to leach barium from shales. He compared leaches using a NaCl brine (4 molal) with and without 10,000 ppm K. He found only a minor increase in the amount of Ba leached when the solution with the added K was used.

Banat et al. (1974) demonstrated that increasing the amount of a synthetic chelating agent increased the amount of mobilized metal in solution. Experiments were run up to 200 hours at 25°C and pH's between 6.6 and 7.0 using nitrilotriacetic (NTA). The trace elements studied were Cd, Cu, Ni, Pb, Zn and Cr from heavy-metal-polluted river sediments. No significant amounts of Cr were leached, possibly because of the low dissociation of $Cr(OH)_3$ at the neutral pH. Increasing the duration of the leach had a positive effect on mobilization of Cu and Cd and a negative effect (less leached) on Zn and Pb. Nickel was not affected by the time of leach. Conclusions based on this work, compared to those of other papers, were:

(1) Increased water hardness suppresses the release of heavy-metal ions, possibly due to the competitive formation of Ca-NTA complexes because of increased ionic strength of the solution.

(2) Protons compete with metals for triacetate and pH values below the neutral point should give a decrease in the amount of complexing;

pH values above the neutral point should also limit the amount of complexing that takes place due to the tendency to form hydroxides and oxides.

Shchylek and Serevkova (1974) studied the compositional changes in aqueous solutions of reactions between a shale containing 47.8 percent pyrite and various brine solutions. They found:

(1) From a starting pH of 7.5 the pH's of the leachate decreased with time of reaction to a point and then leveled off (the longest reaction was two hours).

(2) Increasing the starting TDS resulted in a higher final TDS and lower final pH's.

In summary, the results of previous leaching studies on the process of mobilizing trace elements from shales could be stated as follows:

1. Trace metals are present and concentrated in shales.
2. These metals can be removed from clays (or shales) by a variety of solutions including various acide, ammonium acetate, and various concentrated brine compositions.
3. The elements are not mobilized to the same degree.
4. In general, the effectiveness of the leaching process has been found to increase with increasing temperature and ionic strength of the solution.
5. Increasing the duration of shale-solution contact appears to increase the amount of leaching of some cations.

6. In general, increasing the amount of trace elements that are available to be leached increases the percentage leached from the rock.
7. Leaching efficiency may also be a function of the composition of the solution.

Past research has left these questions unanswered:
1. How does changing the temperature affect the mobilization process? (Is the efficiency linear with temperature change?)
2. What is the mechanism of the mobilization process?
3. How do the different fractions of the shale affect the leaching processes? For example, how do the trace elements held in and removed from the organic fraction compare to those held in and removed from the detrital fraction?
4. What are the effects of relative changes of the components of the leachate (both cation and ligand) on the efficiency of mobilization?

AIM OF THIS STUDY

Based on past experimental research and the theoretical work done here, two processes are considered in this study to be important mechanisms by which a brine can mobilize or collect trace elements from a shale: exchange reactions and extraction. The exchange reactions are similar to base exchanges in which one cation exchanges for another (Carrol, 1959; Weiss and Amstutz, 1966). A working hypothesis is that certain cations present in the brine,

such as K, will work to increase the efficiency of the mobilization process, possibly through base exchange.

The extraction process might work by making the leaching solution a more favorable place for a trace element to exist than the shale. Another working hypothesis for this study is that complexing of trace elements to the various ligands in a brine, such as Cl^-, is a factor in making the solution a more favorable environment for the trace elements.

These hypotheses will be examined by studying the four questions raised by the previous leaching studies, above.

PLAN OF PROCEDURE

In order to investigate the questions raised in the previous section, two general types of experiments were conducted.

The first experiment was an attempt to identify a particular trace element with a certain shale fraction; for example, organic and detrital fractions. This was done by chemically attacking different fractions of the shale using the various techniques reported in the literature (Chester and Hughes, 1967; Nissenbaum, 1972).

Five selective chemical treatments were used: (1) a hydroxylamine hydrochloride-acetic acid leach; (2) a hydrogen peroxide leach; (3) a sodium hypochlorite leach; (4) a lithium metaborate fusion; and (5) an ammonium chloride leach.

Nissenbaum (1974) judged that treatment 1 liberated trace elements associated with carbonates, acid-soluble

sulfides, some iron and manganese oxides, and elements on exchange sites. Both treatments 2 and 3 are designed to attack organic material. Treatment 4 gives the total trace-element content of a shale. The ammonium chloride leach was used for the determination of the exchangeable major cations.

In addition to the above treatments, the total cation exchange capacity was determined.

The second type of experiment was a study of the ability of the various aqueous solutions to mobilize metals from shales. This was done by treating various types of shales with aqueous solutions and, after a specified time, analyzing the leachate for the selected trace elements. The parameters that were varied during the experiment were (1) ionic strength (0I, 0.7I, 2I, and 4I), (2) temperature (25°C, 50°C, and 90°C), (3) composition of the leaching solution, and (4) shale type. For a particular shale, the leaching solutions were NaCl, KCl, $CaCl_2$, and a multication solution. Table 5 shows the leachings that were done on one shale using one composition of leaching solution, e.g. NaCl.

This experimental design resulted in 24 leaching experiments on one particular shale. Leaching experiments were done in triplicate. In addition, experiments were done on some shales with 4I leaching solutions of KF, KBr and KI at 50°c.

SHALE SAMPLES

Four mineralogically and chemically different shale types were picked for this investigation. All were stored

Table 5. Experimental matrix for a one-salt, one-shale combination. Experiments done are marked by X's. These experiments were done on the Eudora and Heumader shales.

	TEMPERATURE OF EXPERIMENT		
IONIC STRENGTH OF SOLUTION	25°C	50°C	90°C
0I			X
.7I			X
2I			X
4I	X	X	X

in polyethylene bottles until treatments were begun. A brief description of each shale follows.

HEUMADER SHALE MEMBER: The Heumader shale is a member of the Lawrence Formation, Shawnee Group, Virgilian Stage, Upper Pennsylvanian Series. It was collected as subsurface samples from Page Airways' storage area in Atchison, Kansas, where little weathering due to exposure to atmosphere had occurred. Its chemistry has probably been influenced by subsurface waters, however. It is a gray, clayey to silty shale containing plant remains. Samples with plant remains were avoided as well as possible for the experiments.

EUDORA SHALE MEMBER: The Eudora shale is a member of the Stanton Limestone, Lansing Group, Missourian Stage, Upper Pennsylvanian Series. It was collected as surface samples from a quarry operated by Martin-Marietta Aggregate Company in Eudora, Kansas. It is a black, hard, fissle shale containing phosphatic and pyrite nodules with iron stains along some bedding planes. Samples with nodules and any evidence of iron stains were carefully avoided in preparing the bulk sample for the experiments.

NINNESCAH SHALE MEMBER: The Ninnescah shale is a member of the Sumner Group, Cimarronian Stage, Permian Series. It was collected from an outcrop along highway 81 just south of Caldwell, Kansas. The shale is red, silty, and massive with some green mottling where collected. The shale is within an evaporite sequence and is associated with the Permian

copper mineralization of south-central Kansas (Long and Angino, 1976).

DAVIS SHALE MEMBER: The Davis shale is a member of the Elvins Group, Upper Cambrian Series. It was collected as a 1-1/4 inch core from near the Boss Mine, east-central Missouri. The core is over the new lead-zinc district comprising the Vibunum Belt. The shale consists of layers of alternating dolomites and gray to purple shale. The bulk sample used in this study was a selected sample of gray shale covering 50 meters of core. The shale was collected from the center few centimeters of the individual gray layers to avoid contamination from the surrounding layers. The total amount collected was 100 centimeters. These individual layers were combined to make the bulk sample.

A fifth shale was also used in a few of the experiments because it was known to contain a variety of metals. A description follows.

HEEBNER SHALE MEMBER: The Heebner shale is a member of the Oread Formation, Shawnee Group, Virgilian Stage, Upper Pennsylvanian Series. It was collected and used in the study by Hathaway et al. (1972). Containing some fossils, it is a black, platey shale, commonly less than three feet thick. This sample was taken from a roadcut along the southeast corner of Lone Star Lake in Douglas County, Kansas (NE, NW, SEC 23, T14S, R18E).

EXPERIMENTAL METHODS

A discussion of the experimental methods comprises three topics: (1) the chemical and mineralogical analysis of the shales and their preparation for leaching, (2) the preparation of the leaching solutions for leaching runs and the conducting of the experiments, and (3) the chemical analysis of the various leachates. A description of these topics follows.

The shales were prepared initially for leaching by washing them with distilled water, during which their outer surfaces were rubbed lightly with a nylon brush. The shales were then dried overnight at 100°C. Subsequent preparation involved breaking up the shales with a mortar and pestle into pieces of about 0.5 cm in diameter, rinsing them with distilled water again, drying them, and grinding them in a titanium carbide shatter box for 90 seconds. Finally the shale was sieved through stainless steel sieves, and the fraction less than 53 microns was collected for the experiments.

Enough bulk shale of each type was prepared to give about 600 grams of sample. Each 600-gram sample was thoroughly mixed to insure as well as possible a homogenized sample. The prepared shales were stored in polyethylene containers. All leaching experiments and shale mineralogy and chemistry were done using these 600-gram samples.

Each shale was analyzed using a General Electric XRD-5 x-ray diffractometer using Cu Kα radiation and a nickel

filter. The mineralogy of each shale was studied on the different fractions: a bulk fraction, the >53 micron fraction, and the <53 micron fraction. The bulk sample was prepared for the x-ray analysis by making a pressed pellet, while samples from the other fractions were prepared by pipetting a homogeneous slurry of the shale onto a glass microscope slide. A comparison of the x-ray diagrams of the different fractions showed no obvious changes in the mineralogy of the sample. Therefore, the <53 micron fraction used for the leaching experiments was determined to be representative of the mineralogy of the whole rock.

The <2 micron fraction was also studied for each shale. It was separated from the <53 micron fraction by centrifuging (Jackson, 1956). Organics were destroyed by treatment with 6 percent sodium hypochlorite (Purex). Samples were treated in a manner suggested by Carrol (1970) and Austings and Leihmeyer (1976) to aid in the identification of the clay minerals. The steps included (1) glycolating the sample, (2) heat treatment to 375°C, and (3) heat treatment to 600°C.

Table 6 summarizes the mineralogy of the shales. Quartz is present in all the shale members. Since the intensity of the major peak of quartz can be used as a qualitative guide to its abundance in a sample, a comparison of the 3.34Å peak for the various samples is also presented in Table 6.

Table 6. Mineralogy of study shales

	Kaolinite	Illite	Chlorite	Dolomite	Feldspar	Quartz*
Ninnescah		P**		P		1,000
Heumader	P	P	P		P	664
Heebner	P	P	P			452
Eudora	P	P	P			350
Davis	P	P			P	200

*Average of determinations of counts per second at 3.34 Å using a 10 second counting time.

** Present

Qualitatively the abundance of quartz in the shales appears to decrease in the order Ninnescah>>Heumader> Heebner>Eudora>Davis. The reverse of this order can serve as a rough guide to the general abundance of clay minerals.

The total trace-element content of the shales was measured by atomic absorption using a modified lithium metaborate fusion method (Perkin Elmer Analytical Methods Manual, 1973). In a graphite crucible 1.00 gram of $LiBO_2$ was thoroughly mixed with 0.20 gram of shale sample. The material was then fused at 1000°C for 20 minutes. Fusing the material for shorter periods of time produced a black material (organic) from the black shales that did not dissolve in the dilute acid. Each sample was stirred after the first 15 minutes of fusion.

After fusion the molten bead was transferred directly to a beaker containing 5 percent HCl and stirred until dissolved. The solution was then analyzed for the trace elements. The total number of fusions included four samples of each shale and four blank determinations using 1 gram of lithium metaborate each.

The hydroxylamine hydrochloride treatment involved leaching 1 gram of sample with 50 ml of 1 molal hydroxylamine hydrochloride in 25 percent (v/v) acetic acid. Reaction time was four hours and was done in 250 ml polyethylene centrifuge tubes with lids at room temperature. A mechanical shaker was used to keep the samples mixed during leaching. After leaching, the samples were centrifuged at

3500 rpm for 30 minutes and the supernatant decanted into polyethylene storage bottles. This treatment was repeated four times on the 1-gram sample and each of the resultant leachates was refrigerated until the chemical analyses could be done, a time less than two days.

The Purex (6 percent sodium hypochlorite) treatment involved treating a shale sample with the 6 percent NaOCl adjusted to a pH of 9.5 with HCl (Lavkulich and Wiens, 1970). This treatment was used on untreated shale samples and on samples that had been treated with the hydroxylamine hydrochloride treatment. One gram of sample was combined with 10 ml of solution in a 100-ml glass centrifuge tube and placed in a boiling water bath. After 15 minutes, 10 ml more of leaching solution was added to the tube and allowed to react for another 15 minutes. After the reaction, the tube was removed from the bath, centrifuged at 2300 rpm for 10 minutes and the supernatant decanted and stored. This process was continued until no reaction resulted from further additions of the Purex. Up to nine treatments were necessary for the Eudora shale.

After the major leaching, the samples were cleaned by (1) two 10-ml treatments with half-strength 1 molal hydroxylamine hydrochloride in 25 percent (v/v) acetic acid, (2) one 10-ml treatment with the Purex solution, and (3) one 10-ml treatment with warm distilled water. All supernatant liquids were combined for subsequent trace-element analysis.

Although the Purex process is an oxidizing treatment, individual (2-gm) samples were also treated with 70 ml of 30% H_2O_2. Hydrogen peroxide was added in 5-ml amounts to the 2-gm sample contained in a 100-ml glass centrifuge tube in a boiling water bath. The total time of the additions was approximately eight hours.

The cation exchange capacity of the shales was determined by a modification of the method proposed by Chapman (1959) in which sodium is used as the exchanging cation. Treatment was done on 3-gm samples in 100-ml polyethylene centrifuge tubes with lids. Thirty-three ml of sodium acetate (pH of 8.2) was added to the sample and allowed to react for five minutes in a shaker. The solution was then centrifuged and the supernatant discarded. This process was repeated three times. The sample was then washed three times with 33 ml of isopropyl alcohol to remove excess sodium. Finally, the sample was treated three times with 33 ml of 1N ammonium acetate (pH of 7). Each treatment was allowed to react five minutes. At the end of each reaction the sample was centrifuged and the supernatant from all reactions combined for analysis of replaced sodium.

The exchangeable cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) were determined by exchanging with ammonium acetate. Twenty ml of 1 molal NH_4OAc (pH of 7) was used to leach 3 grams of sample in a 100-ml polyethylene centrifuge tube. A shaker was used to keep the material mixed. After 15 minutes the reaction was stopped, the sample centrifuged, and the

supernatant stored. This process was repeated five times, the supernatants combined, and the liquid analyzed for Ca, Mg, Na and K.

Leaching experiments were done using two Blue M constant-temperature shaker baths. Agitation rate was chosen to keep the sample and leaching solution mixed and then left constant throughout the experiments. Generally 10 gms of the Heumader, Ninnescah and Davis shales and 5 gms of the Eudora and Heebner shales were used. These sample sizes were chosen on the basis of (1) being small enough to keep the solution and the shale sample mixed and (2) being large enough to allow detection of the presence of a trace element above the background, but small enough so dilution of the leachate was not required before atomic absorption.

A 250-ml pyrex flask with ground glass joint was used as the leaching container in the preliminary experiments. Glassware was soaked overnight prior to use in 10 percent HCl. For the 25°C and 50°C experiments, no loss of leaching solution from the flask occurred due to evaporation. For the 90°C experiments, however, sufficient loss occurred within twenty-four hours to make the results useless. A variety of other methods were tried, including wrapping the ground glass stopper with teflon and securing it to the flask with wire, and using a screw cap pyrex flask with a teflon wrap on the rim and the cap screwed over. Neither of these methods proved successful in maintaining a good seal at 90°C.

In addition, with the screw cap there was danger of trace-element contamination from the plastic cap.

A method that proved to be successful was a "Saran Wrap" technique which was used for all experiments. This method involved wrapping the rim and neck of a 250-ml narrow mouthed Erlenmeyer flask with two layers of teflon. A piece of polyethylene film (Saran Wrap) was put over the top of the flask and secured with bell wire wrapped around the neck. Two wrappings of bell wire were found to be better than one. The bell wire made a very secure seal, holding the film against the teflon tape. The polyethylene was soaked overnight in 10 percent HCl and rinsed with organic-free distilled water prior to use. Blank runs showed no trace-element contamination from the polyethylene or flask for the trace elements studied at the 90°C temperature. Although the seal achieved by this method was good, samples were still occasionally lost due to evaporation. Therefore, multiple runs were needed for some experiments and two or three flasks of the same sample were used per experiment. This permitted some observations on the reproducibility of the experiments, and also provided extra samples in case of evaporation or other experimental loss.

Reactions were allowed to run for 76 hours. In similar types of experiments, O'Connor and Kester (1975) found 36 hours long enough for a steady state to be attained between clay and the reacting solution. Wood (1973) found exchange reactions to be complete in a matter of minutes

using specific ion electrodes to monitor the change. Twenty-four hours appeared to be sufficient to leach trace elements out of shales by Williams (1973). Hathaway et al. (1972) found an increase in leaching with time up to nine days. They also found that successive leaching of the same shale sample extracted significant amounts of trace elements. Studies here with the selective chemical attacks also showed that significant amounts of trace elements are leached rapidly, but that the shale will continue to release trace elements at a low level over a long period of time. In some of the preliminary experiments, up to five days were sometimes necessary for the system to reach a steady state. Seventy-six hours was chosen as the leaching time because: (1) a large number of experiments had to be run; (2) many data suggest the major reactions of the type studied here occur within a 24- to 36-hour time period; (3) the purpose of these experiments was not to study the kinetics of the reactions; and (4) the shorter the leaching period, the less likely significant losses of solution would occur because of evaporation. Results of the leaching experiments are usually presented as the concentration (ppm) of metal in 100 ml of leaching solution for a certain quantity of shale in grams.

The measurement of pH was done with an Orion 701 digital pH meter and a Corning combination pH electrode (0 to 100°C range). The electrode was calibrated against two buffer solutions at the temperature of the solution to be

measured. The pH measurements can only be used as a general indication of the pH of the solutions since the buffers were not adjusted to the ionic strength of the solution.

The leaching solutions were made with ACS grade salts of NaCl, KCl, $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 2H_2O$, Na_2SO_4, KBr, KF, and KI, and were prepared fresh for each leaching. Blanks of the leaching solutions were run with every experiment. Deionized, glass-distilled, organic-free water was used in all leaching solutions and standards. The composition of the multi-cation solution was taken as an approximate average of compositions of solutions from fluid inclusions presented by Roedder (1972). These data are presented in Table 7. Only minerals from Mississippi Valley-type deposits were considered.

The initial pH's of the leaching solutions were not adjusted but normally were in the pH range of 5 to 6. They were weakly buffered solutions. The systems studied may be sensitive to initial pH. Table 8 shows the results of a leaching test using the Eudora shale at 25°C in which the initial pH's of the solutions were controlled. Three pH's were used: 4, 7 and 10. The leaching solution was 4I NaCl and the pH was adjusted using HCl or NH_4OH. Total additions of the adjusting solutions were held to under 2 ml per 500 ml of the leaching solution.

Table 8 shows that the final pH's of the three test solutions are similar, indicating that the final pH of the solution is controlled by the shale. The final pH of

Table 7. Chemical composition of fluid inclusions from Mississippi Valley type ore deposits and chemical composition of the multication brine used in this study. Fluid inclusion data taken from Roedder, 1972. Concentrations are in ppm and percent of the total concentration for that fluid inclusion.

BRINE	TDS*		Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
A	208130	ppm	57100	2700	18000	2400	124600	<3300	30
		%	27	1	9	1	60	2	--
B	227000	ppm	71600	3100	17000	2800	129600	<3000	<80
		%	32	1	7	1	57	1	--
C	199540	ppm	53400	2500	20400	2200	120000	1000	40
		%	27	1	10	1	60	1	--
D	1472000	ppm	39000	3200	18500	3400	83000	---	100
		%	26	2	13	2	56	---	--
Average %			28	1.3	9.8	1.3	58.3	1.3	--
%'s used in this study			27	1	10	1	60	1	--
Molaltites used for 4I multication solution			2.26	0.062	0.499	0.088	3.48	0.009	--

*Total dissolved solids

Brine A taken from sphalerite mineral in sphalerite-galena deposit; Tri State, Okla.
Brine B taken from sphalerite mineral in sphalerite-galena deposit; Cartagena, Spain.
Brine C taken from sphalerite mineral in sphalerite-galena deposit; Upper Miss. Valley.
Brine D taken from galena mineral in sphalerite-galena deposit; Upper Miss. Valley.

Table 8. Results of pH test. Leach of Eudora shale with 4I NaCl solution at 25°C. Initially adjusted pH's of 4, 7, and 10. Experiment was run with duplicates. (Concentrations: ppm found in 100 ml leachate using 5 gm shale samples.)

pH_i*	pH_f**	Zn	Cu	Fe	Ni	Pb	Co
4	7.1	.84	.022	--	.19	.62	--
		.82	.022	--	.20	.61	--
7	7.1	.70	.031	--	.15	.71	--
		.78	.029	--	.18	.57	--
10	7.2	.52	.018	--	.13	.59	--
		.69	.019	--	.16	.60	--

*Initial pH

** Final pH after 3-day leach

the solution could not be controlled without adding buffering agents, which would change the chemistry of the solution to be studied. An analysis of variance using the range method developed by Snedecor and Cochran (1967) showed that there were no significant differences at the 95 percent confidence limit among the three solutions in terms of the trace elements leached. The use of the range method in statistical analyses will be discussed later. From the data in Table 8 it was determined that solutions with starting pH's between 5 and 6 would not affect the conclusions of this paper. Table 8 does suggest that more Zn was leached by solutions with lower starting pH's. More work is necessary, however, to be able to define this observation.

At the end of a leach the pH of one of the replicate solutions was measured. The remaining samples were removed immediately from the water bath and centrifuged at 30,000 rpm for 20 minutes. After centrifuging the supernatant was filtered through a 0.45 μ millipore filter, acidified to a pH of about 2 with HNO_3, and refrigerated in polyethylene bottles until the chemical analysis could be done. The average total time between leaving the water bath and being acidified was about 30 minutes. All chemical analyses were done within 48 hours. Because of the change in solubility with decreasing temperature, the 4I KCl leachate could not be stored refrigerated.

Calcium, magnesium and potassium concentrations in the various solutions were determined by atomic absorption using

a Perkin Elmer model 360 atomic absorption spectrophotometer with deuterium arc background corrector. Sodium content was determined by flame emission using a Zeiss spectrophotometer type PMQ II. All trace-element concentrations in the leaching experiments were determined by atomic absorption using the MIBK-APDC attraction method (Brooks et al., 1967; Sprague and Salvin, 1965). The pH of the solution was adjusted to 4.5 with NaOH or HCl before extraction. Initially a bromphenol blue color indicator was used to adjust the pH. However, color change in the more concentrated solutions was not found to be a reliable indicator of the pH and therefore a pH meter was used for all pH adjustments for the extraction. The matrix for the standards was made with a NaCl solution at the appropriate ionic concentration.

The leachate from the black shales commonly had odors suggesting that organic material had been leached. One concern in the extraction technique is that the presence of organic material in solution might reduce the efficiency of the technique by (1) binding the metals, making them unavailable for the APDC complex, and (2) causing poor aspiration of the solution during analysis (Heltz et al., 1975; Hathaway, personal communication, 1975). Iron is an abundant element in many of the shales that were studied, but the extremely low concentrations of iron in the leachates suggested that organic complexing might be tying up some of the metals.

Attempts at evaporating the leachate to dryness in nitric acid and redissolving in HCl were not found to be

satisfactory in removing the organic material from solution. Although it appeared that organic matter had been destroyed, in some cases not all the material could be brought back into solution. This was especially true of the multi-cation brines at an ionic strength of 4.

A technique for liberating trace metals from seawater without evaporating the sample to dryness was demonstrated by Florence and Batly (1976). Two ml of 2 molar HNO_3 was added to 25 ml of sample (pH 0.7). The sample was boiled gently for ten to fifteen minutes, after which the solution was analyzed for Pb, Zn, Cd and Cu. Results showed complete liberation of the trace elements for extraction. They did not find any increase in the amount of metal liberated using more concentrated acids and evaporating the sample close to dryness.

A modification of this technique was used in this study. Four ml of 2 molar HNO_3 was added to 50 ml of the leachate. The resultant pH varied between 0.4 and 0.6. This solution was then boiled in a 150-ml beaker covered by a ribbed watch glass for twenty minutes. The solution was then diluted to approximately 75 ml with distilled water, the pH adjusted to 4.5 for the trace-element extraction, and the extraction and analysis carried out. A test using 4 ml of 15 molar HNO_3 and evaporating the sample close to dryness showed no more trace elements to be liberated than using the 2 molar HNO_3. Although this technique appeared to work satisfactorily, the problem of organics in

water and trace-element analysis has not been solved and more work is needed in this area.

Test extractions were done on all leaching solutions used at an ionic strength of 4. This was done by spiking the solutions with 1 ppm each of Cu, Pb, Zn, Co, Ni and Fe and then analyzing for these metals by the method outlined above, including the fifteen-minute boiling. The extractions were compared against 1 ppm of the metals in 4I NaCl. All metals could be recovered (>95 percent) from the 4I solutions of NaCl, KCl, $CaCl_2$, $MgCl_2$, KBr and the multication brine. None of the metals could be efficiently extracted from the Na_2SO_4 solutions and for most, no extraction at all was observed. Mobilization of trace elements by the Na_2SO_4 solution therefore could not be studied.

All the trace elements could be recovered from the KI solution except for Fe, which was found to extract at 50 percent efficiency. A test extraction was not done with KF because a trial leaching experiment with KF showed that the resultant pH was unusually high (9) and well buffered. Therefore, pH adjustment for extraction could not be done with reasonable additions of acid. In addition, the solution tended to attack the leaching vessel and precipitate a coating of silicon on the electrode and boiling beaker.

Trace elements in the hydroxylamine hydrochloride-acetic acid leach were analyzed directly by atomic absorption using the deuterium arc background corrector. This method was faster than evaporation with HNO_3 and

redissolution with HCl, as was done by Nissenbaum et al. (1974), and there was less chance of contamination. Trace elements in both oxidizing leaches (Purex and H_2O_2) were analyzed directly after evaporation of the sample and redissolution with 1N HCl.

Table 9 shows a summary of the instrumental variance (means, 95 percent confidence limits, standard deviation) for the determination of Fe, Cu, Pb, Zn, Co and Ni at the different concentrations used as standards. The elements have been extracted from NaCl (4I) and values presented represent five readings for each element at each concentration. The statistics were computed by the methods described by Sokal and Rohlf (1969). Generally instrumental variance increased with increasing concentration of the trace element.

An estimate of the precision of the analytical procedures, including boiling, extraction, and atomic absorption analysis, for each element is: Cu = 5 percent, Pb = 10 percent, Zn = 7 percent, Fe = 6 percent, Co = 5 percent and Ni = 8 percent. These results are comparable to those reported elsewhere (Presley et al., 1972). In order to get an indication of the reproducibility of the leaching experiments, the concentrations of the trace elements mobilized from the Eudora shale during three separate leaches were determined and studied. A KCl solution at an ionic strength of 4 and a temperature of 90°C was used. These leaches resulted in five determinations per element. The coeffi-

Table 9. Instrumental variance for each element. The mean and 95% confidence limit is shown for instrument readings at the concentrations used for the preparation of standards. Included is the standard deviation for each mean.

	0.01ppm	0.05ppm	0.10ppm	0.50ppm	1.00ppm	5.00ppm
Fe M*	4.28 ± 0.20	6.63 ± 0.23	22.65 ± 0.40	85.21 ± 3.60		
S**	0.17	0.23	0.37	2.43		
Cu M	1.63 ± 0.07	5.53 ± 0.21	10.68 ± 0.17	51.58 ± 0.24	95.03 ± 0.69	
S	0.05	0.15	0.12	0.17	0.49	
Pb M	2.98 ± 0.23	4.85 ± 0.29	7.03 ± 0.26	24.45 ± 0.92	48.91 ± 0.58	98.56 ± 0.64
S	0.16	0.19	0.17	0.61	0.38	0.43
Zn M	0.77 ± 0.03	1.42 ± 0.10	2.61 ± 0.11	10.24 ± 0.36	22.62 ± 0.33	97.52 ± 2.10
S	0.03	0.08	0.09	0.29	0.27	1.72
Co M	1.25 ± 0.001	3.04 ± 0.10	5.28 ± 0.10	23.12 ± 0.01	42.63 ± 0.03	
S	0.01	0.06	0.11	0.13	0.34	
Ni M	2.18 ± 0.15	6.25 ± 0.25	11.35 ± 0.44	42.67 ± 0.95	78.00 ± 2.75	
S	0.12	0.20	0.34	0.76	2.22	

*Mean

**Standard deviation

cients of variation were computed for the elements as follows: Cu = 50 percent, Pb = 21 percent, Zn = 35 percent, Co = 31 percent and Ni = 33 percent. Iron could not be detected above background.

The purpose of this investigation was to observe the mobilization process under a variety of experimental conditions. Because of this and the length of time necessary to complete each experimental leach, only two or three replicates were used per sample.

Although the number of replications is small, two types of statistical analysis were used on the data: (1) a t-test to determine confidence limits, and (2) a one-way analysis of variance to determine whether the observed differences among the leaching experiments do exist. Since the number of replications was small, it was assumed that (1) the samples were random, (2) the populations were normally distributed, and (3) the population variances were equal.

Both of the above statistical tests were done using the range methods of Snedecor and Cochran (1967). For the analysis of variance, Tukey's test was used. Although use of the range of the samples is less exact than using the standard deviation and sum of the squares for similar statistical analyses, the range method is faster and, for interval estimates, the efficiency of the range remains above 95 percent for less than five samples (Snedecor and Cochran, 1967). Similar methods were used by Picard and Felback (1976).

RESULTS AND DISCUSSION

Table 10 gives the results of the lithium metaborate fusion experiments to determine the total trace-element concentration of the shales. The mean and 95 percent confidence limits are presented for each shale. The values presented are extrapolated to 10-gm samples of the Ninnescah, Heumader and Davis shales and to 5-gm samples of the Eudora and Heebner shales. These are the respective amounts of material used in the leaching experiments. For comparison the table also presents the trace-element totals for the Heebner shale as determined by Hathaway et al. (1972). Hathaway's data were based on using cation exchange columns and dissolution in HF rather than MIBK-ADDC extraction and lithium metaborate fusion. The values determined by the two independent and different methods compare favorably.

Table 11 gives the results of the attacks using the hydroxylamine hydrochloride-acetic acid solutions (acid-reducing attacks). The table shows the amounts of the various trace elements leached after each of four successive attacks on the individual shales. Values are in ppm calculated for 5 grams of sample per 100 ml of solution for the Eudora and Heebner shales, and 10 grams of sample per 100 ml of solution for the Heumader, Davis and Ninnescah shales. Approximately 15 hours separated treatments two and three.

Table 10. Total concentrations of selected trace elements in the shales as determined by the lithium metaboratē fusion method. (Unless otherwise indicated, concentrations are in ppm found in 100 ml of leachate using 10 gm shale samples.) Mean and 95% confidence limit shown.

	Cu	Co	Ni	Zn	Fe	Mn	Pb
Heumader	5.64 ±1.04	3.50 ±1.15	7.09 ±3.62	9.76 ±1.76	3386 ±47	25.80 ±0.78	8.81 ±1.39
Davis	3.35 ±0.83	3.71 ±1.23	8.78 ±1.97	5.03 ±0.34	3614 ±41	20.20 ±0.47	5.56 ±2.73
Ninnescah	1.57 ±1.10	2.48 ±0.47	5.15 ±0.72	3.36 ±0.11	2029 ±21	73.87 ±1.79	6.14 ±0.32
Eudora 5 gms	4.95 ±0.84	1.20 ±0.43	14.45 ±2.28	50.57 ±6.80	1192 ±144	5.42 ±0.55	2.69 ±1.11
Heebner 5 gms	3.94 ±0.93	0.75 ±0.22	10.92 ±0.68	62.25 ±0.36	1631 ±10	7.47 ±0.40	3.34 ±0.40
Heebner* 5 gms	4.53	0.98	9.75	56.50	2020	8.75	4.68

* Taken from Hathaway et al., 1972

Table 11. The concentrations of trace elements leached by four successive attacks using the acetic acid-hydroxylamine hydrochloride solution. (Unless otherwise indicated the concentrations are in ppm found in 100 ml of leachate using a 10 gm shale sample.)

	Cu	Fe	Ni	Co	Zn	Pb	Mn
Eudora I (5 gm sample)	0.15	46.70	0.84	----	3.63	2.44	0.79
	0.09	18.03	----	----	1.87	0.54	0.11
	0.06	16.38	----	----	2.04	1.04	----
	0.03	10.83	----	----	1.31	0.49	----
Eudora II (5 gm sample)	0.15	49.48	0.84	----	3.63	2.44	0.79
	0.09	21.38	----	----	2.45	0.68	----
	0.06	20.25	----	----	2.68	1.69	----
	0.05	10.28	----	----	1.09	0.25	----
Heumader	1.76	328	0.74	0.48	0.86	0.24	7.60
	0.18	155	----	----	----	----	2.80
	0.06	100	----	----	----	----	0.58
	0.06	82	----	----	----	----	0.34
Ninnescah	0.22	21	----	0.75	----	0.73	49.10
	----	2.78	----	----	----	----	1.44
	----	------	----	----	----	----	----
	----	----	----	----	----	----	----
Davis	0.27	144	----	0.69	0.64	0.25	6.97
	0.12	27.2	----	----	----	----	----
	0.06	29.4	----	----	----	----	----
	0.06	20.55	----	----	----	----	----
Hesbner (5 gm sample)	0.27	63.13	2.82	0.51	18.48	2.12	0.26
	0.12	33.15	0.31	----	4.40	0.18	----
	0.11	43.43	1.85	----	3.63	0.17	----
	0.06	13.60	0.09	----	1.31	----	----

Only one sample per shale was used for the acid-reducing attacks. However, a second set of attacks was done on the Eudora shale in order to get an indication of the reproducibility of the method. Although the values and trends compare favorably, the present state-of-the-art of selective chemical attacks is in need of a statistical study of the reproducibility of the various methods.

Although most of the available metals were removed after the first attack (>60%), in a few cases there was a significant amount of trace element released with subsequent attacks. This continued release did not necessarily appear to be related to the amount of trace element available to be released. For example, the Eudora shale had a low copper content and the Heumader, a high iron content. Yet both continued to release significant amounts of these metals after the first attack. This suggests that the trace element release may be in part a kinetic effect, the rate of release depending on the fraction or fractions attacked. Even after the four attacks, significant amounts of iron were still being released from most of the shales.

In many of the schemes used to determine the partitioning of trace elements in sediments, repeated attacks with the different chemical solutions are made on one sample (cf. Nissenbaum et al., 1972). Because of the continued release of trace elements as shown in this study, partitioning results from successive chemical attacks on one shale should be regarded with caution since the amount of contamination

due to the incomplete leaching of a preceding attack is usually unknown.

The trace elements liberated by this treatment are usually taken to represent those elements associated with carbonates, acid-volatile sulfides, iron-manganese oxides and some exchangeable elements (Nissenbaum, 1974). Since the chemical treatment was done on samples that had no prior chemical treatment, this attack would also liberate cations loosely adsorbed onto clay minerals (Horowitz, 1974).

Table 12 gives the percentage of the total amount of metals leached by the acid-reducing attack. Unfortunately, the percentage of lead leached from the Eudora shale is greater than 100 percent (132 percent). Three possible sources of error for this value are: (1) error in the extraction (acid-reducing attack) procedure, (2) error in the total trace-element procedure, and (3) use of an unhomogeneous shale sample. Since all the experiments were done using the same well mixed batch of shale, the error is probably in one of the procedures. Also, the maximum amount of lead leached by the various aqueous solutions is consistent with the amount of lead leached by the acid-reducing solutions (about 5 to 6 ppm in 100 ml of leachate per 5 gms of sample). This suggests the error in analysis is in determining the total trace-element content of the shale, which is partly supported by the lower lead value found for the Heebner shale in this study compared to the value found by Hathaway et al. (1972) (Table 10). It is suggested, on

Table 12. The percent of the total metal content leached by the acetic acid-hydroxylamine hydrochloride leach.

	Cu	Co	Ni	Zn	Fe	Mn	Pb
Eudora	7.0	----	6.0	19.0	9.0	14.0	>100
Heumader	33.0	13.7	10.4	8.8	19.6	43.9	2.7
Ninnescah	22.0	30.0	----	----	1.1	68.3	11.5
Davis	14.5	18.5	----	12.9	6.1	34.5	4.5
Heebner	14.2	68.00	46.5	44.7	9.4	3.5	74.0

the basis of the aqueous solution leaching experiments and the reducing attack, that the 5 to 6 ppm in 100 ml of leachate total lead per 5 grams of sample is not an unrealistic value for the total lead in the Eudora shale. In any case, the data here indicate that most of the lead in the Eudora is available to be leached by the acid-reducing solution. Much of the lead in the Heebner shale is also available.

Tables 13 and 14 indicate those trace elements released by the 6 percent sodium hypochlorite (Purex) leaches of samples that had been previously treated with the reducing solution and of untreated samples. Sodium hypochlorite is an oxidizing solution and will tend to liberate metals associated with a fraction that can be oxidized, particularly organics. These tables further demonstrate the effect of incomplete leaching on the trace-element partitioning results from successive chemical attacks. Except for possibly Zn and Mn, more trace elements were leached from the sample that had been previously reduced than from the untreated samples. Clearly, trace elements can be carried over to successive attacks.

Table 14 represents two sets of five successive Purex attacks each on the shales. Each attack (10 ml of solution per 1 gm of shale) was allowed to react for 15 minutes, centrifuged, decanted, and combined. It appears few trace elements are liberated from the Heumader, Ninnescah and Davis shales using this oxidizing solution. Copper, nickel and

Table 13. Trace elements leached by one treatment with 6% NaClO (Purex) from previously reduced samples. (Unless otherwise indicated, concentrations are in ppm found in 100 ml of leachate using 10 gm shale samples.)

	Cu	Co	Ni	Zn	Fe	Mn	Pb
Heumader	2.71	2.79	3.74	2.48	29.71	4.23	2.10
Ninnescah	.21	.67	1.29	.87	9.1	--	.61
Davis	2.71	1.45	4.69	.25	30.41	3.53	1.52
Eudora 5 gms	5.81	.25	19.68	21.88	39.61	2.88	8.20

Table 14. Trace elements leached by two treatments with 6% NaClO (Purex) from untreated shales. (Unless otherwise indicated, concentrations are ppm found in 100 ml of leachate using 10 gm shale samples.)

	Cu	Co	Ni	Zn	Fe	Mn	Pb
Heumader	.58	----	----	----	----	3.69	----
	----	----	----	----	----	----	----
Ninnescah	----	----	----	----	----	.17	----
	----	----	----	----	----	.17	----
Davis	----	----	----	----	----	.28	----
	----	----	----	----	----	.17	----
Eudora	2.03	----	6.70	20.9	<.5	.14	----
5 gms	.72	----	----	3.83	----	----	----

cobalt appear to be associated with the oxidizing fraction of the Eudora shale.

Since the data in Table 14 represent attacks on untreated samples, it might be expected that the oxidizing fraction would also contain those metals that are loosely adsorbed. Clearly only minor amounts of metals are contributed to the reducing and oxidizing fractions by the loosely adsorbed fraction in the Heumader, Ninnescah and Davis shales.

The trace elements liberated by an oxidizing attack were also studied using 30 percent H_2O_2 as the attacking solution (Table 15). Generally the results are comparable, with the H_2O_2 solution being slightly more aggressive in some cases. The H_2O_2 attack, however, liberated significantly more Zn from the Eudora shale.

As with the Eudora shale, Ni, Cu and Co are associated with the oxidizable fraction of the Heebner shale, along with iron. Table 16 further demonstrates this by presenting the percent of the total metal content of the shale leached by the oxidizing fraction. Significant amounts of the total metal content of copper, cobalt and nickel are found in the oxidizable fraction in both black shales. Table 16 was compiled using the data from the H_2O_2 attack.

Precise definition of the amount of loosely adsorbed metal in the shales was not possible due to the nature of these experiments. However, comparing Table 16 with Table 12 with respect to the percentage of metal leached from the

Table 15. Results of trace elements leached by 30% H_2O_2 from untreated samples. (Unless otherwise indicated, concentrations are in ppm found in 100 ml of leachate using 10 gm shale samples.)

	Cu	Fe	Ni	Co	Zn	Pb
Eudora (5 gms)	1.09	14.55	7.93	0.38	0.03	0.19
Heumader	0.12	<0.05	0.06	0.02	----	----
Ninnescah	----	<0.05	----	----	----	----
Davis	<0.05	<0.05	<0.04	----	----	----
Heebner (5 gms)	0.92	139.6	7.75	0.42	6.15	0.37

Table 16. Percent of the total trace element concentration in the shales leached by the oxidizing solution of 30% H_2O_2.

	Cu	Co	Ni	Zn	Fe	Pb
Eudora	22.0	31.7	54.9	---	1.2	---
Heumader	2.1	<0.01	<0.01	---	---	---
Ninnescah	---	---	---	---	---	---
Davis	<0.01	---	<0.01	---	---	---
Heebner	23.4	56.0	71.0	9.9	8.6	11.0

reducing fraction suggests that adsorbed metals may be significant in the black shales. This is apparent particularly for cobalt and nickel in the Heebner shale since the total percentage of leachable metal (reducing fraction plus oxidizing fraction) is greater than 100 percent.

Two processes which can account for the mobilization of metals from sediments are cation exchange and ligand extraction. In a Ca, Na-Cl brine, both Na and Ca could act as exchangers. Sodium might be the dominant exchanger because it is usually much more concentrated in the brine. Recently Carpenter et al. (1974) suggested that potassium is the dominant exchanger, causing the concentration of the metals in the brine. This idea would in part explain the unusually high potassium content of fluid inclusions compared to "basin" brines.

The extraction would act by a process in which the solution is made a more favorable place for the metals to exist, possibly caused by the ionic strength of the solution and the type of ligands in solution. The ligands would complex with the trace metals. Earlier in this study it was demonstrated that the nature of the chemical speciation would depend on the major ligands. Metals therefore interact differently with different ligands. There is nothing new in this since it is suggested by the spectrochemical series of the stability of metals with various ligands (Huheey, 1972). The order of decreasing stability is $OH^- > F^- > Cl^- > S^{2-} > Br^- > I^-$. The point to be made is that the

importance of ligands in the mobilizing process can be studied by measuring the metals released from shales as a result of leaching experiments with brines comprising different salt solutions if cation species are held constant.

Table 17a summarizes the results of leaches on the Heebner shale at 50°C using solutions of ionic strength 4 for KBr, KI, KCl, NaCl, $CaCl_2$ and the multi-cation brine. Since the potassium salts contain a common cation, differences in the mobilizing ability of a solution could be attributed to changes in the ligand. With the chloride salts, the difference would be related to changes in the cation. The Heebner shale was used because it has the most leachable metal content of all the shales studied. Except for the KI solution, the final pH's of the leaches are similar. All the pH's are low enough to permit the ligand in the salt to form the dominant complexes; that is, hydroxide complexing would be minor.

Table 17a shows that, except for the KI solution, the amounts of metal leachable by the various salt solutions are similar. The $CaCl_2$ brine appears to leach more zinc, which might account for the slightly higher zinc content of the multi-cation solution. Although the results for the Ca brine are presented on the basis of 5 grams of shale per 100 ml of solution, the original sample-solution ratio was 1 gram to 100 ml; therefore, these comparisons must be regarded with caution. From these data there is no reason to suspect that changes in the cation would have a major effect on the

Table 17a. The results of the leaches of the Heebner shale with various salt solutions at an ionic strength of 4 and at a temperature of 50°C. Salt solutions comprise K with various halogen ligands and Cl with various cations. Concentrations are in ppm found in 100 ml of leachate using 5 gms of shale sample.

Salt Solutions	pH*	Cu	Fe	Ni	Zn	Pb	Co
KCl	4.0	0.50	252.9	3.18	8.28	3.08	0.23
KBr	3.7	0.69	349.5	3.41	8.11	2.86	0.25
KI	5.3	1.16	-----	1.23	0.03	0.08	0.09
NaCl	3.81	0.46	160.5	3.20	8.28	2.68	0.22
$CaCl_2$	---	0.79	97.9	6.05	19.55	2.92	0.24
Brine	---	0.37	>100.0	3.00	10.00	2.42	0.25

* The pH at the end of the leach.

mobilization process. Cation effects on the mobilization process will be discussed further in a later section

The KI solution mobilizes only minor amounts of Fe, Zn, Pb and Co compared to the other salts, but significantly more Cu. This would suggest that the ligand in solution has a significant effect on the mobilization efficiency of the brine.

The selectivity of the KI solution in mobilizing Cu was further studied by leaching the Eudora and Heumader shales with the 4I KCl solution at 50°C (Table 17b). In both cases more Cu was leached than the other trace elements. Table 17b also shows the results of another leach of the Heebner shale with the KI solution compared with a leaching using a NaCl solution. Solution strengths were 4I and 1 gm of shale was used. The results further demonstrate that the KI solution will tend to leach much more Cu than the other trace elements.

Three trends were studied: (1) the amount of metals leached versus shale type, (2) the amount of metals leached versus temperature, and (3) the amount of metals leached versus ionic strength.

Tables 18a through 18d summarize the results of the 90°C leaches of the shales using aqueous solutions with an ionic strength of 4. The value for each shale-metal combination is the average of two or three experiments.

The highest amount of metal was mobilized from the Eudora shale, decreasing in the order Heumader>Davis>

Table 17b. The results of the leaches of the Eudora and Heumader shales with 4I KI solutions at 50°C. Included are the results of the leaches of the Heebner shale with 4I solutions of KI and NaCl at 50°C. Concentrations are in ppm found in 100 ml of leachate using the indicated gram sample size.

Shale Sample Size	Cu	Fe	Ni	Zn	Pb	Co
Eudora 5 gms	1.27	----	0.044	0.002	0.53	0.021
Heumader 10 gms	1.90	----	0.035	0.002	0.014	0.013
Heebner (KI) 1 gm	0.46	----	0.083	0.002	0.019	0.024
Heebner (NaCl) 1 gm	0.22	----	1.03	4.44	0.56	0.055

Table 18. Results of leaches on shales using various salt solutions at 90°C and at an ionic strength of 4. Concentrations are in ppm found in 100 ml of leachate. Shale sample sizes were 10 gms for the Heumader, Davis and Ninnescah, and 5 gms for the Eudora.

a. Multication leach

Shale	Cu	Pb	Zn	Fe	Co	Ni
Eudora	0.01	6.4	5.7	0.3	0.04	0.8
Heumader	0.8	---	0.8	1.0	0.1	---
Davis	0.1	0.09	0.08	---	0.06	---
Ninnescah	---	---	<0.01	---	---	---

b. $CaCl_2$ leach

Shale	Cu	Pb	Zn	Fe	Co	Ni
Eudora	0.01	6.8	6.2	---	0.02	0.48
Heumader	0.22	---	0.75	1.6	0.06	---
Davis	0.18	0.05	0.03	---	0.06	---
Ninnescah	0.04	0.04	0.04	---	0.04	---

c. KCl leach

Shale	Cu	Pb	Zn	Fe	Co	Ni
Eudora	0.01	3.9	4.0	---	---	0.06
Heumader	1.29	---	0.3	---	----	---
Davis	0.03	---	---	---	---	---
Ninnescah	---	---	---	---	---	---

d. NaCl leach

Shale	Cu	Pb	Zn	Fe	Co	Ni
Eudora	0.005	4.2	4.6	---	---	0.04
Heumader	0.22	<0.01	0.56	---	---	---
Davis	0.07	0.01	0.02	---	---	---
Ninnescah	<0.001	0.02	---	---	---	---

Ninnescah. This order is similar to that found for the hydroxylamine hydrochloride-acetic acid leaches. These data indicate that an increase in the amount of metal leached from a shale may be in part related to decreasing quartz content and increasing organic content of the shale. The most lead, zinc and nickel were leached from the Eudora shale and the most copper, from the Heumader. Little iron was leached from any shale, even though the total iron content was high in all samples.

It appears from Tables 18a to d that the bivalent cation solutions were slightly more efficient in mobilizing lead and zinc than the univalent cation solutions, particularly for the Eudora shale. The potassium solution was particularly effective in leaching copper from the Heumader shale.

Table 19 shows the results of analysis-of-variance tests on the data in Tables 18a to d. The bars under the means connect values that are not statistically different at the 95th confidence limit. In general the solutions containing bivalent cations appear to leach more Pb and Zn from the Eudora shale, and more Pb from the Davis shale, than the solutions containing univalent cations. Also the KCl solution appears to leach significantly more Cu from the Heumader shale than the other salt solutions. The other leaches did not show similar trends for Pb, Zn or Cu. This may be due to the low concentrations of the metals in these leaches. From the data in Tables 18a to d and Table 19 it

Table 19. Results of analysis of variance on selected data in Tables 18a-d. Bars under means connect values that are not significantly different at the 95% confidence limit.

	SOLUTIONS			
Shale - Metal	Multi*	$CaCl_2$	NaCl	KCl
Eudora - Pb	6.43	6.76	4.19	3.97
Davis - Pb	0.09	0.05	0.01	
Eudora - Zn	5.70	6.19	4.59	4.00
Davis - Zn	0.08	0.028	0.02	
Heumader - Zn	0.80	0.75	0.56	0.30
Eudora - Cu	0.01	0.01	0.01	0.005

	SOLUTIONS			
Shale - Metal	$CaCl_2$	Multi*	NaCl	KCl
Davis - Cu	0.18	0.10	0.07	0.03

	SOLUTIONS			
Shale - Metal	KCl	Multi*	$CaCl_2$	NaCl
Heumader - Cu	1.29	0.80	0.22	0.22

*Multication solution

is apparent that the type of cation in solution can affect the mobilization process.

In terms of changes in mobilization efficiency as a function of ionic strength and temperature, only Pb and Zn from the Eudora shale and Cu and Zn from the Heumader shale could be studied. The other metal leaches were too low in concentration to permit accurate plotting as a function of ionic strength and temperature.

Payne and Pickering (1975) have demonstrated that the amount of adsorption of a metal will depend on the pH, the nature of the ligands present, and the order of contact of the species. They suggest that complexing of the trace elements will tend to reduce the amount adsorbed. In addition, lower pH's will make H^+ successfully compete for exchange sites and liberate sorpted trace elements.

Increasing the ionic strength of a solution should tend to increase the amount of mobilization by increasing both the amount of extraction and the amount of exchange. Extraction would increase due to the decreased activity coefficients of the metals in solution and the increased amount of complexing (O'Connor and Kester, 1975). Exchange would be enhanced by the increase in cation exchanges.

Figures 15a and b and 16a and b show the effects of increased ionic strength on mobilization for the Heumader and Eudora shales, respectively. As might be predicted, mobilization appears to increase at higher ionic strengths. The diagrams show, however, that the trends are not

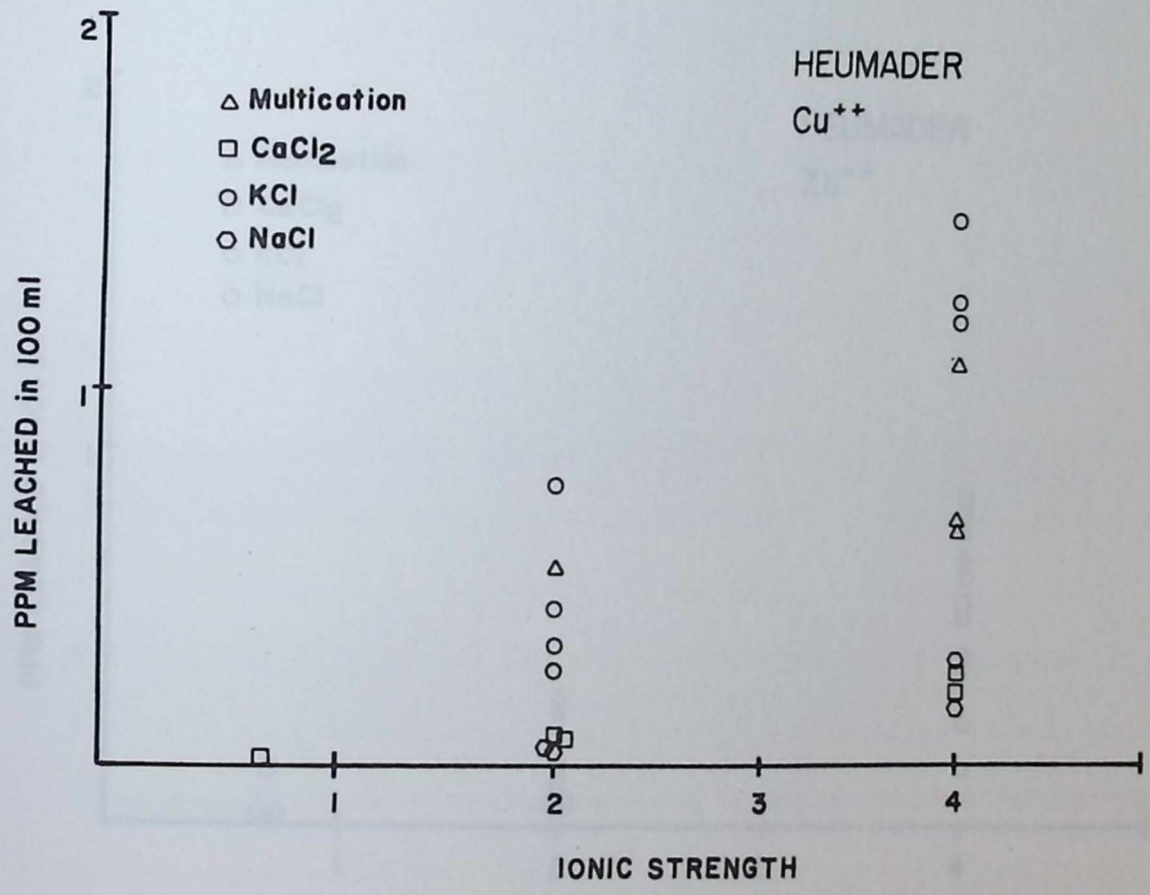


Figure 15a: Changes in the amount of metal removed from the Heumader shale as a function of ionic strength for copper.

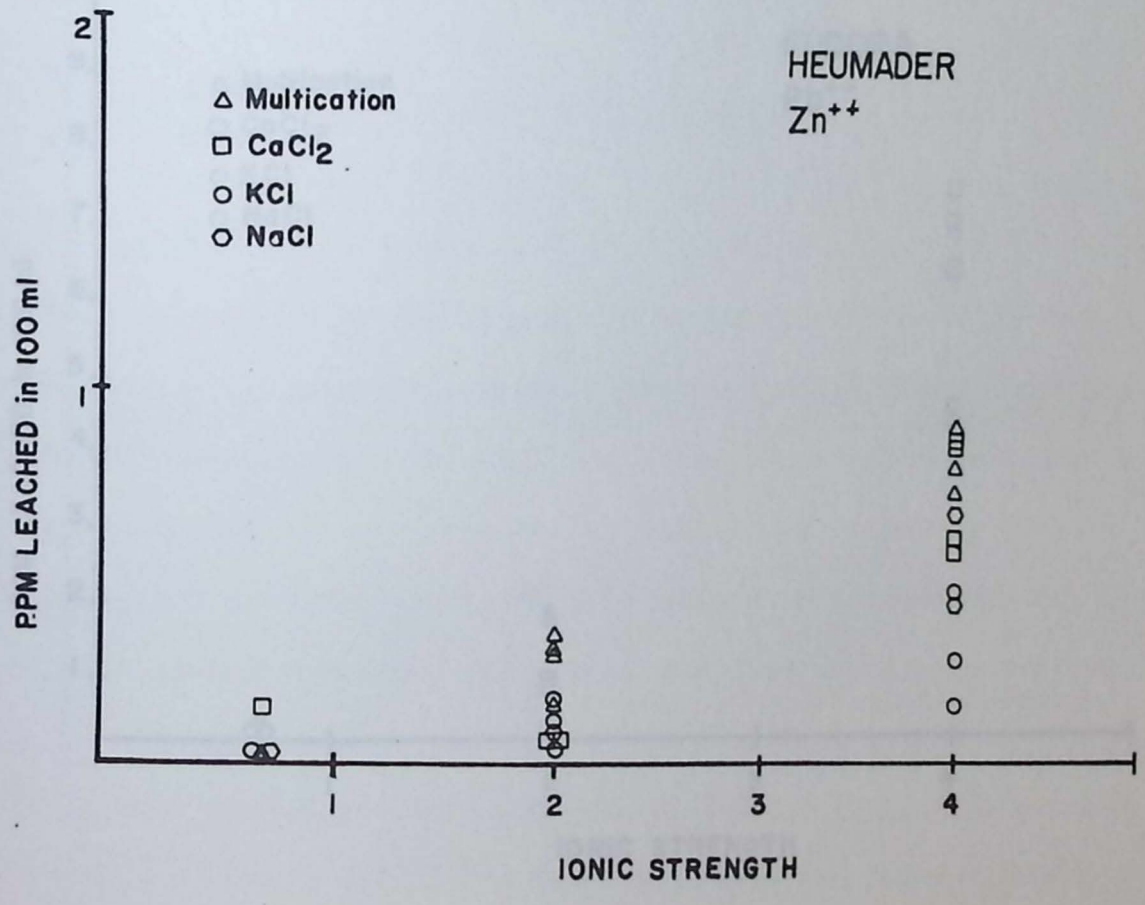


Figure 15b: Changes in the amount of metal removed from the Heumader shale as a function of ionic strength for zinc.

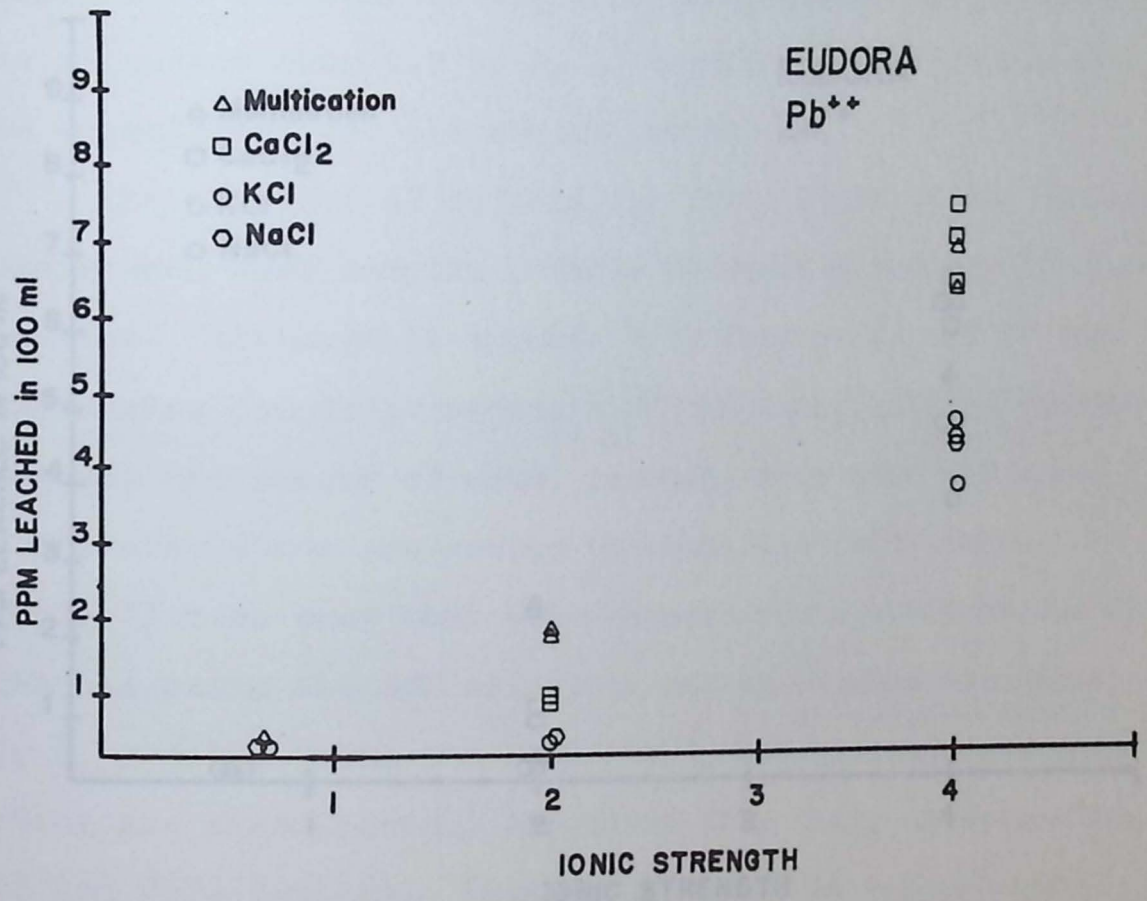


Figure 16a: Changes in the amount of metal removed from the Eudora shale as a function of ionic strength for lead.

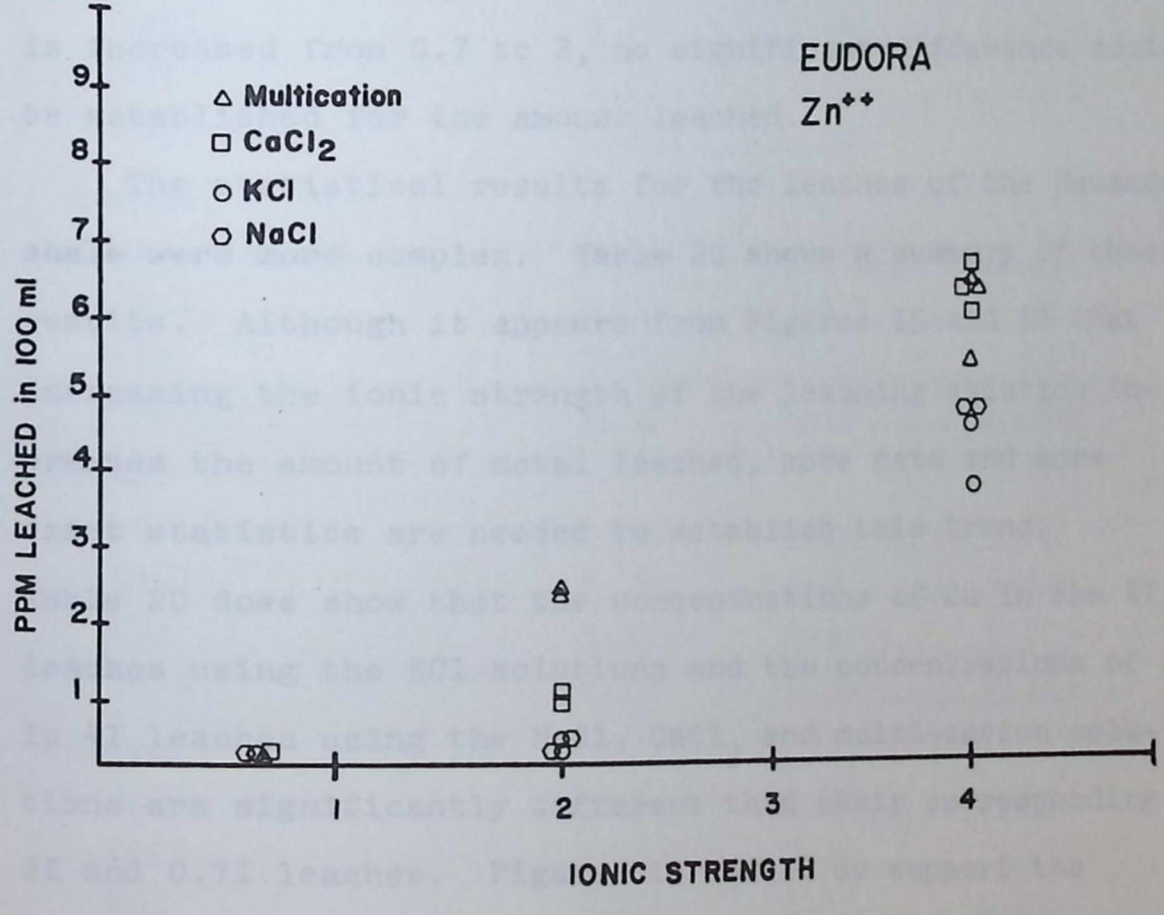


Figure 16b: Changes in the amount of metal removed from the Eudora shale as a function of ionic strength for zinc.

necessarily simple. The means of the metal concentrations of the leachates were compared by an analysis of variance and the results are shown in Table 20. All the leaches of the Eudora shale using solutions at an ionic strength of 4 were found to be significantly different than the leaches with solutions at ionic strengths of 2 and 0.7 at the 95 percent confidence limit. Although the amount of leaching appears to increase as the ionic strength of the solution is increased from 0.7 to 2, no significant difference could be established for the amount leached.

The statistical results for the leaches of the Heumader shale were more complex. Table 20 shows a summary of these results. Although it appears from Figures 15 and 16 that increasing the ionic strength of the leaching solution increases the amount of metal leached, more data and more exact statistics are needed to establish this trend. Table 20 does show that the concentrations of Cu in the 4I leaches using the KCl solutions and the concentrations of Zn in 4I leaches using the NaCl, $CaCl_2$ and multi-cation solutions are significantly different than their corresponding 2I and 0.7I leaches. Figures 15 and 16 do support the observation that more Cu is leached by the K solutions from the Heumader shale, while the bivalent cation solutions tend to leach more Zn and Pb. Clearly the mobilization process is affected by changes in the ionic strength of the leaching solution and also the types of cations in the solution.

Table 20. Results of analysis of variance on the data used to prepare Figures 15a and b and Figures 16a and b. Bars under means connect values that are not significantly different at the 95% confidence limit.

Shale - metal Solution	IONIC STRENGTH 4I	2I	.7I
Heumader - Cu			
multication	0.80ppm	0.22	0.036
$CaCl_2$	0.22	0.04	0.008
KCl	1.29	0.43	
NaCl	0.22	0.18	
Heumader - Zn			
multication	0.08	0.28	
$CaCl_2$	0.75	0.07	0.10
KCl	0.31	0.08	0.033
NaCl	0.56	0.095	0.066
Eudora - Pb			
multication	6.43	1.68	0.25
$CaCl_2$	6.76	0.71	0.058
KCl	3.97	0.13	0.039
NaCl	4.19	0.16	0.012
Eudora - Zn			
multication	5.70	2.32	0.09
$CaCl_2$	6.19	0.90	0.18
KCl	4.00	0.15	0.02
NaCl	4.59	0.25	0.001

The general principles of cation exchange are well known (Carrol, 1959). The reason for the selectivity of certain alkali and alkaline earths in exchanging for certain trace elements, as suggested by these data, is not readily apparent, however. For example, based on ionic radii one might expect that K^+ (ionic radius of 1.33) would be likely to exchange for Pb (ionic radius of 1.2), and Ca^{2+} (0.99), for Cu^{2+} (0.96) and Zn^{2+} (0.74).

A possible reason for the selectivity might be the fraction with which the trace element is associated and how the trace element exists within that fraction. For example, copper could be chelated by the organic fraction in reduced form. The ability of a cation to act as an exchanger might be related not only to the exchanging trace element, then, but also to the fraction in which the exchange takes place.

Presumably an increase in temperature would increase the amount of trace-element mobilization, regardless of the composition of the leaching solution. Hathaway et al. (1972) demonstrated, using distilled water, that increasing the temperature from 25°C to 80°C increased the amount of leaching. This increase might be attributed to (1) an increase in the solubility of a particular phase thereby releasing more trace elements, (2) an increase in desorption, (3) an increase in the amount of complexing, making the metal more soluble, and (4) an increase in the rate of the exchange reactions.

Figures 17a and b show the effects of temperature changes on the ability of the various aqueous solutions to leach Zn and Cu, respectively, from the Heumader shale. The leaching solutions were at an ionic strength of 4. Figures 18a and b show similar types of results for Zn and Pb, respectively, for the Eudora shale.

The means of the metal concentrations of the leachates were compared by analysis of variance. Table 21 summarizes these results. The bars under the means connect values that are not significantly different at the 95 percent confidence limit. Figures 17 and 18 and Table 21 corroborate Hathaway's findings by demonstrating that increasing the temperature of the leaching solution can increase the amount of leaching. The trends of the increases indicated by the various leaching solutions are not the same, however. For example, the amount of Cu leached from the Heumader shale by the KCl solution shows an almost linear increase with temperature change (Figure 17a). The other three solutions show no increase in the amount of leaching from 50°C to 90°C. For these three solutions only the change from 25°C to 50°C is significant (Table 21).

The trends in the leaching of Zn from the Heumader shale (Figure 17b) are reversed. The KCl solutions show a leveling off in the amount of leaching after 50°C, while the other three show an increase in leaching from 50°C to 90°C. The increase in the amount leached is not significant for the $CaCl_2$ solution from 50°C to 90°C, however (Table 21).

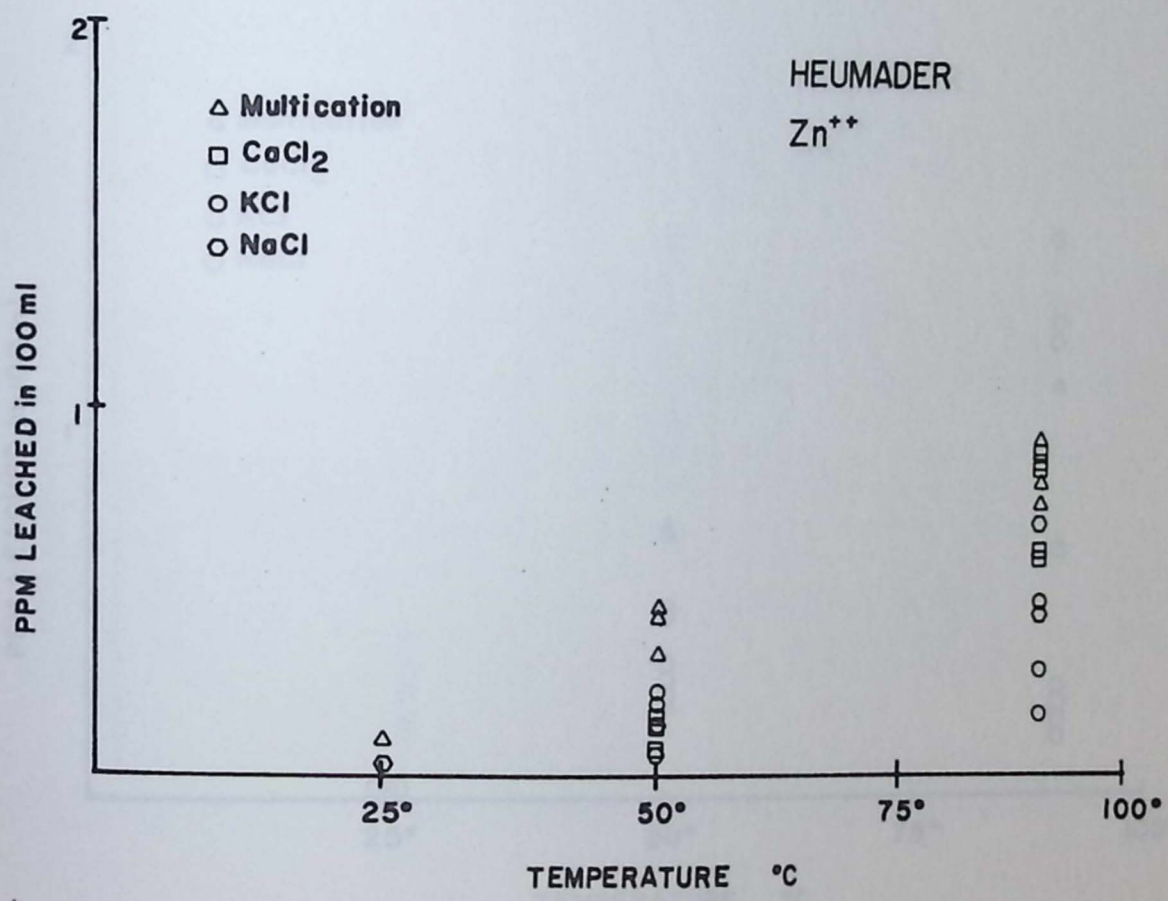


Figure 17a: Changes in the amount of metal removed from the Heumader shale as a function of temperature for zinc.

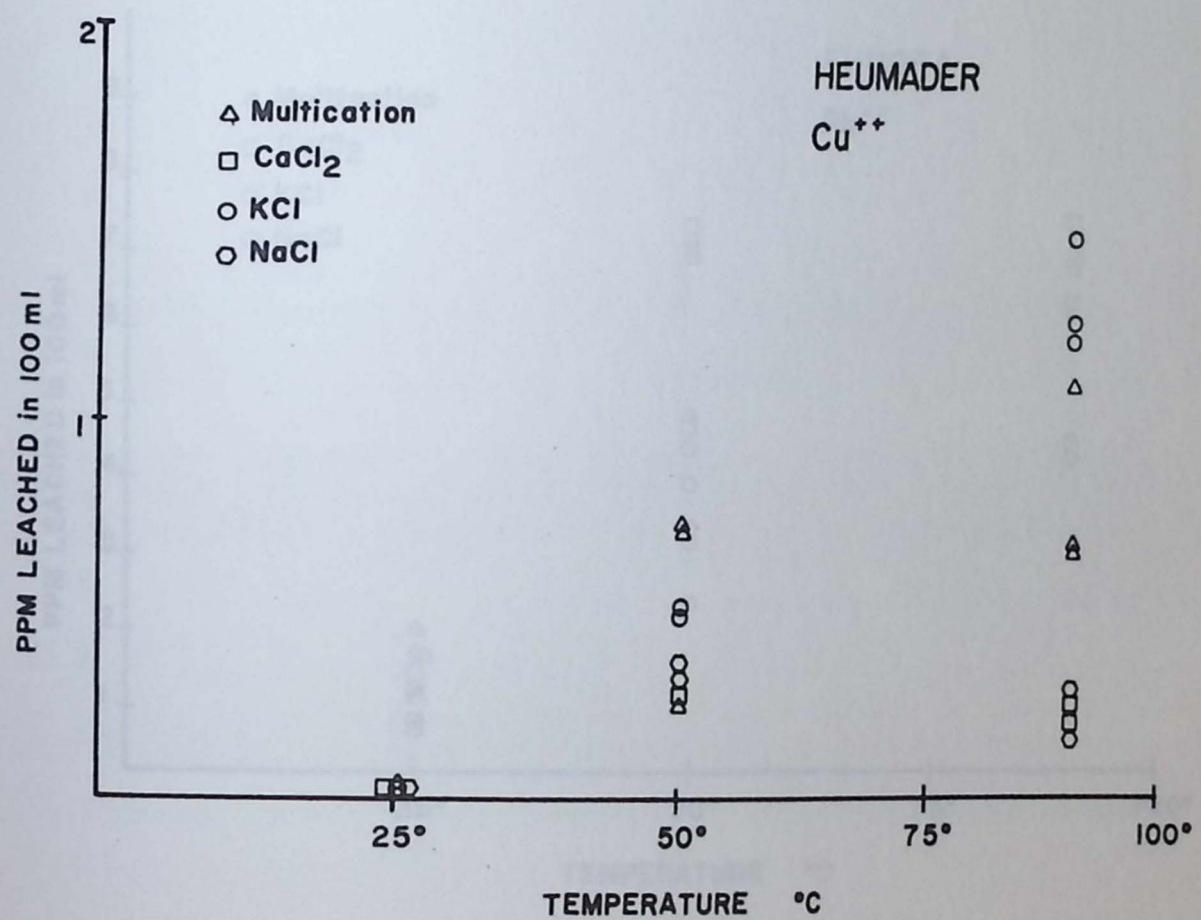


Figure 17b: Changes in the amount of metal removed from the Heumader shale as a function of temperature for copper.

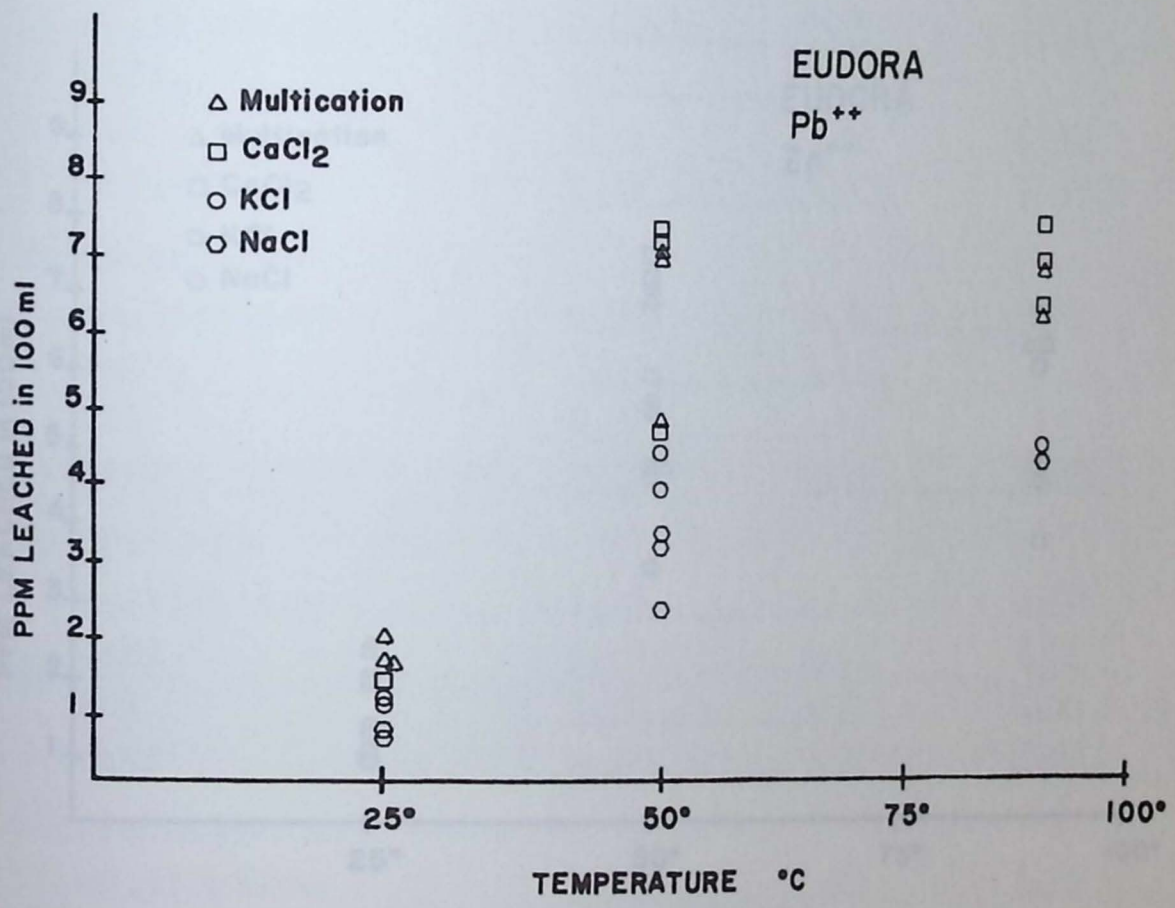


Figure 18a: Changes in the amount of metal removed from the Eudora shale as a function of temperature for lead.

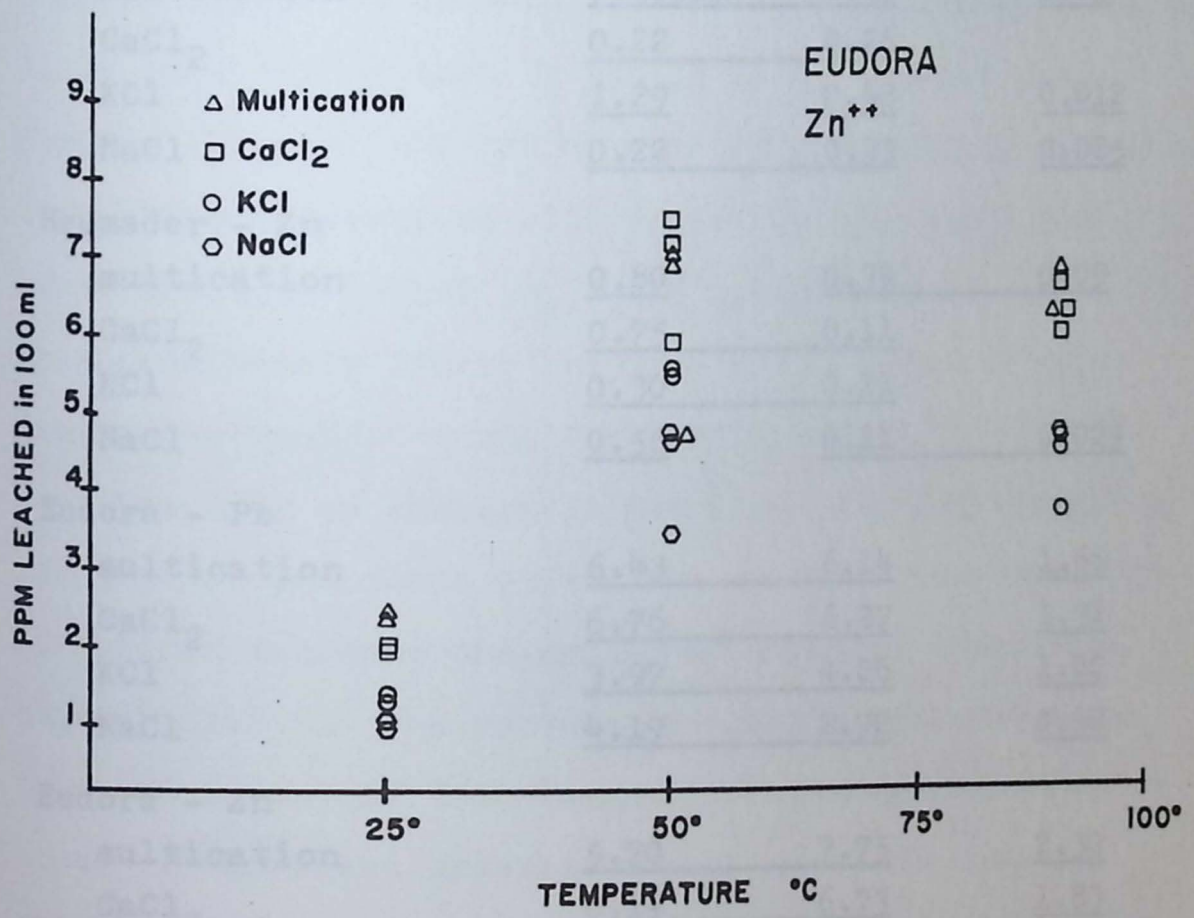


Figure 18b: Changes in the amount of metal removed from the Eudora shale as a function of temperature for zinc.

Table 21. Results of analysis of variance on the data used to prepare Figures 17a and b and Figures 18a and b. Bars under means connect values that are not significantly different at the 95% confidence limit.

Shale - metal Solution	TEMPERATURE 90°C	50°C	25°C
Heumader - Cu			
multication	0.80ppm	0.69	0.03
$CaCl_2$	0.22	0.26	
KCl	1.29	0.48	0.012
NaCl	0.22	0.33	0.025
Heumader - Zn			
multication	0.80	0.39	0.09
$CaCl_2$	0.75	0.11	
KCl	0.30	0.21	
NaCl	0.56	0.11	0.029
Eudora - Pb			
multication	6.43	6.14	1.66
$CaCl_2$	6.76	6.27	1.32
KCl	3.97	4.06	1.00
NaCl	4.19	2.92	0.62
Eudora - Zn			
multication	5.70	7.75	2.30
$CaCl_2$	6.19	6.73	1.83
KCl	4.00	5.38	1.18
NaCl	4.59	4.16	0.94

The trends of the metal leachings from the Eudora shale (Figures 18a and b and Table 21) are similar for Pb and Zn. In all the leaching solutions there was no significant increase in the amount of leaching above 50°C.

As might have been anticipated on the basis of the experiments with different ionic strengths, the KCl solution is more effective in mobilizing Cu while the multivalent cations appear to be more effective in mobilizing Pb and Zn. It is interesting that Cu and Zn in the Heumader shale leaches (Figures 17a and b) show similar leaching changes with increasing temperature with respect to each one's more efficient mobilizer; that is, K and the multivalent cations show an approximately linear increase in the amount of metal leached between 25°C and 90°C for Cu and Zn.

The data on changes in metal leaching with changes in temperature and ionic strength demonstrate that increasing either can increase the amount of leaching. These data suggest that (1) the cations in solution will affect the type and amount of leaching, (2) the phases with which the trace elements are associated will affect the type and amount of leaching, and (3) increasing the temperature will not necessarily mean a continuous increase in the amount of leaching in the systems studied.

Previous discussions have demonstrated the effects of changes in cations on leaching efficiency. By comparing the leaching data for Cu, Zn and Pb in the different phase attacks (Table 22), in the different aqueous solution

Table 22. Results of the comparison of percent leached between the acid-reducing attack (AR) and the oxidizing attack (O).

		Cu	Co	Fe	Zn	Ni	Pb
Heebner	AR	14.2%	68.0	9.4	44.7	46.5	74.0
	O	23.4	56.0	8.6	9.9	71.0	11.1
Eudora	AR	0.07	----	9.0	19.0	6.0	>100.0
	O	22.0	31.7	1.2	----	54.9	----
Heumader	AR	33.0	13.7	19.6	8.8	10.4	2.7
	O	2.1	<0.01	----	----	<0.01	----
Davis	AR	14.5	18.5	6.1	12.9	----	4.5
	O	<0.01	----	----	----	<0.01	----
Ninnescah	AR	22.0	30.0	1.1	----	-----	----
	O	----	----	----	----	----	----

attacks (Tables 18a to d), and the maximum percent leached from the shales (Table 23), the phases that liberate the most metals can be studied. These tables suggest that of the three shale fractions defined by this study (those trace elements liberated by the acid-reducing attack, those liberated by the oxidizing attack, and those in the residue), the acid-reducing attack liberates the most trace elements. Similar interpretations can be made by comparing the amounts of Ni and Co leached from the shales by the different attacking solutions.

The aqueous solutions leached more Cu and Zn from the Heumader shale than other trace elements (Co, Ni and Fe). The acid-reducing attacks leached 33 percent of the total Cu from the Heumader shale and 9 percent of the total Zn, while only 2.1 percent and 0 percent, respectively, were leached by the oxidizing attack (H_2O_2 solution) (Table 22). More Zn and Pb were leached from the Eudora shale by the aqueous solutions than other trace elements. The acid-reducing attack liberated 19 percent of the Zn and 100 percent of the Pb. Less than 1 percent of these metals was leached by the oxidizing solution. The Eudora shale contains more total Cu than the Heumader. Tables 18 to 23 show that little Cu was mobilized from the Eudora shale by any of the aqueous solutions. More Cu was liberated by the oxidizing solution (22 percent) than the acid-reducing solution (0.07 percent). Thus metals that tend to be mobilized by the acid-reducing fraction also tend to be mobilized by

Table 23. Maximum percentage of metals leached considering all the salt solutions used, excluding KI.

	Cu	Co	Fe	Zn	Ni	Pb
Heebner	9.4%	33.9	2.1	36.0	46.0	90.0
Eudora	0.2	4.2	----	12.9	7.3	>100.0
Heumader	25.6	2.8	----	9.1	3.0	0.1
Davis	5.1	1.6	----	1.6	----	1.6
Ninnescah	4.0	1.6	----	1.2	----	0.6

the aqueous solutions. The oxidizing fraction is apparently not attacked by the aqueous solutions used in this study. The leaching data for the Heebner shale support this interpretation.

The Heebner aqueous leaches contain high concentrations of Pb and Zn relative to other metals. More Pb and Zn were mobilized by the acid-reducing solutions (74 percent and 44.7 percent, respectively) than by the oxidizing solutions (11.1 percent and 9.9 percent, respectively. There is more total Cu in the Heebner shale than in the Heumader, yet similar to the Eudora shale, little Cu was leached by the aqueous solutions (Table 23). Twenty-three percent of the Cu in the Heebner shale was mobilized by the oxidizing solution and 14.2 percent, by the acid-reducing attack. The greater amount of Cu mobilized from the Heebner shale by the aqueous solutions compared to the Eudora (9.4 percent and 0.2 percent, respectively) is consistent with the greater amount of Cu leached from the Heebner shale by the acid-reducing solution compared to the Eudora (14.2 percent and 0.07 percent, respectively).

Data in Table 23 for the aqueous leaches of the Davis and the Ninnescah shales show that more Cu was mobilized from each of these shales than any of the other trace elements. More Cu was mobilized by the acid-reducing solution (Davis, 14.7 percent and Ninnescah, 22 percent) with only minor amounts mobilized by the oxidizing solution (Davis, <0.01 percent and Ninnescah, 0 percent).

Although the aqueous solutions appeared to be mobilizing metals from the acid-reducing fraction, not all of the metals were mobilized to the same efficiency under the conditions of this study. For example, whereas 68 percent of the Co in the Heebner shale was released by acid-reducing solution, only half that percentage was mobilized by the aqueous solutions. Only 2.8 percent of Co and 3.0 percent of Ni were mobilized by the aqueous solutions from the Heumader shale, much less than the 13.7 percent and 10.4 percent of the metals released, respectively, by the acid-reducion solution. Iron shows very high concentrations in the acid-reducing fractions of all the shales. Except for the Heebner shale, which leached 2 percent in the aqueous solutions, little Fe leaching by these solutions was detected. Clearly, however, the aqueous solutions are preferentially attacking certain phases of the sediment.

Finally, it appears that increasing the temperature above 90°C would not necessarily mean an increase in the amount of metal leaching. It is not known how much metal would become available from other fractions of the shale as the temperature is raised. For example, more metal might be released due to the breakdown of the organic fraction. Perhaps the amount leaching at 90°C would be similar to that leaching at 200°C.

SUMMARY OF THE EXPERIMENTAL RESULTS

(1) Increasing the temperature of the leaching solution can increase the amount of metal mobilized. The change is not necessarily linear with time.

(2) The composition of the brine in terms of both the absolute and relative amounts will affect the mobilizing efficiency. Increasing the ionic strength will increase the amount of mobilization. Changes in the ligand and cation type will affect the mobilizing efficiency. Except for copper in the KI brines, the chloride and bromide brines mobilized the greatest amounts of metals. In terms of the cations, more copper was mobilized by the K^+ solutions than the Ca^{2+}, Na^+ and multi-cation solutions; and more Pb^{2+} and Zn^{2+} were mobilized by the multivalent cations solutions than the K^+ solutions.

(3) From comparison of the KBr, KCl, KI, NaCl, $CaCl_2$ and multi-cation leaches (Table 18), it appears that changes in the ligand type can have a greater effect on the mobilization process than changes in the cation.

(4) Except for Fe and Co, the percent of the total concentration in the various shales of each element mobilized by the aqueous solutions compared favorably with the percentage of metal mobilized by the acid-reducing attack.

(5) Except for the amounts of Fe and Zn, the Purex attack (6 percent NaClO) on the shales produced results similar to the H_2O_2 attack. The Purex leached more Zn, and H_2O_2, more Fe.

(6) Experiments using selective chemical attacks on the shales showed significant contamination caused by metal carry-over if the attacks were successive on one shale sample. The results suggest that if successive attacks are used, the oxidizing attack should be done first to avoid significant carry-over.

MODEL

The results of the leaching experiments and the theoretical calculations support the hypothesis of a low-temperature origin for some strata-bound ores. Figure 19 is a flow chart for the origin of a low-temperature strata-bound ore deposit, such as the Mississippi Valley type. It is a synthesis of the works of Jackson and Beales (1969), Helgeson (1968), and Noble (1962). These works suggest that the origin of the deposits is related to a developing sedimentary basin.

As the sediments are deposited, trace elements are concentrated in the sediments from the overlying marine water. The major processes of concentration are scavenging by organics, scavenging by oxides, and adsorption onto clays. During the process of diagenesis the concentrations of the major species (Ca, Mg, Na, etc.) are being altered toward a Ca, Na-Cl brine-like composition. The trace elements are in part changing solid phases and in part becoming enriched in the interstitial water due to the reduction of the oxides and the formation of complexes. Further burial and diagenesis cause the interstitial water composition to be modified by membrane filtration (reverse osmosis) and/or reactions with evaporite minerals. This further modification increases the concentrates of Ca, Na and Cl in the interstitial water. As a result of the increased concentration, chloride complexing of trace elements and exchange

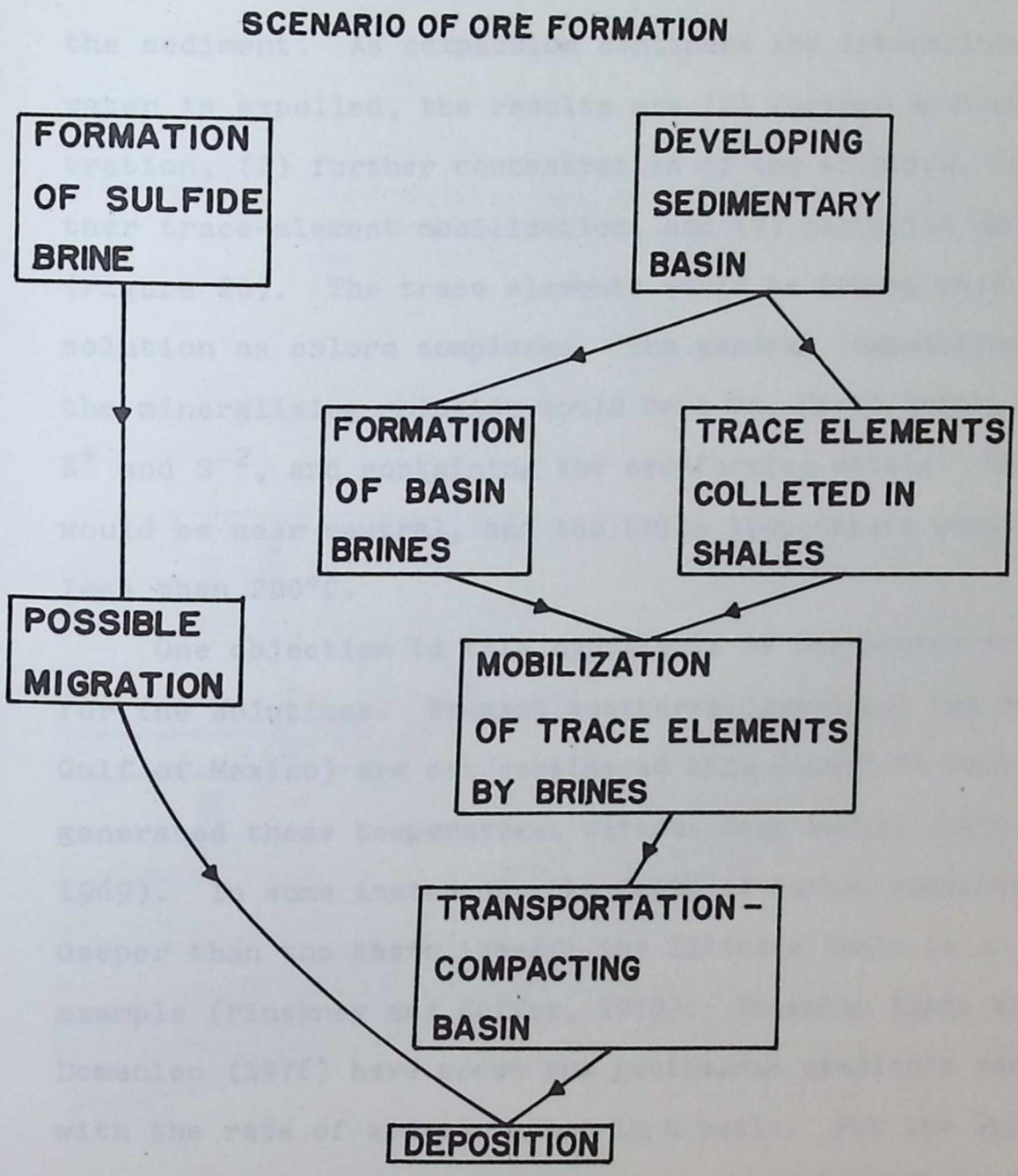


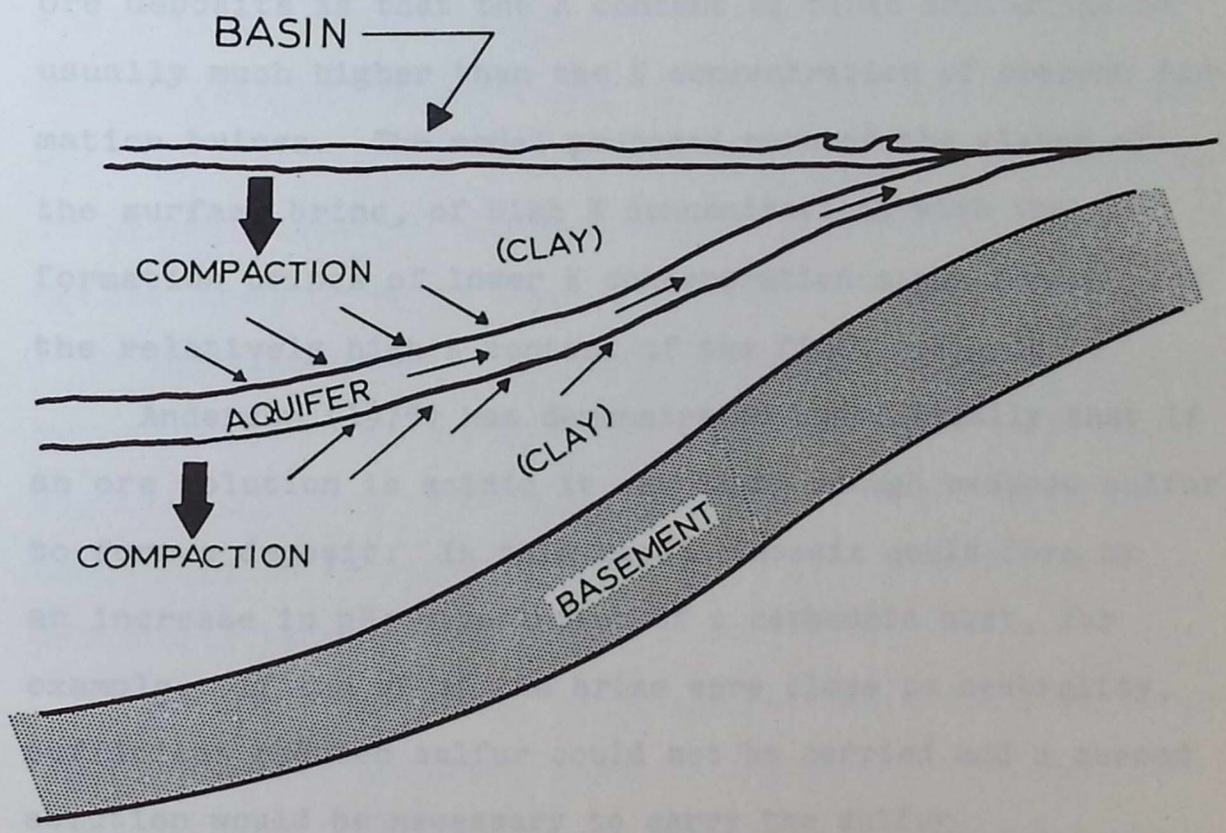
Figure 19. Flow chart for the origin of a low-temperature strata-bound ore deposit.

reactions become more important and tend to increase the amount of trace elements in solution by mobilizing them from the sediment. As compaction continues and interstitial water is expelled, the results are (1) further membrane filtration, (2) further concentration of the solution, (3) further trace-element mobilization, and (4) migration upward (Figure 20). The trace elements would be transported in solution as chloro complexes. The general composition of the mineralizing solution would be a Ca, Na-Cl brine, low in K^+ and S^{-2}, and containing the ore-forming metals. The pH would be near neutral, and the brine temperature would be less than 200°C.

One objection to this hypothesis is the source of heat for the solutions. Present geothermal gradients (as in the Gulf of Mexico) are not considered high enough to have generated these temperatures without deep burial (Heyl, 1969). In some instances, the depth of burial required is deeper than the basin itself; the Illinois basin is an example (Pinckney and Haffty, 1970). Recently Sharp and Domenico (1976) have shown how geothermal gradients can vary with the rate of sedimentation in a basin. For the Gulf of Mexico they demonstrated that the geothermal gradient during periods of low sediment influx to the basin could have been as high as 30°C/km. A gradient such as this could account for the temperatures of the ore-forming fluids.

While the deep mineralizing brine is forming, another brine could form closer to the surface which might be

Figure 20. Diagrammatic representation of formation of low-temperature ore deposits. (Modified from Noble, 1962.)



analogous to the sabkha-type brine. The composition of this brine would be higher in S^{2-} and K^{+} than the deeper brine. This brine would usually be contained in carbonate rocks and may or may not migrate. At some point in the development of the basin, the deeper brines moving upward due to compaction mix with the shallow brines, and the ore minerals are precipitated.

A problem in models for the formation of sedimentary ore deposits is that the K content of fluid inclusions is usually much higher than the K concentration of present formation brines. The model proposed here of the mixing of the surface brine, of high K concentration, with the formation brines of lower K concentration might account for the relatively high K content of the fluid inclusion.

Anderson (1975) has demonstrated theoretically that if an ore solution is acidic it can carry enough reduced sulfur to form a deposit. In this case a deposit could form by an increase in pH; dissolution of a carbonate host, for example. If the pH of the brine were close to neutrality, sufficient reduced sulfur could not be carried and a second solution would be necessary to carry the sulfur.

Both Anderson (1975) and Beales (1975) have demonstrated, by observing what minerals were at equilibrium with the ore solution during deposition, that the ore solution was probably close to a neutral pH during deposition of the metals. These investigations support an ore-forming model utilizing two solutions. The importance of this model is

that it is strictly a low-temperature (<200°C), low-pressure (<400 bars), non-igneous, sedimentary process for the origin of an economic ore deposit.

Billings et al. (1969) used the leaching results of Williams (1968) to demonstrate that shales could easily supply enough metal to form an ore deposit. The shales used in the leaching experiments were from outcrops (see Previous Leaching Studies) and might be expected to have had some of their metal content removed by weathering or made more mobile than in unaltered shale. Although sufficient metal was removed from the shales, the leaching solution used was 1N ammonium acetate and might not be directly comparable to metals expected to be removed by brine solutions.

The experimental results of this study demonstrate that brine solutions at temperatures below 100°C and at an ionic strength of 4 can remove metals from shales at concentrations similar to those found by Williams (1967) to form ore deposits (Table 24).

One could speculate, after incorporating the results of this study into the model shown in Figure 19, that the formation of a sedimentary ore deposit does not have to be a unique (catastrophic) event as, for example, was thought to be the case for magmatic related ores. Many magmatic ores are now seen to be closely related to the chemical processes involved in plate tectonics (Dunham, 1972; Tourtelot and Vine, 1976).

Table 24. Comparison of data from Williams (1967) with data from this study. The values are the amount of metal leached from the shales in ppm of rock.

Metal	Mean Leachate Williams (1967)	Heebner	Eudora	Heumader	Davis	Ninnescah
Zn	8.3	448.2	131.5	9.8	1.0	.3
Cu	2.1	7.4	.2	14.7	1.8	.4
Fe	61.0	<500.0	-----	----	----	----
Mn	11.0	----	----	----	----	----
Pb	NP*	59.9	54.0	0.1	1.1	.3
Co	NP	5.1	1.0	1.0	.7	.2
Ni	NP	100.0	21.1	2.1	----	----

*Not presented by Williams, 1967

Similarly, the processes of sedimentary ore formation may be related to the chemical and physical evolution of sedimentary basins. The occurrence of these ore deposits might be related to the availability of a "trapping" mechanism and the availability of metals in the basin. The "trapping mechanism" for the ore solutions would be chemical (Boyle, 1968) and would be related to the presence of the sulfide brine solution. If one were to accept this hypothesis, then to find these types of ores one should look for likely areas to have had a chemical "trap" for the metals.

The basins may not have had the metals to be mobilized. Therefore, although the processes suggested earlier were operating in a developing basin, the brines would not have been able to mobilize enough trace elements. In other words, if the metals had been available there might have been a deposit. The unavailability of the metals would be a function of (1) low metal concentrations in the shales, and (2) a brine composition that was unable to attack the fraction of the shale that contained the trace elements.

Another importance of this model is that it does not necessarily restrict the origin of low-temperature ores to Pb-Zn deposits. Rather, a similar process might account for certain other "sedimentary" deposits such as the Permian copper sulfides of the mid-continent (Long and Angino, 1976). The segregation of the various minerals in the ore deposits might be the result of the availability of metals in the source area. The mobilization process could also

account for the segregation of ore minerals. Results from this study demonstrated that mobilization is a selective process which could be caused by (1) the fraction of the shale that contains the metal, (2) the composition of the brine, and (3) the nature of the metal itself.

Finally, the selective nature of the depositional process could also account for the segregation of the minerals in low-temperature ore deposits. For example, the different affinities of metals such as Pb, Zn and Cu for sulfide are commonly considered to be the cause of mineral zonation in some ore deposits (Renfro, 1975). Results from this study demonstrated that the trace elements have different chemical speciation in aqueous solutions. Perhaps chemical speciation is also an important factor in the selective nature of ore mineral deposition. (See section on the application of brine-freshwater mixing models to the formation of sedimentary ore deposits.)

CONCLUSIONS

It was the purpose of this study to investigate the ability of shales to act as sources of metal in the formation of mineralizing solutions. Direct application can be made to a model for the formation of a low-temperature ore deposit (Mississippi Valley type) based on the physical and chemical evolution of a sedimentary basin. Both theoretical and experimental techniques were used. Theoretical calculations can also be used to study the types of chemical speciation to be expected for metals in various aqueous solutions. The results of this study are as follows:

(1) As might be predicted, elements with similar outer orbital structures, such as Cd and Zn, exhibit similar theoretical speciation in aqueous solutions.

(2) The amount of complexing in the same solutions follows the order Pb>Zn>Cu. As the ionic strength of the solution increases, the chemical speciation of Zn becomes more like Pb. In dilute solutions (<1I) Zn speciation is similar to Cu.

(3) The major controls on the amount and type of inorganic complexing that takes place in various natural water solutions are the absolute and relative concentrations of the competing inorganic ligands.

(4) Incorporating the equation $\log \gamma = -0.5I$ for the γ of neutral species (Reardon and Langmuir, 1976) drastically changed the results of the speciation calculations by stabilizing the neutral complexes.

(5) Increasing the temperature of a solution increases the amount of complexing.

(6) The type and amount of speciation change with different coordinating halogens. For lead the amount of complexing decreases in the order I>F>Cl>Br.

(7) Although shales normally contain enough trace elements to form an ore solution, whether or not shales can act as a source will depend on how easily the metals can be mobilized from the shale. This will be a function of the fraction with which the metal is associated. Different fractions will release different amounts of trace elements. Two fractions were studied, (1) the fraction that released metals when attacked by hydroxylamine hydrochloride-acetic acid (acid-reducing fraction), and (2) the fraction that released metals when attacked by an oxidizing solution (hydrogen peroxide or sodium hypochlorite). Within the conditions of this study the metals mobilized by the aqueous solutions came mostly from the acid-reducing fraction.

(8) An increase in either ionic strength or temperature increased the amount of mobilization, but the trends were not linear or simple. Increasing the ionic strength over 4I or the temperature over 90°C might further increase the amount of metals leached, but there is an indication that the mobilization efficiency will not continue to increase. Therefore, a brine of ionic strength 10 at 120°C might not be any more effective in leaching trace elements than a 5I brine at 90°C. In many of the experiments leaching

efficiency changed little between 50°C and 90°C at an ionic strength of 4. Trace element contributions from other phases at temperatures and ionic strengths greater than 90°C and 4I are unknown.

(9) Both extraction and exchange reactions as defined by this study contribute to the mobilizing process. In deep basin brines in which the chloro ligand is dominant, subtle differences in the concentrations of the major cations might be more important in determining the type of mobilization that takes place than changes in the ligand concentrations. In this study Ca^{2+} was found to be an efficient mobilizer of Zn and Pb, while K^{+} was found to be efficient in mobilizing Cu.

RECOMMENDATIONS FOR FUTURE WORK

The following is a list of potential future projects that could be used to test some of the observations of this research and add further insights into the problem of mobilization of trace elements from shales.

1. Two hypotheses should be statistically tested. They are that (a) Ca will mobilize more Pb and Zn from shales than K, and K will mobilize more Cu from shales than Ca, and (b) changing the starting pH's of the leaching solutions will change the amount of metal mobilized even though the pH's at the end of the leaches are the same for a given shale.

2. More work is needed on the selective chemical attacks on sediment. A good statistical test of the reproducibility of the different methods is needed. The attacks should be standardized so that comparisons can be made between papers. It is suggested that five fractions could be defined: (a) the loosely adsorbed water-soluble fraction, (b) the acid-oxidizing fraction, (c) the acid-reducing fraction, (d) the base-oxidizing fraction, and (e) the base-reducing fraction. Work could also be done using organic attacking solutions such as 2-propanol or benzene.

3. More attacks are needed using different brine compositions. In this study, the mobilizing brine was based on the chemical composition of fluid inclusions. The hypothesis proposed on this study for the origin of low-temperature ore

deposits suggests that the composition of fluid inclusions may not be the same as the composition of the brine that mobilized the metals. It would be interesting to study how other brine compositions would affect the mobilization process.

4. The model for the origin of ores proposed here could be studied by theoretically mixing brines (the "sabkha" type and the "deep-basin" type) and determining what type of ore deposits could be formed.

5. The theoretical models developed in this paper for Cu were based on Cu^{2+}. Since the reduced form of copper, Cu^{+}, can occur in shales and brines, it would be interesting to develop theoretical models for copper based on Cu^{+}.

6. The chemical behavior of Ag may parallel Cu during the process of ore formation. Studies such as the theoretical and experimental approaches of this research should be done on Ag and the results compared to those found for Cu.

7. It was suggested in this paper that the processes needed for the formation of sedimentary ore deposits are a natural consequence of a developing sedimentary basin. One reason for the lack of the widespread occurrence of such deposits might be that the basin shales did not have enough trace elements to be mobilized. It would be interesting to make a tally of all the occurrences of sedimentary-type ores, from subeconomic to major deposits. One might find

from this that "mineralization" occurrences are much more prevalent than presently thought.

8. The possible relationship between low-temperature ore deposits and the occurrence, formation and migration of petroleum was not discussed in this paper. The hypothesis for the origin of some low-temperature ore deposits suggested here closely parallels the hypothesis for the origin of petroleum. More work needs to be done to determine if there are common aspects of origin between ore deposits and petroleum.

REFERENCES

Anderson G. M. (1973) The hydrothermal transport and deposition of galena and sphalerite near 100°C. Econ. Geol. 68, 480-492.

Anderson G. M. (1975) Precipitation of Mississippi Valley-type ores. Econ. Geol. 70, 937-942.

Angino E. E. (1974) Mineralogy of suspended sediment and concentration of Fe, Mn, Ni, Zn, Cu and Pb in water and Fe, Mn and Pb in suspended load of selected Kansas streams. Water Resources Res. 10, 1187-1191.

Angino E. E. and Billings G. K. (1972) Atomic Absorption Spectometry in Geology, 1098 pp. Elsevier.

Angino E. E., Magnuson L. M. and Stewart G. F. (1972) Effects of urbanization on storm water runoff quality: a limited experiment, Naismith Ditch, Lawrence, Kansas. Water Resources Res. 8, 135-140.

Angino E. E. and Schneider H. I. (1975) Trace element, mineralogy and size distributions of suspended material samples from selected rivers in eastern Kansas. Kansas Water Resources Research Institute Contribution No. 169, 58 pp.

Austings G. S. and Leihmeyer R. K. (1976) The effect of heat treating sedimented mixed-layer illite-smectite as related to quantitative clay mineral determination. J. Sediment. Petrol. 46, 206-215.

Banat K., Forstner U. and Muller G. (1974) Experimental mobilization of metals from aquatic sediments by nitrilotriacetic acid. Chem. Geol. 14, 199-207.

Beales F. W. (1975) Precipitation mechanisms for Mississippi Valley-type ore deposits. Econ. Geol. 70, 943-948.

Beales R. G., Staples B. R. and Robinson R. A. (1970) Ionic hydration and single ion activities in unassociated chlorides at high ionic strengths. Analyt. Chem. 70, 943-948.

Belewzew Ja. N., Fomenko W. Ju., Kutscher W. N. and Kusenko S. W. (1972) Die mobilizierung von metallen aus sedimentaren und metamorphen gesteinen durch wabrige losungen. Geologitscheskij shurnal 32, 42-51.

Bender M. L. and Shultz C. (1969) The distribution of trace metals in cores from a transverse across the Indian Ocean. Geochim. Cosmochim. Acta 33, 292-297.

Benes P. and Steinnes E. (1975) Migration forms of trace elements in natural fresh waters and the effect of the water storage. Water Res. 9, 741-749.

Berner R. A. (1971) Principles of Chemical Sedimentology, 240 pp. McGraw-Hill.

Berry F. A. F. (1969) Relative factors influencing membrane filtration effects on geologic environments. Chem. Geol. 4, 295-301.

Billings G. K., Kesler S. E. and Jackson S. A. (1969) Relation of zinc-rich formation waters, northern Alberta, to the Pine Point ore deposit. Econ. Geol. 64, 385-391.

Bischoff J. L. and Ku T. L. (1970) Pore fluids of recent marine sediments. 1. Oxidizing sediments of 20°N, continental rise to mid-Atlantic range. J. Sediment. Petrol. 40, 960-972.

Bischoff J. L. and Ku T. L. (1971) Pore fluids of recent marine sediments. 2. Anoxic sediments of 35°S to 45°N, Gibralter to mid-Atlantic ridge. J. Sediment. Petrol. 41, 1008-1017.

Bostrom K. (1972) Geochemistry of sediments: modern. In Encyclopedia of Geochemistry and Environmental Sciences (editor R. Fairbridge), IV-A, 428-434.

Boyle R. W. (1968) The source metals and gangue elements in epigenetic deposits. Mineral Deposita 3, 174-177.

Boyle R. W. and Lynch J. J. (1968) Speculations on the source of zinc, cadmium, lead, copper and sulfur in Mississippi Valley and similar types of lead-zinc deposits. Scientific Communications, Econ. Geol. 63, 421-422.

Brooks R. R., Kaplan I. R. and Peterson M. N. A. (1969) Trace element composition of Red Sea geothermal brine and interstitial water. In Hot Brines and Recent Heavy Metal Deposits in the Red Sea (editors D. A. Ross and E. T. Degens), 600 pp. Springer-Verlag.

Brooks R. R., Presley B. J. and Kaplan I. R. (1967) APDC-MIBK extraction system for the determination of trace elements in saline waters by atomic-absorption spectrophotometry. Talanta 14, 809-816.

Brooks R. R., Presley B. J. and Kaplan I. R. (1968) Trace elements in the interstitial waters of marine sediments. Geochim. Cosmochim. Acta 32, 397-414.

Brown A. C. (1973) An epigenetic origin for stratiform Cd-Pb-Zn sulfides in the lower Nonesuch shale, White Pine, Michigan. Econ. Geol. 69, 271-274.

Burst J. F. Jr. (1966) Diagenesis of Gulf Coast clayey sediments and its possible relation to petroleum migration. Bull. Am. Assoc. Petrol. Geol. 50, 607.

Bush P. R. (1970) Chloride-rich brines from sabkha sediments and their possible role in ore formation. Trans. Institute of Mining and Metallurgy, Sec. B, Applied Earth Science 79, B137-B144.

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

Carpenter A. B., Trout M. L. and Dickett E. E. (1974) Preliminary report on the origin and chemical evolution of lead- and zinc-rich oil field brines in central Mississippi. Econ. Geol. 69, 1191-1206.

Carroll D. (1959) Ion exchange in clays and other minerals. Bull. Geol. Soc. Amer. 70, 749-780.

Carroll D. (1970) Clay minerals: a guide to their x-ray identification. Geol. Soc. Amer. Special Paper 126.

Chao T. T. and Anderson B. J. (1974) The scavenging of silver by manganese and iron oxides in stream sediments collected from two drainage areas of Colorado. Chem. Geol. 14, 159-166.

Chapman H. D. (1965a) Cation exchange capacity. In Methods of Soil Analysis, Part 2 (editor C. A. Black), 891-901.

Chapman H. D. (1965b) Total exchange bases. In Methods of Soil Analysis, Part 2 (editor C. A. Black), 902-904.

Chester R. and Hughes M. J. (1966) The distribution of manganese, iron and nickel in a north Pacific deep-sea clay core. Deep-Sea Res. 13, 627-634.

Chester R. and Hughes M. J. (1967) A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. Chem. Geol. 2, 249-262.

Chester R. and Hughes M. J. (1969) The trace element geochemistry of a north Pacific pelagic clay core. Deep-Sea Res. 16, 639-654.

Chilingarian G. V. and Rieke H. H. III (1969) Some chemical alterations of subsurface waters during diagenesis. Chem. Geol. 4, 235-252.

Chow T. J., Broland K. W., Bertein K., Soutar A., Koide M. and Goldberg E. D. (1973) Lead pollution in southern California coastal sediments. Science 181, 551-552.

Cody R. D. (1971) Adsorption and the reliability of trace elements as environmental indicators for shales. J. Sediment. Petrol. 41, 461-471.

Collins A. G. (1975) Geochemistry of oil field waters. Developments in Petrol. Sci. 1, 496 pp.

Connor J. J. and Shacklette H. T. (1975) Background geochemistry of some rocks, soils, plants and vegetables in the coterminous United States. U.S. Geol. Surv. Prof. Paper 574-F.

Cronan D. S. and Garrett D. E. (1973) Distribution of elements in metalliferous Pacific sediments collected during the deep sea drilling project. Nature Phys. Sci. 242, 88-89.

Davidson C. F. (1965) A possible mode of origin of strata-bound copper ores. Econ. Geol. 60, 942-954.

Davidson D. F. and Lakin H. W. (1961) Metal content of some black shales of the western United States. U.S. Geol. Surv. Short Papers in the Geologic and Hydrologic Sciences C-329, 147-299.

Davies C. W. (1962) Ion Association, 190 pp. Butterworths.

Degens E. T. and Chilingar G. V. (1967) Diagenesis of subsurface waters. In Developments in Sedimentology (editors G. Larsen and G. V. Chilingar), Vol. 8.

DeGroot A. J. and Allersma E. (1973) Field observations on the transport of heavy metals in sediments. Conf. on Heavy Metals in the Aquatic Environment, Nashville (Tenn.), Dec. 4-7, 1973.

De Sitter L. U. (1947) Diagenesis of oil-field brines. Bull. Am. Assoc. Petrol. Geol. 31, 2030-2040.

Doe B. R. and Delevaux M. H. (1972) Source of lead in south-east Missouri galena ores. Econ. Geol. 67, 409-425.

Doe B. R., Hedge C. E. and White D. E. (1966) Preliminary investigation of the source of lead and strontium in deep geothermal brines underlying the Salton Sea geothermal area. Econ. Geol. 61, 462-483.

Duce R. A., Quinn J. G., Olney C. E., Piotrowicz S. R., Ray B. J. and Wade T. L. (1972) Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, R. I. Science 176, 161-163.

Duchart D., Calvert S. E. and Price N. B. (1973) Distribution of trace metals in the pore waters of shallow water marine sediments. Limnol. Oceanogr. 18, 605-610.

Dunham K. C. (1970) Mineralization by deep formation waters: a review. Trans. Institute of Mining and Metallurgy, Sec. B, Applied Earth Science 79, B127-B136.

Dunham K. C. (1972) Basic and applied geochemists in search of ore. Trans. Institute of Mining and Metallurgy, Sec. B, Applied Earth Science 81, B13-B18.

Elder John F. (1975) Complexation side reactions involving trace metals in natural water systems. Limnol. Oceanogr. 20, 96-102.

Ellis A. J. (1968) Natural hydrothermal systems and experimental hot-water/rock interaction: reactions with NaCl solutions and trace metal extraction. Geochim. Cosmochim. Acta 32, 1356-1363.

Engelhardt W. and Gaida K. H. (1963) Concentration changes of pore solutions during the compaction of clay sediments. J. Sediment. Petrol. 33, 919-930.

Ernst R., Allen H. E. and Mancy K. H. (1975) Characterization of trace metal species and measurement of trace metal stability constants by electrochemical techniques. Water Res. 9, 969-979.

Ferguson J. and Bubela B (1974) The concentration of Cu (II), Pb (II), and Zn (II) from aqueous solutions by particulate algal matter. Chem. Geol. 13, 163-186.

Florence T. M. and Batley G. E. (1976) Trace metal species in sea water. I.Removal of trace metals from sea water by a chelating resin. Talanta 23, 179-186.

Gad M. A. and LeRiche H. H. (1966) A method for separating the detrital and non-detrital fractions of trace elements in reduced sediments. Geochim. Cosmochim. Acta 30, 841-846.

Gardiner J. (1974) The chemistry of cadmium in natural water. I. A study of cadmium complex formation using the cadmium specific-ion electrode. Water Res. 8, 23-30.

Garrels R. M. and Christ C. L. (1965) Solutions Minerals and Equilibria, 450 pp. Harper and Row.

Garrels R. M. and MacKenzie F. T. (1971) Evolution of Sedimentary Rocks, 397 pp. Norton.

Garrels R. M. and Thompson M. E. (1962) A chemical model for seawater at 25°C and one atmosphere total pressure. Amer. J. Sci. 260, 57-66.

Gibbs R. J. (1973) Mechanisms of trace metal transport in rivers. Science 18, 71-73.

Goldberg E. D. and Arrhenius G. O. S. (1958) Chemistry of Pacific pelagic sediments. Geochim. Cosmochim. Acta 13, 153-212.

Hathaway L. R., Galle O. K. and Evans T. (1972) Brine leaching of the Heebner shale (Upper Pennsylvanian) of Kansas. Kansas Geol. Surv. Bull. 204, Part 1, 18.

Helgeson H. E. (1969) Thermodynamics of hydrothermal systems at elevated temperatures and pressures. Amer. J. Sci. 266, 729-804.

Heyl A. V. (1969) Some aspects of genesis of zinc-lead-barite-fluorite deposits in the Mississippi Valley, U.S.A. Trans. Institute of Mining and Metallurgy, Sec. B, Applied Earth Science 78, B148-B160.

Hirst D. M. (1971) Considerations of a sedimentary source for the heavy metal content of ore-forming fluids. Trans. Institute of Mining and Metallurgy, Sec. B, Applied Earth Science 80, B1-B3.

Hirst D. M. and Nicholls G. D. (1958) Techniques in sedimentary geochemistry: separation of the detrital and non-detrital fractions of limestones. J. Sediment. Petrol. 28, 468-481.

Hitchon B., Billings G. K. and Klovan J. E. (1971) Geochemistry and origin of formation waters in the western Canada sedimentary basin--III. Factors controlling chemical composition. Geochim. Cosmochim Acta 35, 567-598.

Hitchon B. and Horn M. K. (1974) Petroleum indicators in formation waters from Alberta, Canada. Bull. Amer. Assoc. Petrol. Geol. 58, 464-473.

Hitchon B. and Krouse H. R. (1972) Hydrogeochemistry of the surface waters of the MacKenzie River drainage, Canada --III. Stable isotopes of oxygen, carbon and sulphur. Geochim. Cosmochim. Acta 36, 1337-1357.

Hoagland A. D. (1971) Appalachian strata-bound deposits: their essential features, genesis and the exploration problem. Econ. Geol. 66, 805-810.

Holland H. D. (1972) Granites, solutions, and base metal deposits. Econ. Geol. 67, 281-301.

Horowitz A. (1974) The geochemistry of sediments from the northern Reykjanes Ridge and the Iceland-Faroes Ridge. Marine Geol. 17, 103-122.

Horowitz A. and Cronan D. S. (1976) The geochemistry of basal sediments from the North Atlantic Ocean. Marine Geol. 20, 205-228.

Hower J., Eslinger E. V., Hower M. E. and Perry E. A. (1976) Mechanism of burial metamorphism of argillaceous sediment: mineralogical and chemical evidence. Bull. Geol. Soc. Amer. 87, 725-737.

Huheey J. E. (1972) Inorganic Chemistry: Principles of Structure and Reactivity, 737 pp. Harper and Row.

Jackson M. L. (1956) Soil Chemical Analysis: Advanced Course. Published by author, 31-251.

Jackson S. A. and Beales F. W. (1967) An aspect of sedimentary basin evolution: the concentration of Mississippi Valley-type ores during late stages of diagenesis. Bull. Can. Petrol. Geol. 15, 383-433.

Jenne E. A. (1968) Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water, the significant role of hydrous Mn and Fe oxides. In Trace Inorganics in Water, Advances in Chemistry Series (editor R. E. Gould) 73, 337-387.

Jones A. S. G. (1973) Letter section: The concentration of copper, lead, zinc and cadmium in shallow marine sediments, Cardigan Bay (Wales). Marine Geol. 14, M1-M9.

Jones P. H. and Wallace R. H. Jr. (1974) Hydrogeologic aspects of structural deformation in the northern Gulf of Mexico basin. J. Res. U. S. Geol. Surv. 2, 511-517.

Kennedy V. C. (1965) Mineralogy and cation-exchange capacity of sediments from selected streams. U. S. Geol. Surv. Prof. Paper 433-D.

Kharaka Y. K. and Barnes I. (1973) SOLMNEQ: Solution-mineral equilibrium computations. NTIS/PB/215 899.

Kharaka Y. K. and Berry F. A. F. (1973) Simultaneous flow of water and solutes through geological membranes--I. Experimental investigation. Geochim. Cosmochim. Acta 37, 2577-2603.

Kharaka Y. K. and Berry F. A. F. (1974) The influence of geological membranes on the geochemistry of subsurface waters from Miocene sediments at Kettleman North Dome in California. Water Resources Res. 10, 313-327.

Kharaka Y. K., Berry F. A. F. and Friedman I. (1973) Isotopic composition of oil-field brines from Kettleman North Dome, California, and their geologic implications. Geochim. Cosmochim. Acta 37, 1899-1908.

Kielland J. (1937) Individual activity coefficients of ions in aqueous solutions. J. Amer. Chem. Soc. 59, 1675.

Kodama H. and Schnitzer M. (1974) Further investigations on fulvic acid-Cu^{2+}-montmorillonite interactions. Clay Clay Minerals 22, 107-110.

Korte N. E., Skopp J., Nibebla E. E. and Fuller W. H. (1975) A base-line study on trace metal elution from diverse soil types. Water, Air and Soil Pollution 5, 149-156.

Kramer J. R. (1969) Subsurface brines and mineral equilibria. Chem. Geol. 4, 37-50.

Krauskopf K. B. (1976) Factors controlling the concentrations of thirteen rare metals in sea-water. Geochim. Cosmochim. Acta 9, 1-32.

Krishnaswami S. (1976) Authigenic transition elements in Pacific pelagic clays. Geochim. Cosmochim. Acta 40, 425-434.

Kronfeld J. and Navrot J. (1975) Aspects of trace metal contamination in the coastal rivers of Israel. Water, Air and Soil Pollution 4, 127-134.

Krumbein W. C. and Garrels R. M. (1952) Origin and classification of chemical sediments in terms of pH and oxidation reduction potentials. J. Geol. 60, 1-33.

Kunkel R. and Manahan S. E. (1973) Atomic absorption analysis of strong heavy metal chelating agents in water and waste water. Analyt. Chem. 45, 1465-1468.

Laganathan P. and Burav R. G. (1973) Sorption of heavy metal ions by hydrous manganese oxide. Geochim. Cosmochim. Acta 37, 1277-1293.

Langmuir D. (1968) Stability of calcite based on aqueous solubility measurements. Geochim. Cosmochim. Acta 32, 835-851.

Lavkulich L. M. and Wiens J. H. (1970) Comparison of organic matter destruction by hydrogen peroxide and sodium hypochlorite and its effects on selected mineral constituents. Soil Sci. Soc. Amer. Proc. 34, 755-758.

Leland H. V., Shukla S. S. and Shimp N. F. (1973) Factors affecting the distribution of lead and other trace elements in sediments of southern Lake Michigan. In Trace Metals and Metal-Organic Interaction in Natural Waters (editor P. C. Singer), Ann Arbor Science.

Livingstone D. (1963) Chemical composition of rivers and lakes. Data of Geochem., U. S. Geol. Surv. Prof. Paper 440-G.

Long D. T. and Angino E. E. (1976) Occurrence of copper sulfides in the (Permian Age) Milan dolomite, south-central Kansas. Econ. Geol. 71, 656-661.

Manahan S. E. (1975) The environmental chemistry of humic materials as related to trace substances: results of a computerized WBSIC bibliographic literature search. Ninth Annual Conf. on Trace Substances in Environmental Health, University of Missouri, Columbia.

Mangel M. S. (1971) Letter section: A treatment of complex ions in sea water. Marine Geol. 11, M24-M26.

Manheim F. T. (1974) Comparative studies on extraction of sediment from interstitial waters: discussion and comment on the current state of interstitial water studies. Clay Clay Minerals 22, 337-343.

Maugh T. H. II (1973) Trace elements: a growing appreciation of their effects on man. Research News. Science 181, 253-254.

McLerran C. J. and Holmes C. W. (1974) Deposition of zinc and cadmium by marine bacteria in estuarine sediments. Limnol. Oceanogr. 19, 998-1001.

Mesmer R. E. and Baes C. F. Jr. (1975) The hydrolysis of cations. ORNL-NSF-EATC-3, Part III. Oak Ridge National Laboratories.

Morel F. and Morgan J. (1972) A numerical method for computing equilibria in aqueous chemical systems. Environmental Sci. and Tech. 6, 58-67.

Nissenbaum A. (1972) Distribution of several metals in chemical fractions of sediment core from the Sea of Okhotsk. Israel J. Earth Sci. 21, 143-154.

Nissenbaum A. (1974) Trace elements in Dead Sea sediments. Israel J. Earth Sci. 23, 111-116.

Nissenbaum A., Baedecker M. J. and Kaplan I. R. (1972) Organic geochemistry of Dead Sea sediments. Geochim. Cosmochim. Acta 36, 702-727.

Nissenbaum A., Presley B. J. and Kaplan I. R. (1972) Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia--I. Chemical and isotopic changes in major components of interstitial water. Geochim. Cosmochim. Acta 36, 1007-1027.

Noble E. A. (1963) Formation of ore deposits by water of compaction. Econ. Geol. 58, 1145-1156.

Nriagu J. O. (1971) Expressions for calculating the solubilities of metal sulfides in hydrothermal solutions. Can. J. Earth Sci. 8, 813-819.

Nriagu J. O. and Anderson G. M. (1970) Calculated solubilities of some base-metal sulphides in brine solutions. Trans. Institute of Mining and Metallurgy, Sec. B, Applied Earth Science 29, 208-212.

Nriagu J. O. and Anderson G. M. (1971) Stability of lead (II) chloride complexes at elevated temperatures. Chem. Geol. 7, 171-183.

O'Connor T. P. and Kester D. R. (1975) Adsorption of copper and cobalt from fresh and marine systems. Geochim. Cosmochim. Acta 39, 1531-1544.

Ostrom M. E. (1957) Trace elements in Illinois Pennsylvanian limestones. Ill. State Geol. Surv. Circ. 243.

Payne K. and Pickering W. F. (1975) Influence of clay-solute interactions on aqueous copper ion levels. Water, Air and Soil Pollution 5, 63-69.

Pearson R. G. (1963) Hard and soft acids and bases. J. Amer. Chem. Soc. 85, 3533-3539.

Perry E. A., Gieskes J. M. and Lawrence J. R. (1976) Mg, Ca, O^{18}/O^{16} exchange in the sediment-pore water system, hole 149, DSDP. Geochim. Cosmochim. Acta 40, 413-423.

Perry E. A. and Hower J. (1970) Burial diagenesis in Gulf Coast pelagic sediments. Clay Clay Minerals 18, 165-177.

Picard G. L. and Felback G. T. Jr. (1976) The complexation of iron by marine humic acid. Geochim. Cosmochim. Acta 40, 1347-1350.

Pinckney D. M. and Hafpty J. (1970) Content of zinc and copper in some fluid inclusions from the Cave-in-Rock District, southern Illinois. Econ. Geol. 65, 451-458.

Pita F. W. and Hyne N. J. (1975) The depositional environment of zinc, lead and cadmium in reservoir sediments. Water Res. 9, 701-706.

Polzer W. L. and Roberson C. E. (1967) Calculation of ion activity products for a brine from the Bonneville Salt Flats, Utah. U. S. Geol. Surv. Prof. Paper 575-C, C116-C119.

Powers M. C. (1967) Fluid release mechanisms in compacting marine mudrocks and their importance in oil exploration. Bull. Amer. Assoc. Petrol. Geol. 51, 1240-1254.

Presley B. J., Kolodny Y., Nissenbaum A. and Kaplan I. R. (1972) Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia--II. Trace element distribution in interstitial water and sediment. Geochim. Cosmochim. Acta 36, 1073-1090.

Price L. C. (1976) Aqueous solubility of petroleum as applied to its origin and primary migration. Bull. Amer. Assoc. Petrol. Geol. 60, 213-244.

Proctor R. M. (1962) Semi-quantitative clay mineralogy in subsurface studies. J. Alberta Soc. Petrol. Geol. 10, 257-270.

Rashid M. A. (1974) Adsorption of metals on sedimentary and peat humic acids. Chem. Geol. 13, 115-123.

Reardon E. J. and Langmuir D. (1974) Thermodynamic properties of the ion pairs, $MgCO_3$ and $CaCO_3$ from 10 to 50°C. Amer. J. Sci. 274, 599-612.

Reardon E. J. and Langmuir D. (1976) Activity coefficients of $MgCO_3^\circ$ and $CaSO_4^\circ$ ion pairs as a function of ionic strength. Geochim. Cosmochim. Acta 39, 549-554.

Renfro A. R. (1974) Genesis of evaporite-associated stratiform metalliferous deposits-a sabkha process. Econ. Geol. 69, 33-45.

Rieke H. H. and Chilingarian G. V. (1974) Compaction of argillaceous sediments. Developments in Sedimentology Series, No. 16.

Riffald R. and Levi-Minzi R. (1975) Adsorption and desorption of Cd on humic acid fraction of soils. Water, Air and Soil Pollution 5, 179-184.

Rittenhouse G. (1967) Bromine in oil-field waters and its use in determining possibilities of origin of these waters. Bull. Amer. Assoc. Petrol. Geol. 51, 2430-2440.

Rittenhouse G. (1969) Minor elements in oil-field waters. Chem. Geol. 4, 367-371.

Roberson H. E. (1974) Early diagenesis: expansible soil clay-sea water reactions. J. Sediment. Petrol. 44, 441-449.

Robinson R. A. and Stokes R. H. (1959) Electrolyte Solutions, 599 pp. Butterworths.

Roedder E. (1967) Environment of deposition of stratiform (Mississippi Valley-Type) ore deposits, from studies of fluid inclusions. Econ. Geol. Mon. 3, 349-362.

Roedder E. (1968) Temperature, salinity and origin of the ore-forming fluids at Pine Point, Northwest Territories, Canada, from fluid inclusion studies. Econ. Geol. 63, 439-450.

Roedder E. (1971) Fluid-inclusion evidence on the environment of formation of mineral deposits of the southern Appalachian Valley. Econ. Geol. 66, 777-791.

Roedder E. (1972) Composition of fluid inclusions. U. S. Geol. Surv. Prof. Paper 440-JJ.

Ruch R. R., Gluskoter H. J. and Shimp N. F. (1974) Occurrence and distribution of potentially volatile trace elements in coal: a final report. Ill. State Geol. Surv. Environ. Geol. Notes, No. 72.

Sawkins F. J. (1972) Sulfide ore deposits in relation to plate tectonics. J. Geol. 80, 377-397.

Sayles F. L., Wilson T. R. S., Hume D. N. and Mangelsdorf P. C. Jr. (1973) In situ sampler for marine sedimentary pore waters: evidence for potassium depletion and calcium enrichment. Science 181, 154-156.

Schmidt G. W. (1971) Interstitial water composition and geochemistry of deep Gulf Coast shales and sands, 121 pp. M. S. Thesis, University of Tulsa.

Schnitzer M. and Skinner S. I. M. (1967) Organic-metallic interactions in soils. 7. Stability constants of Pb^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Ca^{2+} and Mg^{2+}-fulvic acid complexes. Soil Sci. 103, 247-257.

Sharp J. M. Jr. and Domenico P. A. (1976) Energy transport to thick sequences of compacting sediment. Bull. Geol. Soc. Amer. 87, 390-400.

Shulyak V. E. and Sevrikova S. D. (1974) Change in chemical composition of chloride waters as a result of the reaction with a pyrite-containing rock. Izv. Vyssh. Ucheb. Zaved. Geol. Razved 17, 95-98 (in Russian).

Sillen L. G. and Martell A. E. (1964) Stability constants of metal-ion complexes. I. Inorganic ligands. Chem. Soc. London Spec. Pub. 17, 764 pp.

Sillen L. G. and Martell A. E. (1971) Supplement No. 1 to Stability Constants of Metal Ion Complexes. Chem. Soc. London Spec. Pub. 25.

Slowey F. J. and Hood D. W. (1971) Copper, manganese and zinc concentrations in Gulf of Mexico waters. Geochim. Cosmochim. Acta 35, 121-128.

Smith G. E. (1974) Deposition systems, San Angelo formation (Permian), north Texas-faces control of red-bed copper mineralization. Tex. Bur. Econ. Geol. Report of Invest. 80, 73 pp.

Snyder F. G. (1967) Criteria for the origin of stratiform ore bodies with application to southwest Missouri. Econ. Geol. Mon. 3.

Sokal R. and Rohlf F. J. (1969) Biometry, 776 pp. W. H. Freeman.

Spears D. A. (1974) Relationship between water-soluble cations and paleosalinity. Geochim. Cosmochim. Acta 38, 567-575.

Spencer D. W., Brewer P. G. and Sachs P. L. (1972) Aspects of the distribution of trace element composition of suspended matter in the Black Sea. Geochim. Cosmochim. Acta 36, 71-86.

Sprague S. and Salvin W. (1964) Determination of very small amounts of copper and lead in KCl by organic extraction and atomic absorption spectrophotometry. Atomic Absorption Newsletter 20, 11-15.

Stanton R. L. (1972) Ore Petrology, 713 pp. McGraw-Hill.

Steele K. F. and Wagner G. A. (1975) Trace metal relationships in bottom sediments of a fresh water stream--the Buffalo River, Arkansas. J. Sediment. Petrol. 45, 310-319.

Stiff M. J. (1971) Copper/bicarbonate equilibria in solutions of bicarbonate ion at concentrations similar to those found in natural water. Water Res. 5, 171-176.

Stumm W. and Morgan J. J. (1970) Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters, 583 pp. Wiley-Interscience.

Temple K. L. and LeRoux N. W. (1964) Syngenesis of sulfide ores: description of adsorbed metal ions and their precipitation as sulfides. Econ. Geol. 59, 647-655.

Tiller K. G. and Hodgson J. F. (1960) The specific sorption of cobalt and zinc by layer silicates. Proc. Ninth National Conf. Clays Clay Minerals, pp. 393-403.

Tooms J. S. (1970) Review of knowledge of metalliferous brines and related deposits. Trans. Institute of Mining and Metallurgy, Sec. B, Applied Earth Science 79, B116-B126.

Tourtelot E. B. and Vine J. D. (1976) Copper deposits in sedimentary and volcanogenic rocks. U. S. Geol. Surv. Prof. Paper 907-C.

Truesdell A. H. and Jones B. F. (1969) Ion association in natural brines. Chem. Geol. 4, 51-62.

Turekian K. K. and Wedepohl K. H. (1961) Distribution of the elements in some major units of the earth's crust. Bull. Geol. Soc. Amer. 72, 175-192.

Van Everdingen R. O. (1968) Mobility of main ion species in reverse osmosis and the modification of subsurface brines. Can. J. Earth Sci. 5, 1253-1260.

Van Everdingen R. O. (1968) Studies of formation waters in western Canada: geochemistry and hydrodynamics. Can. J. Earth Sci. 5, 523.

Vine J. D. and Tourtelot E. B. (1970) Geochemistry of black shale deposits-a summary report. Econ. Geol. 65, 253-272.

Vinogradov A. P. (1953) The elementary chemical composition of marine organisms. Sears Foundation for Marine Research, Yale University, New Haven.

Walker A. C., Bray V. B. and Johnston J. (1927) Equilibrium in solutions of alkali carbonates. J. Amer. Chem. Soc. 49, 1235-1256.

Weiler R. R. (1973) The interstitial water composition in the sediments of the Great Lakes. 1. Western Lake Ontario. Limnol. Oceanogr. 18, 918-931.

Weiss A. and Amstutz G. C. (1966) Ion-exchange reactions on clay minerals and cation selective membrane properties as possible mechanisms of economic metal concentration. Mineralium Deposita 1, 60-66.

White D. E. (1965) Saline waters of sedimentary rocks. In Fluids in Subsurface Environments--A Symposium. Amer. Assoc. Petrol. Geol. Mem. 4.

White D. E. (1968) Environments of generation of some base-metal ore deposits. Econ. Geol. 63, 301-334.

White D. E. (1974) Diverse origins of hydrothermal ore fluids. Econ. Geol. 69, 954-973.

White D. E., Hem J. D. and Waring G. A. (1963) Chemical composition of subsurface waters. In Data of Geochemistry, 67 pp. U. S. Geol. Surv. Prof. Paper 440-F.

Whitfield M. (1972) The electrochemical characteristics of natural redox cells. Limnol. Oceanogr. 17, 383-393.

Whitfield M. (1974) The ion-association model and the buffer capacity of the carbon dioxide system in sea-water at 25°C and 1 atmosphere total pressure. Limnol. Oceanogr. 19, 235-248.

Whitfield M. (1975) The extension of chemical models for seawater to include trace components at 25°C and 1 atmosphere pressure. Geochim. Cosmochim. Acta 39, 1545-1557.

Williams H. H. (1967) Some aspects of ion exchange in shales, 182 pp. M. S. Thesis, University of Calgary.

Wood J. R. (1975) Thermodynamics of brine-salt equilibria--1. The systems NaCl-KCl-$MgCl_2$-$CaCl_2H_2O$ and NaCl-$MgSO_4$-H_2O at 25°C. Geochim. Cosmochim. Acta 39, 1147-1163.

Wood W. W. (1973) Rapid reaction rates between water and a calcareous clay as observed by specific-ion electrodes. J. Res. U. S. Geol. Surv. 1, 237-241.

Zeller D. E. (1968) The stratigraphic succession in Kansas. Bull. Kans. State Geol. Surv. 189, 78 pp.

Zirino A. and Yamamoto S. (1972) A pH-dependent model for the chemical speciation of copper, zinc, cadmium and lead in sea water. Limnol. Oceanogr. 17, 661-671.

APPENDIX A. Stability constants for trace element and major element species used in the calculations. Values are the logarithms of the association constants.

A - 1. Values of trace element complexes for calculations at 25°C.

METAL	Cl^-	OH^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}
Pb: $\log\beta_{11}$	1.6 (2)	6.2 (6)	2.9 (1)	6.3 (3)	2.7 (6)
$\log\beta_{12}$	1.78 (2)	10.9 (6)		10.64(3)	3.47(6)
$\log\beta_{13}$	1.68 (2)	13.9 (6)			
$\log\beta_{14}$	1.38 (2)	16.3 (6)			
Cu: $\log\beta_{11}$	0.02(2)	6.37(6)	2.7 (1)	5.97(3)	2.25(6)
$\log\beta_{12}$	-0.71(2)	14.3 (6)		9.83(4)	
$\log\beta_{13}$	-2.3 (2)	15.0 (6)			
$\log\beta_{14}$	-4.6 (6)	16.0 (6)			
Cd: $\log\beta_{11}$	2.0 (6)	5.0 (6)	2.1 (1)	4.1 (5)	2.3 (6)
$\log\beta_{12}$	2.7 (6)	10.6 (6)			
$\log\beta_{13}$	2.1 (6)	10.0 (6)			
$\log\beta_{14}$		10.0 (6)			
Zn: $\log\beta_{11}$	0.43(2)	4.4 (6)	2.1 (1)	5.3 (1)	2.3 (6)
$\log\beta_{12}$	0.61(2)	12.89(6)			
$\log\beta_{13}$	0.53(2)	14.0 (6)			
$\log\beta_{14}$	0.2 (2)	15.0 (6)			

(1) Zirino and Yamamoto (1972)

(2) Helgeson (1969)

(3) Ernest *et al.* (1975)

(4) Mesmer and Baes (1975)

(5) Gardiner (1974)

(6) Sillen and Martel (1964)

A - 2. Values of trace element complexes for calculations at 50°C and 90°C. Data taken from Kharaka and Barnes, 1973 and Kharaka, personal communication, 1975.

SPECIES	CONSTANT 50°C	90°C
$PbCl^{+}$	1.63	1.60
$PbCl_2^{o}$	1.85	1.78
$PbCl_3^{-}$	1.81	1.68
$PbCl_4^{2-}$	1.59	1.38
$CuCl^{+}$	0.53	1.27
$CuCl_2^{o}$	-0.08	0.89
$CuCl_3^{-}$	-1.49	-0.26
$CuCl_4^{2-}$	-3.56	-2.00
$ZnCl^{+}$	0.90	1.64
$ZnCl_2^{o}$	1.12	1.94
$ZnCl_3^{-}$	1.14	2.02
$ZnCl_4^{2-}$	0.89	1.90

A - 3. Values of major element complexes for calculations at 25°C, 50°C and 90°C. Data taken from Kharaka and Barnes, 1973 and Kharaka, personal communication, 1975.

	TEMPERATURE		
SPECIES	25°C	50°C	90°C
$CaCO_3^o$	3.2	3.40	3.80
$CaHCO_3^+$	1.26	1.64	2.27
$CaSO_4^o$	2.30	2.40	2.63
$CaOH^+$	1.23	1.35	1.57
$MgCO_3^o$	3.40	3.42	3.51
$MgHCO_3^+$	0.90	1.52	2.52
$MgSO_4^o$	2.25	2.60	3.08
$MgOH^+$	2.60	2.70	2.99
$NaCO_3^-$	1.27m	1.81	2.68
$NaHCO_3^o$	-0.25	-0.25	-0.25
$NaSO_4^-$	1.06	1.35	1.82
$NaOH^o$	-0.70	-0.70	-0.70
KSO_4^-	0.83	1.00	1.25

A - 4. Values of lead complexes with the halogen ligands (F^-, Cl^-, Br^-, and I^-). Data taken from Sillen and Martel, 1964.

Complex with lead	F^-	Cl^-	Br^-	I^-
β_1	<0.80	1.60	2.23	2.00
β_2	2.27	1.78	-1.46	3.15
β_3	3.42	1.68	-0.94	3.92
β_4	3.10	1.38	0.267	4.47