GEOCHEMISTRY OF GROUND WATER IN THE MIOCENE OAKVILLE SANDSTONE— A MAJOR AQUIFER AND URANIUM HOST OF THE TEXAS COASTAL PLAIN

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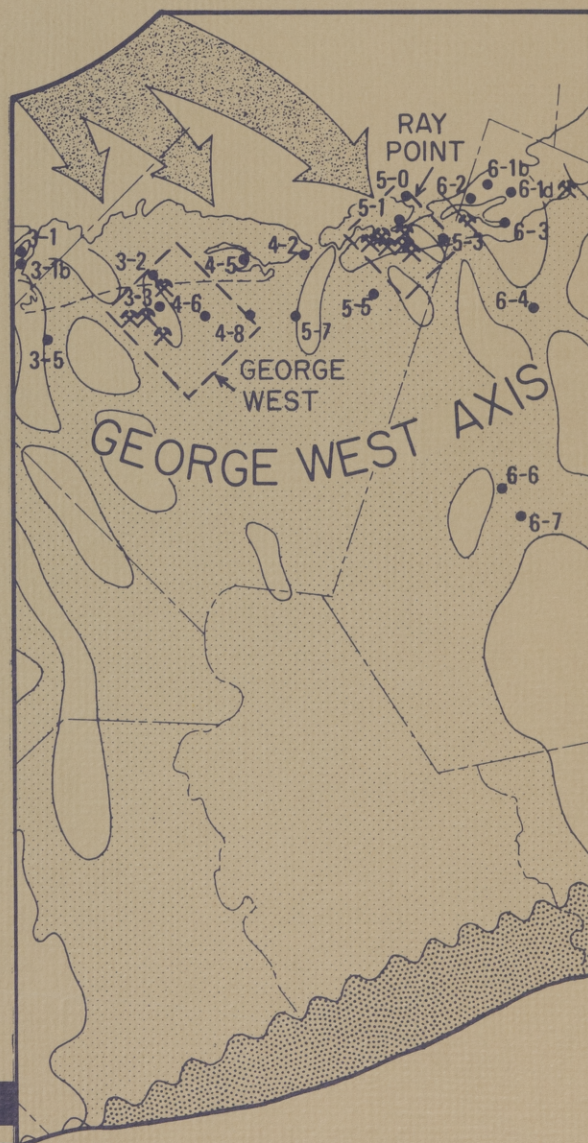
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ABSTRACT

The Oakville Sandstone is a major aquifer and a major host of uranium deposits in the Texas Coastal Plain. This report discusses the geochemistry — including major ions, the trace elements uranium, molybdenum, arsenic, and selenium, and oxidation-reduction potential — of Oakville ground water to evaluate the potential effect of uranium mining on water quality. Ground-water chemistry was investigated both regionally and in two major uranium mining districts.

Major ion composition of Oakville ground water shows a regional variation. East Texas water has low to moderate dissolved solids (350 to 1,100 mg/L) and evolves from a calcium-magnesium-bicarbonate water in near-surface recharge areas to a sodium-bicarbonate composition downdip. The composition and evolution result from calcite solution and cation exchange. South Texas water has higher dissolved solids (up to 3,000 mg/L) dominated by sodium, chloride, and sulfate. The high dissolved solids result from solution of evaporites within the Oakville and from the discharge along faults into the Oakville of high-dissolved-solids water from deeper aquifers.

There are three oxidation-reduction zones within the Oakville: (1) an oxidizing zone with Eh values greater than 300 mV, controlled by the presence of measurable concentrations of dissolved oxygen, (2) an intermediate zone with Eh values between 110 and 10 mV, probably controlled by ferrous-ferric mineral reactions, and (3) a reducing zone with Eh values less than -40 mV, probably controlled by the presence of FeS_2.

Uranium, molybdenum, arsenic, and selenium show regional variations in concentrations, with trace element values in South Texas water distinctly higher than in East Texas water. The higher concentrations may result either from secondary dispersion from uranium deposits, which are more abundant in South Texas than in East Texas, or from a residual primary source in South Texas. Uranium closely follows behavior predicted from thermodynamic data; equilibrium with coffinite determines uranium concentrations in intermediate-Eh and reducing water. The other three elements do not follow predicted behavior, probably because no data are available on complexing.

Analysis of water chemistry around the two uranium mining districts gives results similar to those found in the regional study. Very high concentrations of trace elements occur only in a few samples within ore zones. These high concentrations probably result from natural dispersal from the deposits, although this is not a widespread phenomenon.

INTRODUCTION

The Miocene Oakville Sandstone of the Texas Coastal Plain is important economically for at least two reasons: (1) it is a major source of ground water for both domestic and agricultural uses, and (2) it is a major host of uranium deposits. Uranium is now being mined from the Oakville by both open-pit and in situ leach methods. Extensive exploration during the last few years has identified many additional uranium deposits, which suggests that mining will expand in the future. Although use of ground water and uranium mining are not mutually exclusive, mining can potentially alter ground-water quality and hydrologic characteristics around a mine site. Because of this possibility, it is necessary to understand the potential impact of mining on ground water and to determine ways in which any deleterious impact can be mitigated.

This report focuses on the hydrochemistry — the chemical composition of the ground water — of the Oakville Sandstone. Although determining the impact of mining is a primary goal of this study, other objectives are also important. Understanding the chemical composition of Oakville ground water will aid in exploration for and production of ground water and in exploration for uranium deposits.

To accomplish these goals we have (1) determined existing Oakville ground-water chemistry, including major ion composition, oxidation-reduction status, and concentrations of uranium and its associated trace elements, molybdenum, arsenic, and selenium, both regionally and around two major uranium mining districts, and (2) examined the theoretical or experimentally determined controls of pertinent trace element concentrations in water. Uranium and its associated elements are concentrated where oxidizing ground water encounters a reducing zone within the subsurface flow system; redox status and the concentration and distribution of trace elements in ground water have long been used as exploration tools for uranium deposits. Also ground-water com-

position around a uranium deposit or mine influences the natural or induced dispersion of trace elements. The approach to understanding water chemistry and evolution used in this study should be applicable to other aquifers, whether or not they are or will be affected by mining.

This report is derived from a more comprehensive contract report (Galloway and others, 1982a) prepared by the Bureau of Economic Geology for the U.S. Environmental Protection Agency on the depositional systems, hydrology, use, and hydrochemistry of the Oakville Sandstone. Although much of the data in the comprehensive report is essential for interpreting Oakville hydrochemistry, the findings can only be mentioned briefly in this topical report. For a thorough discussion of these other data the reader is referred to Galloway and others (1982a), to Galloway and others (1982b), who discuss physical stratigraphy, and to Smith and others (in press), who discuss hydrodynamics. In a concluding report, Henry and others (in press) discuss the potential impact of uranium mining on the Oakville aquifer.

GEOLOGY OF THE OAKVILLE SANDSTONE

The Oakville Sandstone is composed of the deposits of a major sand-rich fluvial system deposited by several major and minor rivers that drained the interior of Texas and surrounding states during the Miocene (Galloway and others, 1982b). Broad bed-load fluvial axes (fig. 1), including the Hebbronville, George West, and New Davy trends, lie south of the San Marcos Arch and host significant reserves of uranium. To the north of the arch, the Moulton streamplain consists of deposits of numerous small, intermittent to ephemeral streams that drained the inland margin of the coastal plain. The Burton/Penn mixed-load fluvial axes traverse the coastal plain in the general area of the modern Colorado and Brazos Rivers. Downdip, the fluvial sand axes merge with strike-oriented, coastal-deltaic and strandline sand systems. A small area in the southernmost part of the study area is believed to contain sediments deposited in a playa-floodplain environment (fig. 1). The Oakville is cut by a number of normal faults (fig. 2), some of which were active during Oakville deposition and strongly influenced sedimentation.

Each fluvial axis consists of characteristic facies deposited in channel, crevasse splay, and marginal floodplain environments. Sand percentage, sand-body dimensions and lateral relations, and composition vary systematically among the various axes. The overall transmissivity of the Oakville Sandstone, which closely corresponds to the Jasper aquifer system of conventional hydrostratigraphic terminology, correlates directly with mapped facies composition and trend. The size of

uranium deposits shows a strong positive correlation with aquifer transmissivity.

Commercial uranium deposits lie within channel and interbedded sheet-splay sands in or along the margin of major fluvial belts, typically close to shallow faults. Mineralization occurs as narrow, elongate fronts that separate altered, but commonly resulfidized, host sand from epigenetically sulfidized, reduced sand. Deposits show pronounced spatial zoning across the mineralization front of trace metals, iron sulfides, carbonate, and, in places, clay minerals.

OAKVILLE GROUND-WATER SAMPLING PROGRAM

Oakville hydrochemistry was examined by collecting and analyzing 58 water samples from wells along 10 dip-oriented regional cross sections (lines 1 through 10, fig. 1; apps. A and B). Sections chosen represent different physical environments, that is, the different depositional systems within the Oakville aquifer. For instance, line 7 falls within the Burton/Penn fluvial axes, whereas lines 8 and 9 are within the Moulton streamplain facies. Additionally, 21 water samples were collected from wells around two major uranium districts to facilitate understanding of water chemistry in more detail in these critical areas, as well as to supplement regional information (app. A). Sampling procedures, samples collected, and types of treatment and preservation used are discussed in Galloway and others (1982a).

To ensure that all sampled wells produce from the Oakville aquifer, cross sections were constructed from electric logs used in the depositional systems study (app. B). Only those wells for which we had accurate information on depth and on screened or perforated interval were used. Many wells identified within the Oakville aquifer by the Texas Department of Water Resources do not produce from the Oakville as it is defined in this study. In addition, many wells do not have sufficient information on completion to identify positively their producing interval. Such wells were not used for this study.

Numerous wells occur in the relatively densely populated, eastern part of the study area. However, some difficulty was encountered in finding deep Oakville wells in the eastern part because most wells produce from shallower aquifers. In the southern part of the area, the population density is lower, and there are proportionately fewer Oakville wells. Locating wells with sufficient documentation to verify producing intervals was difficult; many of those found were abandoned or windmill driven. Consequently, the dip section lines are irregularly oriented to include the most suitable wells.

Well locations for water samples were chosen on the theory that the physical and chemical framework of the Oakville aquifer should control water chemistry. The

aquifer's framework includes properties such as geometry, transmissivity, mineralogy and chemical composition of the aquifer matrix, and structure. Mineralogy of framework grains and cements varies locally and regionally (Galloway and others, 1982b). Thus, different depositional environments in the Oakville may be characterized by different water chemistries. Because the Oakville is principally of fluvial origin in the area studied, most water wells produce from fluvial sandstones. However, several wells in the southern part of the area may produce from the postulated playa-floodplain facies.

The general assumption in examination of hydrochemical data from dip profiles is that ground water is recharged in outcrop and flows generally downdip. Smith and others (in press) document this general flow pattern for the Oakville aquifer and also show that flow is strongly deflected toward topographic lows along major drainages crossing the Oakville outcrop. Therefore, downdip water chemistry should evolve from updip water chemistry. Using these assumptions, one can then study the evolution of water chemistry by sampling a series of wells from the recharge area into the subsurface. The assumption, however, is imperfect: the aquifer is highly anisotropic, and ground-water flow is not directly downdip (Smith and others, in press). Additional recharge water enters the Oakville from both above and below. Although overlying clayey beds are qualitatively considered aquicludes, they do have finite permeability; water can pass through these beds and enter the upper part of the Oakville. Rate of flow and total amount of recharge per unit area from this process depends on the relative permeability of the Oakville and overlying beds, and on hydraulic head in both. Water may enter the Oakville from below, especially along fault zones that serve as avenues of vertical permeability in otherwise low-permeability strata. Upward discharge of deeper, highly reducing water is well documented both by previous studies and by the results of this study.

Interpretation of water chemistry and its downdip evolution must incorporate these variables and uncertainties because, like any natural system, the Oakville aquifer is complex.

MODELING OF GROUND-WATER CHEMISTRY

Understanding water chemistry requires sophisticated sampling and analytical techniques and careful interpretation of analytical results. We have reviewed the available literature on aqueous chemistry and behavior of uranium, molybdenum, arsenic, and selenium, and have used a modified version of the computer model WATEQF (Plummer and others, 1976) to interpret the analytical results. WATEQF calculates speciation of dissolved ions and determines saturation with respect to a variety of minerals. The saturation index of a mineral equals the log of the ratio of the ionic activity product (IAP) to the equilibrium constant of the reaction that produces the mineral, at a given temperature (KT). A saturation index of zero indicates equilibrium, whereas positive and negative values indicate oversaturation and undersaturation, respectively. Because the trace elements uranium, molybdenum, selenium, and arsenic are of critical concern in evaluating the impact of uranium mining, thermodynamic data on their speciation and mineral formation have been added to the program. Sources for these data include Wagman and others (1969) for copper; Naumov and others (1971) for arsenic, copper, molybdenum, and selenium; Howard (1977) for selenium; Kaback (1977) for molybdenum; and Langmuir (1978) for uranium.

Eh-pH diagrams have been constructed or adapted from the literature to predict the form, whether dissolved ion or stable mineral species, that trace metals assume under various conditions. Construction of the diagrams followed procedures described by Garrels and Christ (1965). This approach is particularly appropriate because the solubility of the elements is Eh dependent, and Eh varies greatly within the Oakville aquifer.

A number of assumptions or approximations are necessary to use Eh-pH diagrams and chemical models such as WATEQF and to interpret water chemistry in general. The following brief discussion is based on the work of others: Garrels and Christ (1965), concerning the use of Eh-pH diagrams; Truesdell and Jones (1974) and Plummer and others (1976), concerning WATEQF; Kaback (1977), Howard (1977), Langmuir (1978), and Ferguson and Gavis (1972), concerning molybdenum, selenium, uranium, and arsenic, respectively; and Jenne (1979), concerning the application of chemical modeling in general.

Both Eh-pH diagrams and chemical modeling rely entirely upon available thermodynamic data, including free energies of formation and dissociation constants for various reactions. These values are accurately known to varying degrees. Equilibrium constants involving most major ions and minerals are well documented; however, constants for trace metal complexes are commonly unavailable or unreliable. Complexing of uranium is much better understood than is complexing of molybdenum, selenium, or arsenic.

Some minerals are complex solid substitutions. To determine the free energies of such minerals accurately, it is necessary to analyze specific examples from the geologic unit under examination. For example, we have used solubility data from Kaback (1977) for ferrimolybdite because she determined the actual composition of a naturally occurring sample. However, whether that particular ferrimolybdite is appropriate for the Oakville is not known. Other minerals, such as ferric hydroxides for example, which are of critical importance to this study because of their role in adsorption, vary in
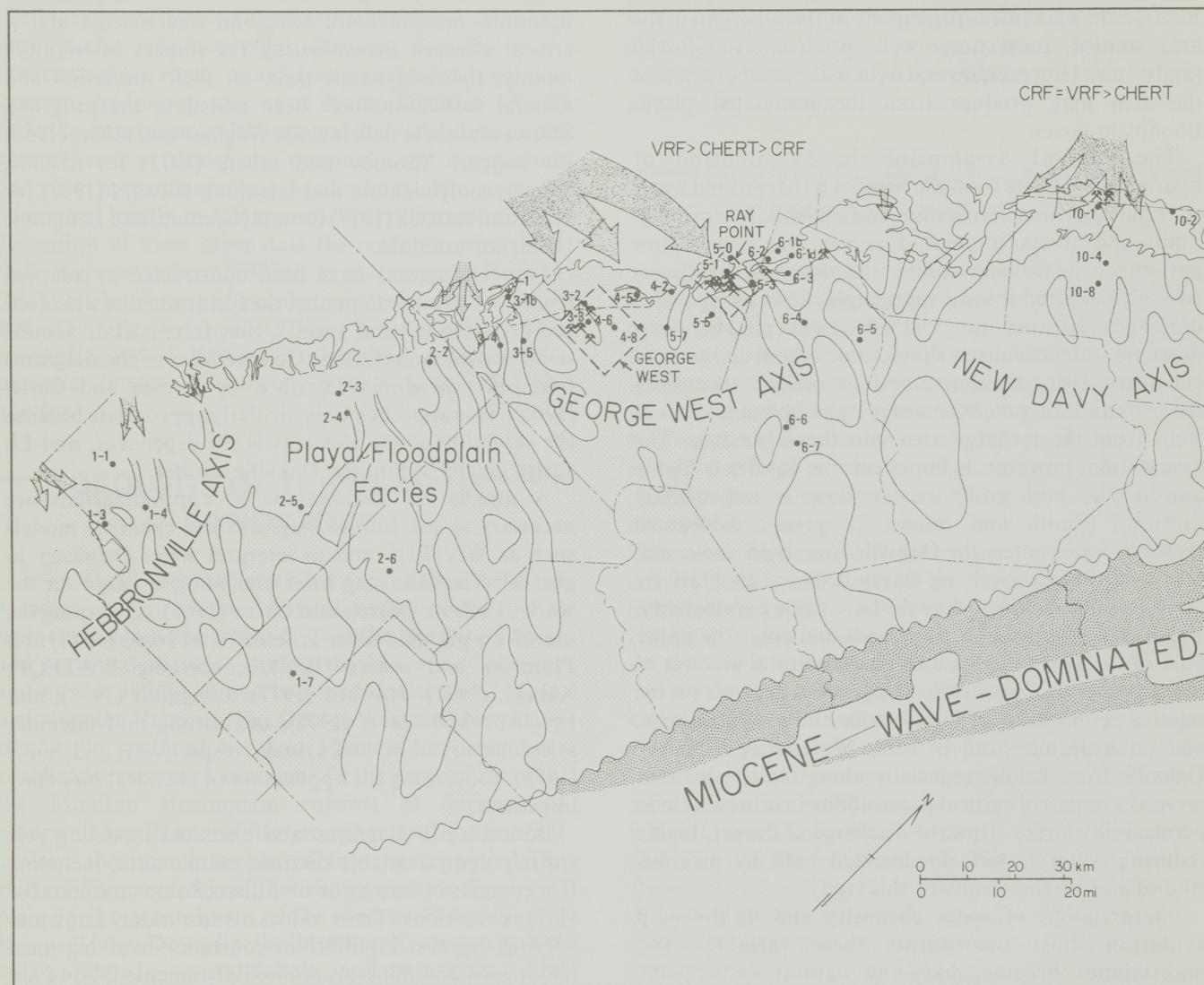
Figure 1. Depositional elements of the Oakville fluvial system. Points of entry of major rivers onto the Coastal Plain are recorded by the Hebbronville (which lies largely south of the study area), George West, New Davy, and Burton/Penn fluvial axes. The Moulton streamplain is a broad, interaxial area characterized by deposits of numerous local, flashy to ephemeral streams. The dip-oriented fluvial elements emerge downdip with strike-

CRF>VRF>CHERT

CRF≫CHERT≥VRF

8-1
8-1.5
8-2
8-3
8-4
8-5
8-6

9-1
9-2
9-4
9-3
9-6
9-7

10-9

7-1
7-2
7-3
7-4
7-5
7-7
7-8

BURTON/PENN AXES

MOULTON STREAMPLAIN

DELTA AND BARRIER SYSTEM
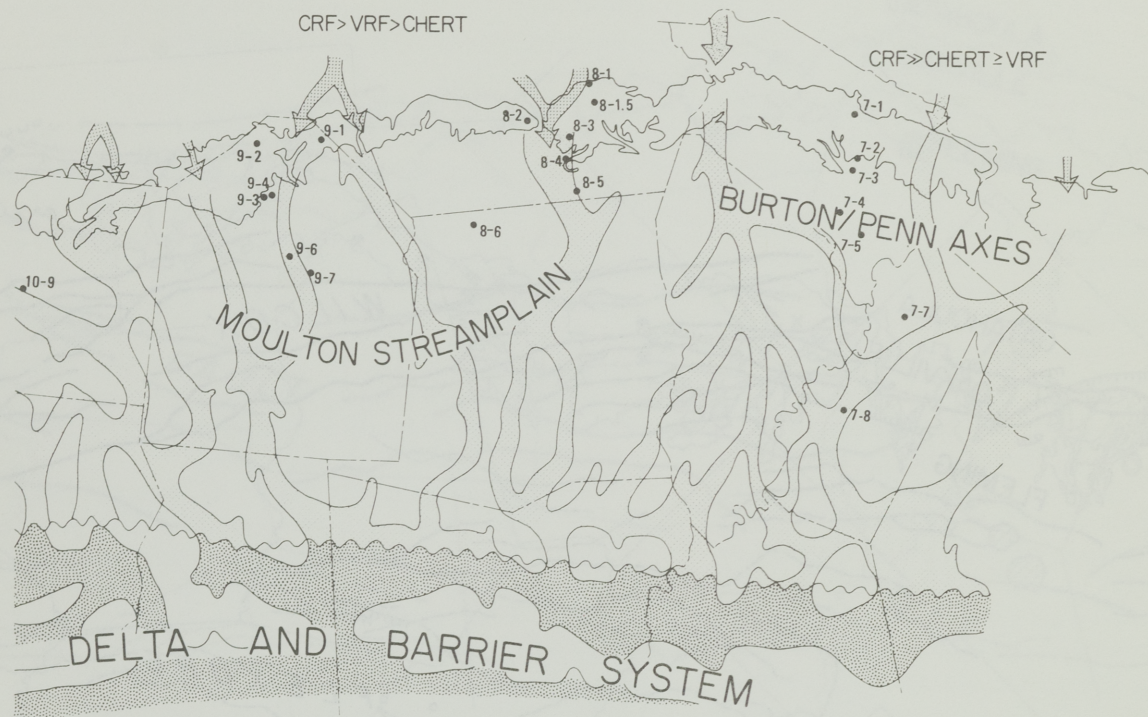
EXPLANATION

Pebble to cobble
Granule to coarse sand
} Sediment input axes

Channel trends

• 1-1   Ground-water sampling points

⚒ Uranium mine

VRF (Volcanic rock fragment)
CRF (Carbonate rock fragment) } Sand composition
CHERT

oriented facies of the equivalent strandline sands of Miocene delta and barrier systems. Composition of lithic grains in sands confirms the presence of at least three different source terranes for the rivers. Numbered circles indicate ground-water sampling sites.

Figure 2. Generalized distribution of faults and diapiric intrusions mapped within or below the

6
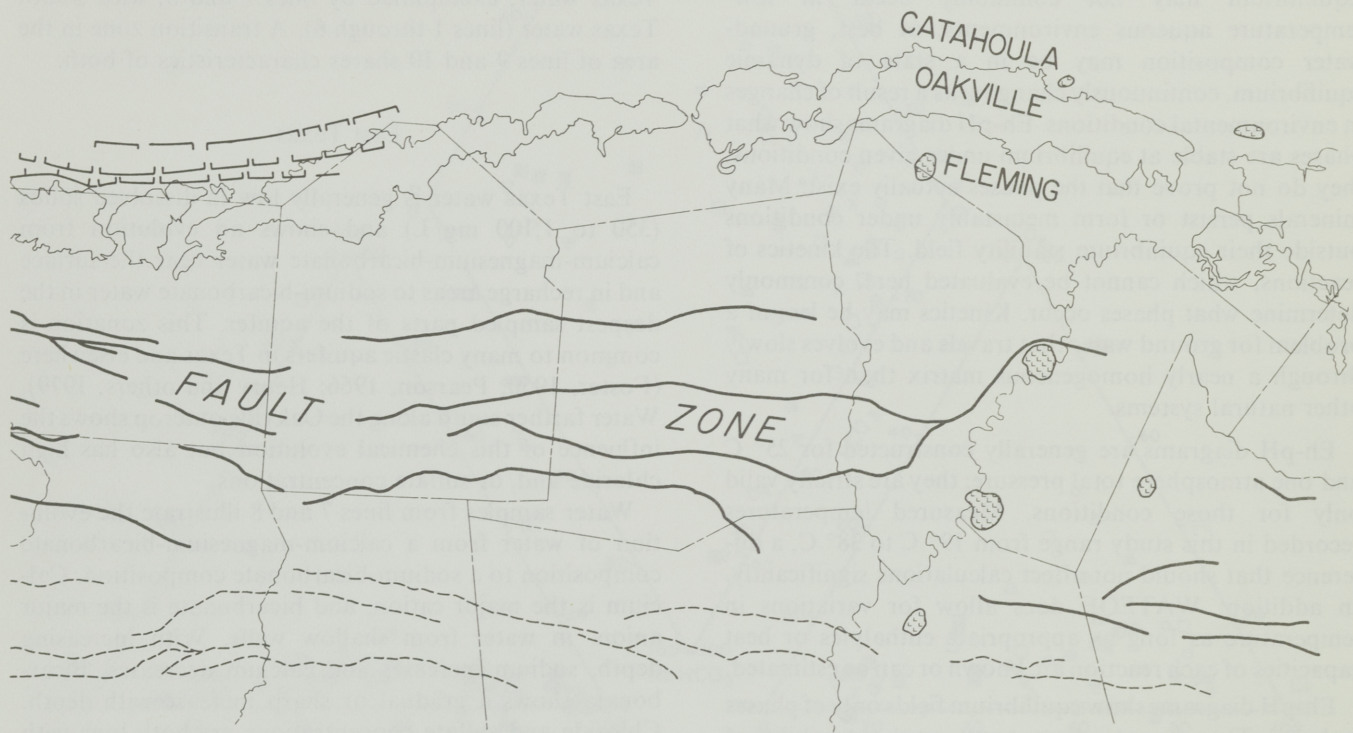
MAJOR SUBSURFACE FAULT ZONES

⊏⊐ Lower Cretaceous

╱ Upper Wilcox / Carrizo

╱ Jackson

╱ Catahoula / Frio Sand.

⌇⌇ Outcrop fault

GEOLOGIC FEATURES

⬯ Salt diapirs

° ₀ Shale diapirs

⚒,x Uranium mine ; deposit

Oakville Sandstone. Mapping horizon is indicated by style of line. Compiled from various sources.

chemistry and degree of crystallinity; both factors affect their solubility products. Because most studies have not specified the precise form of ferric hydroxide, we have used the general term "ferric hydroxide" to designate all. By necessity, we have relied on the judgment of others to evaluate thermodynamic data.

Calculations by WATEQF and constructions of Eh-pH diagrams are based on an assumption of equilibrium. Equilibrium may not commonly occur in low-temperature aqueous environments; at best, ground-water composition may be in a state of dynamic equilibrium, continuously changing as a result of changes in environmental conditions. Eh-pH diagrams show what phases are stable at equilibrium under given conditions; they do not prove that the phases actually exist. Many minerals persist or form metastably under conditions outside their equilibrium stability field. The kinetics of reactions, which cannot be evaluated here, commonly determine what phases occur. Kinetics may be less of a problem for ground water that travels and evolves slowly through a nearly homogeneous matrix than for many other natural systems.

Eh-pH diagrams are generally constructed for 25° C and one atmosphere total pressure; they are strictly valid only for those conditions. Measured temperatures recorded in this study range from 19° C to 38° C, a difference that should not affect calculations significantly. In addition, WATEQF does allow for variations in temperature as long as appropriate enthalpies or heat capacities of each reaction are known or can be estimated.

Eh-pH diagrams show equilibrium fields only of phases included. They do not indicate anything about stability of phases not included in the diagram. WATEQF, obviously, cannot calculate the degree of saturation of a mineral not included in the program or for which the appropriate ions were not analyzed. A mineral that was not considered may be the most stable phase under a given set of conditions and may control the solubility of a trace element. Organic material is known to be an important adsorbent of some trace elements, and organic ligands may be significant in complexing trace metals in solution (Jenne, 1979). Unfortunately, far too little is known about the role of organic complexes; nothing is known about their occurrence and distribution in the Oakville aquifer. Consequently, this study is limited exclusively to inorganic compounds.

Solubility calculations are only as good as the accuracy of input analytical data. Two of the most critical values in the Oakville system are Eh and pH; pH can be determined adequately but measurement of Eh is complex, and its significance in an aquifer is uncertain. This problem is discussed more thoroughly below. In addition, collection and analysis of water samples for trace element concentrations at the μg/L level present additional difficulties. (Analytical methods for uranium, molybdenum, selenium, and arsenic are given in appendix C.)

REGIONAL WATER CHEMISTRY

MAJOR ION CHEMISTRY

Oakville water encompasses a wide variety of chemical types (fig. 3; app. A). Total dissolved solids range from about 350 mg/L to about 3,000 mg/L. Geographic zonation of chemical types is evident by comparing East Texas water, exemplified by lines 7 and 8, with South Texas water (lines 1 through 6). A transition zone in the area of lines 9 and 10 shares characteristics of both.

East Texas

East Texas water is generally low in dissolved solids (350 to 1,100 mg/L) and shows an evolution from calcium-magnesium-bicarbonate water near the surface and in recharge areas to sodium-bicarbonate water in the deepest sampled parts of the aquifer. This zonation is common to many clastic aquifers in Texas and elsewhere (Foster, 1950; Pearson, 1966; Henry and others, 1979). Water farther south along the Oakville outcrop shows the influence of this chemical evolution but also has high chloride and/or sulfate concentrations.

Water samples from lines 7 and 8 illustrate the evolution of water from a calcium-magnesium-bicarbonate composition to a sodium-bicarbonate composition. Calcium is the major cation, and bicarbonate is the major anion, in water from shallow wells. With increasing depth, sodium increases and calcium decreases. Bicarbonate shows a gradual or sharp increase with depth. Chloride and sulfate concentrations are both low; with only a few exceptions, they are less than 100 mg/L (app. A). Henry and others (1979) attributed similar chemical evolution of water in the Wilcox Group (Eocene) of East Texas to a combination of calcite solution and cation exchange with smectite. The reactions involved are

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^- \qquad (1)$$

$$Ca^{2+} + Na\text{-}clay = 2Na^+ + Ca\text{-}clay \qquad (2)$$
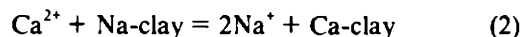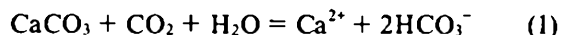
As calcite dissolves, the water approaches equilibrium with respect to calcite; at the same time, calcium exchanges with clays, releasing sodium ions. As calcium is depleted by exchange, the water becomes undersaturated with respect to calcite and more calcite can dissolve; thus, a continuous process occurs.

The initial composition is determined by solution of calcite in the soil zone and shallow subsurface. Calculated saturation indices for even the shallowest water in East Texas indicate equilibrium with calcite (table 1), consistent with the presence of abundant carbonate fragments in the Oakville (Galloway and others, 1982a).

Chloride and sulfate concentrations are low in East Texas water simply because little chloride or sulfate-

Figure 3. Piper (trilinear) diagram: Oakville ground water. Numbers under "Explanation" indicate sample lines.

bearing sediment exists in the aquifer. The sediments were deposited in a fresh-water environment and have been extensively flushed by fresh water. The presence of dissolved oxygen at depth (discussed below) is another indication of flushing. Detrital substances such as volcanic glass, which once may have been a significant framework constituent, have already been altered and soluble material flushed out. Pyrite also must be a minor phase because oxidation of pyrite would have contributed significant amounts of sulfate.

South Texas

Water in South Texas has higher total dissolved solids (up to 3,000 mg/L) than does water in East Texas. Chloride concentrations illustrate this point: almost all are greater than 100 mg/L, and they range as high as 1,000 mg/L. The water samples having the highest dissolved solids in East Texas contain sodium and bicarbonate resulting from downflow evolution. Water samples in

South Texas with high dissolved solids contain sodium, chloride, and sulfate. Nevertheless, South Texas water shares several characteristics with East Texas water. Saturation indices show that almost all South Texas water samples are approximately in equilibrium with calcite (table 1), further reflecting the abundance of carbonate fragments in the Oakville.

Cation exchange also has a significant effect in South Texas. Along several lines (for example, lines 1 and 6), calcium and magnesium concentrations decrease with increasing depth. Sodium concentrations increase irregularly with depth, because sodium is contributed both by cation exchange and by other processes discussed below.

There are two major processes responsible for the higher total dissolved solids in South Texas water: (1) solution of evaporites within low permeability parts of the Oakville, and (2) discharge of chloride-rich water with high total dissolved solids along faults into the Oakville. The influence of evaporites can be observed in samples

Table 1. Saturation indices (log IAP/KT) for major element minerals (regional wells).

Sample	Calcite	Chalcedony	Silica gel	Siderite	FeOH₃*	FeS*	FeS₂
1-1	0.24	0.64	0.14	-1.8	3.0	—	—
1-3	0.11	0.15	-0.36	-3.7	2.9	—	—
1-4	0.15	0.32	-0.18	-0.3	0.6	—	—
1-7	0.08	-0.03	-0.53	0.5	-0.9	1.4	15
2-2	0.00	0.06	-0.44	-0.6	1.8	—	—
2-3	0.02	0.37	-0.13	-1.2	2.5	—	—
2-4	-0.06	0.00	-0.51	-0.1	-3.4	1.5	14
2-5	-0.01	0.02	-0.49	0.1	-0.2	0.0	15
2-6	-0.11	-0.05	-0.55	0.2	-1.0	-0.3	13
3-1	0.19	0.36	-0.15	-2.0	2.9	—	—
3-1b	0.06	0.54	0.03	-1.7	2.9	—	—
3-2	0.06	0.47	-0.04	-1.5	2.4	—	—
3-3	0.10	0.39	-0.12	-2.2	2.9	—	—
3-4	0.06	0.27	-0.23	0.4	-0.7	0.4	17
3-5	0.21	0.21	-0.30	-0.7	-1.6	—	—
4-2	0.15	0.55	0.04	-1.0	3.1	—	—
4-5	0.13	0.52	0.01	-1.0	3.0	—	—
4-6	0.13	0.27	-0.23	0.2	0.1	—	—
4-7	0.32	0.00	-0.51	0.6	-1.6	0.0	13
4-8	0.19	0.26	-0.25	-0.3	0.9	—	—
5-0	0.16	0.40	-0.10	-2.1	2.7	—	—
5-1	0.16	0.61	0.11	-1.8	2.6	—	—
5-3	0.15	0.47	-0.04	-0.9	-5.2	1.3	14
5-5	0.14	0.05	-0.45	-0.1	0.4	—	—
5-7	0.30	0.00	-0.50	0.6	-1.6	0.0	13
6-1b	0.23	0.67	0.16	-0.4	1.9	—	—
6-1d	0.11	0.36	-0.15	0.5	-0.8	0.2	15
6-2	0.11	0.39	-0.11	-0.3	-3.6	0.5	14
6-3	0.30	0.08	-0.43	0.2	0.8	NC	NC
6-4	0.26	0.01	-0.49	0.3	-2.6	1.9	15
6-5	0.15	0.01	-0.49	0.4	-0.9	0.8	15
6-6	0.30	-0.05	-0.56	1.0	0.6	0.8	16
6-7	0.47	-0.05	-0.55	0.8	-3.3	0.1	7.4
7-1	0.09	0.23	-0.28	-3.1	2.5	—	—
7-2	-0.07	0.16	-0.34	-1.6	2.4	—	—
7-3	-0.06	0.27	-0.23	-1.6	2.5	—	—
7-4	0.13	0.34	-0.17	-2.7	2.5	—	—
7-5	0.02	0.13	-0.38	0.1	-0.2	—	—
7-7	-0.04	0.34	-0.17	0.2	-0.4	—	—
7-8	-0.04	0.00	-0.50	-0.1	0.3	—	—
8-1	0.02	0.24	-0.26	-4.1	2.4	—	—
8-1.5	0.08	0.13	-0.38	-2.8	2.5	—	—
8-2	0.20	0.31	-0.20	-0.5	0.3	—	—
8-3	-0.11	0.67	0.16	-0.6	-0.3	—	—
8-4	-0.08	0.64	0.14	0.6	1.0	—	—
8-5	-0.01	0.64	0.14	0.4	-0.2	-0.2	17
8-6	0.12	0.60	0.10	0.8	0.2	0.1	16
9-1	-0.04	0.33	-0.18	-2.5	2.7	—	—
9-2	0.06	0.43	-0.08	-0.8	-1.6	-0.2	18
9-3	-0.03	0.21	-0.30	-0.4	0.3	—	—
9-4	0.21	0.35	-0.15	-0.5	1.4	—	—
9-6	0.01	0.41	-0.09	0.5	1.3	-0.1	19
9-7	-0.11	0.55	0.05	0.4	-2.5	1.4	15
10-1	0.22	0.41	-0.09	-1.7	2.8	—	—
10-2	0.34	0.42	-0.09	-0.6	-1.8	-0.5	16
10-4	0.0008	0.26	-0.24	-0.4	0.4	—	—
10-8	-0.097	0.18	-0.32	0.2	-0.5	—	—
10-9	-0.22	0.03	-0.47	0.6	-0.5	—	—

— Sulfide below level of detection
NC Not calculated
* Amorphous

from line 2, which lies within the postulated playa-floodplain facies. Water samples from line 2 have high chloride concentrations, probably resulting from solution of evaporite minerals within these sediments. Sample 2-5, which has the lowest chloride concentration of samples from line 2, is at the edge of the Hebbronville fluvial axis, where flux of meteoric water should be greater than in the playa-floodplain facies. Sulfate concentrations in water samples from line 2 are irregular, with the highest concentrations in the two deepest wells. The playa-floodplain facies were deposited in a nonmarine environment and may contain erratic sulfate concentrations.

Samples from line 1 may also illustrate the influence of evaporite solution. Sample 1-1 has a high chloride concentration and is within a low-transmissivity (sand-poor) part of the Oakville. Other samples on line 1 are from higher net-sand, and consequently higher transmissivity, parts of the Oakville that exhibit lower chloride concentrations. Although other factors may be involved, it is likely that the finer grained, less permeable sediment initially contained more soluble material and has been less flushed with meteoric water than more permeable parts of the Oakville. However, transmissivity alone generally does not show a good correlation with total dissolved solids.

Fault-related discharge into the Oakville of water containing high concentrations of dissolved solids has been documented in several uranium mining districts (Goldhaber and others, 1978; Reynolds and Goldhaber, 1978). The exact composition of such water and whether the process is occurring today are not known, however. Nevertheless, water discharged along faults is high in dissolved solids, particularly sodium and chloride, and is extremely reducing because of high concentrations of H_2S.

Sample 5-3 (and samples Z-205 and Z-217 of the detailed Ray Point study) may be representative of fault-discharge water or at least discharge water modified by mixing with meteoric water. These three samples contain high and nearly uniform dissolved solids (~2,500 mg/L), composed of sodium and chloride; they contain H_2S and are also extremely reducing. The sample sites are close to a fault where discharge is known to have occurred in the past.

Uncertainties with a fault-discharge interpretation include: (1) The reducing conditions may be controlled by the presence of pyrite from previous fault discharge, but the discharge water subsequently has been flushed by meteoric water. (2) Other nearby water samples, such as sample 5-0, have moderately high dissolved solids ($\sim$1,400 mg/L) and high sodium and chloride concentrations similar to the inferred fault-discharge water; however, they are highly oxidizing and contain measurable dissolved oxygen. Possibly this latter water was derived from discharge but has been oxidized by mixing with meteoric water. Nevertheless, it is difficult to envision how, by mixing, water as reducing as that found in well 5-3 could become as oxidizing as water in well 5-0 without losing all of its chemical identity. Probably no fault-discharge water has been preserved unchanged; the highly reducing water is probably the closest relict example available but it has been modified by mixing with meteoric water.

Fault discharge should be more common in South Texas than in East Texas because faults are far more abundant in South Texas, especially in shallow parts of the Oakville Sandstone (fig. 2). Faults have not been identified in the areas of lines 7 and 8 except for several that cut the Oakville at the extreme downdip end of line 7. The density of faults is greatest in South Texas between lines 2 and 10. Most evidence of fault-discharge of water has been documented in this area. Such evidence includes (1) saline ground water having low Eh, (2) pyrite-rich sediment adjacent to fault zones, and (3) stable isotope composition of calcite and pyrite formed by discharge (Goldhaber and others, 1978). The Ray Point and George West uranium districts, two areas where fault discharge is known to have occurred, are discussed in more detail in a later section.

OXIDATION AND REDUCTION

The oxidation state of Oakville ground water was investigated because of its importance in evaluating oxidation-reduction reactions and trace element solubility. Oxidation state was determined in several ways. Dissolved oxygen and Eh were measured directly at the time of sampling; procedures are given in Galloway and others (1982a). Eh was also calculated from the oxidized-reduced couples NO_3-NH_3 and SO_4-H_2S by means of the Nernst equation (Langmuir, 1971). Measured Eh was also compared with Eh values predicted from dissolved oxygen concentrations calculated using different assumptions. All measured and calculated Eh values are given in table 2. Eh could have been calculated from ferrous and ferric iron concentrations, had they been determined. This method would be a useful test of some of the conclusions drawn below, but it was not used in this study.

Interpretation of Eh measurements of natural water is complex. In this study, measured Eh values and values determined from the nitrogen or sulfur couples generally do not agree. As noted by Morris and Stumm (1967), many reactions, including those involving nitrogen and sulfur, are slow unless biologically mediated; thus, they are rarely in equilibrium. Because ground water moves slowly through the subsurface and has greater time for equilibration, Eh values determined for ground water might be more indicative of equilibrium. Morris and Stumm (1967) suggest that most measured Eh values represent mixed potentials; that is, the various couples are not in equilibrium, and the measured potential is a mixture of the individual potentials. For this reason, Eh values cannot be quantitatively interpreted. We have attempted to use all the Eh determinations, along with knowledge of water chemistry and host-rock mineralogy, to interpret oxidation-reduction controls.

It is well known that Eh values within an aquifer decrease from areas of recharge into the subsurface (Back and Barnes, 1965; Edmunds, 1973; Champ and others, 1979). The decrease is attributed to a sequence of oxidation-reduction reactions that consume oxidants, especially dissolved oxygen, in recharge water. For example, Champ and others (1979) designated three redox zones in ground-water flow systems from areas of recharge to areas of discharge: (1) oxygen-nitrate, Eh$\geqslant$300 mV; (2) iron-manganese, Eh=300 to 100 mV; and (3) sulfide, Eh$\leqslant$100 mV.

Measured Eh values of this study also cluster in three groups (fig. 4), but the groups do not coincide exactly with the zones of Champ and others (1979). Eh values show a regular pattern of decrease with depth and distance from recharge only in part of the Oakville aquifer (lines 1, 3, 7, 8). In other parts, Eh values show an irregular pattern exhibiting reversals in Eh with depth, although an overall decrease exists (lines 2, 4, 5, 6, 9, 10).

All water samples with Eh values greater than 300 mV contain measurable dissolved oxygen. This indicates an oxidizing zone that occurs in areas of recharge and extends to variable depths within the Oakville. An intermediate zone with Eh values of 110 to 10 mV occurs downdip of the oxidizing zone. About half of these water samples contain low yet detectable concentrations of hydrogen sulfide. In some areas (lines 3, 7, 8), the deepest wells sampled fall within this intermediate zone. A highly reducing zone with Eh less than -40 mV occurs in the deepest parts of some lines (1, 4, 9, 10) but also at very shallow depths along other lines (2, 5, 6). Along these latter lines, the shallow reducing water appears to be associated with faults that have served as conduits for the rise of highly reducing, sulfide-rich water from deeper formations (Goldhaber and others, 1978). All reducing water samples contain dissolved hydrogen sulfide.

Table 2. Measured and calculated Eh, dissolved oxygen, and hydrogen sulfide (regional wells).

Sample	Measured Values			Eh (mV) Calculated From:			
	Eh (mV)	DO (ppm)	H₂S (ppm)	DO	Sato (1960)	H₂S-SO₄	NH₄-NO₃
1-1	370	4.3	0	787	197	—	360
1-3	430	1.7	0	756	165	—	326
1-4	110	0	0	—	—	—	—
1-7	-120	0	0.74	—	—	-309	247
2-2	180	0	0	—	—	—	335
2-3	300	5.1	0	786	192	—	362
2-4	-150	0	2.32	—	—	-247	322
2-5	-40	0	0.03	—	—	-269	276
2-6	-80	0	0.02	—	—	-272	271
3-1	—	6.2	0	810	212	—	389
3-1b	380	5.7	0	810	211	—	391
3-2	350	2.2	0	799	206	—	385
3-3	390	4.5	0	788	198	—	—
3-4	30	0	0.06	—	—	-207	357
3-5	10	0	*	—	—	—	330
4-2	320	6.1	0	789	193	—	—
4-5	320	ND	0	—	—	—	—
4-6	25	0	0	—	—	—	—
4-7	-80	0	0.02	—	—	-233	—
4-8	110	0	0	—	—	—	—
5-0	360	7.6	0	—	—	—	—
5-1	340	6.3	0	785	188	—	357
5-3	-150	0	9.54	—	—	-206	—
5-5	70	0	0	—	—	—	317
5-7	-80	0	0.02	—	—	-233	—
6-1b	260	0.4	0	792	189	—	—
6-1d	-40	0	0.02	—	—	-226	—
6-2	-100	0	0.38	—	—	-204	—
6-3	90	0	0	—	—	—	331
6-4	-170	0	2.98	—	—	-302	—
6-5	-70	0	0.13	—	—	—	—
6-6	-50	0	0.06	—	—	—	245
6-7	-270	0	0.02	—	—	—	—
	-50	0	0.02	—	—	—	—
7-1	420	7.6	0	808	197	—	371
7-2	350	5.5	0	812	207	—	378
7-3	350	4.3	0	807	202	—	—
7-4	390	2.4	0	791	186	—	355
7-5	70	0	0	—	—	—	—
7-7	30	0	*	—	—	—	311
7-8	30	0	0	—	—	—	287
8-1	470	6.4	0	—	—	—	369
8-1.5	430	5.9	0	803	208	—	378
8-2	110	0	0	—	—	—	334
8-3	100	0	0	—	—	—	—
8-4	60	0	0	—	—	—	303
8-5	40	0	0.04	—	—	-246	311
8-6	10	0	0.02	—	—	—	—
9-1	410	4.1	0	802	201	—	372
9-2	50	0	0.29	—	—	—	—
9-3	70	0	0	—	—	—	310
9-4	170	0	0	—	—	—	—
9-6	90	0	0.03	—	—	-266	—
9-7	-130	0	1.42	—	—	—	—
10-1	360	6.3	0	799	198	—	375
10-2	20	0	0.08	—	—	-211	357
10-4	160	1.0	0	796	198	—	—
10-8	40	0	*	—	—	—	—
10-9	-70	0	*	—	—	—	—

DO Dissolved oxygen
* Odor detected at well head
— Could not be calculated
ND Not determined

Oxidizing Zone

Water samples from shallow wells along every line except possibly line 6 contain measurable dissolved oxygen and have Eh values greater than 300 mV. For example, six samples along lines 7 and 8 (samples 7-1 through 7-4, 8-1, and 8-1.5) have dissolved oxygen concentrations ranging from 2.4 to 7.6 mg/L; by comparison, water in equilibrium with the atmosphere should contain about 10 mg/L. Measured Eh ranges from 350 to 470 mV. Within this range, dissolved oxygen concentration and Eh values do not correlate; obviously, dissolved oxygen concentration is not the sole control of Eh.

The general range of Eh values and dissolved oxygen concentrations in the Oakville Sandstone is consistent with an equilibrium of dissolved oxygen and hydrogen peroxide in the water (Sato, 1960). Sato suggested that Eh of water containing dissolved oxygen is controlled not by equilibrium between oxygen and water, an extremely sluggish reaction, but by equilibrium between oxygen and hydrogen peroxide. The reaction is

$$H_2O_2 = O_2 + 2H^+ + 2e^- \qquad (3)$$
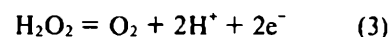
Eh of this reaction at equilibrium is given by the equation

$$Eh = 0.682 - 0.0591\ pH + 0.0295 \log \frac{P_{O_2}}{[H_2O_2]} \qquad (4)$$

Calculation of an exact Eh value from dissolved oxygen concentrations is impossible without knowledge of the hydrogen peroxide concentration. Sato (1960) estimated a possible range of P_{O_2}/H_2O_2 ratios and used these to calculate a range of possible Eh-pH environments. He assumed that hydrogen peroxide concentration could not exceed the concentration of dissolved oxygen from which it formed, thus resulting in a minimum ratio of 1. As a maximum value, he assumed an arbitrary value of 10^6. Reaction-equilibrium lines using both assumptions are shown in figure 4. Eh-pH values of almost all Oakville water samples containing dissolved oxygen plot between these two lines. Those few samples containing measurable dissolved oxygen that plot below the lower line

display very low oxygen concentrations. The concentrations may in fact be below detection levels but may appear positive because of the difficulty of measuring low concentrations. All Eh values calculated by WATEQF, assuming equilibrium between dissolved oxygen and water (table 2), are much greater than those obtained by direct measurement. This observation supports Sato's conclusion that the dissolved oxygen-water reaction does not control Eh.

Eh values calculated from the nitrate-ammonia couple fall within the same range as measured Eh values but they are not considered meaningful for reasons discussed below. Nevertheless, almost all water samples containing dissolved oxygen also contain detectable nitrate; many water samples with lower Eh values do not. Eh cannot be determined from the sulfur couple because none of the oxidizing water samples contain measurable hydrogen sulfide.

Measurable dissolved oxygen and high Eh values extend to a depth of at least 125 m (410 ft) along line 7 but only to 34 m (112 ft) along line 8, the nearest adjacent line. Apparently reductants to consume dissolved oxygen are more abundant along line 8 than along line 7, or the flux of meteoric water is greater along line 7. Line 8, which lies within the Moulton stream-plain, has a lower net-sand content and higher percentage of low-permeability muds than line 7, which lies within the permeable Burton/Penn fluvial axes. Possibly oxygen consumption is related to more reducing conditions in muds than in sands. Also, no correlation exists between dissolved oxygen values and the depth at which the aquifer becomes confined. Along line 7, dissolved oxygen extends into the confined part of the aquifer, whereas on line 8, dissolved oxygen drops to zero well before confinement. The presence of dissolved oxygen does not simply reflect recharge in the outcrop area.

Lines 3, 7, and 8 exhibit similar redox patterns, even though chemical composition of the water samples is markedly different. Measurable dissolved oxygen extends to a depth of 119 m (390 ft) in well 3-3. Because wells along line 3 are irregu-

larly distributed, the depth at which dissolved oxygen is consumed is unknown. In well 4-6, Eh is 25 mV, and dissolved oxygen is depleted even though it is within 8 km (5 mi) of, and at about the same depth as, well 3-3.

Line 1 exhibits a redox pattern that is similar to redox patterns along lines 3, 7, and 8. However, several features of line 1 are notable:

(1) The Oakville Sandstone does not crop out in this area. It is totally buried beneath the Goliad Formation. Recharge water containing dissolved oxygen must be passing through the Goliad to enter the Oakville.

(2) Even though the aquifer here is confined, dissolved oxygen extends to the greatest depth of any line, 238 m (780 ft). Along line 2, dissolved oxygen was found only in sample 2-3 at a depth of 95 m (310 ft).

(3) Line 1 lies in the Hebbronville fluvial axis, where flushing by meteoric water should be greater than in the low-permeability playa-floodplain facies transected by line 2. From the distribution and depth of dissolved-oxygen-bearing water, we conclude that overall permeability of the aquifer in a given area largely controls the depth to which oxygen-bearing water extends.

Figure 4. Eh-pH diagram showing hypothesized controls on the oxidation-reduction state of Oakville water. Reaction-equilibrium lines are drawn for ionic and other concentrations as shown. Dots indicate measured Eh and pH values of this study. Based in part on Sato (1960).
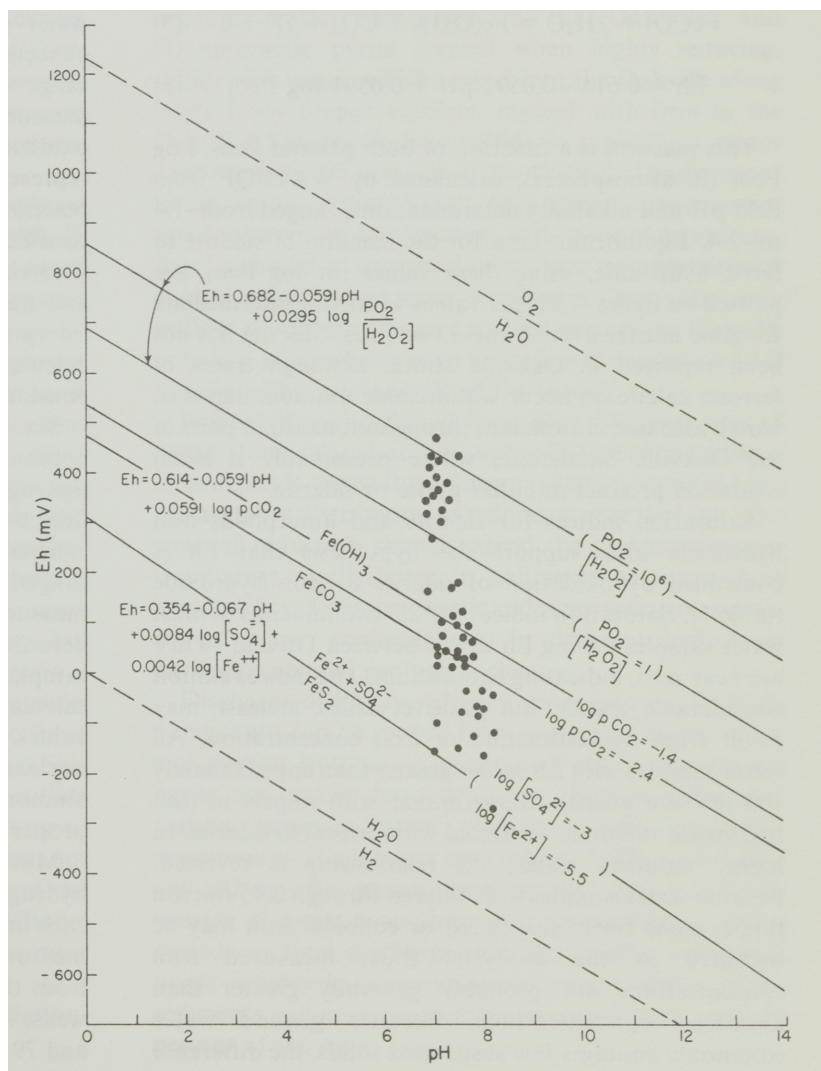
Intermediate Eh Zone

Champ and others (1979) identified the zone between 300 and 100 mV as the iron and manganese zone; however, very few measured Eh values of this study fall within that range. At least one that does, sample 2-2, was from oily water that may have coated the platinum electrode, leading to erroneous results. The Eh level of Oakville water generally drops to approximately 100 mV once dissolved oxygen is consumed. Eh values along lines 1, 7, and 8 illustrate this pattern. Edmunds (1973) observed a very similar relationship between Eh and dissolved oxygen concentrations. Along lines 7 and 8, once Eh drops to approximately 100 mV, wells farther downdip show a progressive, slight decrease in Eh, but never fall below 0 mV. As noted above, many Eh values generally cluster in the range from 110 to 10 mV.

Eh in the intermediate range may be controlled by ferrous-ferric mineral reactions. For example, Sato (1960) proposed that Eh in many sedimentary rocks occurring in the "depth environment" is controlled by the oxidation of siderite to ferric hydroxide:

$$FeCO_3 + 2H_2O = Fe(OH)_3 + CO_2 + H^+ + e^- \quad (5)$$
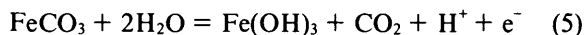
$$Eh = 0.614 - 0.0591 \text{ pH} + 0.0591 \log Pco_2 \quad (6)$$

This reaction is a function of both pH and Pco_2. Log Pco_2 (in atmospheres), calculated by WATEQF from field pH and alkalinity determinations, ranged from -1.4 to -2.4. Equilibrium lines for the reaction of siderite to ferric hydroxide, using these values for log Pco_2, are plotted on figure 4. Eh-pH values within the intermediate Eh zone cluster around these two lines. Siderite has not been reported in Oakville strata, although traces of ferroan calcite do occur within some uranium deposits. Iron hydroxide is abundant throughout oxidized parts of the Oakville Sandstone, where presumably it is an oxidation product of either pyrite or siderite.

Saturation indices for siderite and amorphous iron hydroxide also support the hypothesis that Eh is controlled by oxidation of siderite to iron hydroxide (table 1). Saturation indices for the two minerals in most water samples having Eh values between 110 and 10 mV are near zero, indicating equilibrium. The indices exhibit considerable scatter, but positive values, at least, may result from overestimation of iron concentration. All water samples with Eh values greater than approximately 100 mV are greatly oversaturated with respect to iron hydroxide and undersaturated with respect to siderite. In highly reducing water, the relationship is reversed. Because water samples were filtered through 0.45-micron filters, some finely suspended or colloidal iron may be included in the analysis; thus, measured iron concentrations are probably generally greater than dissolved concentrations. Because ground water commonly contains few suspended solids, the difference between measured and dissolved concentrations may not be great. Nevertheless, saturation indices for the iron-bearing minerals must be interpreted cautiously.

Control of Eh by oxidation of Fe^{2+} (either as siderite, ferroan calcite, or iron-bearing smectite) to Fe^{3+} as iron hydroxide is consistent with observed Eh values and with calculated equilibrium. Useful tests of this conclusion would be (1) to compare Eh values calculated from ferrous and ferric iron concentrations with measured Eh values and (2) to identify ferrous iron minerals in sediments within the intermediate zone.

Both iron and manganese exhibit maximum concentrations in the intermediate Eh zone. Because some iron and manganese may occur in colloidal form, the true dissolved concentrations are uncertain. However, there is no reason to assume that iron occurs preferentially as colloids in any of the water samples, so probably all of the iron values are proportionately high. Thus, although the absolute Eh range in the Oakville differs, the intermediate Eh zone is similar to the iron-manganese zone of Champ and others (1979).

Eh values could be calculated from the nitrate-ammonia couple for six out of the 20 intermediate zone water samples. The other 14 had nitrate or ammonia concentrations below detection levels. Calculated values range from 357 to 287 mV, are much higher than measured values, and resemble values determined for oxidizing water (table 2). These high values probably represent metastable persistence of nitrate; the inorganic reaction is slow, and bacterial mediation is generally considered necessary for reduction of nitrate to ammonia (Morris and Stumm, 1967). The discrepancy in calculated and measured Eh values demonstrates the problems of interpreting Eh measurements. For this reason, Eh values calculated from nitrate and ammonia concentrations are considered unreliable.

Six water samples had measurable hydrogen sulfide concentrations. Three others had detectable odors of hydrogen sulfide, but concentrations were below the detection limit of 0.02 mg/L (app. A). Eh values could be calculated for only four of the six water samples and ranged from -207 to -266 mV. Two water samples with measurable sulfide had sulfate concentrations below detection limits. Maximum Eh values for thése two samples could be about -220 to -250 mV. Thus, all calculated values are very much less than measured values. The significance of the calculated values is unclear, but, like values calculated from the nitrate-ammonia couple, they demonstrate the problems of proper Eh interpretation.

Most of the intermediate Eh water samples containing hydrogen sulfide are the deepest and most reducing on each line. For example, samples 8-5 and 8-6 have low but measurable concentrations of hydrogen sulfide and are from the two deepest wells along line 8. However, two wells, 9-2 and 10-2, are relatively shallow (67 m [220 ft] and 79 m [260 ft], respectively), yet they have the highest

sulfide concentrations among water samples exhibiting intermediate Eh values. Lines 9 and 10 display sharp drops and reversals in Eh; deeper wells along both lines have higher Eh values or no dissolved sulfide or both. The high sulfide concentrations in these water samples may be caused by discharge of sulfide-rich water along fault zones.

Reducing Zone

A reducing zone characterized by measured Eh values of less than -40 mV, and possibly as low as -270 mV, occurs downdip of the intermediate Eh zone along lines 1, 4, 6, 9, and 10. Similar reducing conditions also occur at very shallow depths along lines 5 and 6, where reducing conditions coincide with major uranium districts. All reducing water samples have detectable dissolved hydrogen sulfide.

Nitrate concentrations in many of the reducing water samples (for example, most samples from line 6) are below detection limits, as they should be. However, many others have detectable nitrate concentrations; Eh values calculated from the nitrate-ammonia couples all cluster around 300 mV, which is very much different from measured values. Possibly nitrate is persisting metastably for long periods in the subsurface; oxidation of ammonia to nitrate during sampling is also a possible source, although care was taken to avoid oxidation.

Eh values calculated from the sulfate-sulfide couple are all considerably lower than measured Eh values (table 2); the differences in calculated and measured values range from 220 to 60 mV. Dissolved hydrogen sulfide can coat the platinum electrode, leading to erroneously high Eh readings (Langmuir, 1971). However, the best agreement between measured and calculated Eh values occurs in water samples having the highest sulfide concentrations (for example, samples 2-4 and 5-3). Because many reactions involving trace elements are Eh dependent, understanding the significance of measured and calculated Eh in the Oakville reducing zone is necessary. Equilibrium calculations for the reduced uranium silicate, coffinite, suggest that measured Eh is more accurate. Formation of coffinite is Eh dependent but independent of dissolved sulfide concentration. Consequently, if sulfide is coating the platinum electrode, producing unrealistically high Eh readings, coffinite saturation indices would decrease with increasing sulfide concentration. Water samples having the highest sulfide concentrations would appear to be most undersaturated with respect to coffinite. In fact, this relationship does not occur (fig. 5). In general, sulfide-bearing water of the Oakville is nearly in equilibrium with respect to coffinite; waters with the highest sulfide concentrations are most oversaturated. Coffinite equilibrium implies that measured Eh is a realistic appraisal of oxidation-reduction status of the reducing water.

The major control of Eh potential in the reducing zone is probably oxidation of pyrite. Pyrite is known to be a major constituent of the Oakville, occurring both in reduced sediment surrounding uranium districts and elsewhere in deeper parts of the aquifer. Most measured Eh values (table 2) are greater than Eh values predicted by the reaction

$$FeS_2 + 8H_2O = Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^- \quad (7)$$
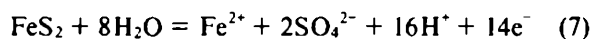
$$Eh = 0.345 - 0.067 \text{ pH} + 0.0084 \log [SO_4^{2-}] + 0.0042 \log [Fe^{2+}] \quad (8)$$

The predicted Eh is a function of the activities of sulfate and ferrous iron, but, even assuming very high activities, predicted Eh values are well below those observed. Also, all sulfide-bearing water samples are highly oversaturated with respect to pyrite, a relationship also found in Oakville water by Potter and others (1979). Amorphous iron sulfide is commonly near equilibrium (table 1), but its occurrence in the Oakville Sandstone is speculative.

Two possible sources of pyrite (or marcasite) are (1) syngenetic species formed by reduction of sulfate by organic matter deposited in the Oakville, and (2) epigenetic pyrite formed when highly reducing, sulfide-rich water, which leaked into the Oakville along faults from deeper aquifers, reacted with iron in the Oakville. Syngenetic iron sulfide is typically a minor constituent (<0.5 percent) of the Oakville Sandstone of South Texas. It should form only where organic matter was not destroyed by oxidation at the time of deposition. Also, it should be preserved only where postdepositional oxidation by ground water is unlikely. Thus, syngenetic sulfides should be restricted to deep parts of the Oakville or to low-permeability parts at shallower depths; well 1-7 may be within an example of the former.

Epigenetic pyrite should form near discharge sites of deeper, fault-related, sulfidic water. Extent of the reduced zone depends on the flux of deep, reducing water and the permeability distribution of sediments near the fault. The zone of reduction should extend the greatest distance from areas of discharge in sediments having highest permeability. Thus, epigenetic and syngenetic iron sulfide should occur predominantly in different hydrologic environments and geologic facies.

Discharge of highly reducing water into the Oakville along faults can be proved from analysis of stable sulfur and carbon isotopes in pyrite and calcite. Syngenetic pyrite and calcite have distinctly different sulfur and carbon isotopic ratios compared with epigenetic counterparts (Goldhaber and others, 1978). Goldhaber and others also present evidence for more than one episode of pyrite formation, each representing different periods of fluid discharge into the aquifer. Epigenetic pyrite commonly composes up to several percent of the sediments and in rare circumstances forms as much as 40 percent of the rock.
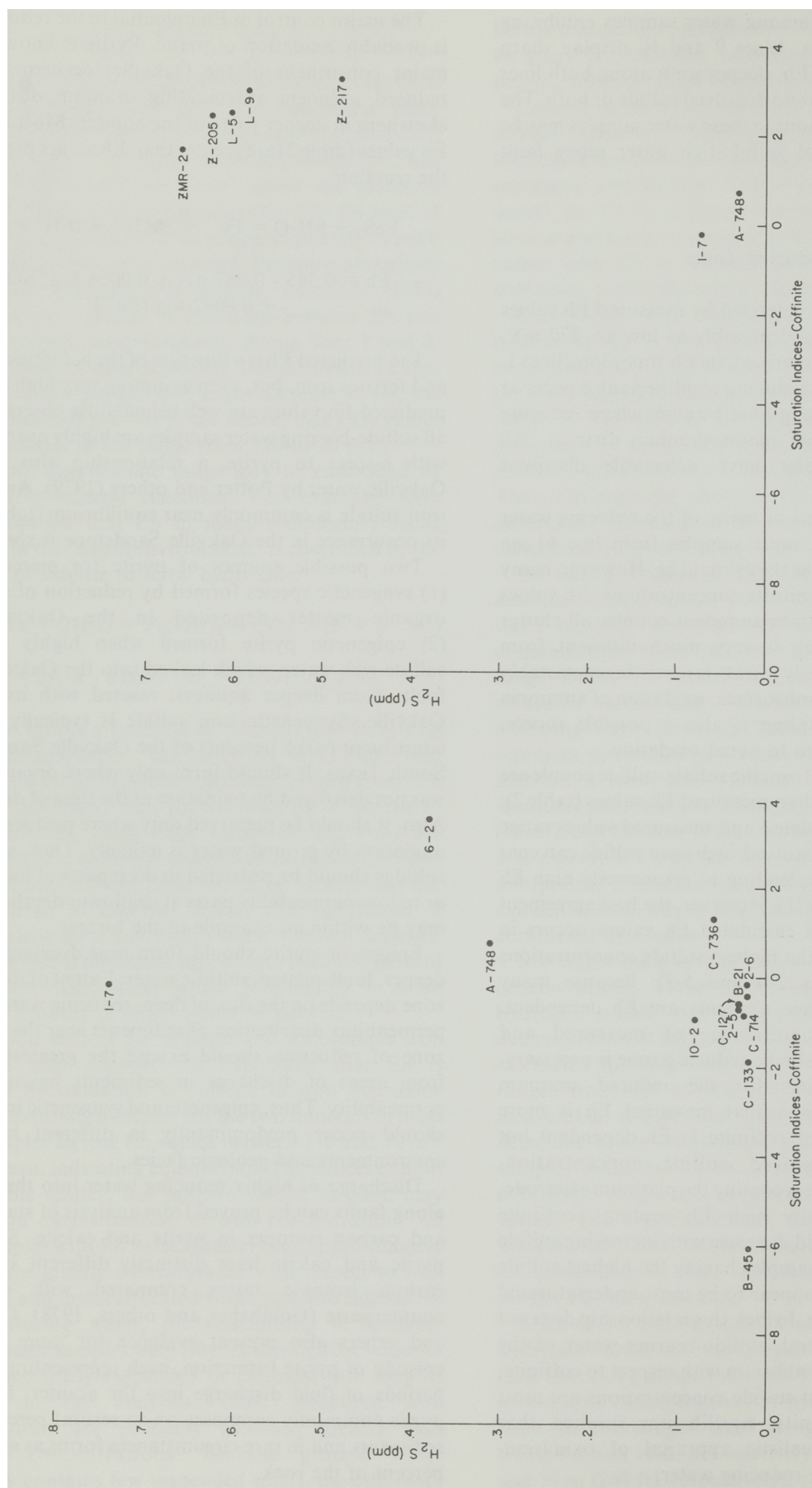
Figure 5. Plot of coffinite (USiO₄) saturation indices versus dissolved H₂S, in ppm, for selected Oakville water samples. (A) H₂S = 0 to 1 ppm; (B) H₂S = 0 to 10 ppm.

Discharge of water into the Oakville aquifer is known to have occurred along faults in the Ray Point and George West uranium districts. Well 5-3 within the Ray Point district has the lowest Eh value and highest hydrogen sulfide concentration encountered in the Oakville. Line 3 crosses the George West district but does not encounter the extremely low Eh values that may exist locally. However, water sampled in the more detailed study of the George West district, discussed below, does exhibit low Eh values. Also, the presence of reducing water at very shallow depth, reversals in the Eh gradient, and the presence of faults show that reduction has occurred along line 6. Potter and others (1979) measured Eh potentials within a uranium deposit near line 6, using techniques similar to those used in this study. Measured Eh values ranged from -70 to -140 mV, in good agreement with our results.

Similar discharge of sulfidic water into the aquifer is indicated along lines 9 and 10. Samples 9-2 and 10-2 exhibit intermediate Eh values but greater hydrogen sulfide concentrations than do most intermediate Eh water samples. Both samples are from shallow depths and reversals in the Eh gradient characterize both lines. Both wells are near fault zones mapped in underlying Cretaceous strata, but extension of the faults upward into the Oakville Sandstone is uncertain. An alternative explanation is that wells 9-2 and 10-2 are in low-permeability parts of the Oakville aquifer where syngenetic reductants have been preserved. Water from well 10-2 is low in total dissolved solids and contains low chloride concentrations, especially in comparison to sample 10-1, which has an Eh value of 360 mV but much higher concentrations of chloride and dissolved solids. The Oakville Sandstone near well 10-1 probably does not have low permeability. The Oakville there may have experienced reduction by deeper water, but the deep water has been subsequently flushed out and partly reoxidized by normal, oxidizing Oakville water.

Sample 9-2 contains high total dissolved solids and has a relatively high chloride concentration. The water composition may reflect the composition of deep reducing water that has been partially oxidized to an intermediate Eh. Alternatively, both the intermediate Eh and high dissolved solids could indicate that well 9-2 is in a low-permeability, unoxidized part of the Oakville aquifer.

Summary of Oxidation-Reduction Patterns

In summary, there appear to be three zones, each exhibiting a different redox potential. These zones include (1) an oxidizing zone with Eh values greater than 300 mV, controlled by the presence of measurable concentrations of dissolved oxygen, (2) an intermediate zone with Eh values between 110 and 10 mV, probably controlled by ferrous-ferric mineral reactions, and (3) a reducing zone with Eh values less than -40 mV, probably controlled by the presence of FeS_2. The basic processes creating these zones are the influx of oxygen-bearing recharge water, the consumption of oxygen and other oxidants in the flow path, and the influx of sulfidic, reducing water from deeper formations. The exact reactions involved are imperfectly known, and equilibrium may not be attained in most cases. Reactions involving NH_3^+ and NO_3^-, and H_2S and SO_4^{2-}, are clearly out of equilibrium; Eh values calculated from these couples are meaningless. Measured Eh is the best available indicator of redox potential.

The overall geometry of oxidizing and reducing water and the distribution of pyrite depend on the initial abundance of syngenetic pyrite, the amount of pyrite formed by one or more discharges into the aquifer of deep reducing water, and the extent of continuing oxidation by recharging ground water. In places, pyrite-rich environments along faults are preserved only as small pods isolated by oxidizing ground water.

DISTRIBUTION OF TRACE ELEMENTS

Uranium, molybdenum, arsenic, and selenium exhibit similar geochemical behavior; their occurrence together in epigenetic uranium deposits is one indicator of their similarity. All of these elements exist in two or more common oxidation states. In oxidized valence states, molybdenum, arsenic, and selenium can form soluble oxyanions in water (for example, molybdate $[MoO_4^{2-}]$, arsenate $[AsO_4^{3-}]$, and selenite $[SeO_3^{2-}]$). Uranium in the oxidized 6+ valence forms the uranyl ion (UO_2^{2+}), which commonly forms negatively charged complexes with inorganic ligands such as carbonate or phosphate. Reduction from the higher to lower valences leads to formation of relatively insoluble minerals, including sulfides (arsenopyrite, orpiment, molybdenite), oxides (uraninite, ilsemannite), silicates (coffinite), or the native elements (arsenic, selenium). This reduction is the general basis for formation of uranium ore deposits and accumulation of molybdenum, arsenic, and selenium with the uranium. Some other elements, such as vanadium, behave similarly but are not considered here because they are not known to be concentrated in South Texas deposits.

Adsorption and mineral precipitation control solubility of the elements. In general, oxidized valence minerals of the elements are highly soluble, and do not significantly limit concentrations in oxidizing water, except under unusual circumstances. Adsorption by a variety of natural colloids, especially amorphous iron hydroxide, probably determines concentrations and mobility in oxidizing ground water. Equilibrium with insoluble reduced minerals should determine the concentrations of the trace elements in reducing water.

Precipitation

Uranium

Because of the economic significance of uranium, much is known about its geochemistry. Recently, Langmuir (1978) reviewed thermodynamic data for uranium, considerably revising ideas about uranium migration in ground water. Eh-pH diagrams (fig. 6) are from Langmuir (1978), and Galloway and Kaiser (1980). They show dominant uranium species but not necessarily all possible or important complexes. Historically, emphasis has been on the reduction of U^{6+} to U^{4+} to form uraninite (UO_2) or coffinite ($USiO_4$), the primary ore minerals of most uranium deposits. Both minerals occur in Oakville deposits; coffinite is more common.

In oxidizing water, uranium exists as the UO_2^{2+} ion and is almost entirely complexed with various inorganic ligands. Which ligand is dominant depends upon pH and the concentration of the different ligands. In a pH range from 4 to 10 and with typical ground-water compositions, complexes with phosphate and carbonate species are dominant.

A wide variety of U^{6+} minerals is found around oxidized uranium deposits; several, including autinite [$Ca(UO_2)_2(PO_4)_2 \cdot 10H_2O$] and uranophane [$Ca(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$], are common in South Texas. Most have high solubilities and do not significantly limit uranium concentrations in oxidizing water. Also, the minerals generally require high concentrations of other constituents such as phosphate or silica. South Texas uranium deposits are notably deficient in vanadium, and carnotite has not been observed. Therefore, equilibrium with carnotite or other uranium vanadates should not control uranium concentrations.

Reduction of uranium-bearing water can cause precipitation of the U^{4+} minerals, uraninite and coffinite, at nearly equivalent Eh (fig. 6). Silica concentrations determine whether uraninite or coffinite forms. Langmuir (1978) and Galloway and Kaiser (1980) suggest that silica concentrations greater than approximately 60 mg/L are necessary to form coffinite in preference to uraninite. Amorphous varieties of the two minerals may form initially by reduction to Eh values well below those necessary to precipitate the crystalline varieties (fig. 6). Possible reductants include dissolved sulfide, pyrite, dissolved ferrous iron, or organic matter. The solubility of the reduced uranium minerals is so low that uranium should be undetectable in a solution that is in equilibrium with the minerals. However, both dissolved carbonate and phosphate greatly increase uraninite solubility through formation of uranium carbonate or phosphate complexes.

Molybdenum

The Eh-pH diagrams in figure 7 have been adapted from Kaback (1977). Because little is known of molybdenum (or selenium or arsenic) complexing, the actual species occurring in water may be different from those shown in figure 7. In oxidizing water, molybdenum occurs as MoO_4^{2-} or $HMoO_4^-$ ions. Most molybdate minerals are highly soluble. A uranylmolybdate, iriginite, has been found in oxidized uranium deposits in South Texas (Bunker and MacKallor, 1973). Several other molybdate minerals also could form in molybdenum-rich environments; these include wulfenite ($PbMoO_4$), which is the most common molybdenum mineral after molybdenite (MoS_2) (Palache and others, 1944), and powellite ($CaMoO_4$). Precipitation of wulfenite requires high lead concentrations. Although lead concentrations have not been determined in this study, lead is not concentrated in uranium deposits, and, given the high-pH waters characteristic of the Oakville aquifer, concentrations should be especially low. Powellite is more likely to form, but only around oxidized uranium deposits. Molybdenum concentrations would have to be near the mg/L level to form either mineral.

Ferrimolybdite is stable at low pH (between 2 and 4) and high Eh (approximately 700 mV) (Kaback, 1977). It could form around oxidized molybdenum and sulfide-rich uranium deposits or in an in situ leach operation where an acid leach is used. However, ferrimolybdite is not stable in normal ground water and should not form around a leach mine where an alkaline leach is used. Ferrimolybdite has not been reported in South Texas.

Reduction of molybdenum-bearing ground water can lead to precipitation of molybdenite (MoS_2) or ilsemannite (Mo_3O_8). Molybdenite forms only at very low Eh, approximately -200 mV at pH 7.5, which is well below that required for ilsemannite. However, at molybdenum concentrations typical of normal ground water, ilsemannite forms only at low pH (fig. 7A). At higher concentrations, the ilsemannite field expands to higher pH (fig. 7B). Thus, at low concentrations in normal or alkaline water, ilsemannite should be unstable, and reduction to very low Eh would be necessary to precipitate molybdenite and remove molybdenum from solution. In acidic water or at higher concentrations of molybdenum, ilsemannite can precipitate at higher Eh. Because molybdenite and ilsemannite have low solubilities, concentrations of molybdenum in equilibrium with them should be low, well below the detection limit of 0.2 mg/L.

Molybdenum-bearing minerals have not been identified in South Texas deposits, except for ilsemannite, which occurs in one deposit in the Whitsett Formation (Bunker and MacKallor, 1973) and umohoite,
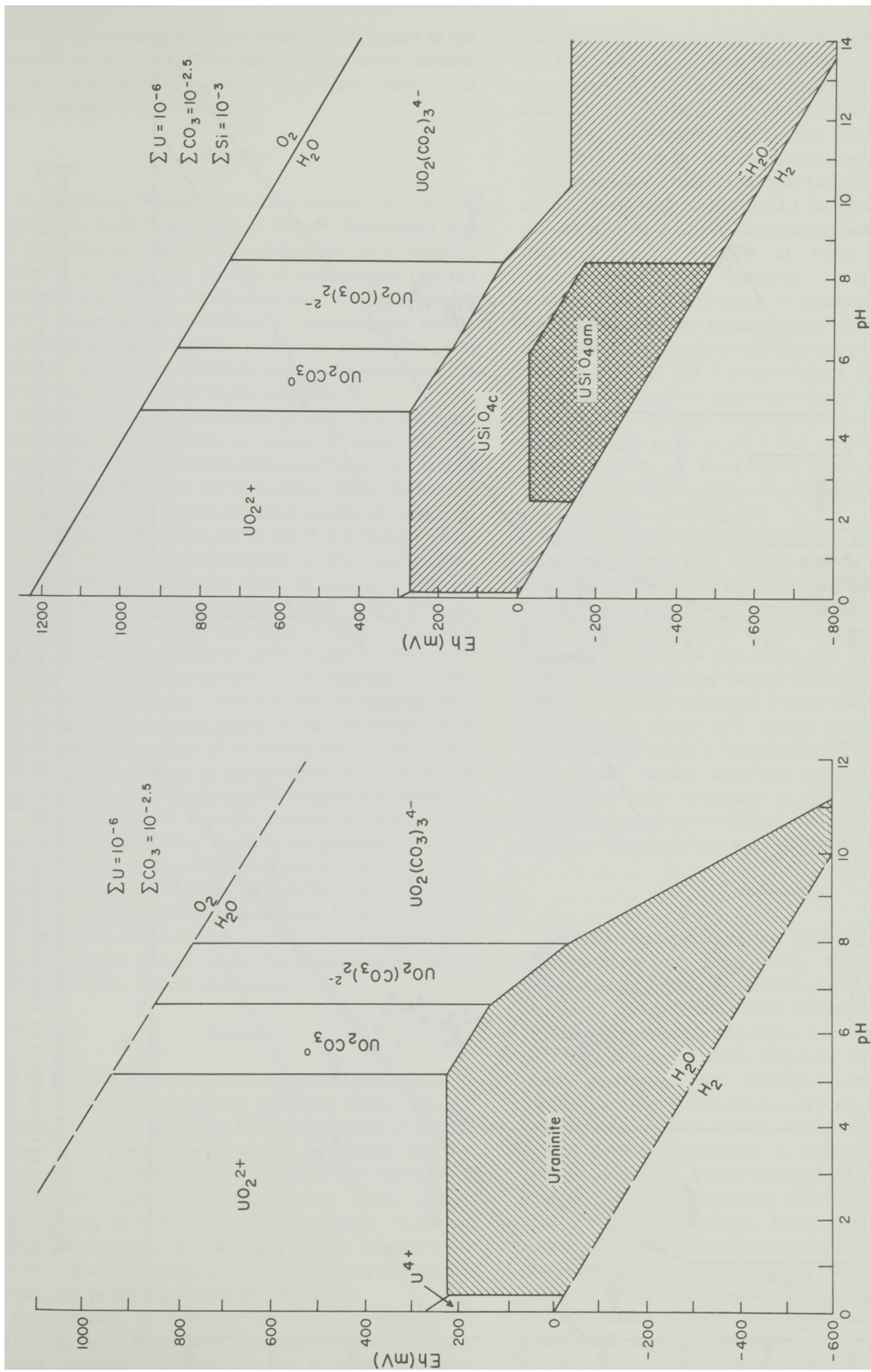
Figure 6. Eh-pH diagrams for uranium species at 25° C, 1 atm. (A) U-CO_2 system; P$co_2 = 10^{-2}$ atm. Crystalline uraninite-solution boundary shown for dissolved uranium = 10^{-6} M (from Langmuir, 1978). (B) U-CO_2-SiO_2 system; total carbonate = 200 mg/L = $10^{-2.5}$ M; total silica as $H_4SiO_4 = 60$ mg/L = 10^{-3} M; total uranium = 240 μg/L = 10^{-6} M. Stability fields of both crystalline and amorphous USiO$_4$ shown (from Galloway and Kaiser, 1980).
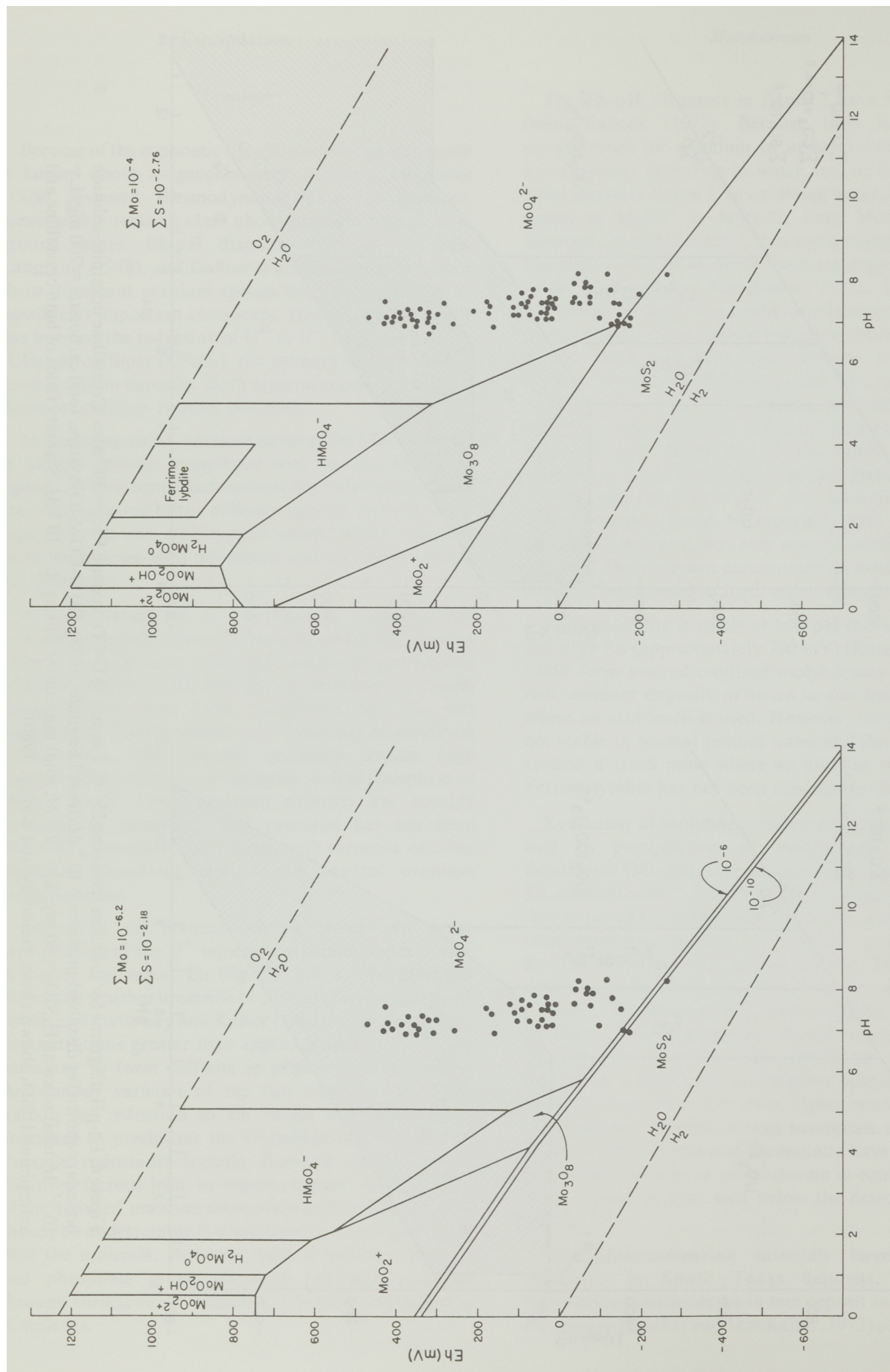
Figure 7. Eh-pH diagrams for molybdenum species at 25° C, 1 atm, adapted from Kaback (1977). Dots indicate measured Eh and pH values of this study. (A) Total molybdenum = $10^{-6.2}$ M; total sulfur = $10^{-2.18}$ M. MoS_2 boundary shown for 10^{-6} M and 10^{-10} M dissolved molybdenum. (B) Total molybdenum = 10^{-4} M; total sulfur = $10^{-2.76}$ M.

a rare uranium-molybdenum oxide, which occurs in the Oakville in the Ray Point district. The latter mineral should not generally be a significant control of molybdenum concentrations.

Selenium

In oxidizing water, selenium occurs as the 4+ oxyanions, SeO_3^{2-} (selenite) or $HSeO_3^-$ (biselenite) (fig. 8). Existence of a still more oxidized 6+ form, selenate (SeO_4^{2-}), is less certain. Studies of soils suggest that the selenate form may be common in soils, whereas Howard (1977) suggests that oxidation to selenate may not be possible because of kinetic problems. Precipitation of selenium minerals in oxidizing water is unlikely because all selenite minerals are highly soluble.

Reduction of selenium-bearing ground water can cause precipitation of selenium as native selenium (Se), as ferroselite ($FeSe_2$), or as selenium substituted for sulfur in pyrite (FeS_2) (Howard, 1977; Lisitsin, 1969). Reduction of selenite to native selenium occurs at relatively high Eh, approximately 150 to 80 mV at pH 7 to 8 (fig. 8). Thus, selenium commonly accumulates at the most upflow (updip) and least reduced parts of uranium deposits (Harshman, 1974; Galloway and Kaiser, 1980). Because native selenium is highly insoluble, it seems likely that nearly all selenium would be precipitated before the Eh stability fields of either ferroselite or selenium in pyrite are reached. However, Howard (1977) suggests that consumption of reducing agents in the rock would allow selenium-bearing water of moderate Eh to enter more reduced zones, leading to precipitation of ferroselite or selenium in pyrite. Harshman (1974) states that selenium in various uranium deposits occurs as both native selenium and ferroselite. Possibly the presence of a very steep Eh gradient and kinetic delays would allow some selenite to enter the stability fields of ferroselite or pyrite before precipitation as native selenium. Kinetic problems are important because high concentrations of dissolved selenium might persist under Eh conditions in which native selenium should precipitate.

Arsenic

The behavior of arsenic in water is complex because it has four naturally occurring oxidation states. The 5+ (arsenate) and 3+ (arsenite) forms are soluble to low Eh values over a wide range of pH conditions (fig. 9). Ferguson and Gavis (1972) attribute the well-known toxicity of arsenic to the 3+ valence. Thus, arsenic toxicity may be a function of its speciation. However, little is known about complexing of arsenic. Arsenic in the lowest valence (3-) exists as arsenic hydrite at very low Eh values and is not significant for this study.

Precipitation of arsenate or arsenite minerals in oxidizing water is unlikely, with the possible exception, under certain conditions, of barium arsenate

$[Ba_3(AsO_4)_2]$ (Wagemann, 1978). Barium arsenate (pK = -50.1) is much less soluble than other arsenates. Barium concentrations were not determined in this study; thus, to evaluate the significance of barium arsenate, it is necessary to assume that barite ($BaSO_4$) solubility controls barium concentrations. Because the concentrations of sulfate in most Oakville water samples are relatively high (>100 mg/L), barium concentrations should be low, and barium arsenate should be highly undersaturated except at very high arsenic concentrations. For example, water with sulfate concentrations of 600 mg/L in equilibrium with barite will have a barium concentration of only 3.8 μg/L. Dissolved total arsenic would have to be 418 μg/L at pH 8 and 10 mg/L at pH 7 to precipitate barium arsenate. Water with a sulfate concentration of 50 mg/L would have 46 μg/L barium. Total dissolved arsenic would be limited to 225 μg/L at pH 7 and only 9 μg/L at pH 8. Thus, solubility of $Ba_3(AsO_4)_2$ could be a significant factor controlling arsenic concentrations at low sulfate concentrations and high pH.

Under mildly reducing conditions, arsenic occurs as soluble arsenious acid species (fig. 9). At sufficiently reducing conditions so that sulfide is present, orpiment (As_2S_3) and realgar (AsS) are stable at low to moderate pH. However, there is some disagreement over the relative solubility of the solid and dissolved arsenic sulfides. Ferguson and Gavis (1972) state that the solid sulfides are stable below pH 5 only, and, under reducing conditions at higher pH, arsenic occurs as dissolved arsenic sulfide (AsS_2^-). Wagemann (1978) states that less than 2×10^{-7} molar dissolved sulfide can occur in equilibrium with orpiment at pH 7 or less. Under extremely reducing conditions, native arsenic is stable; such low Eh conditions were not found in this study.

Conclusion

The role that precipitation plays in controlling the concentrations of some trace elements (uranium, selenium, molybdenum, and arsenic) in oxidizing water should be insignificant except immediately adjacent to oxidized deposits resulting either from natural oxidation or from mining. In these instances oxidized minerals could precipitate, but concentrations of the trace elements in solution would remain high. Reduction leads to precipitation of a variety of minerals; precipitation should limit concentrations to values below detection limits of this study. At intermediate pH, reduction occurs around 130 mV for selenium, 100 mV for uranium, and -200 mV for molybdenum. Thus, mineral deposits are commonly zoned with selenium concentrated upflow and molybdenum concentrated downflow from the zone of uranium accumulation. The behavior of arsenic is less well established; its location in this zonation is uncertain. Price (1980) suggests that arsenic is restricted to deposits containing abundant carbonaceous matter.
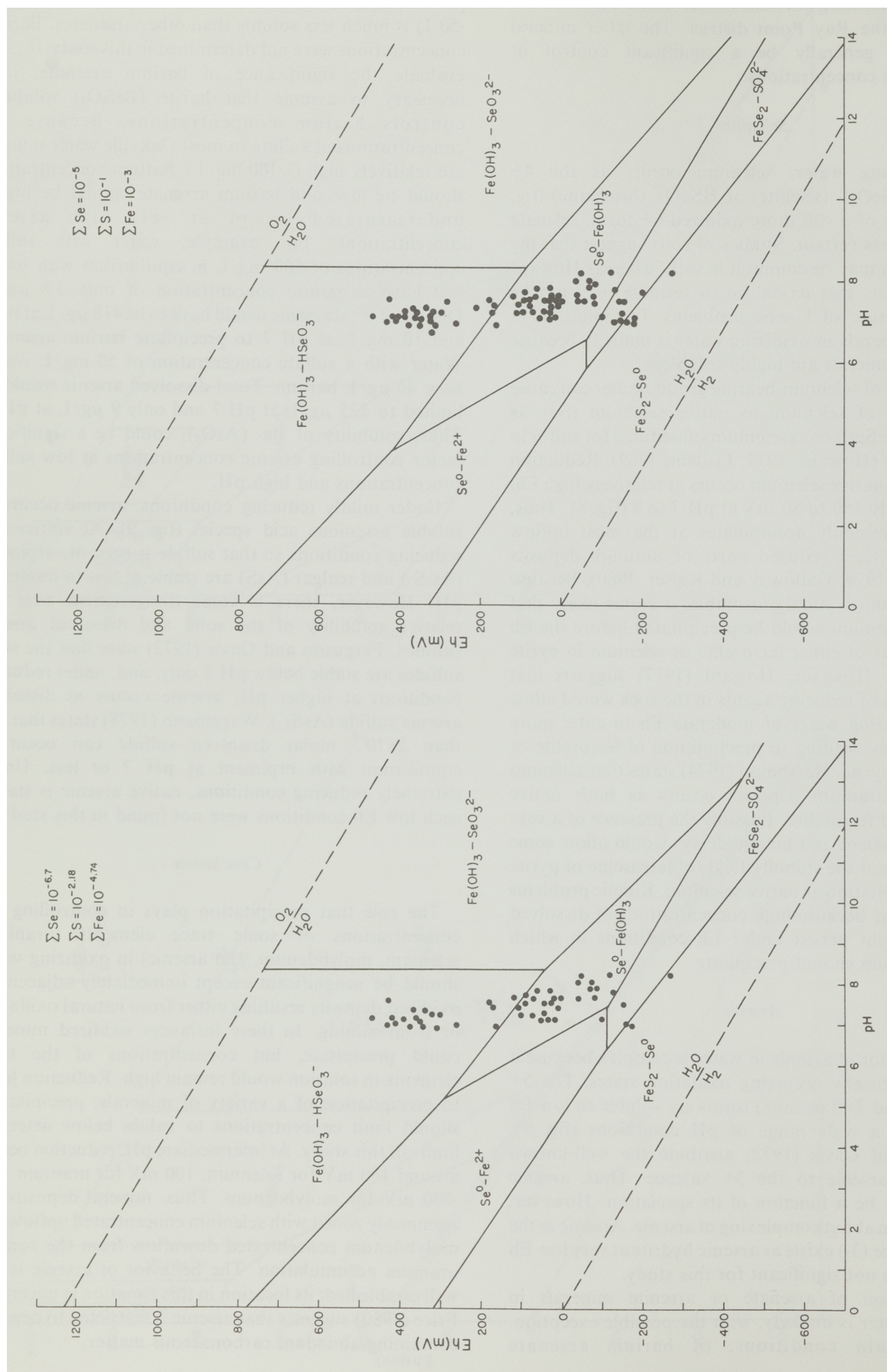
Figure 8. Eh-pH diagrams for selenium species at 25° C, 1 atm, adapted from Howard (1978). Dots indicate measured Eh and pH values of this study. (A) Total selenium = $10^{-6.7}$ M; total sulfur = $10^{-2.18}$ M; total iron = $10^{-4.74}$ M. (B) Total selenium = 10^{-5} M; total sulfur = 10^{-1} M; total iron = 10^{-3} M.

Adsorption

In oxidizing ground water, adsorption probably influences trace element concentrations far more than mineral precipitation does. Studies of adsorption of uranium (Szalay, 1964; Doi and others, 1975; Langmuir, 1978), molybdenum (Jones, 1957; Reisenauer and others, 1962; Hingston and others, 1972; Kaback, 1977), selenium (Howard, 1972, 1977; Hingston and others, 1968, 1972), and arsenic (Ferguson and Gavis, 1972; Bacso and others, 1978; Gupta and Chen, 1978; Gulens and others, 1979; and Holm and others, 1979) show that these elements are strongly adsorbed by a variety of common materials. Both the effectiveness of adsorption and the equilibrium concentrations of elements in solution in contact with the adsorbents are functions of the element and its speciation (particularly complexing), surface properties of the adsorbent, and composition, pH, and temperature of the solution.

Studies of adsorption of uranium, molybdenum, selenium, and arsenic show that they behave in a broadly similar manner. Amorphous ferric hydroxides (variously termed iron hydroxides, hydrous ferric oxides, or goethite) are the best adsorbers; other oxides and clay minerals are also effective. All four elements show maximum adsorption at acidic or intermediate pH; adsorption decreases with an increase in pH (fig. 10). For example, uranium adsorption decreases rapidly above approximately pH 9 (Langmuir, 1978) and molybdenum is nearly completely desorbed at pH 10 (Hingston and others, 1972). Complexing clearly decreases adsorption of uranium and probably the other three elements, but only the effect on uranium has been evaluated. Langmuir (1978) showed that an increase in P_{CO_2} (increased carbonate complexing) decreases adsorption at high pH (fig. 10), whereas increases in sulfate or fluoride concentrations decrease adsorption at low pH. Several studies also indicated that adsorption can be limited by saturation.

Although complexing of elements other than uranium has not been evaluated, speciation of the elements does influence adsorption. For example, Howard (1977) states that selenite (Se^{4+}) is strongly adsorbed by ferric hydroxides whereas selenate (Se^{6+}) is not. Also Gulens and others (1979) found greater adsorption of As^{5+} than As^{3+} by ferric hydroxide in oxidizing neutral water.

We have evaluated adsorption controls on solubility only in a qualitative way. Although there have been recent
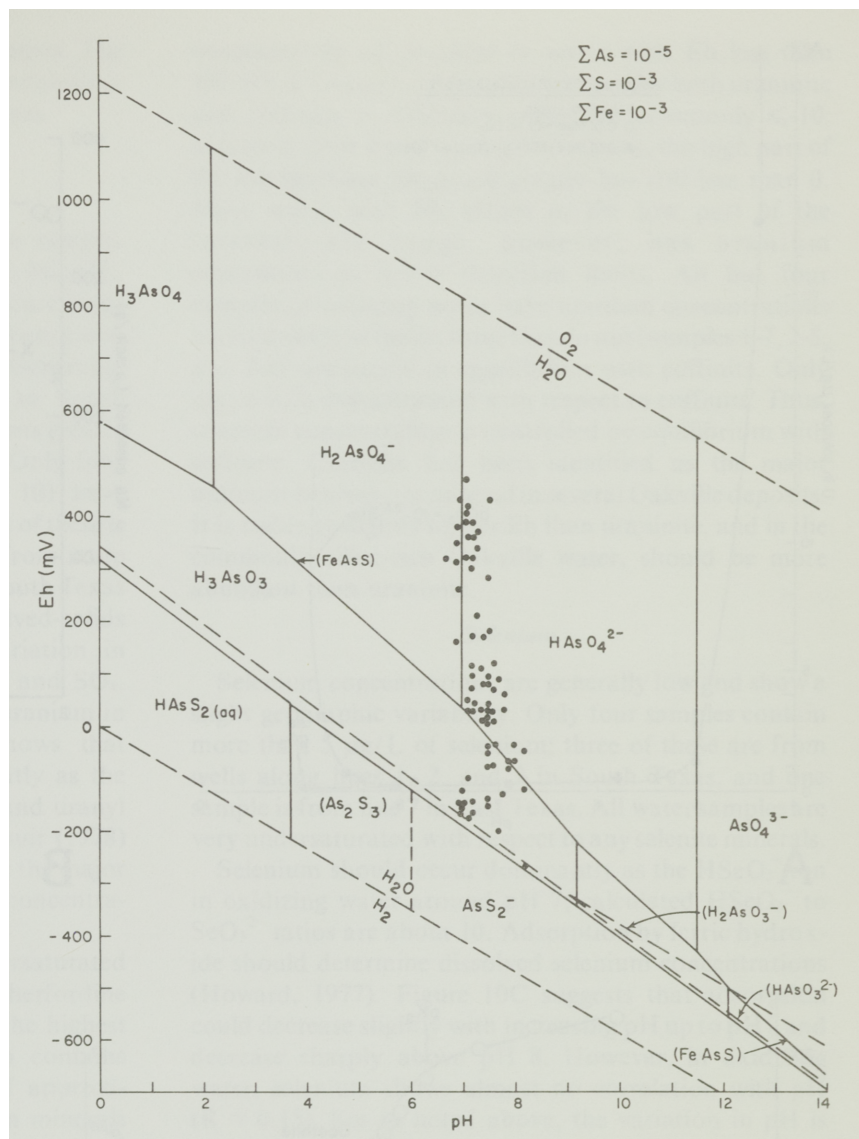
Figure 9. Eh-pH diagram for arsenic species at 25° C, 1 atm; total arsenic = 10^{-5} M; total sulfur = 10^{-3} M; total iron = 10^{-3} M. Dots indicate measured Eh and pH values of this study.

attempts to determine adsorption quantitatively there were too many constraints for such an approach in this study.

Implications of Regional Distribution

Adsorption in oxidizing water, and reduction and precipitation in reducing water are the major processes controlling trace element concentrations predicted from theoretical and experimental data. Evaluating the effectiveness of these processes requires an understanding of how well they operate in natural systems. We analyzed the effectiveness of these processes by (1) examining elemental concentrations regionally throughout the Oakville Sandstone, and (2) examining elemental concentrations immediately adjacent to areas of uranium mineralization, where active oxidation of deposits may

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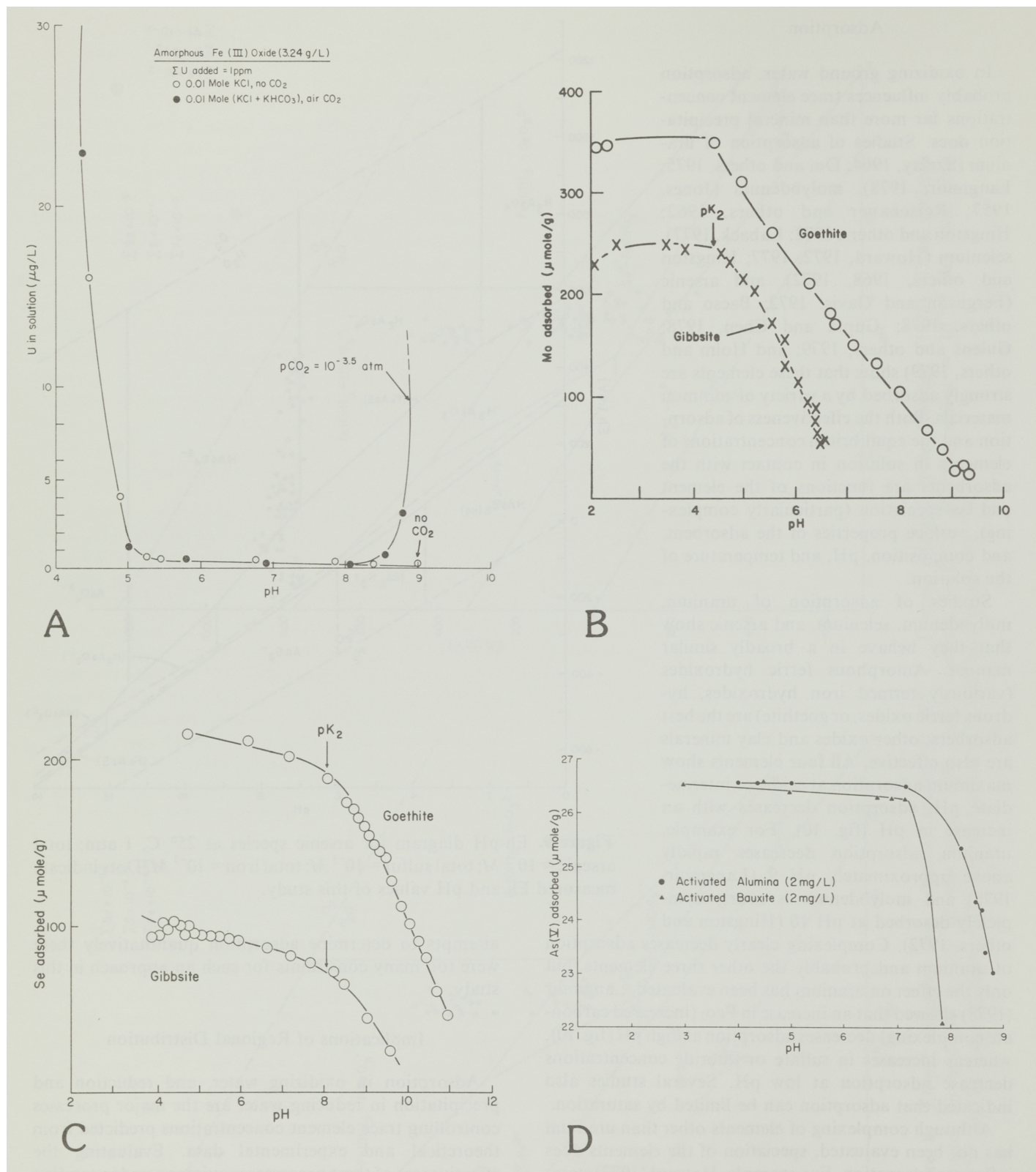
Figure 10. Adsorption characteristics of trace elements. (A) Adsorption of uranyl ion onto amorphous ferric hydroxide as a function of pH and CO_2 content. Plotted points are residual uranium in solution initially containing 1 mg/L (from Langmuir, 1978). (B) Adsorption of molybdenum onto goethite and gibbsite as a function of pH (from Hingston and others, 1972). (C) Adsorption of selenium onto goethite and gibbsite as a function of pH (from Hingston and others, 1972). (D) Adsorption of arsenic onto activated alumina and activated bauxite as a function of pH (from Gupta and Chen, 1978).

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have led to natural dispersal of the trace elements. The regional analysis is discussed here; the local analysis is discussed in sections on the two producing areas.

Uranium

Uranium concentrations in Oakville water samples range from below detection limits (0.2 μg/L) to 99 μg/L. However, only four water samples have concentrations greater than 10 μg/L, and the highest value is from a well just updip from the Ray Point mining area. Generally, high uranium concentrations are restricted to South Texas; the four water samples with concentrations greater than 10 μg/L are from wells in that area. Only four samples from East Texas (lines 7, 8, 9, 10) have concentrations greater than 1 μg/L; the highest of these is only 6.7 μg/L. These differences may result from more abundant or more active uranium sources in South Texas or from greater complexing in the higher-dissolved-solids water of South Texas. However, most variation in composition of dissolved solids involves Cl and SO_4, which do not form important complexes of uranium in these waters. Speciation by WATEQF shows that uranium in oxidizing water occurs dominantly as the uranyl dicarbonate ion; uranyl tricarbonate and uranyl biphosphate are of lesser importance. Langmuir (1978) suggested that phosphate complexes should be the major form in most ground water, but phosphate concentrations in Oakville water samples are low.

All Oakville water samples are highly undersaturated with respect to any U^{6+} minerals. Rutherfordine (UO_2CO_3) and schoepite ($UO_3 \cdot 2H_2O$) show the highest saturation indices; even sample 5-1, which contains 99 μg/L uranium, has saturation indices of approximately -4. Precipitation of oxidized uranium minerals does not affect uranium concentrations in water.

Adsorption should control uranium concentrations in oxidizing water but the process is difficult to evaluate quantitatively. Adsorption should decrease with increasing pH, so uranium concentrations could be expected to increase with higher pH. In fact, uranium in oxidizing water samples shows a very slight negative correlation with pH (R = -0.26). However, pH varies only slightly from 6.7 to 7.6. Probably most of the variability in uranium concentrations in oxidizing water reflects differences in source availability. Adsorption may complement the source variation.

Reduction of U^{6+} to U^{4+} occurs within the intermediate Eh range of Oakville water. Thus, reduction to intermediate or lower Eh levels should lead to uraninite or coffinite precipitation and removal of most dissolved uranium. Examination of table 3 and figure 6 shows that actual behavior closely follows this predicted behavior. Uranium concentrations clearly vary with Eh, although the correlation is not particularly good (R = 0.29). High uranium concentrations are restricted to water with Eh values greater than approximately 180 mV. The highest

concentration of uranium in water with Eh less than 180 mV is 1.4 μg/L. Saturation indices for both uraninite and coffinite in oxidizing water are commonly $\leqslant$-10; indices in most water having Eh values in the high part of the intermediate range are greater but still less than 0. Most water with Eh values in the low part of the intermediate range, however, has uranium concentrations below detection limits. All but four samples of reducing water have uranium concentrations below detection limits; three that do not (samples 1-7, 2-5, and 2-6) are nearly in equilibrium with coffinite. Only one, 6-2, is oversaturated with respect to coffinite. Thus, uranium concentration is controlled by equilibrium with coffinite. Coffinite has been identified as the major uranium-bearing ore mineral in several Oakville deposits. It is stable at slightly higher Eh than uraninite, and in the commonly silica-rich Oakville water, should be more abundant than uraninite.

Selenium

Selenium concentrations are generally low and show a slight geographic variability. Only four samples contain more than 5 μg/L of selenium; three of these are from wells along lines 1, 2, and 3 in South Texas, and one sample is from line 7 in East Texas. All water samples are very undersaturated with respect to any selenite minerals.

Selenium should occur dominantly as the $HSeO_3^-$ ion in oxidizing water around pH 7; calculated $HSeO_3^-$ to SeO_3^{2-} ratios are about 10. Adsorption by ferric hydroxide should determine dissolved selenium concentrations (Howard, 1977). Figure 10C suggests that adsorption could decrease slightly with increasing pH up to pH 8 and decrease sharply above pH 8. However, in oxidizing water, selenium shows almost no correlation with pH (R = 0.15), but as noted above, the variation in pH is small.

Native selenium is stable at relatively high Eh, so that reduction from oxidizing water to intermediate Eh water should be sufficient to precipitate native selenium (fig. 8). However, neither selenium concentrations nor saturation indices of native selenium demonstrate this relationship (table 3). In oxidizing water, native selenium is several orders of magnitude undersaturated; in most intermediate Eh or reducing water, native selenium is very oversaturated. Detectable concentrations of selenium remain in both intermediate Eh and reducing water.

Selenium does show some correlation with Eh (R = 0.33), but the concentrations show a relatively uniform decrease with decrease in Eh potential. No sharp drop in concentration exists between oxidizing and intermediate Eh values, as would be expected if native selenium were precipitated. Selenium concentrations are below detection in many water samples exhibiting various Eh values.

There are several possible explanations for the pattern of selenium concentrations and the apparent oversaturation of native selenium in Oakville water:

Table 3. Saturation indices (log IAP/KT) for trace element minerals (regional wells).*

Sample	Uranium		Molybdenum			Selenium		Arsenic		
	Uraninite (UO₂)	Coffinite (USiO₄)	Molybdenite (MoS₂)¹	Molybdenite (MoS₂)²	Ilsemannite (Mo₃O₈)	Selenium (Se)	Ferroselite (FeSe₂)	Orpiment (As₂S₃)	Realgar (AsS)	Arsenopyrite (FeAsS)
1-1	•	•	•	—	•	•	•	—	—	—
1-3	•	•	•	—	•	•	•	<—	<—	<—
1-4	-6.4	-5.2	•	—	•	-0.8	•	—	—	—
1-7	-1.1	-0.2	•	1.6	•	4.4	7.6	1.3	-2.6	•
2-2	-6.9	-5.8	•	—	•	-4.7	•	—	—	—
2-3	-9.8	-8.5	•	—	•	•	•	—	—	—
2-4	<	<	•	6.6	•	2.3	4.8	6.6	0.8	-8.9
2-5	-1.7	-0.7	•	-2.3	•	5.8	8.0	-4.3	-5.8	•
2-6	-1.1	-0.1	•	-0.9	•	4.8	7.1	-3.6	-4.7	•
3-1	•	•	•	—	•	•	•	—	—	—
3-1b	•	•	•	—	•	•	•	—	—	—
3-2	•	-9.6	<	<—	<	•	•	—	—	—
3-3	•	•	•	—	•	•	•	—	—	—
3-4	<	<	•	-0.4	•	7.4	10	3.1	-2.9	•
3-5	<	<	•	—	•	6.2	6.9	—	—	—
4-2	•	-9.3	<	<—	<	<	<	—	—	—
4-5	•	-9.5	<	<—	<	<	<	—	—	—
4-6	<	<	<	<—	<	<	<	<—	<—	<—
4-7	<	<	•	1.0	•	4.3	7.0	1.6	-1.9	•
4-8	-5.6	-4.4	•	—	•	<	<	—	—	—
5-0	•	•	•	—	•	•	•	—	—	—
5-1	•	-9.3	<	<—	<	•	•	•	2.8	-7.0
5-3	<	<	<	<—	<	<	<	<—	<—	<—
5-5	<	<	<	<—	<	<	<	—	—	—
5-7	<	<	•	1.0	•	4.3	7.0	1.6	-1.9	•
6-1b	-8.5	-6.8	•	—	•	-7.1	•	—	—	—
6-1d	<	<	•	-2.6	•	5.8	8.8	<	<	<
6-2	2.2	3.6	•	4.7	•	<	<	<	<	<<
6-3	-4.9	-3.8	NC	NC	•	0.2	-7.2	—	—	—
6-4	<	<	<	<	<	2.4	5.5	7.1	1.0	-8.2
6-5	<<	<<	<—	-1.3	•	4.9	7.7	1.2	-2.9	•
6-6	<<	<<	—	-4.2	•	4.0	4.9	-5.6	-6.6	•
6-7	<	<	—	1.8	•	-1.6	0.8	-2.0	-1.0	-6.7
7-1	•	•	•	—	•	<	<	—	—	—
7-2	•	•	<	<—	<	•	•	—	—	—
7-3	•	•	•	—	•	•	•	<—	<—	<—
7-4	•	•	NC	—	•	<	<	—	—	—
7-5	<	<	NC	—	•	<<	<<	—	—	—
7-7	<	<	—	—	•	<<	<<	—	—	—
7-8	-3.7	-2.7	•	—	•	2.2	-1.7	—	—	—
8-1	<	<	<	<—	<	<	<	<—	<—	<—
8-1.5	•	•	NC	—	•	•	•	<—	<—	<—
8-2	-6.1	-4.8	•	—	•	0.3	-8.0	—	—	—
8-3	<	<	•	—	•	2.1	-4.0	—	—	—
8-4	-4.9	-3.3	•	—	•	1.8	-2.9	—	—	—
8-5	<	<	•	-2.4	•	4.1	2.1	-2.4	-6.1	•
8-6	<	<	—	-3.4	•	4.5	4.3	<	<	<
9-1	•	•	•	<	•	•	•	—	—	—
9-2	<	<	<—	<	<	<	<	<	<	<
9-3	<	<	—	—	•	<	<	—	—	—
9-4	-7.4	-6.1	—	—	•	<	<	—	—	—
9-6	<	<	•	-6.5	•	-0.8	-9.4	<	<	<<
9-7	<	<	<—	<	<	2.7	4.8	<	<	<<
10-1	<	<	•	—	•	•	•	—	—	—
10-2	-2.4	-1.0	•	0.1	•	<	<	4.0	-2.4	•
10-4	-5.7	-4.4	•	—	•	-0.3	•	<—	<—	<—
10-8	<	<	•	—	•	4.9	4.1	—	—	—
10-9	<	<	•	—	•	5.2	8.0	—	—	—

¹Calculated from sulfate reaction
²Calculated from sulfide reaction
*Positive values indicate oversaturation; negative values indicate undersaturation; values less than -10 denoted by •
< U, Mo, Se, or As below level of detection
— Sulfide or sulfate below level of detection
NC Not calculated

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(1) Many of the selenium concentrations in low Eh water samples are near the detection limit. It is possible that analyses were inaccurate at this level and concentrations actually are below detection. If so, oversaturation may not exist.

(2) Assuming all analyses are accurate, dissolved selenium may persist metastably for kinetic reasons even though formation of native selenium is thermodynamically favored.

(3) The most likely explanation is that selenium forms complexes that have not been taken into account in calculation of saturation indices. Lisitsin (1969) observed similar oversaturation in low Eh water; he suggested that soluble complexes, particularly with organic compounds, were responsible.

Molybdenum

Concentrations of molybdenum in Oakville water samples range from below detection limits (0.2 μg/L) to 57 μg/L. Subtle geographic variations are apparent, with higher concentrations in southern and central areas and lower concentrations in East Texas. Dissolved molybdenum occurs almost entirely as the MoO_4^{2-} ion; calculated $HMoO_4^-$ concentrations are two to three orders of magnitude lower, dependent upon pH.

Equilibrium with molybdate minerals clearly does not control molybdenum concentrations in Oakville water. All oxidizing water is undersaturated with respect to all molybdate minerals; as expected, molybdate minerals should not control molybdenum concentrations in nonmineralized water. Powellite ($CaMoO_4$) has the highest saturation index, approximately -2, reflecting its relatively low solubility and the high concentrations of calcium in many shallow oxidizing water samples. All other molybdate minerals are even more undersaturated. Ferrimolybdite is also undersaturated in intermediate pH waters of the Oakville system.

The geographic distribution of molybdenum concentrations in Oakville water suggests that differences in source materials may be the dominant influence on concentrations. However, the actual concentrations may be affected by both source material and equilibrium of dissolved and adsorbed molybdenum. Adsorption should decrease with an increase in pH, so molybdenum concentrations in oxidizing or intermediate Eh water would be expected to vary with pH. However, Mo concentrations do not correlate with pH (R = 0.11).
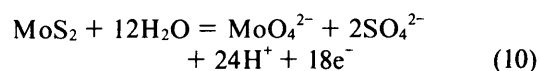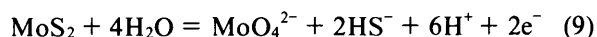
The drop in Eh between oxidizing and intermediate Eh water should not affect molybdenum concentration; much lower Eh values are necessary to form molybdenite, and ilsemannite forms only at low pH (fig. 7). Saturation indices for both minerals in intermediate Eh water are all much less than 0 (table 3).

Control of molybdenum concentrations in reducing Oakville water by equilibrium with molybdenite is uncertain. Correlation of molybdenum with Eh is poor

(R = -0.20); the highest molybdenum concentrations found in the Oakville aquifer are in reducing water (for example, samples 1-7, 2-5, 2-6, and 4-7). However, with the exception of these four samples, molybdenum in Oakville water samples does decrease with decreasing Eh. Concentrations of molybdenum may drop at approximately Eh = 0 mV, but the decrease is gradual, and does not reflect the sharp change that is predicted from thermodynamic data.

Evaluating molybdenite saturation in reducing water is complicated for two reasons:

(1) The molybdenite formation reaction can be written either with sulfate or sulfide:

$$MoS_2 + 4H_2O = MoO_4^{2-} + 2HS^- + 6H^+ + 2e^- \quad (9)$$

$$MoS_2 + 12H_2O = MoO_4^{2-} + 2SO_4^{2-} + 24H^+ + 18e^- \quad (10)$$

(2) Measured Eh values in reducing water may not reflect true oxidation-reduction relationships for molybdenum.

The molybdenite stability field (fig. 7) has been drawn using the sulfate reaction (representing oxidation of both molybdenum and sulfur), following the example of Lisitsin (1969) and Kaback (1977). However, saturation indices have been determined for both the sulfate and sulfide reactions. The sulfide reaction is preferable to the sulfate reaction because it is much less susceptible to minor analytical errors. Given that the coefficients for H^+ and e^- are large in the sulfate reaction, even small errors in measurement of pH and Eh would create large changes in calculated saturation indices. Although Kaback drew the stability field using the sulfate reaction, she determined molybdenite saturation by using the sulfide reaction, in which only molybdenum is involved in oxidation and reduction. Saturation indices determined by the sulfate reaction in the Oakville study are all considerably less than zero even though sulfate concentrations are quite high in many samples.

One problem with interpreting molybdenite saturation is that measured Eh values in Oakville water are well above the molybdenite stability field as drawn from the sulfate reaction. Some saturation indices calculated using the sulfide reaction are greater than zero, dominantly (and expectably) for water samples with high sulfide concentrations. A few water samples with high sulfide concentration have molybdenum concentrations below detection. This could indicate that molybdenum concentrations are maintained at low levels by precipitation of molybdenite.

The second problem is that measured Eh values and Eh values calculated from the sulfate-sulfide couple do not agree. Measured Eh values for only three samples (5-3, 6-4, and 6-7) are sufficiently low to be in the molybdenite stability field determined from the sulfate reaction, and, as noted above, the measured Eh value of sample 6-7 is

questionable. Molybdenum concentrations in samples 5-3 and 6-4 are below detection levels, and the concentration in sample 6-7 is only 0.6 μg/L. Using calculated Eh values, most reducing water plots within the molybdenite field on an Eh-pH diagram (drawn using the sulfate reaction, however). Although saturation indices have not been determined using calculated Eh values, all samples with measurable molybdenum concentrations would be oversaturated.

Lisitsin (1969) stated that neither low Eh potential nor presence of dissolved sulfide is sufficient to precipitate molybdenite. He did not state what additional conditions were necessary but speculated that formation of stable complexes accounted for oversaturation of water with respect to molybdenite. By Lisitsin's calculations, molybdenite, where it does precipitate, does so in an Eh range of -210 to -230 mV at pH 7.5. Although not the only requirement, dissolved sulfide is necessary for molybdenite precipitation. Several sulfide-rich water samples (for example, samples 5-3, 9-2, and 9-7) have molybdenum concentrations below detection and may be in equilibrium with molybdenite; however, several other sulfide-rich water samples (for example, samples 1-7 and 2-4) have very high molybdenum concentrations and are greatly oversaturated (table 3).

Thus, molybdenite solubility may not control molybdenum concentrations. The observed high concentrations in many samples of reducing water suggest that measured Eh values are a better indicator of molybdenite stability, consistent with the interpretation deduced from coffinite saturation. Calculated Eh values suggest that many reducing water samples are highly oversaturated with respect to molybdenite. However, no combination of reactions or calculated or measured Eh gives consistent, unambiguous results. We have to conclude that we do not fully understand molybdenite stability nor the effectiveness of reduction and precipitation on molybdenum concentrations in Oakville water. Apparently, present-day conditions commonly do not remove molybdenum from solution.

Arsenic

Arsenic concentrations range from below detection (1 μg/L) to 39 μg/L and exhibit a variable geographic distribution. Nine of the 12 Oakville water samples containing greater than 10 μg/L are from South Texas. Three samples from East Texas (line 8) have concentrations greater than 10 μg/L.

Arsenic is present mostly as arsenate (5+) species in water having Eh potential greater than 0 mV. The pK$_2$ of arsenic acid is approximately 7, so that arsenic is approximately equally distributed between $H_2AsO_4^-$ and $HAsO_4^{2-}$ at pH 7. With increasing pH, $HAsO_4^{2-}$ is the dominant species; at pH 8, the $HAsO_4^{2-}$ to $H_2AsO_4^-$ ratio is approximately 10. Figure 10D shows that maximum

adsorption should occur at pH = pK$_2$, with a rapid drop at higher pH. This suggests that arsenic concentration in oxidizing or intermediate Eh water should increase with pH. Although the correlation is poor (R = -0.32) the opposite occurs: highest concentrations exist at low pH, even considering only water in which arsenate species is dominant.

Equilibrium of dissolved arsenic with barium arsenate may be important. The few arsenate minerals for which saturation indices were calculated are highly undersaturated, with saturation indices of approximately -10. As noted above, barium concentrations ought to be relatively high in water having low sulfate concentrations; high barium concentrations would maintain low arsenic concentrations. However, there is no correlation (R = -0.09) between arsenic and sulfate in Oakville water, even though East Texas water, which generally has low sulfate concentrations, has low arsenic concentrations.

Reduction of As^{5+} to As^{3+} occurs at Eh levels of less than approximately 0 mV, coinciding with reducing water in the Oakville aquifer. H_3AsO_3 is the dominant species in water with pH less than 9. Adsorption may still determine arsenic concentrations in reducing water. However, ferric hydroxides are unstable at these low Eh values, so other phases would have to account for the adsorption.

Precipitation of As^{3+} sulfides is uncertain and shares many of the interpretation problems noted for molybdenite. Measured Eh values barely reach the arsenic sulfide stability field, as shown in figure 9. Arsenic does exhibit a general decrease in concentration with a decrease in Eh (R = 0.54), but the decrease in arsenic does not coincide with any predicted equilibrium boundaries.

Calculation of saturation indices using a sulfate reaction indicates general undersaturation of all arsenic sulfides. Calculation using a sulfide reaction indicates that several low-Eh, sulfide-rich water samples are oversaturated with respect to orpiment; several of these samples have arsenic concentrations well above detection levels (table 3). Eh values calculated from sulfate-sulfide couples place most Oakville water samples in the orpiment stability field. Calculation of saturation indices using calculated Eh has not been done but should indicate oversaturation of arsenic sulfides in many other Oakville water samples.

WATER CHEMISTRY IN URANIUM DISTRICTS

RAY POINT DISTRICT

The Ray Point district lies at the north margin of a broad belt of fluvial facies, called the George West axis (fig. 1). Detailed descriptions of geology and ore deposits are given by Galloway and others (1982b). Water from six
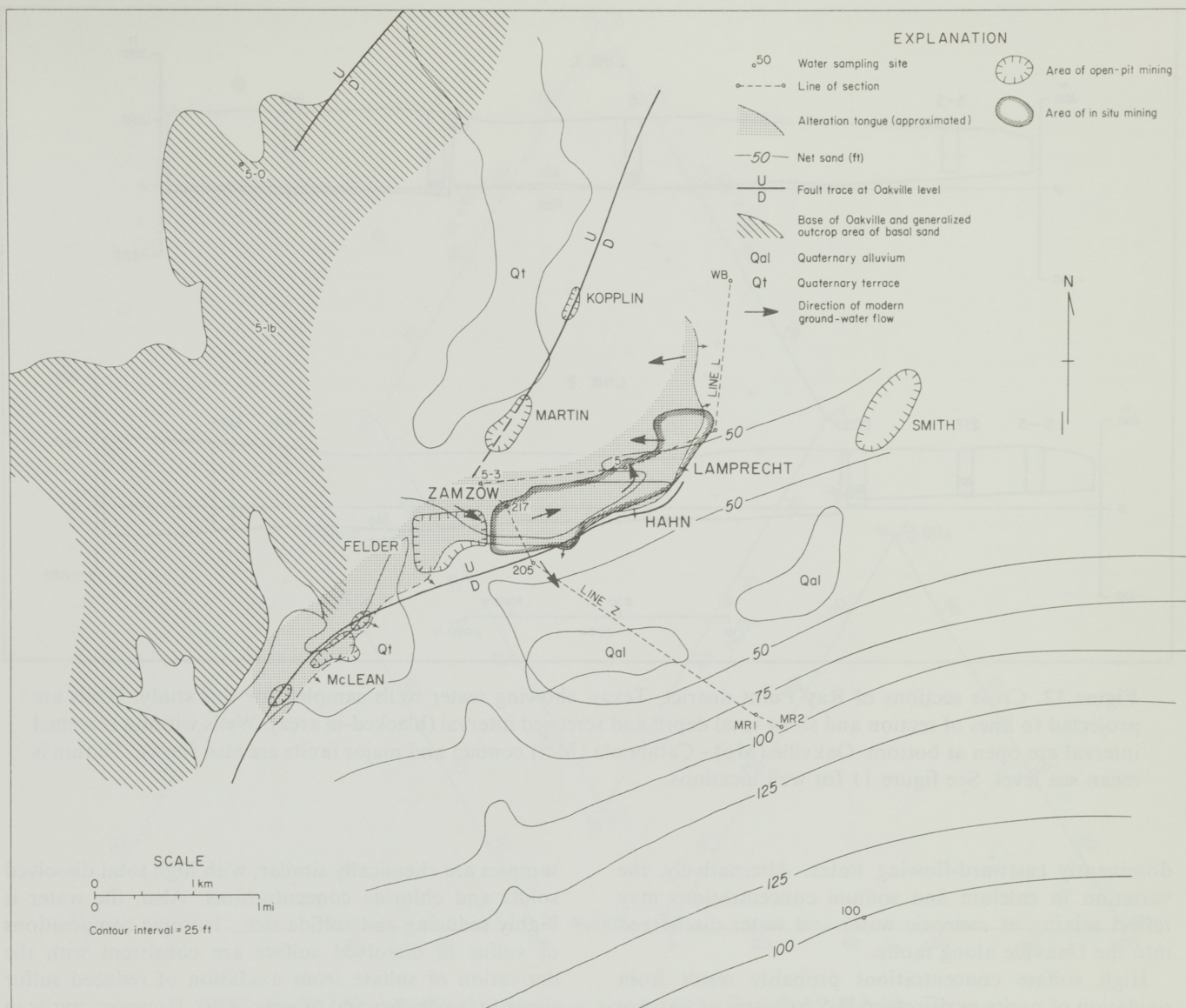
Figure 11. Ray Point area, South Texas, showing sample locations, Oakville net sand, and areas of mining. Location of Ray Point area shown in figure 1.

additional wells was sampled in and around deposits of the Ray Point area to supplement the samples collected for regional study. The location of these wells and wells of line 5 of the regional study, the location of faults in the Ray Point area, and the approximate location of the mineralization front are shown in figure 11. Together, the regional wells of line 5 and the wells of the Ray Point area form a line crossing the area of mineralization from northwest to southeast, with an arm extending northeast parallel to and approximately coincident with mineralization. Figure 12 is a cross section of the area showing the wells and their screened interval, the base of the Oakville, and faults in the area. Wells Z-205, Z-217, L-5, and L-9 are monitor wells installed by mining companies adjacent to solution mines; other wells are domestic or stock wells.

Major Ion Chemistry

Ray Point area water samples (fig. 13) can be divided into two chemically contrasting groups — those within and those away from mineralized zones. All water samples are slightly oversaturated with respect to calcite (table 4).

Water in the mineralized zone is compositionally uniform, exhibiting high total dissolved solids (1,300 to 3,500 mg/L) and high sodium, chloride, and H_2S concentrations; all samples are strongly reducing. With one exception, sulfate concentrations are greater than 500 mg/L. However, within these water samples there are both large- and small-scale variations in composition. Samples 5-3, Z-205, and Z-217 contain about twice as much calcium as samples L-5, L-9, and LWB, suggesting that cation exchange may be an important process in the

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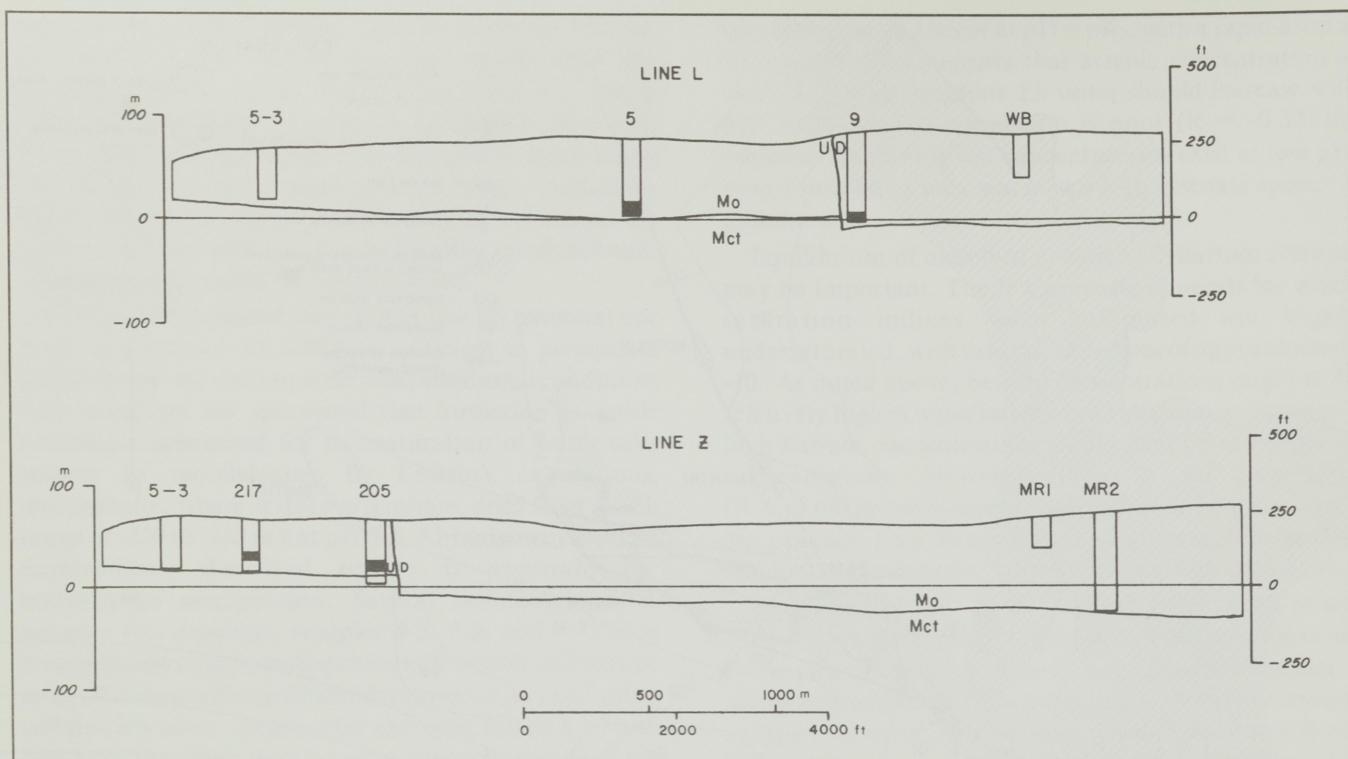
Figure 12. Cross sections of Ray Point district, Texas, showing water wells sampled for this study. Wells are projected to lines of section and show total depth and screened interval (blacked-in area). Wells without screened interval are open at bottom. Oakville (Mo) - Catahoula (Mct) contact and major faults are also shown. Datum is mean sea level. See figure 11 for well locations.

dominantly eastward-flowing water. Alternatively, the variation in calcium and sodium concentrations may reflect mixing of meteoric water and water discharged into the Oakville along faults.

High sulfate concentrations probably result from oxidation of pyrite or dissolved H_2S by water recharging the sands from the surface (Goldhaber and others, 1979). Most of the wells in the area of mineralization are shallow; surface oxidation should be prominent. In contrast, sample ZMR-2, which contains a much lower concentration of sulfate than other wells in the Ray Point area, is from a deeper well where surface oxidation is prevented either by intervening impermeable beds or by depth.

One of the two updip, oxidizing samples (sample 5-1) is lower in dissolved solids and in most individual ion concentrations than are water samples in the area of mineralization. However, the other oxidizing water (sample 5-0) is chemically very similar to the reducing water but it has a very much lower sulfate concentration.

Two uncertainties concerning the origin of reducing water in the Ray Point area are (1) whether water is now discharging into the Oakville along faults, and (2) whether the Oakville water is wholly or in part the product of present-day discharge. Several lines of evidence suggest that discharge is occurring. All water

samples are chemically similar, with high total dissolved solids and chloride concentrations. Also, the water is highly reducing and sulfide rich. Isotopic compositions of sulfur in dissolved sulfate are consistent with the derivation of sulfate from oxidation of reduced sulfur species (Goldhaber and others, 1979). However, pyrite in the sediment is isotopically distinct and cannot be the source of the sulfate. The sulfate probably formed by oxidation of H_2S from water now being discharged into the aquifer, but the sources of present-day discharge and discharge responsible for previous reduction and pyrite formation are different.

A problem with postulating an origin of fault-related discharge for Oakville water in the Ray Point area is that nonreducing water also has high chloride concentrations. Sample 5-0 is chloride rich and chemically similar to most of the reducing water, yet it is oxidizing. It may be a formerly reducing water oxidized near the surface, but oxidation of such a water without major compositional change seems unlikely. Alternatively, similar chemical compositions may result from processes not involving fault discharge. The present-day reducing conditions may be related only to the presence of abundant pyrite created by previous reduction. Previous discharge into the aquifer from faults is documented; present-day discharge is likely but cannot be proven with the available data.
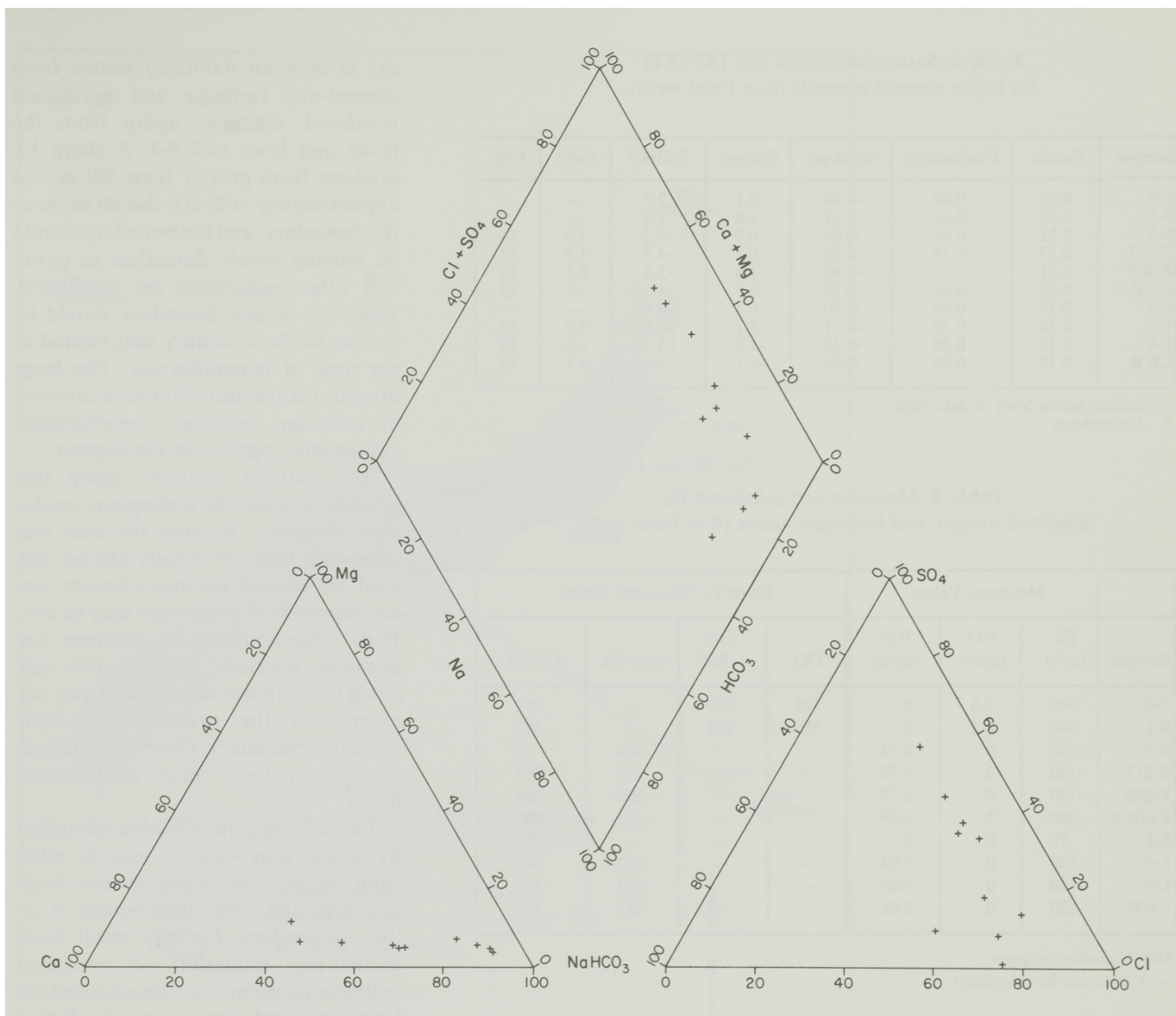
Figure 13. Piper (trilinear) diagram: water of the Ray Point district, Texas.

Oxidation-Reduction

Measured Eh levels of Oakville water from the Ray Point area range from 360 to -200 mV (table 5; fig. 14). The two samples from shallow updip wells, 5-0 and 5-1, have high Eh values, detectable dissolved oxygen, and high concentrations of nitrate. The waters are oxidizing because they are from shallow wells in a recharge area. Potential reductants in the Oakville, other than those in the soil zone, have been entirely consumed in this area.

Seven wells in and near the area of mineralization have extremely low Eh values, ranging from -130 to -200 mV, and consistently high dissolved sulfide concentrations. Calculated Eh values from the sulfide couple are all lower than measured Eh values but only by 30 to 70 mV. These water samples show the lowest measured Eh values and the best agreement between measured and calculated Eh of any samples of this study.

Water from well 5-5, obliquely downdip from the area of mineralization, has an Eh value of 70 mV, placing it in the intermediate Eh zone. It contains neither dissolved oxygen nor sulfide. Saturation indices show that the water is nearly in equilibrium with both siderite and amorphous ferric hydroxide. As suggested for other samples from the intermediate Eh zone, the oxidation state here may result from ferrous-ferric mineral equilibrium.

Rereduction of the Oakville aquifer matrix by highly reducing water introduced along fault zones undoubtedly contributes to the low Eh of many water samples. Reduction by discharging sulfide-rich water produced a zone of abundant pyrite adjacent to a fault zone. Equilibrium with pyrite alone could produce the Eh values, but all samples are highly oversaturated with respect to pyrite even though they have relatively low iron concentrations (table 4). Alternatively, reducing, sulfide-

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Table 4. Saturation indices (log IAP/KT)
for major element minerals (Ray Point wells).

Sample	Calcite	Chalcedony	Silica gel	Siderite	FeOH₃*	FeS*	FeS₂
5-0	0.15	0.40	-0.10	-2.1	2.7	—	—
5-1	0.16	0.61	0.11	-1.8	2.6	—	—
5-3	0.15	0.47	-0.04	-0.9	-5.2	1.3	14
Z-217	0.17	0.15	-0.36	-0.7	-4.7	1.2	14
Z-205	0.21	0.10	-0.40	-1.5	-5.8	0.5	13
ZMR-2	0.33	-0.23	-0.73	-0.3	-4.3	1.7	13
5-5	0.14	0.05	-0.50	-0.1	0.4	—	—
L-5	0.16	0.39	-0.11	-1.1	-5.0	0.9	14
L-9	0.18	0.36	-0.15	-1.0	-5.2	1.0	13
LWB	0.16	-0.04	-0.54	-1.1	-5.9	0.7	12

— Sulfide below level of detection
* Amorphous

Table 5. Measured and calculated Eh,
dissolved oxygen, and hydrogen sulfide (Ray Point wells).

	Measured Values			Eh (mV) Calculated From:			
Sample	Eh (mV)	DO (ppm)	H₂S (ppm)	DO	Sato (1960)	H₂S-SO₄	NH₄-NO₃
5-0	360	7.6	0	789	193	—	361
5-1	340	6.3	0	785	188	—	357
5-3	-150	0	9.54	—	—	-206	—
Z-217	-130	0	4.78	—	—	-204	363
Z-205	-150	0	6.27	—	—	-205	364
ZMR-2	-200	0	6.59	—	—	-261	309
5-5	70	0	0	—	—	—	317
L-5	-150	0	6.04	—	—	-222	345
L-9	-170	0	5.85	—	—	-225	345
LWB	-180	0	5.88	—	—	-215	353

DO Dissolved oxygen
— Could not be calculated

rich water could still be discharging into the Oakville along the fault zone, and the presence of dissolved H_2S could be controlling Eh. However, the lowest Eh values are from wells LWB and ZMR-2, some distance away from the probable discharging fault.

All of the reducing water exhibits low but detectable concentrations of nitrate, and calculated Eh values from the nitrate couple are all greater than 300 mV. Although the calculated and measured Eh values do not agree, the large differences in nitrate concentrations distinguish the oxidizing and reducing waters in a qualitative way. Also, nitrate in the reducing water may result from present-day, near-surface oxidation of ammonia in the water.

The precise geometry of the oxidation-reduction zones within the Oakville in the Ray Point area and the events that produced the zones are not entirely known. Fault discharge and reduction by sulfide-rich water have occurred at least twice and were superimposed upon previous oxidation. An intermediate Eh zone has not been recognized between wells 5-1 and 5-3, a distance of approximately 3 km (2 mi). Probably the present bound-

ary is between oxidizing waters from present-day recharge and pyrite-rich rereduced sediment updip from the faults and from well 5-3. A sharp Eh gradient from greater than 300 mV to approximately -150 mV should occur at this boundary, and the boundary should be moving slowly downflow as pyrite and other reductants are consumed. Thus, the present boundary should be similar to the boundary that existed at the time of mineralization. The large drop in Eh accounts for the occurrence of uranium, selenium, molybdenum, and arsenic together in the deposit.

Any reduced sediment along this boundary should be undergoing oxidation. However, because the area was rereduced from previously altered and oxidized ground, the trace element concentrations in this sediment may be low. High concentrations in sediment are probably restricted to a narrow belt along the uranium ore zone and may not extend to the present oxidation-reduction boundary. Chemical evidence to support these ideas is discussed below.

The intermediate Eh zone identified by water from well 5-5 may be relict from earlier oxidation before fault discharge and subsequent reduction, or the intermediate Eh may result from present-day oxidation of rereduced sediment by water that flows around the highly reduced zone along the faults. Structural trends and sand-body geometries are complex, and they complicate interpretation of the geometry of oxidizing and reducing ground-water zones. The total extent of reduction and the existence and extent of subsequent oxidation is unknown. Location of the boundary between reducing water and intermediate Eh water also is unknown, other than that it lies between wells ZMR-2 and 5-5. Nevertheless, the zone of reduction is remarkably large, extending at least from ZMR-2 to well 5-3, a distance of 3 to 4 km (approximately 2 mi) and an unknown distance beyond either well. The total area of reduction before modification by present-day oxidation would be even larger.

Present oxidation of the central part of the rereduced zone (fig. 14), especially the area of uranium ore, should not be occurring by lateral encroachment of oxidizing water. Such encroachment should be restricted to the trace-element-deficient edges of the reducing zone. Oxidation is known to be occurring by downward movement of oxidizing water in the upper Oakville Sandstone, and this oxidation is probably responsible for the high sulfate concentrations in much of the reducing water.
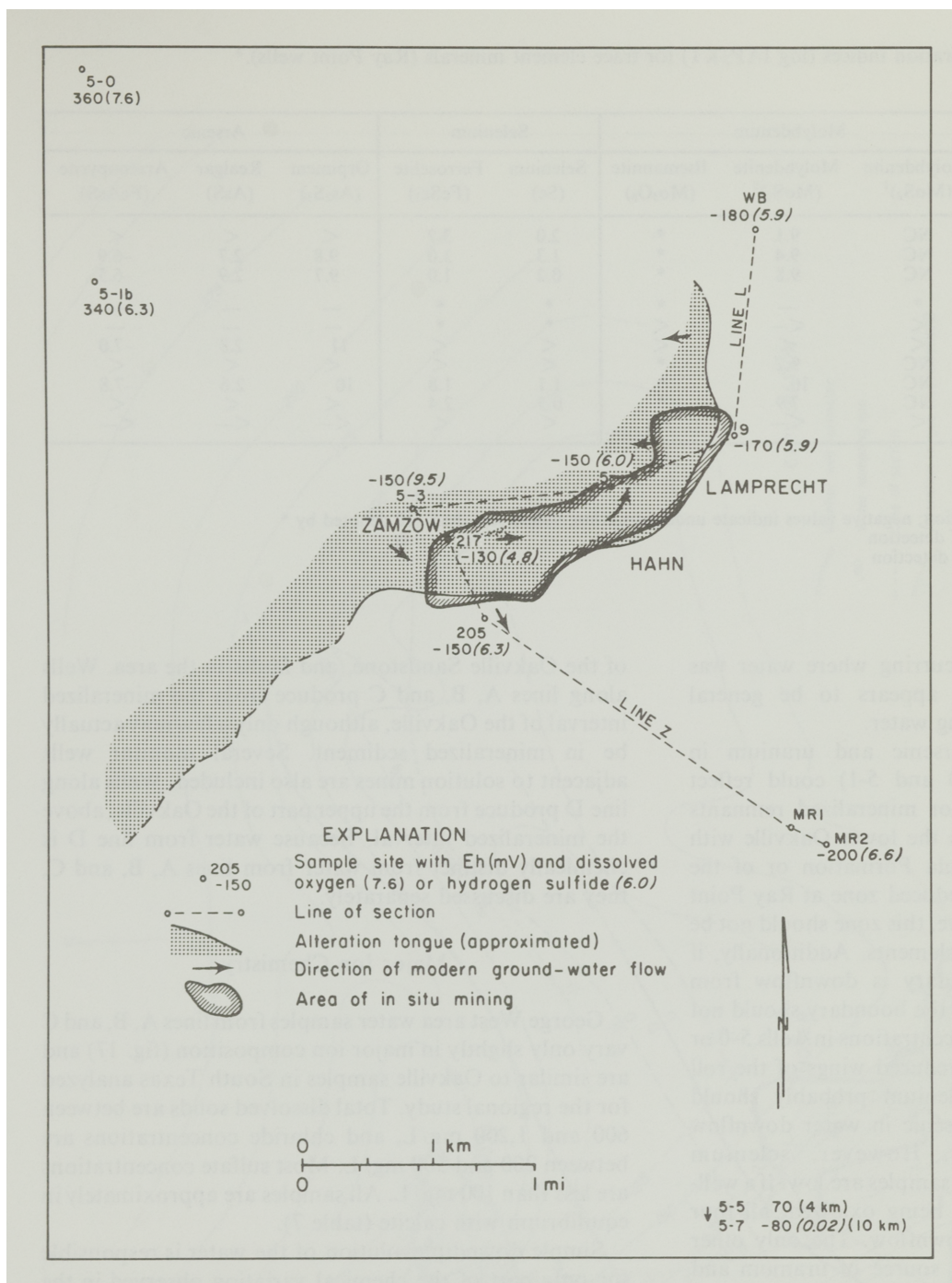
Figure 14. Distribution of Eh values and concentrations of dissolved oxygen and hydrogen sulfide in water of the Ray Point district, Texas.

Trace Element Concentrations

Trace element concentrations in water samples of the Ray Point area definitely reflect Eh conditions of the water. High concentrations occur only in samples 5-0 (arsenic = 45 μg/L) and 5-1 (arsenic = 39 μg/L; uranium = 99 μg/L). Although these values are relatively high, the samples are undersaturated with respect to all arsenic and uranium minerals considered in the investigation.

Concentrations of trace elements in reducing water are generally low and relatively uniform, but are mostly above detection limits. For example, uranium varies only from 0.1 to 0.6 μg/L, and arsenic varies from less than 1.0 to 3.0 μg/L. Nevertheless, the samples are oversaturated with respect to most of the reduced minerals (table 6). Many of the uranium concentrations are near detection limits and may be lower than can be accurately measured, but most molybdenum values are distinctly above detection. Oversaturation may be a result of complexing not considered by our chemical model or of minor oxidation of the deposits with release of the trace elements. Concentrations in well 5-5 are all below detection limits even though the Eh is low enough only for reduction of uranium and selenium. Significant natural mobilization of trace elements from the Ray Point

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Table 6. Saturation indices (log IAP/KT) for trace element minerals (Ray Point wells).*

Sample	Uranium		Molybdenum			Selenium		Arsenic		
	Uraninite (UO$_2$)	Coffinite (USiO$_4$)	Molybdenite (MoS$_2$)[1]	Molybdenite (MoS$_2$)[2]	Ilsemannite (Mo$_3$O$_8$)	Selenium (Se)	Ferroselite (FeSe$_2$)	Orpiment (As$_2$S$_3$)	Realgar (AsS)	Arsenopyrite (FeAsS)
L-5	1.1	2.5	NC	9.1	*	2.0	3.7	<	<	<
L-9	1.7	3.0	NC	9.4	*	1.3	3.0	9.8	2.7	-6.9
LWB	1.7	2.7	NC	9.8	*	0.2	1.0	9.7	2.9	-6.5
5-0	*	*	*	—	*	*	*	—	—	—
5-1	*	-9.3	<	<—	<	*	*	—	—	—
5-3	<	<	<	<	<	<	<	11	2.8	-7.0
Z-217	2.1	3.3	NC	9.2	*	<	<	<	<	<
Z-205	1.3	2.5	NC	10	*	1.1	1.8	10	2.6	-7.8
ZMR-2	0.9	1.7	NC	7.9	*	0.5	2.4	<	<	<
5-5	<	<	<	<—	<	<	<	<—	<—	<—

[1]Calculated from sulfate reaction
[2]Calculated from sulfide reaction
*Positive values indicate oversaturation; negative values indicate undersaturation; values less than -10 denoted by *
< U, Mo, Se, or As below level of detection
— Sulfide or sulfate below level of detection
NC Not calculated

deposits apparently is not occurring where water was sampled, even though there appears to be general oxidation by downward-moving water.

High concentrations of arsenic and uranium in oxidizing water (samples 5-0 and 5-1) could reflect oxidation or leaching of minor mineralized remnants along the contacts of sands in the lower Oakville with reduced muds of the Catahoula Formation or of the Oakville. Oxidation of the rereduced zone at Ray Point should occur but, as noted above, this zone should not be particularly enriched in trace elements. Additionally, if the oxidation-reduction boundary is downflow from wells 5-0 and 5-1, oxidation at the boundary should not contribute to trace element concentrations in wells 5-0 or 5-1. If previously oxidized, rereduced wings of the roll front are being oxidized, selenium probably should dominate over uranium or arsenic in water downflow from the oxidation front. However, selenium concentrations in all Ray Point samples are low. If a well-developed front or wing were being oxidized, all four elements should be present downflow. The only other explanation is that a primary source of uranium and arsenic, such as volcanic ash, still exists in the Oakville sediments and is being altered at present. No evidence of such a primary source has been found, however.

GEORGE WEST DISTRICT

The George West district lies at the southern margin of the George West fluvial axis (fig. 1). Detailed descriptions of geology and ore deposits are given by Galloway and others (1982b). Twenty-one additional wells, arranged in four lines designed to cross the oxidation-reduction fronts, were sampled in the district to supplement the regional program (fig. 15). Figure 16 shows cross sections of the area with the location and depth of the wells, base

of the Oakville Sandstone, and faults in the area. Wells along lines A, B, and C produce from the mineralized interval of the Oakville, although only a few may actually be in mineralized sediment. Several monitor wells adjacent to solution mines are also included. Wells along line D produce from the upper part of the Oakville, above the mineralized interval. Because water from line D is chemically distinct from water from lines A, B, and C, they are discussed separately.

Major Ion Chemistry

George West area water samples from lines A, B, and C vary only slightly in major ion composition (fig. 17) and are similar to Oakville samples in South Texas analyzed for the regional study. Total dissolved solids are between 600 and 1,200 mg/L, and chloride concentrations are between 200 and 500 mg/L. Most sulfate concentrations are less than 100 mg/L. All samples are approximately in equilibrium with calcite (table 7).

Simple downdip evolution of the water is responsible for only part of the chemical variation observed in the George West district. Cation exchange is probably responsible for the variation in relative proportions of sodium and calcium. Low calcium concentrations in samples from line C probably result from cation exchange in the deepest and most downflow wells of the area. Some samples from lines A and B that have low calcium concentrations occur where deep, reducing, and probably sodium-rich water once discharged into the Oakville. The low calcium and high sodium concentrations of these samples from lines A and B probably reflect exchange with smectite that has been enriched in sodium by the discharging water.

Likewise, the shallowest, most updip water on line A is nearly in equilibrium with silica gel and is oversaturated
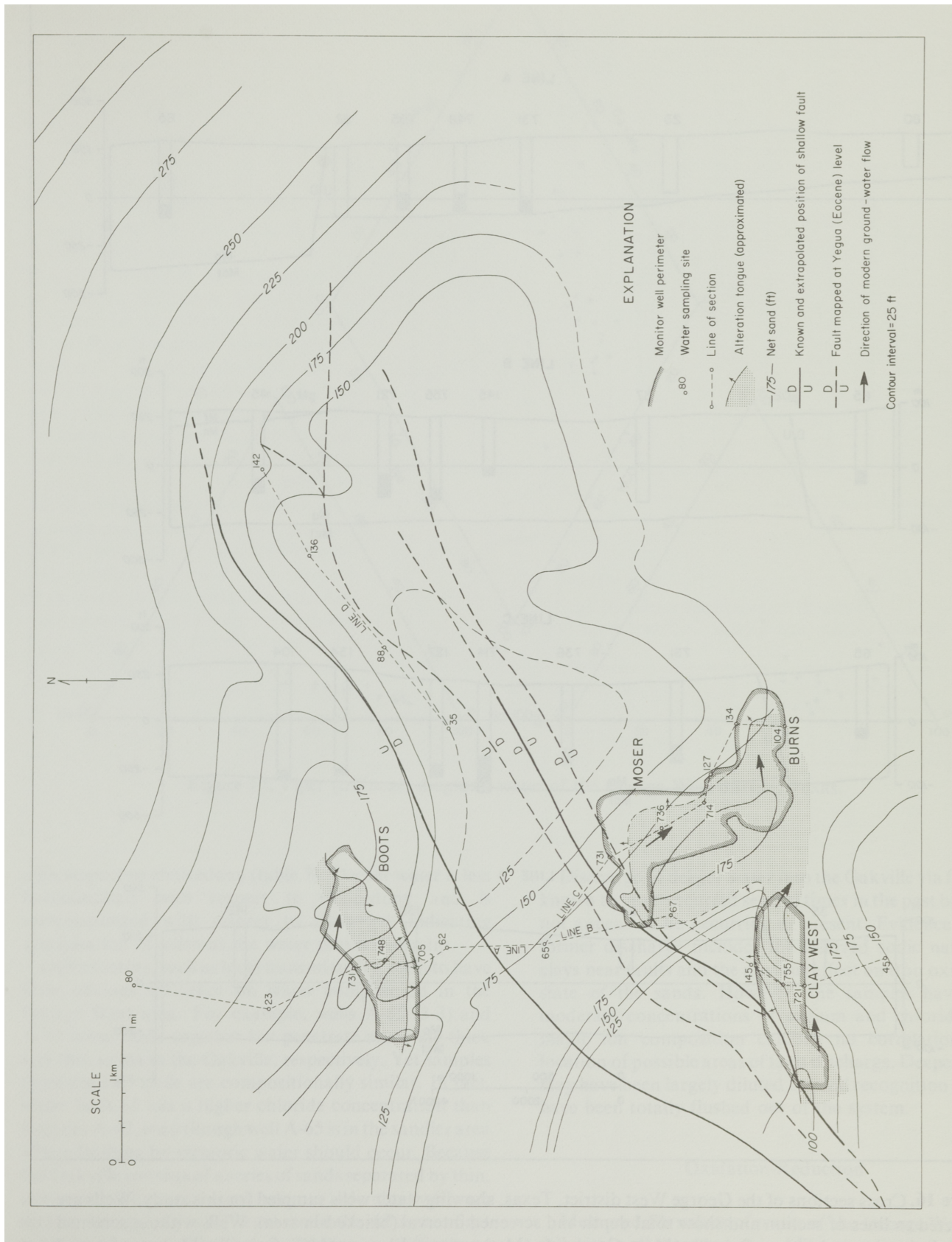
Figure 15. George West area, South Texas, showing sample locations, Oakville net sand, and areas of mining. Location of George West area shown in figure 1.

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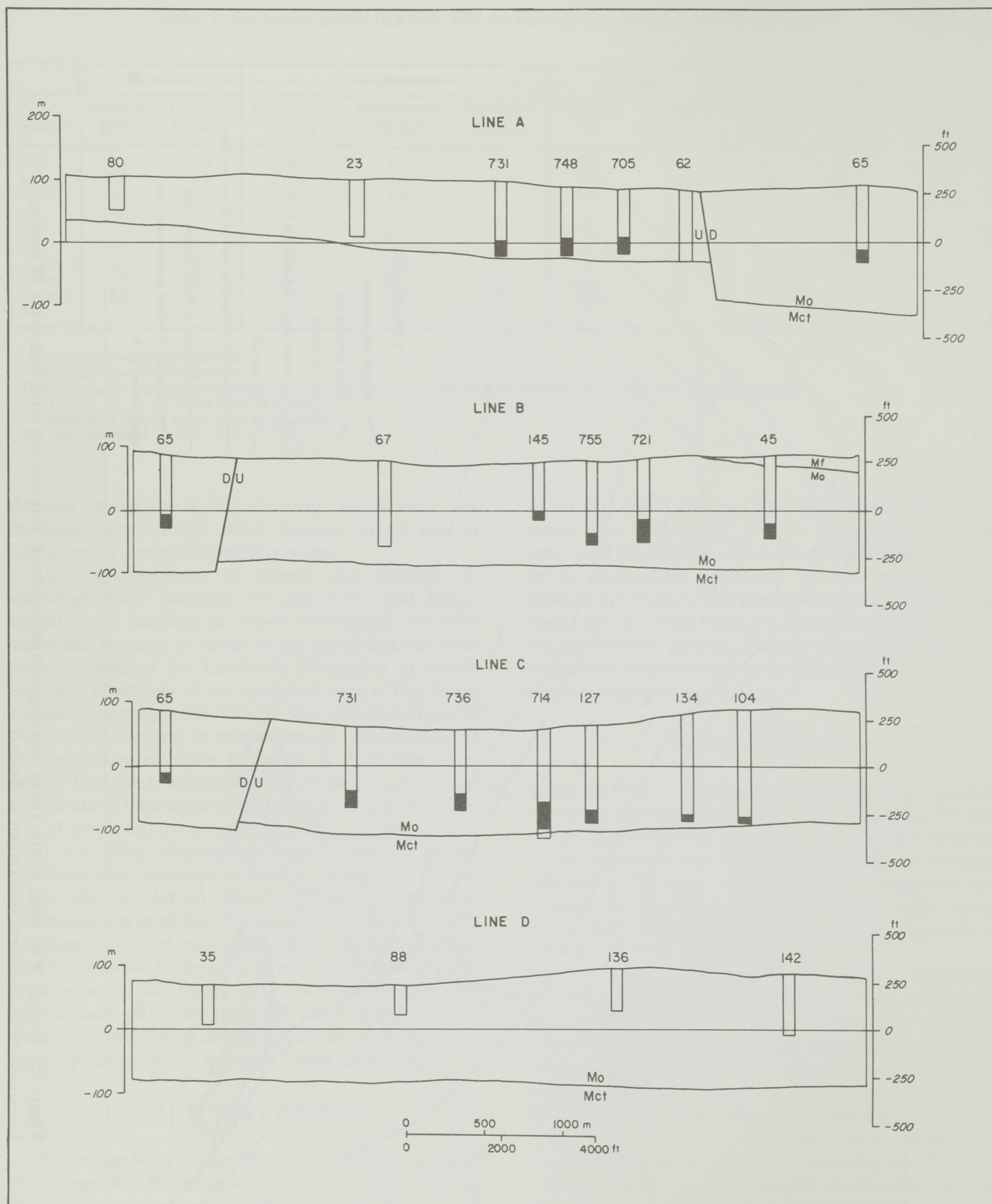
Figure 16. Cross sections of the George West district, Texas, showing water wells sampled for this study. Wells are projected to lines of section and show total depth and screened interval (blacked-in area). Wells without screened interval are open at bottom. Oakville (Mo) - Catahoula (Mct) contact, Fleming (Mf) - Oakville (Mo) contact, and faults are also shown. Datum is mean sea level. Well location shown in figure 15.
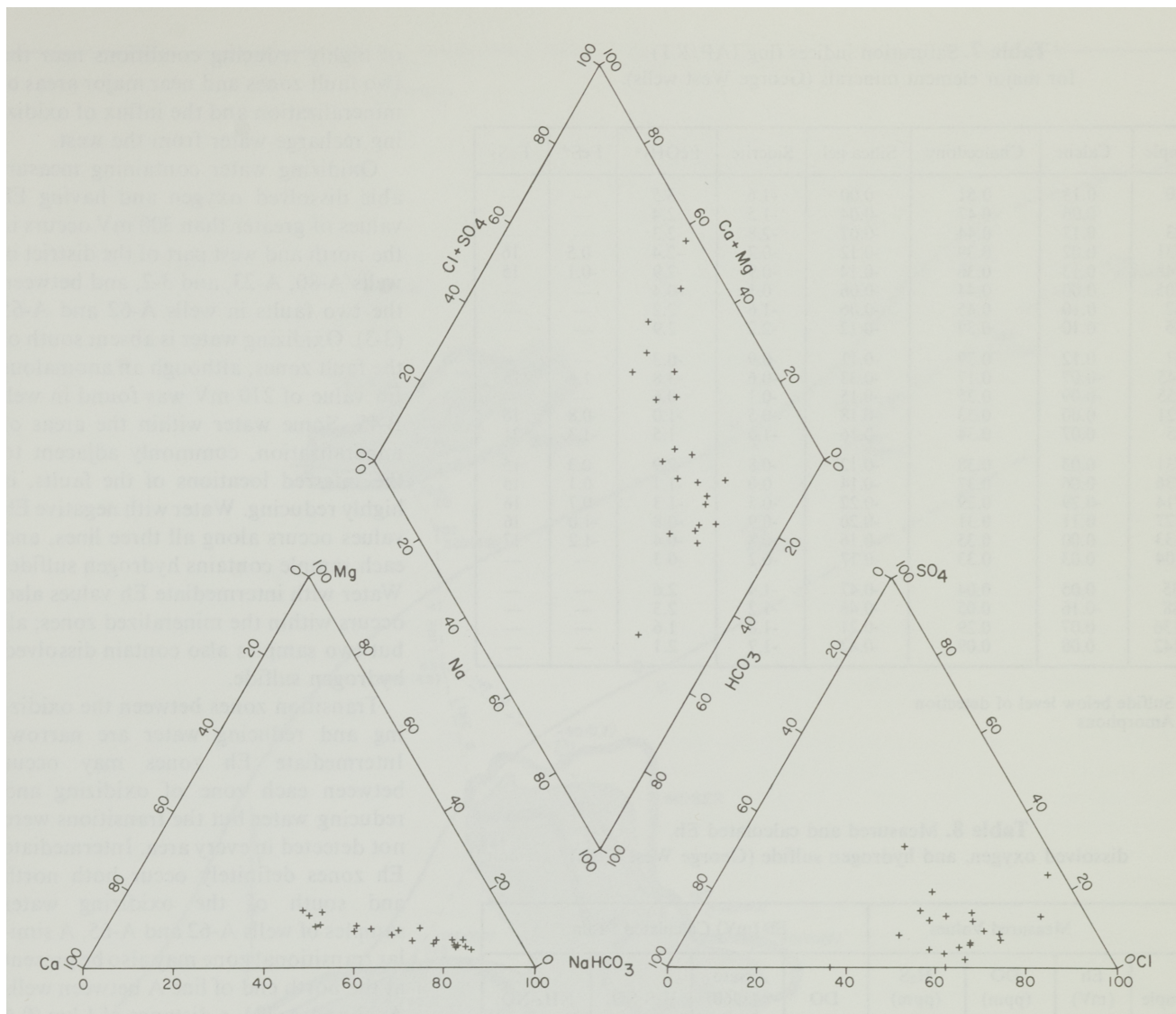
Figure 17. Piper (trilinear) diagram: water of the George West district, Texas.

with respect to chalcedony (table 7). Deeper water is less oversaturated with respect to chalcedony and is undersaturated with respect to silica gel, indicating precipitation of silica as the water moves downdip.

Other factors, such as local transmissivity, seem to have little obvious influence on water composition in the George West area. For example, wells A-65 (3-3) and A-62 occur close together but penetrate relatively thick and thin sands in the Oakville, respectively. Yet samples from the two wells are compositionally similar. In fact, water in A-65 has a higher chloride concentration than water in A-62, even though well A-65 is in the sandier area where flushing by meteoric water should occur. Because the Oakville consists of a series of sands separated by thin, low-permeability lenses and because individual wells are screened irregularly in different sands, the influence of net sand on degree of meteoric flushing is difficult to evaluate.

Discharge of deeper water into the Oakville via faults is known to have occurred several times in the past but does not appear to be occurring at present. Evidence of the former discharge includes the inferred sodic nature of clays near faults and the obvious effect on iron oxidation state of the sands. However, the samples have only moderate concentrations of sodium and chloride, and major ion composition exhibits no correlation with location of possible areas of fault discharge. Deeper water may have been largely diluted beyond recognition or may have been totally flushed out of the system.

Oxidation-Reduction

Measured Eh values of water of the George West area fall within all three recognized Eh zones (table 8; fig. 18). The distribution of Eh values clearly shows the influence

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Table 7. Saturation indices (log IAP/KT) for major element minerals (George West wells).

Sample	Calcite	Chalcedony	Silica gel	Siderite	FeOH₃*	FeS*	FeS₂
A-80	0.13	0.51	0.00	-1.6	3.5	—	—
3-2	0.06	0.47	-0.04	-1.5	2.4	—	—
A-23	0.17	0.44	-0.07	-2.8	2.3	—	—
A-731	0.02	0.39	-0.12	-0.7	-2.4	0.5	16
A-748	0.13	0.36	-0.14	-0.9	-2.9	-0.1	15
A-705	0.00	0.44	-0.06	0.1	-0.4	—	—
A-62	0.10	0.45	-0.06	-1.6	2.2	—	—
A-65	0.10	0.39	-0.12	-2.2	2.9	—	—
B-67	0.12	0.39	-0.11	-0.9	-0.3	—	—
B-145	-0.07	0.17	-0.33	-0.6	-3.8	1.4	15
B-755	-0.09	0.35	-0.15	-0.1	-0.6	—	—
B-721	0.00	0.33	-0.18	-0.5	-1.0	-0.8	16
B-45	0.07	0.34	-0.16	-1.0	1.5	-1.3	21
C-731	0.03	0.38	-0.12	-0.8	-2.9	0.3	15
C-736	0.06	0.37	-0.14	0.0	-1.1	0.1	15
C-714	-0.29	0.29	-0.22	-0.5	-1.3	-0.7	16
C-127	0.11	0.31	-0.20	-0.9	-0.8	-1.0	16
C-133	0.00	0.35	-0.16	-0.8	-0.4	-1.2	17
C-104	0.03	0.33	-0.17	-0.2	-0.3	—	—
D-35	0.05	0.04	-0.47	-1.4	2.6	—	—
D-88	-0.16	0.05	-0.46	-1.2	2.3	—	—
D-136	0.07	0.29	-0.21	-1.8	1.6	—	—
D-142	0.08	0.09	-0.42	-1.7	2.1	—	—

— Sulfide below level of detection
* Amorphous

Table 8. Measured and calculated Eh, dissolved oxygen, and hydrogen sulfide (George West wells).

	Measured Values			Eh (mV) Calculated From:			
Sample	Eh (mV)	DO (ppm)	H₂S (ppm)	DO	Sato (1960)	H₂S-SO₄	NH₄-NO₃
A-80	390	5.4	0	791	198	—	356
3-2	310	2.2	0	799	206	—	385
A-23	380	2.9	0	781	189	—	352
A-731	-50	0	0.76	—	—	—	319
A-748	-50	0	0.31	—	—	-220	—
A-705	20	0	0	—	—	—	317
A-62	320	5.6	0	795	200	—	358
A-65	390	4.5	0	788	198	—	—
B-65	390	4.5	0	788	198	—	—
B-67	110	0.5	0	769	175	—	342
B-145	-140	0	6.96	—	—	—	—
B-755	10	0	0	—	—	—	318
B-721	30	0	0.02	—	—	-220	332
B-45	210	0	ND	764	173	-218	—
C-65	390	4.5	0	788	198	—	—
C-731	-80	0	0.67	—	—	-245	—
C-736	-40	0	0.06	—	—	-244	—
C-714	30	0	0.03	—	—	-211	—
C-127	40	0	0.03	—	—	-232	—
C-133	80	0	0.02	—	—	-220	—
C-104	80	0	*	—	—	—	—
D-35	285	7.0	0	768	179	—	324
D-88	170	0.6	0	772	179	—	351
D-136	320	8.0	0	819	224	—	397
D-142	320	4.1	0	794	201	—	365

DO Dissolved oxygen
* Odor detected at well head
— Could not be calculated
ND Not determined

of highly reducing conditions near the two fault zones and near major areas of mineralization and the influx of oxidizing recharge water from the west.

Oxidizing water containing measurable dissolved oxygen and having Eh values of greater than 300 mV occurs in the north and west part of the district in wells A-80, A-23, and 3-2, and between the two faults in wells A-62 and A-65 (3-3). Oxidizing water is absent south of the fault zones, although an anomalous Eh value of 210 mV was found in well B-45. Some water within the areas of mineralization, commonly adjacent to the inferred locations of the faults, is highly reducing. Water with negative Eh values occurs along all three lines, and each sample contains hydrogen sulfide. Water with intermediate Eh values also occurs within the mineralized zones; all but two samples also contain dissolved hydrogen sulfide.

Transition zones between the oxidizing and reducing water are narrow. Intermediate Eh zones may occur between each zone of oxidizing and reducing water but the transitions were not detected in every area. Intermediate Eh zones definitely occur both north and south of the oxidizing water samples of wells A-62 and A-65. A similar transitional zone may also be present at the north end of line A between wells A-23 and A-731, a distance of 1 km (0.6 mi); however, there are no wells in this area. At the southern ends of both lines B and C, Eh values rise through the intermediate Eh zone, but the presence of oxidizing water farther south is uncertain. At the time of mineralization, each front must have represented a drop in Eh from oxidizing to reducing conditions because all trace elements and both pyrite and iron hydroxide occur within the mineralized front in the thermodynamically appropriate settings.

As was the case with the regional water samples, measured and calculated Eh values of water of the George West area do not agree. Eh values calculated from the sulfur couple are 170 to 300 mV lower than measured Eh values, showing that equilibrium is not established. The greatest discrepancies in Eh values occur in intermediate Eh water containing measurable hydrogen
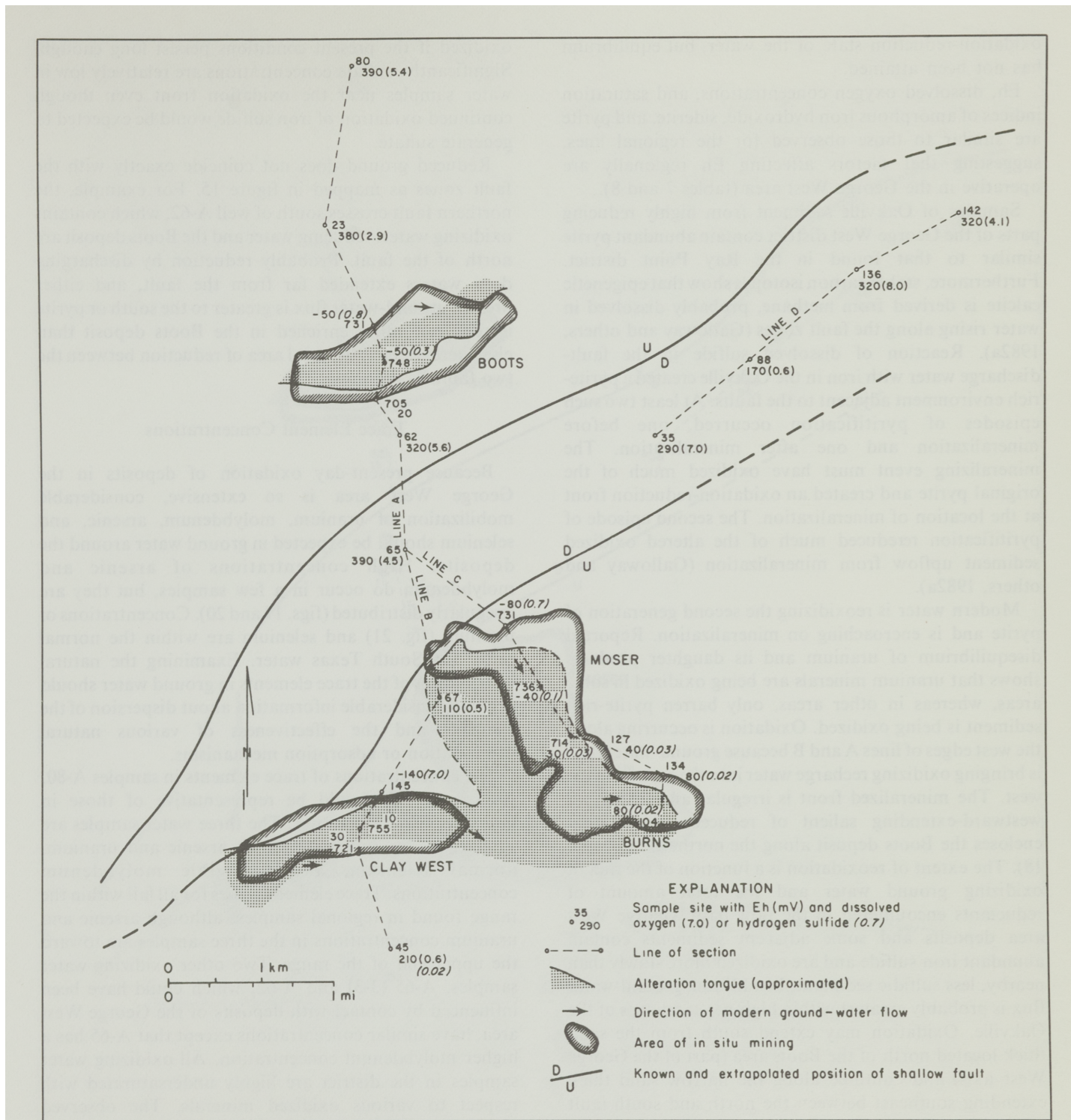
Figure 18. Distribution of Eh values and concentrations of dissolved oxygen and hydrogen sulfide in water of the George West district, Texas.

sulfide; reducing water shows lesser Eh differences. Possibly hydrogen sulfide is leaking continuously from highly reducing water into intermediate Eh water but too quickly to establish equilibrium.

Eh values calculated from the nitrogen couple also do not agree with measured values. Where determined, all calculated Eh values are greater than 300 mV. However, high nitrate concentrations (1 to 9 mg/L) are restricted to oxidizing water samples, and many intermediate Eh and reducing water samples contain no detectable nitrate. Also, where detectable, nitrate concentrations in reducing or intermediate Eh water samples are no greater than 0.40 mg/L. Thus, in a qualitative way, the oxidized and reduced nitrogen species reflect the

oxidation-reduction state of the water, but equilibrium has not been attained.

Eh, dissolved oxygen concentrations, and saturation indices of amorphous iron hydroxide, siderite, and pyrite are similar to those observed for the regional lines, suggesting that factors affecting Eh regionally are operative in the George West area (tables 7 and 8).

Samples of Oakville sediment from highly reducing parts of the George West district contain abundant pyrite similar to that found in the Ray Point district. Furthermore, stable carbon isotopes show that epigenetic calcite is derived from methane, probably dissolved in water rising along the fault zones (Galloway and others, 1982a). Reaction of dissolved sulfide in the fault-discharge water with iron in the Oakville created a pyrite-rich environment adjacent to the faults. At least two such episodes of pyritification occurred, one before mineralization and one after mineralization. The mineralizing event must have oxidized much of the original pyrite and created an oxidation-reduction front at the location of mineralization. The second episode of pyritification rereduced much of the altered oxidized sediment upflow from mineralization (Galloway and others, 1982a).

Modern water is reoxidizing the second generation of pyrite and is encroaching on mineralization. Reported disequilibrium of uranium and its daughter products shows that uranium minerals are being oxidized in some areas, whereas in other areas, only barren pyrite-rich sediment is being oxidized. Oxidation is occurring along the west edges of lines A and B because ground-water flow is bringing oxidizing recharge water into the area from the west. The mineralized front is irregular and displays a westward-extending salient of reduced ground that encloses the Boots deposit along the northern fault (fig. 18). The extent of reoxidation is a function of the flux of oxidizing ground water and the total amount of reductants encountered in the flow path. George West area deposits and some adjacent sediments contain abundant iron sulfide and are oxidized more slowly than nearby, less sulfidic sediment. In addition, ground-water flux is probably greatest within high-net-sand axes of the Oakville. Oxidation may extend south from the sand thick located north of the Boots area (part of the George West axis) and continue along the narrow sand thick extending southeast between the north and south fault zones (figs. 15 and 18). Thus, the Boots deposit is a remnant of reduced pyrite-rich sediment surrounded on the north, west, and south by oxidizing water. Oxidizing water may also be encroaching from the west along the south border of the Clay West deposit (fig. 18). Polarity of the mineralization front shows that a component of flow of the mineralized, oxidizing fluids was from the south. Following mineralization, Oakville sediment south of the Clay West and Moser deposits must have been oxidized; present Eh values, however, are in the intermediate Eh range. All of the George West area deposits will be totally oxidized if the present conditions persist long enough. Significantly, sulfate concentrations are relatively low in water samples near the oxidation front even though continued oxidation of iron sulfide would be expected to generate sulfate.

Reduced ground does not coincide exactly with the fault zones as mapped in figure 15. For example, the northern fault crosses south of well A-62, which contains oxidizing water; reducing water and the Boots deposit are north of the fault. Probably reduction by discharging deep waters extended far from the fault, and either present ground-water flux is greater to the south or pyrite is relatively more enriched in the Boots deposit than elsewhere. In fact, the total area of reduction between the two faults is unknown.

Trace Element Concentrations

Because present-day oxidation of deposits in the George West area is so extensive, considerable mobilization of uranium, molybdenum, arsenic, and selenium should be expected in ground water around the deposits. High concentrations of arsenic and molybdenum do occur in a few samples, but they are irregularly distributed (figs. 19 and 20). Concentrations of uranium (fig. 21) and selenium are within the normal range for South Texas water. Examining the natural distribution of the trace elements in ground water should provide considerable information about dispersion of the elements and the effectiveness of various natural precipitation or adsorption mechanisms.

The concentrations of trace elements in samples A-80, A-23, and 3-2 should be representative of those in inflowing, oxidizing water. The three water samples are similar, having moderately high arsenic and uranium, normal selenium, and negligible molybdenum concentrations. Trace element values for all fall within the range found in regional samples, although arsenic and uranium concentrations in the three samples are toward the upper end of the range. Two other oxidizing water samples, A-65 (3-3) and A-62, which could have been influenced by contact with deposits of the George West area, have similar concentrations except that A-65 has a higher molybdenum concentration. All oxidizing water samples in the district are highly undersaturated with respect to various oxidized minerals. The observed concentrations are probably the result of several factors, including availability of sources, complexing, and adsorption, particularly by ferric hydroxide. Unfortunately, none of these factors can be tested quantitatively.

Oxidation of reduced sediment should be occurring along the north and west edge of the Boots deposit (fig. 18). Ground-water flow should transport dissolved trace elements either back into reduced sediments within the deposit (wells A-731, A-748, A-705), where the elements could be rereduced and precipitated, or into oxidized

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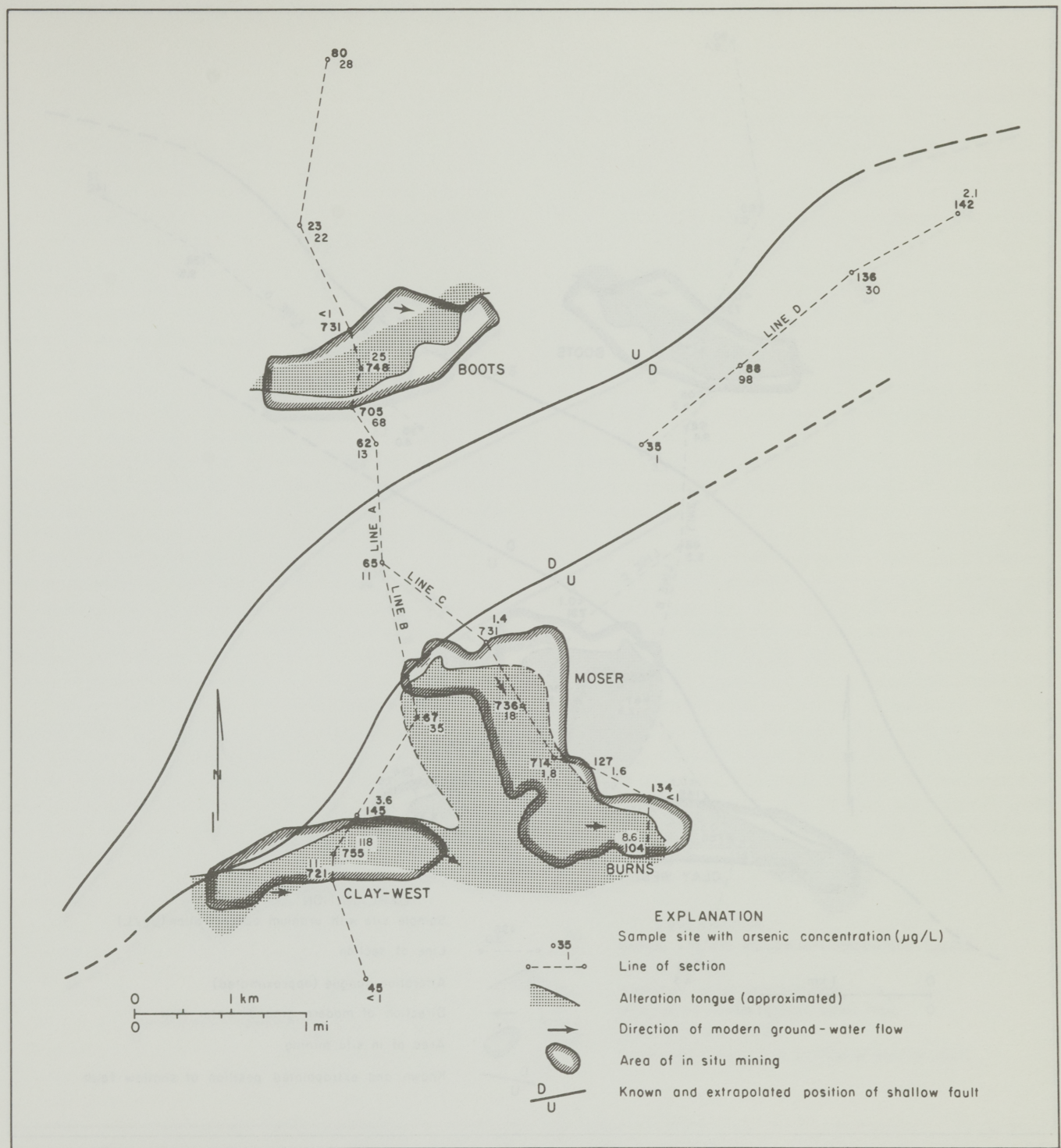
Figure 19. Distribution of arsenic concentrations in water of the George West district, Texas.

sediments south of the Boots area (wells A-62 and A-65), where rereduction would not occur. Trace elements in these samples are irregularly distributed. High concentrations are found only in samples A-748 (molybdenum = 700 μg/ L), A-705 (arsenic = 68 μg/ L), and possibly A-65 (molybdenum = 24 μg/ L). Enrichment of trace elements, if it is occurring, is not uniform from well to well or among different elements in a single well. Either the trace elements are being released in different proportions because of locally different distributions of oxidation potentials, or some are preferentially removed from the water before they reach the sampled wells. Probably the high concentrations of the elements are more a function of what is occurring in the aquifer immediately adjacent

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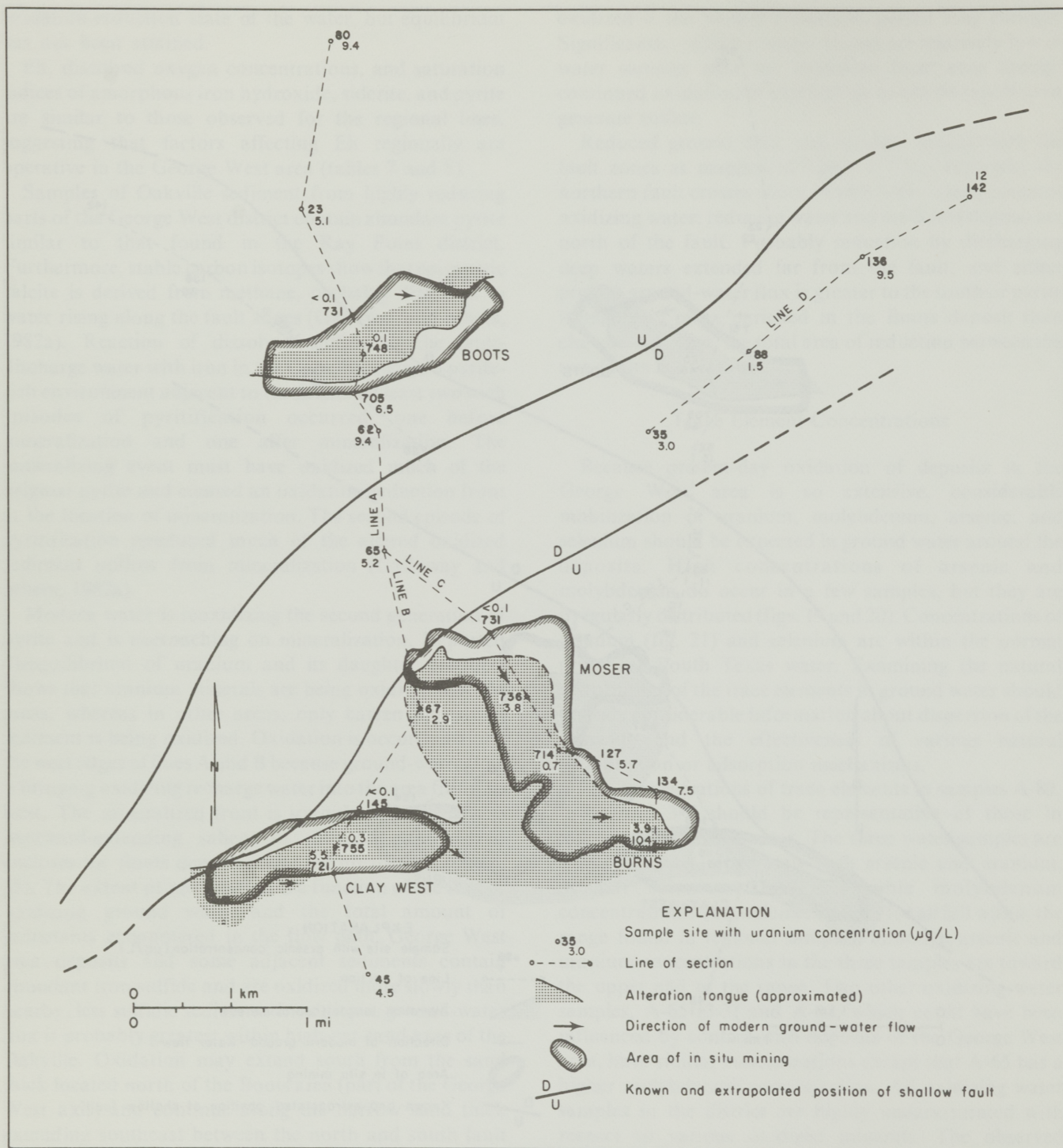
Figure 20. Distribution of molybdenum concentrations in water of the George West district, Texas.

to the well than a function of oxidation along the regional oxidation-reduction front. That is, the very high molybdenum concentration in A-748 may result from oxidation of mineralized sediments at or near the well rather than from inflow from an external source. In fact, oxidation at the regional front may be affecting primarily pyrite-rich but trace-element-barren, resulfidized, altered sediment.

Water from well A-748 is highly oversaturated with respect to molybdenite, native selenium, ferroselite, and orpiment; water from well A-705 is oversaturated with respect to native selenium and ferroselite (table 9). Selenium oversaturation is common in regional wells and probably has no special significance. The very high concentration of molybdenum and oversaturation with respect to molybdenite in sample A-748 is unusual and
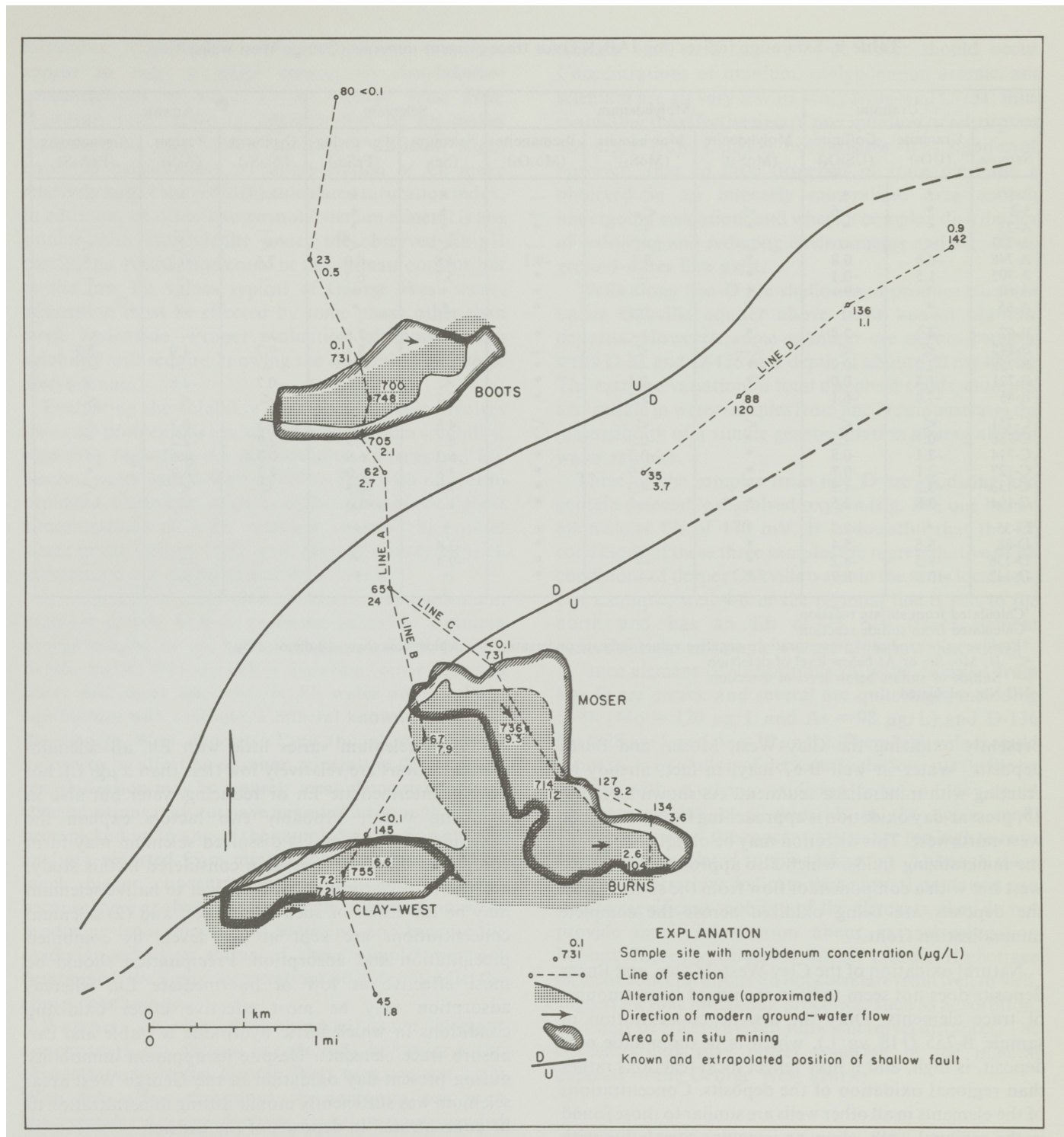
Figure 21. Distribution of uranium concentrations in water of the George West district, Texas.

difficult to explain from the available data. Apparent oversaturation of both samples probably results from nonequilibrium and inadequate knowledge of complexing.

The two oxidizing samples between the Boots and Moser deposits, samples A-62 and A-65, also have normal trace element concentrations, with the possible exception of molybdenum in A-65 (24 μg/L). The

molybdenum concentration, although higher than in oxidizing water upflow, is not unusually high compared with concentrations in regional samples. Natural oxidation of the Boots deposit has not released large quantities of trace elements, at least not to the wells sampled.

Samples A-65 and B-67 (although the latter is in the intermediate Eh zone) are representative of the water

Table 9. Saturation indices (log IAP/KT) for trace element minerals (George West wells).*

Sample	Uranium		Molybdenum			Selenium		Arsenic		
	Uraninite (UO$_2$)	Coffinite (USiO$_4$)	Molybdenite (MoS$_2$)[1]	Molybdenite (MoS$_2$)[2]	Ilsemannite (Mo$_3$O$_8$)	Selenium (Se)	Ferroselite (FeSe$_2$)	Orpiment (As$_2$S$_3$)	Realgar (AsS)	Arsenopyrite (FeAsS)
A-80	•	•	<	<—	—	•	•	—	—	—
3-2	•	-9.6	<	<—	—	•	•	—	—	—
A-23	•	•	•	—	•	•	•	—	—	—
A-731	<	<	<—	<	—	<	<	<	<	<
A-748	-0.6	0.8	•	5.4	-9.1	4.8	6.0	7.6	0.2	•
A-705	-1.5	-0.1	•	—	•	5.7	6.3	—	—	—
A-62	•	-9.1	•	—	•	•	•	—	—	—
A-65	•	•	•	—	•	•	•	—	—	—
B-67	-4.2	-2.8	•	—	•	0.7	-7.6	—	—	—
B-145	<	<	<—	<	—	2.9	5.1	9.7	1.9	-8.7
B-755	-2.2	-0.9	•	—	•	6.0	7.0	—	—	—
B-721	-1.4	0.0	•	-2.1	•	<	<	-0.7	-4.8	•
B-45	-7.4	-6.1	•	-8.4	•	-6.7	•	<	<	<
C-731	<	<	<	<	<	4.5	6.2	5.5	-0.7	•
C-736	-0.1	1.3	•	-0.3	•	6.1	8.9	2.9	-2.2	•
C-714	-2.1	-0.8	•	-0.7	•	6.3	6.8	-0.3	-4.6	•
C-127	-2.1	-0.7	•	-2.9	•	3.8	1.0	-4.3	-6.9	•
C-133	-3.2	-1.9	•	-4.3	•	1.7	-4.5	<	<	<
C-104	-3.8	-2.5	•	—	•	1.3	-5.0	—	—	—
D-35	•	-9.7	•	—	•	•	•	—	—	—
D-88	-6.5	-5.4	•	—	•	-3.4	•	—	—	—
D-136	-9.5	-8.2	•	—	•	-9.4	•	—	—	—
D-142	-10	-8.9	•	—	•	•	•	—	—	—

[1]Calculated from sulfate reaction
[2]Calculated from sulfide reaction
*Positive values indicate oversaturation; negative values indicate undersaturation; values less than -10 denoted by •
< U, Mo, Se, or As below level of detection
— Sulfide or sulfate below level of detection
NC Not calculated

presently oxidizing the Clay West, Moser, and Burns deposits. Water in well B-67 may, in fact, already be reacting with mineralized sediment. As shown by figure 15, present-day oxidation is approaching from the west or west-northwest. This direction may be oblique to flow of the mineralizing fluids, which also approached from the west but with a component of flow from the south. Thus, the deposits are being oxidized across the complete mineralization front.

Natural oxidation of the Clay West, Moser, and Burns deposits does not seem to have mobilized large amounts of trace elements. Only the arsenic concentration of sample B-755 (118 μg/L), which is in the middle of a deposit, is high, and it may reflect local reactions rather than regional oxidation of the deposits. Concentrations of the elements in all other wells are similar to those found in the regional wells, show an irregular correlation with Eh, and are generally not in equilibrium with solid phases. For example, sample B-145 has the lowest measured Eh (-140 mV) and highest hydrogen sulfide concentration (7.0 mg/L) found in the George West area. Both molybdenum and uranium concentrations in sample B-145 are below detection; selenium and arsenic were both detected, and the samples are highly oversaturated with respect to selenium, ferroselite, orpiment, and realgar (table 9).

Almost all samples in the George West area are oversaturated with respect to selenium and ferroselite.

Although selenium varies little with Eh, all selenium concentrations are relatively low (less than 5 μg/L), not only in intermediate Eh or reducing water but also in oxidizing water. Probably two factors explain the behavior of selenium: (1) dissolved selenium may form complexes that have not been considered in this study; apparent oversaturation with respect to native selenium may be the result of such complexes, and (2) selenium concentrations are kept at low levels by combined precipitation and adsorption. Precipitation should be most effective at low or intermediate Eh, whereas adsorption may be most effective under oxidizing conditions in which ferric hydroxide is stable and can absorb trace elements. Despite its apparent immobility during present-day oxidation in the George West area, selenium was sufficiently mobile during mineralization to be concentrated in deposits of the district.

Almost all samples in the George West district are either highly undersaturated with respect to molybdenite (calculated using measured Eh values and the sulfide reaction), or molybdenum or sulfide concentrations are below detection. Molybdenite saturation indices would be even lower if calculated from concentrations of sulfate and measured Eh. The use of Eh values calculated from the sulfur couple would probably indicate oversaturation of many of the samples, but this method is probably least appropriate. Two samples, C-736 and C-714, are nearly in equilibrium with molybdenite, which may simply be

fortuitous. Equilibrium with molybdenite does not appear to exert a major control on molybdenum concentrations in water of the George West area. However, uncertainty in interpretation of Eh makes evaluation of molybdenite saturation difficult; slight errors in measurement or interpretation of Eh make relatively large changes in the calculated saturation index. In addition, no other known molybdenum mineral is less soluble than molybdenite under the observed Eh-pH conditions. Adsorption could be the ultimate control, but at the low Eh values typical of George West water, adsorption must be effected by some phase other than ferric hydroxide. Proper evaluation of molybdenum solubility will require knowing the mineralogical site of molybdenum.

Evaluating the solubility controls of arsenic involves the same problems as evaluating molybdenum solubility, especially regarding the interpretation of measured Eh. Several water samples are oversaturated with respect to orpiment. Curiously, arsenic exhibits some of the highest concentrations of trace elements observed in ground water in the George West area, although analyzed rock samples are not highly enriched in arsenic.

In contrast to molybdenum, arsenic, and selenium, uranium closely follows predicted behavior. Uranium concentrations in the most reducing samples (A-731, B-145, and C-731) are below detection; other reducing water and most intermediate Eh water are nearly in equilibrium with coffinite, a mineral known to occur in the George West deposits. Even though oxidation is known to be affecting uranium minerals in the deposits, remobilization may be a purely local phenomenon; high concentrations may not have migrated far enough to have been picked up in any of the sampled wells. Some water analyses reported from mining company data do show much higher concentrations of uranium. However, because these analyses are commonly of water from wells producing from mineralized sediment, and because the oxidation-reduction status of these samples was not determined, the high concentrations do not contradict the above conclusions.

Whether or not the observed trace element concentrations follow predicted behavior, the concentrations in the George West area are not high. With only a few exceptions, the concentrations, even from samples very near deposits, are below recommended public health limits. Natural oxidation apparently is not significantly mobilizing the trace elements in this area. A limitation is that our sample sites are not ideally situated to detect natural oxidation of mineral deposits or to follow trace elements once they are released. A better test would be to sample wells that are closely spaced along a line parallel to ground-water flow and that produce from a variety of Eh and other conditions. Only line C of this study is oriented roughly parallel to flow; other lines are oriented obliquely to flow. Line C shows no effect of oxidation at the northwest end (C-731), where initial

contact with oxidizing recharge water should occur. Concentrations of uranium, molybdenum, arsenic, and selenium are all very low in water from well C-731; thus, evaluating the effectiveness of precipitation or adsorption downflow from C-731 is not possible. It is significant, however, that so little dispersal of trace elements is observed in an intensely mineralized area actively undergoing oxidation, and where a complex distribution of oxidizing and reducing environments and significant ground-water flux exist.

Wells along line D are shallow and produce from the upper Oakville aquifer above most known uranium deposits. However, some uranium ore occurs between wells D-88 and D-136 at a depth of about 120 m (400 ft). The extreme variation in total dissolved solids, chloride, and sulfate in water samples from line D demonstrates the impossibility of a simple genetic relation among all four water samples.

Three of the samples from line D are oxidizing and contain detectable dissolved oxygen (fig. 18); one has an anomalous Eh of 170 mV. It is doubtful that the Eh conditions of these three samples are representative of Eh conditions of deeper Oakville water in the same locations. For example, well 4-6 of the regional line is just to the north and has an Eh of 25 mV (trace element concentrations in sample 4-6 are all below detection).

Trace element concentrations of water samples from line D are erratic and several are quite high, including D-88 (Mo = 120 μg/L and As = 98 μg/L) and D-136 (Se = 28 μg/L and As = 30 μg/L). These high values could result from oxidation of deposits in the lower Oakville by contact with overlying oxidizing water, or they could represent oxidation of minerals in the upper sand. Certainly some of the concentrations are too high to have any source unrelated to mineralization. Although these high concentrations indicate that natural oxidation can lead to significant mobility of the elements, they do not provide much information about natural mitigation because the concentrations are so erratic. High trace element concentrations do not correlate from well to well, suggesting that mitigating processes, such as adsorption, may only be effective given sufficient travel distances. The concentrations may reflect zonation of the mineral deposits of the George West district.

CONCLUSIONS

EVALUATION OF GEOCHEMICAL CONTROLS OF TRACE ELEMENT CONCENTRATIONS

Concentrations of molybdenum, selenium, arsenic, and uranium in Oakville water are relatively low considering that the Oakville Sandstone is a mineralized aquifer. In reducing water, trace element concentrations

should be low, but in oxidizing water, higher concentrations would be expected. Only samples in and immediately adjacent to the George West and Ray Point uranium districts contain unusually high concentrations of the trace elements. All of these high concentrations may result from naturally occurring, local dispersion from mineral deposits, although this is not a widespread phenomenon.

The lack of high trace element concentrations suggests that an active source of trace elements does not exist. Volcanic ash, largely within the underlying Catahoula Formation, is considered to have been the source of uranium and other trace elements in many South Texas deposits. Whether volcanic ash ever existed in the Oakville Sandstone and overlying Fleming Formation is uncertain. Abundant clay-rich sediments within the Oakville may include altered ash, but petrographic evidence to confirm this has been largely destroyed by alteration. Whatever the source of uranium — whether the Fleming, the Oakville, or the Catahoula Formations — that source has now been effectively depleted. Thus, because no presently active source exists, the elemental concentrations in Oakville water are low, except near deposits where higher concentrations probably result from dispersal. The generally higher concentration of all elements in South Texas water compared with East Texas water implies that either (1) there are more uranium deposits in South Texas leading to more secondary dispersion, or (2) there is some residual primary source remaining in South Texas.

The actual concentrations of trace elements observed in oxidizing water may reflect equilibrium between dissolved and adsorbed elements. Appropriate adsorbents are abundant in the Oakville; however, it is not possible to evaluate adsorption quantitatively. Correlation between dissolved elemental concentrations and pH (as it affects efficiency of adsorption) is irregular; however, any pH correlation may be obscured by the effect of Eh. In any event, the results are not diagnostic. Therefore, it is impossible to quantify effectiveness of adsorption in controlling trace element concentrations.

Ground water near uranium deposits commonly flows from oxidized sediments into reduced sediments. Exceptions occur where present-day hydrology is very different from that which created the extant oxidation-reduction pattern. Migration of oxidizing, trace-element-rich water (for example, an excursion from a solution mine or drainage from an abandoned open-pit mine) into an adjacent reducing environment should lead to rereduction and reprecipitation of the trace elements. In a sense, the process should recreate the mineralization process, which at one time was extremely efficient in concentrating the elements.

Present-day reduction does not remove low concentrations of dissolved trace elements. Only uranium closely follows behavior predicted from thermodynamic data, probably because so much more is known about uranium and its complexing than about the other elements. The other three elements, selenium, arsenic, and molybdenum, persist in concentrations greater than those predicted by the sparse available thermodynamic data. Although the three other elements do decrease somewhat with a decrease in Eh in the regional Oakville wells, the decrease does not coincide with expected Eh boundaries. Instead, the decrease is more gradual. Selenium definitely does not follow predicted behavior. Molybdenum and arsenic may actually follow predicted behavior, but the ambiguity of the meaning of measured Eh values makes evaluation uncertain. Whatever the explanation, it is clear that high concentrations of the trace elements other than uranium could persist in mine drainage even if the water reenters a reducing part of the aquifer.

There are at least three possible reasons why observed and predicted behavior of dissolved trace elements are different:

(1) There could be major errors in the analytical or thermodynamic data used to predict geochemical behavior. Although this is a significant possibility, it cannot be evaluated in the scope of this study.

(2) The chemical model used undoubtedly does not account for all important solubility controls. For example, complexing by organic or inorganic ligands may increase the total concentration of trace elements allowed in equilibrium with reduced minerals.

(3) The kinetics of reactions may be slow and may allow oversaturation to persist. Because some of the wells are many kilometers down hydrologic gradient from the oxidation-reduction boundaries, disequilibrium would have to last thousands of years. Although this seems unlikely, the discrepancy between calculated and measured Eh values indicates that disequilibrium can occur.

In intermediate Eh water, neither adsorption nor reduction may be effective in removing molybdenum or arsenic. Eh under these conditions is not low enough to remove molybdenum or arsenic as insoluble sulfides. Adsorption may also be less effective because ferric hydroxide, the major identified adsorbent, is unstable at intermediate Eh, breaking down to form ferrous minerals, such as siderite, or dissolved ferrous iron.

The fact that the four elements were concentrated at the time of mineralization and that their distribution follows thermodynamically predicted behavior seems to contradict the findings reported here. However, the present-day geochemical setting may be very different from the setting at the time of mineralization. Eh and Eh gradients may be different, but, more importantly, the concentrations of the elements in solution are probably vastly different. Concentrations of trace elements at the time of mineralization are not known but may have been much higher than at present. For example, Granger and Warren (1978) postulate that ground water containing 50 μg/L uranium, which is less than the concentrations in

some present-day Oakville ground water, could serve as an ore-forming fluid. If uranium or the other elements approached the mg/L level, removal of 90 percent of them would produce major ore deposits but would still leave high dissolved concentrations. Although nearly complete removal by precipitation is still predicted by the model we have used, we have not necessarily accounted for all factors controlling solubility. Better knowledge of trace element complexes, trace element mineralogy in the uranium districts, and thermodynamic properties of both is necessary to understand the behavior of the trace elements.

EH GRADIENTS

Recognition and mapping of oxidized and reduced sediment are major uranium exploration tools. Most commonly, recognition is based on examining core or cuttings from wells drilled expressly for uranium exploration. The coloration and mineralogy of the sediments indicate their oxidation state. Oxidation state can also be determined by measurement of Eh in ground water, as we have done. Our method has some advantages over the more common method, such as the ability to recognize more subtle Eh differences including the presence of three distinct redox zones as opposed to only two zones — oxidized and reduced. Also, direct measurement should be less expensive, at least initially, when a regional pattern can be obtained by taking measurements of water in existing wells. For example, the Eh data of this report could be used for just such a purpose.

Both Eh measurements and observation of the oxidation-reduction state of sediments indicate the current redox potential. The redox potential at the time of mineralization may have been different. The most obvious difference occurs where discharge into the aquifer of highly reducing sulfidic water via faults has rereduced formerly oxidized sediment located updip from the mineralization front. In this situation, which has occurred in both the Ray Point and George West uranium districts, the present-day oxidation-reduction boundary is updip of the boundary as it existed at the time of mineralization. Nevertheless, the original oxidation-reduction and mineralization boundary has not migrated such long distances that Eh measurements could not still be used to focus on favorable areas.

Uranium, molybdenum, arsenic, and selenium reduce and precipitate at different Eh values at a given pH. Thus the elements should occur together in a deposit only if the Eh gradient is steep and spans the complete range of Eh values at which the various elements precipitate. For example, from the oxidizing zone to the intermediate zone, reduction involves a drop in Eh value from greater than 300 mV to about 100 to 10 mV. Under these circumstances, only uranium and selenium should precipitate; molybdenum and arsenic should remain

dissolved. In general, uranium deposits in Texas contain uranium, selenium, and molybdenum, all of which are distributed in the mineral deposit according to their redox potentials; that is, selenium occurs updip and molybdenum downdip of uranium. Thus an Eh gradient from the oxidizing zone to the reducing zone must have existed across these deposits at the time of mineralization. Arsenic may be restricted to deposits in which carbonaceous material acted as an important reductant (Price, 1980). However, high arsenic values occur in some Catahoula deposits that lack carbonaceous material.

Our data show the existence of a broad zone of intermediate Eh water in the Oakville aquifer in East Texas and in some parts of South Texas. The Eh pattern in South Texas is complicated by the abundance of rereduced zones superimposed on the "normal" Eh pattern. Our data suggest that uranium deposits in East Texas should contain only uranium and selenium (Henry and others, 1980), but only if the present-day Eh pattern reflects the pattern at the time of mineralization. Also, mineralization in East Texas might be diffuse if the transition from oxidizing conditions to intermediate Eh is gradual. Conceivably a second mineralization front containing molybdenum or arsenic could exist farther downdip if a reducing zone were encountered; we did not find such a zone along either lines 7 or 8. However, if pH also drops across the mineralization front (from oxidation of pyrite or marcasite), all four elements could be concentrated together (see figs. 4, 5, 6, and 7).

The oxidizing and reducing zones could occur together in East Texas and all four trace elements could be concentrated together in a deposit in two general geologic settings: (1) in contact zones between highly permeable channel deposits and less permeable interchannel deposits, and (2) in as-yet-undiscovered sites of pyritization resulting from deep discharge of sulfidic water into the aquifer via faults. In the first setting, the permeable channel deposits would be oxidized because of repeated flushing by oxidizing meteoric water. Adjacent impermeable sediments would be considerably less flushed and could contain preserved carbonaceous matter or syngenetic pyrite formed from carbonaceous matter. A steep Eh gradient would occur between the oxidized channel deposits and the unoxidized interchannel sediments. Crevasse splays from the main channel might be favorable areas for exploration. These hypotheses can be better evaluated as data become available on East Texas deposits.

As discussed in the section on oxidation and reduction, areas of fault discharge into the Oakville have not been found in East Texas and are unlikely to occur there because of the paucity of faults. However, potential areas of deep discharge occur as far east as Lavaca County (lines 9 and 10), and discharge of sulfidic water could also occur near salt domes, which are found in East Texas.

Pyritic zones resulting from fault-controlled discharge of sulfidic water are seemingly abundant in the Oakville

of South Texas. The pyritic, reducing zones are probably superimposed on an otherwise normal Eh gradient similar to what is found in East Texas. This is best illustrated along line 5 where intermediate Eh conditions are encountered downdip of the Ray Point uranium district. Such zones are particularly favorable for formation of uranium deposits because they assure that highly oxidizing and highly reducing water are juxtaposed. Uranium mineralization in the Oakville in South Texas may in fact be restricted to such zones. At present, we know of no South Texas Oakville uranium deposits that do not occur in such a setting.

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APPENDIX A: ANALYTICAL DATA

Table A-1. Regional samples.

Analyzed Constituents*	Line 1				Line 2						Line 3		
	1-1	1-3	1-4	1-7	2-2	2-3	2-4	2-5	2-6	3-1	3-1b	3-2	
Temp (°C)	28.0	27.5	34.0	38.5	27.0	26.5	29.0	31.5	37.0	25.0	24.5	27.0	
pH	7.1	7.6	7.4	8.2	7.5	7.2	7.5	8.0	7.9	6.9	6.9	6.9	
Eh	370	430	110	-120	180	300	-150	-40	-80	ND	380	350	
DO	4.3	1.65	<0.02	ND	ND	5.1	ND	ND	ND	6.2	5.7	2.2	
H_2S	<0.02	<0.02	<0.02	0.74	<0.02	<0.02	2.3	0.03	0.02	<0.02	<0.02	<0.02	
Ca^{2+}	214	50.5	67.6	7.7	60.3	118	43.1	20.1	16.4	494	378	278	
Mg^{2+}	64.6	15.3	17.2	0.46	18.9	34.2	13.8	2.0	1.1	34.6	53.6	47.4	
Na^+	373	209	433	608	723	753	1,060	702	664	148	306	391	
K^+	21.3	10.0	15.5	2.3	15.1	26.0	19.5	7.6	2.8	16.0	25.2	18.0	
Cl^-	826	246	482	492	1,050	1,060	1,380	380	462	1,040	1,100	1,020	
SO_4^{2-}	110	75	185	405	114	374	282	638	594	61.2	112	101	
HCO_3^-	302	270	303	409	272	332	353	263	263	237	234	284	
NO_3^-	40.0	19.4	<0.01	0.94	8.0	38.9	1.6	0.14	0.55	42.4	102	14.2	
SiO_2	85.0	27.1	47.1	24.4	21.8	43.8	19.6	22.2	21.8	40.6	60.5	55.0	
Fe	0.14	0.10	0.22	0.16	0.17	0.11	0.32	0.24	0.25	0.16	0.22	0.11	
PO_4^{3-}	0.05	0.03	0.04	0.05	0.04	0.03	0.03	0.03	0.03	0.03	0.04	0.03	
NH_3	0.23	0.27	0.24	0.06	0.06	0.06	0.10	0.02	0.07	0.06	0.10	0.02	
Al	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.08	0.02	ND	
Mn	0.03	0.04	0.05	0.02	0.03	0.02	0.05	0.02	0.02	0.03	0.01	0.01	
Mo (µg/L)	3.5	3.0	4.9	30	23	13	2.7	57	46	0.7	1.1	<0.1	
U_3O_8 (µg/L)	7.9	6.1	0.1	0.2	4.9	21	<0.2	0.9	0.2	3.7	12	7.6	
Se (µg/L)	1.3	5.9	4.9	3.2	4.2	9.0	1.3	1.5	0.7	1.0	1.7	1.4	
As (µg/L)	12	<1.0	5.0	13	1.0	1.0	1.0	6.0	3.0	20	33	19	
Cu	0.009	0.007	0.005	0.005	0.007	0.040	0.007	0.005	0.005	0.16	0.013	0.028	
TDS	1,880	790	1,400	1,740	2,150	2,610	3,000	1,900	1,890	1,990	2,250	2,060	
Screened interval m (ft)	110 to 128 (360 to 420)	238+ (780+)	271+ (890+)	710 to 747 (2,330 to 2,450)	49 to 64 (160 to 210)	107+ (350+)	168 to 177 (550 to 580)	305 to 352 (1,000 to 1,155)	564 to 579 (1,850 to 1,900)	24 to 30 (80 to 100)	43+ (140+)	88 to 94 (290 to 310)	

* All in mg/L except where noted and for pH (standard units) and Eh (mV)
ND Not determined
DO Dissolved oxygen

Table A-1 (cont.)

Analyzed Constituents*	Line 3 (cont.)			Line 4					Line 5			
	3-3	3-4	3-5	4-2	4-5	4-6	4-7	4-8	5-0	5-1	5-3	5-5
Temp (°C)	28.0	27.5	28.5	25.6	25.0	26.3	27.5	26.0	26.0	25.5	25.0	25.0
pH	7.1	7.1	7.4	7.2	7.2	7.6	7.6	7.6	7.2	7.3	7.0	7.6
Eh	390	30	10	320	320	25	-80	110	360	340	-150	70
DO	4.5	ND	ND	6.1	ND	<0.02	ND	<0.02	7.55	6.25	ND	<0.02
H_2S	<0.02	0.06	<0.02	<0.02	<0.02	<0.02	0.02	<0.02	<0.02	<0.02	9.5	<0.02
Ca^{2+}	169	151	86.6	141	121	35.4	62.1	49.9	132	72.6	312	41.0
Mg^{2+}	32.0	42.2	22.2	21.0	16.8	8.3	19.4	13.6	14.4	10.2	29.2	15.0
Na^+	194	658	320	241	138	218	908	317	373	254	491	576
K^+	6.6	16.0	13.1	18.0	6.3	6.4	18.0	11.0	7.6	5.1	22.0	7.8
Cl^-	462	1,150	449	380	225	204	966	197	568	232	773	736
SO_4^{2-}	78	123	129	184	62.7	15.6	371	201	85.8	66.0	642	9.6
HCO_3^-	245	316	334	300	306	322	522	376	298	447	330	404
NO_3^-	9.1	1.2	0.55	14.1	15.7	0.30	0.20	0.01	63.9	121	<0.10	0.30
SiO_2	47.0	35.0	31.5	63.9	59.0	35.0	19.0	33.5	46.4	74.5	52.0	20.3
Fe	0.10	2.80	0.09	0.26	0.23	0.37	0.99	0.15	0.07	0.06	0.28	0.22
PO_4^{3-}	0.03	0.03	0.02	0.02	0.01	0.02	0.06	0.02	0.02	0.05	0.04	0.03
NH_3	<0.01	0.05	0.07	<0.01	<0.01	<0.01	<0.01	<0.01	0.10	0.25	1.07	0.15
Al	0.05	ND	<0.01	0.04	0.10	0.04	<0.01	0.01	ND	0.02	0.01	0.13
Mn	<0.01	0.14	0.16	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	0.19	0.01
Mo (µg/L)	24	2.1	1.4	<0.1	<0.1	<0.1	47	1.7	1.4	<0.1	<0.1	<0.1
U_3O_8 (µg/L)	5.2	<0.2	<0.2	6.1	3.6	0.2	<0.2	1.2	5.2	99	<0.2	<0.2
Se (µg/L)	4.5	6.1	0.8	<0.25	<0.25	<0.25	0.5	<0.25	3.2	1.7	<0.25	<0.25
As (µg/L)	11	12	2.0	23	22	<1.0	4.4	1.2	45	39	1.4	<1.0
Cu	0.015	0.007	0.005	0.006	0.010	0.002	0.007	0.004	0.009	0.008	0.007	0.004
TDS	1,120	2,330	1,220	1,210	800	680	2,620	1,010	1,440	1,060	2,490	1,610
Screened interval m	104 to 119	122 to 143	110 to 168	58 to 70	76 to 91	94 to 116	128 to 137	107 to 152	18+	37+	50+	82 to 91
(ft)	(340 to 390)	(400 to 470)	(360 to 550)	(190 to 230)	(250 to 300)	(310 to 380)	(420 to 450)	(350 to 500)	(60+)	(120+)	(165+)	(270 to 300)

*   All in mg/L except where noted and for pH (standard units) and Eh (mV)

ND Not determined

DO Dissolved oxygen

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Table A-1 (cont.)

Analyzed Constituents*	Line 5 (cont.) 5-7	Line 6 6-1b	6-1d	6-2	6-3	6-4	6-5	6-6	6-7	Line 7 7-1	7-2	7-3
Temp (°C)	27.5	23.0	19.0	24.0	24.5	29.0	25.5	34.0	34.5	20.5	22.5	22.5
pH	7.6	7.0	7.7	7.1	7.5	8.0	7.9	8.2	8.2	7.1	6.9	7.0
Eh	-80	260	-40	-100	90	-170	-70	-50	-270	420	350	350
DO	ND	0.40	ND	ND	ND	ND	ND	ND	ND	7.6	5.5	4.3
H_2S	0.02	<0.05	0.02	0.38	ND	3.0	0.13	0.06	0.02	<0.02	<0.02	<0.02
Ca^{2+}	62.1	162	38.7	150	78.8	18.1	23.2	7.4	11.6	121	123	119
Mg^{2+}	19.4	20.2	5.2	18.3	10.6	2.7	6.8	0.45	2.1	2.0	3.6	5.0
Na^+	908	296	190	282	445	529	475	546	738	23.5	44.9	81.0
K^+	18.0	15.4	12.5	19.8	17.9	5.1	7.7	8.3	10.0	1.1	1.2	3.4
Cl^-	966	380	120	300	520	590	660	550	760	38.4	67.7	134
SO_4^{2-}	371	135	69.9	420	169	0.2	<0.1	<0.1	<0.1	27.0	24.4	31.6
HCO_3^-	522	642	375	377	434	456	357	600	670	348	348	336
NO_3^-	0.20	0.07	<0.10	<0.10	0.88	<0.10	<0.10	0.10	<0.1	13.9	7.3	1.9
SiO_2	19.0	79.4	34.8	43.2	21.2	20.7	18.8	20.5	20.8	27.0	24.4	31.6
Fe	0.99	0.38	0.86	0.52	0.57	0.17	0.37	0.33	0.23	0.06	0.09	0.09
PO_4^{1-}	0.06	<0.01	0.04	<0.01	<0.01	0.03	0.12	0.15	0.07	0.08	0.04	0.03
NH_1	<0.01	<0.01	0.05	0.12	0.12	<0.01	0.36	0.15	0.33	0.72	0.66	<0.01
Al	<0.01	0.02	0.04	0.04	0.04	0.01	0.03	0.01	0.04	0.06	0.04	0.03
Mn	0.02	0.01	0.11	0.13	0.06	0.02	0.02	0.01	<0.01	<0.01	<0.01	<0.01
Mo ($\mu g/L$)	47	7.8	0.4	0.3	42	<0.1	0.5	1.4	0.6	0.9	<0.1	2.6
U_3O_8 ($\mu g/L$)	<0.2	18	<0.2	1.4	1.0	<0.2	<0.2	<0.2	<0.2	0.9	6.7	0.1
Se ($\mu g/L$)	0.5	2.1	0.5	<0.25	0.1	2.5	0.5	0.2	0.3	<0.25	0.4	7.0
As ($\mu g/L$)	4.4	9.6	<1.0	<1.0	2.1	4.7	0.8	7.1	1.8	2.2	3.0	<1.0
Cu	0.007	0.020	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.006	0.011	0.008
TDS	2,620	1,400	660	1,270	1,480	1,390	1,370	1,430	1,870	430	470	570
Screened interval m	128 to 137	32 to 38	46(?)	46+	70 to 76	244	191 to 198	413 to 463	436 to 485	15+	30 to 35	59 to 67
(ft)	(420 to 450)	(105 to 125)	(150(?))	(150+)	(230 to 250)	(800+)	(625 to 650)	(1,355 to 1,520)	(1,430 to 1,590)	(50+)	(100 to 115)	(193 to 220)

* All in mg/L except where noted and for pH (standard units) and Eh (mV)

ND Not determined

DO Dissolved oxygen

Table A-1 (cont.)

Analyzed Constituents*	Line 7 (cont.)				Line 8						
	7-4	7-5	7-7	7-8	8-1	8-1.5	8-2	8-3	8-4	8-5	8-6
Temp (°C)	22.5	27.5	31.0	30.0	23.0	26.0	23.5	24.0	24.5	29.0	31.0
pH	7.2	7.2	7.5	7.8	7.1	7.0	7.4	7.2	7.8	7.5	7.6
Eh	390	70	30	30	470	430	110	100	60	40	10
DO	2.35	<0.02	ND	<0.02	3.4/6.4	5.9	<0.02	<0.02	<0.02	ND	ND
H_2S	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.04	0.02
Ca^{2+}	102	63.0	12.4	14.4	87.3	129.2	61.1	50.8	9.3	12.3	15.4
Mg^{2+}	6.36	5.89	0.86	1.29	2.0	1.3	5.6	5.6	0.82	0.34	0.21
Na^+	28.7	60.7	293	231	25.3	22.4	89.2	76.4	390	402	385
K^+	3.8	7.2	6.3	2.2	2.2	3.0	9.4	14.2	7.1	11.5	9.4
Cl^-	42.0	33.4	90.4	106	24.4	41.3	29.9	53.5	94.9	121	181
SO_4^{2-}	36.6	25.8	<0.10	102	0.5	1.7	23.0	20.3	28.3	4.4	<0.5
HCO_3^-	352	348	727	337	345	362	392	358	632	964	693
NO_3^-	0.70	<0.01	1.24	0.28	9.58	26.7	0.79	<0.01	0.35	0.24	<0.01
SiO_2	36.6	25.8	45.6	20.6	30.0	24.9	35.2	81.5	78.0	87.5	84.0
Fe	0.06	0.63	0.18	0.12	0.04	0.05	0.13	0.17	0.38	0.25	0.67
PO_4^-	0.04	0.03	0.13	0.04	0.02	0.02	0.02	0.02	0.06	0.14	0.24
NH_3	0.20	0.18	0.30	0.23	0.10	0.11	0.23	0.60	0.39	0.39	0.28
Al	0.06	0.04	0.03	0.05	0.03	0.06	0.03	0.03	0.03	<0.01	<0.01
Mn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.10	0.09	0.02	0.03	0.03
Mo (µg/L)	0.7	5.3	2.5	8.7	<0.1	8.4	0.6	3.2	2.9	11	1.9
U_3O_8 (µg/L)	5.2	<0.1	<0.1	0.8	<0.1	0.2	0.1	<0.1	1.2	<0.1	<0.1
Se (µg/L)	<0.25	<0.25	<0.25	0.6	<0.25	1.3	0.8	1.2	1.4	3.1	1.0
As (µg/L)	2.2	2.4	9.8	6.6	<1.0	<1.0	6.2	14	20	10	<1.0
Cu	0.009	0.003	0.004	0.012	0.010	0.012	0.007	0.007	0.008	0.007	0.006
TDS	430	390	810	640	350	430	450	480	920	1,110	1,020
Screened interval m	116 to 125	226 to 238	335 to 399	488+	29 to 35	29 to 34	34 to 40	61 to 67	91 to 110	183 to 219	283 to 293
(ft)	(380 to 410)	(740 to 780)	(1,100 to 1,310)	(1,600+)	(95 to 115)	(95 to 112)	(110 to 130)	(200 to 220)	(300 to 360)	(600 to 720)	(930 to 960)

* All in mg/L except where noted, and for pH (standard units) and Eh (mV)
ND Not determined
DO Dissolved oxygen

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Table A-1 (cont.)

Analyzed Constituents*	Line 9 9-1	9-2	9-3	9-4	9-6	9-7	10-1	10-2	Line 10 10-4	10-8	10-9
Temp (°C)	24.0	25.0	25.0	26.0	30.0	30.0	24.0	25.5	25.0	30.0	31.5
pH	7.0	7.1	7.6	7.4	7.7	7.8	7.1	7.1	6.9	7.3	8.0
Eh	410	50	70	170	90	-130	360	20	160	40	-70
DO	4.1	ND	<0.02	<0.02	ND	ND	6.3	ND	1.0	ND	ND
H$_2$S	<0.02	0.29	<0.02	<0.02	0.03	1.42	<0.02	0.08	<0.02	<0.02	<0.02
Ca^{2+}	99.5	134	30.5	93.7	10.0	5.9	188.2	90.9	163.3	44.0	4.6
Mg^{2+}	4.7	10.5	4.6	9.4	0.26	0.25	12.9	3.8	9.1	5.0	0.5
Na$^+$	36.7	429	341	568	404	436	163	51	60	173	349
K$^+$	2.8	17.0	6.5	12.9	8.3	8.0	3.9	4.6	6.8	10.6	5.4
Cl$^-$	38.9	732	408	958	228	150	354	36.9	181	111	193
SO$_4^{2-}$	11.7	<0.1	<0.1	<0.5	0.9	<0.1	36.3	24.8	32.3	86.3	58.7
HCO$_3^-$	346	353	308	345	775	914	333	316	304	353	480
NO$_3^-$	8.79	<0.01	0.32	<0.01	<0.01	<0.01	33.9	0.76	0.51	<0.01	<0.01
SiO$_2$	37.2	48.0	29.1	41.2	52.7	73.5	45.2	47.5	33.0	31.3	23.1
Fe	0.08	0.16	0.14	0.19	0.26	0.15	0.13	0.19	0.66	0.75	0.26
PO$_4^{3-}$	0.03	0.02	0.02	0.02	0.08	0.11	0.02	0.04	<0.01	0.01	0.06
NH$_3$	0.32	0.66	0.85	0.76	0.39	0.73	0.05	0.06	0.09	0.36	0.42
Al	0.03	0.05	0.06	<0.01	0.01	0.01	0.02	0.02	0.07	0.03	0.05
Mn	0.02	0.16	0.04	0.07	<0.01	0.02	<0.01	0.02	0.01	0.01	0.01
Mo (µg/L)	0.7	<0.1	4.8	0.5	1.1	<0.1	0.8	1.6	3.3	6.8	3.3
U$_3$O$_8$ (µg/L)	1.2	<0.1	<0.1	0.6	<0.1	<0.1	<0.1	0.1	0.8	<0.1	<0.1
Se (µg/L)	1.3	<0.25	<0.25	<0.25	1.4	0.4	2.9	<0.25	2.9	1.4	0.7
As (µg/L)	1.8	<1.0	3.2	2.0	<1.0	<1.0	7.2	5.5	<1.0	2.8	4.6
Cu	0.010	0.010	0.008	0.013	0.010	0.004	0.009	0.005	0.008	0.008	0.008
TDS	400	1,550	970	1,850	1,090	1,130	970	420	640	640	870
Screened interval											
m	29+	68+	94 to 104	146 to 153	256 to 268	283 to 299	27 to 30	70 to 79	64 to 174	280 to 296	323 to 366
(ft)	(94+)	(223+)	(310 to 340)	(480 to 503)	(840 to 880)	(930 to 980)	(90 to 100)	(230 to 260)	(210 to 570)	(920 to 970)	(1,060 to 1,200)

* All in mg/L except where noted and for pH (standard units) and Eh (mV)

ND Not determined

DO Dissolved oxygen

Table A-2. Ray Point area samples.

Analyzed Constituents*	5-0	5-1	5-3	Z-205	Z-217	ZMR-2	5-5	L-5	L-9	LWB
Temp (°C)	26.0	25.5	25.0	26.3	26.0	28.0	25.0	26.2	27.0	26.0
pH	7.2	7.3	7.0	7.0	7.0	7.7	7.6	7.2	7.2	7.1
Eh	360	340	-150	-150	-130	-200	70	-150	-170	-180
DO	7.55	6.25	ND	ND	ND	ND	<0.02	ND	ND	ND
H_2S	<0.02	<0.02	9.54	6.27	4.78	6.59	<0.02	6.04	5.85	5.88
Ca^{2+}	132	72.6	312	350	345	40.8	41.0	161	175	163
Mg^{2+}	14.4	10.2	29.2	50.5	27.2	14.0	15.0	18.6	20.3	49.8
Na^+	373	254	491	333	361	413	576	495	466	1,100
K^+	7.6	5.1	22.0	27.9	20.5	11.0	7.8	22.9	23.6	24.0
Cl^-	568	232	773	517	357	469	736	561	606	1,540
SO_4^{2-}	85.8	66.0	642	750	960	106	9.6	540	633	378
HCO_3^-	298	447	330	342	322	503	404	344	324	500
NO_3^-	63.9	121	<0.1	0.87	0.78	1.29	0.30	1.07	1.57	0.83
SiO_2	46.4	74.5	52.0	23.2	25.8	10.9	20.3	45.5	43.0	16.6
Fe	0.07	0.06	0.28	0.07	0.44	0.08	0.22	0.08	0.10	0.08
PO_4^{1-}	0.02	0.05	0.04	0.03	0.03	0.02	0.03	0.04	0.02	0.02
NH_1	0.10	0.25	1.07	0.29	0.22	0.33	0.15	0.40	0.21	0.40
Al	ND	0.02	0.01	ND	ND	ND	0.13	0.12	0.04	ND
Mn	<0.01	<0.01	0.19	0.13	0.19	0.01	0.01	0.13	0.11	0.06
Mo (µg/L)	1.4	<0.1	<0.1	1.9	1.2	1.2	<0.1	2.0	1.2	0.3
U_3O_8 (µg/L)	5.2	99	<0.2	0.1	0.6	0.2	<0.2	0.1	0.4	0.3
Se (µg/L)	3.2	1.65	<0.25	0.3	<0.25	0.6	<0.25	1.4	1.2	0.3
As (µg/L)	45	39	1.4	1.6	<1.0	<1.0	<1.0	<1.0	3.0	1.5
Cu	0.009	0.008	0.007	0.008	0.009	0.005	0.004	0.009	0.008	0.015
TDS	1,440	1,060	2,490	2,220	2,260	1,310	1,610	2,020	2,140	3,520
Screened interval										
m	18+	37+	50+	46 to 49	41 to 44	104+	82 to 91	61 to 70	79 to 85	49+
(ft)	(60+)	(120+)	(165+)	(152 to 162)	(133 to 143)	(340+)	(270 to 300)	(200 to 230)	(260 to 280)	(160+)

* All in mg/L except where noted and for pH (standard units) and Eh (mV)
ND Not determined
DO Dissolved oxygen

Table A-3. George West area samples.

| Analyzed Constituents*	A-80	A-23	A-731	A-748	A-705	A-62	A-65 (3-3)	B-67	B-145	B-755	B-721	B-45
Temp (°C)	26.5	27.0	27.0	27.0	27.0	26.0	28.0	26.5	26.5	27.5	27.5	27.5
pH	7.1	7.2	7.5	7.3	7.5	7.1	7.1	7.2	7.5	7.5	7.4	7.3
Eh	390	380	-50	-50	20	320	390	110	-140	10	30	210
DO	5.40	2.90	ND	ND	ND	5.60	4.45	0.45	ND	0.02	0.02	0.60
H_2S	<0.02	<0.02	0.76	0.31	<0.02	<0.02	<0.02	<0.02	6.96	<0.02	<0.02	0.02
Ca^{2+}	154	142	39.8	81.8	38.5	149	169	108	23.8	42.4	66.7	96.2
Mg^{2+}	25.1	23.3	8.7	15.2	9.1	22.4	32.0	21.2	8.8	10.5	15.2	19.0
Na^+	200	256	251	220	250	183	194	201	186	283	198	210
K^+	17.2	13.2	15.5	10.7	16.4	9.6	6.6	9.0	10.3	17.1	14.7	12.7
Cl^-	411	520	307	282	310	235	462	373	132	362	281	354
SO_4^{2-}	106	66.2	<0.5	114	23.2	264	78.0	44.3	<0.5	68.1	31.5	111
HCO_3^-	292	282	322	357	322	338	245	294	397	232	247	248
NO_3^-	4.45	7.65	<0.14	<0.01	0.04	2.55	9.05	<0.40	<0.01	0.17	0.30	<0.01
SiO_2	60.0	51.8	46.1	43.8	52.5	51.8	47.0	46.0	27.8	43.4	41.0	42.2
Fe	0.43	0.03	0.07	0.08	0.47	0.05	0.10	0.10	0.06	0.39	0.20	0.09
PO_4^{3-}	0.05	0.01	0.04	0.02	0.04	0.02	0.03	0.02	0.18	0.02	0.03	0.02
NH_4	0.25	0.18	0.19	0.29	0.08	0.31	<0.01	0.15	0.10	0.11	0.07	0.14
Al	0.06	0.04	0.03	0.04	0.03	0.02	0.05	0.01	0.07	0.03	0.07	ND
Mn	<0.01	<0.01	0.01	0.03	0.01	<0.01	<0.01	1.06	0.01	0.14	0.01	0.01
Mo (μg/L)	<0.1	0.5	<0.1	700	2.1	2.7	24	7.9	<0.1	6.6	7.2	1.8
U_3O_8 (μg/L)	9.4	5.1	<0.1	0.1	6.5	9.4	5.2	2.9	<0.1	0.3	5.5	4.5
Se (μg/L)	0.8	1.4	<0.25	0.3	<1.9	6.0	4.5	0.8	2.1	1.2	0.25	0.6
As (μg/L)	28	22	<0.1	25	68	13	11	35	3.6	118	11	<1.0
Cu	0.008	0.025	0.008	0.004	0.007	0.029	0.015	0.003	0.004	0.007	0.006	0.005
TDS	1,120	1,220	830	940	860	1,090	1,120	950	590	940	770	970
Screened interval m (ft)	55+ (180+)	85 to 91 (280 to 300)	94 to 117 (310 to 385)	82 to 107 (270 to 350)	79 to 102 (260 to 334)	107+ (350+ (?))	104 to 119 (340 to 390)	134+ (440+ (?))	79 to 91 (260 to 300)	114 to 131 (375 to 430)	99 to 136 (325 to 445)	110 to 131 (360 to 430)

* All in mg/L except where noted and for pH (standard units) and Eh (mV)
ND Not determined
DO Dissolved oxygen

Table A-3 (cont.)

| Analyzed Constituents*	C-731	C-736	C-714	C-127	C-133	C-104	D-35	D-88	D-136	D-142
Temp (°C)	27.5	27.5	27.5	28.0	28.5	29.0	28.0	26.5	26.0	27.0
pH	7.5	7.6	7.2	7.5	7.4	7.5	7.5	7.2	6.7	7.0
Eh	-80	-40	30	40	80	80	285	170	320	320
DO	ND	ND	ND	ND	ND	ND	7.00	0.60	8.00	4.10
H_2S	0.67	0.06	0.03	0.03	0.02	0.02	<0.02	<0.02	<0.02	<0.02
Ca^{2+}	38.7	30.7	41.2	58.2	51.6	46.2	41.6	56.9	996	276
Mg^{2+}	9.6	8.3	10.3	10.4	10.5	13.9	9.7	17.5	201	59.4
Na^+	328	236	255	199	234	289	197	226	1,070	365
K^+	13.5	12.7	13.2	16.6	13.4	19.0	9.0	10.2	97.0	17.5
Cl^-	367	257	325	307	296	280	198	268	3,000	947
SO_4^{2-}	15.4	27.8	36.9	39.4	93.8	150	46.8	84.0	1,320	217
HCO_3^-	313	307	287	238	285	302	313	308	218	217
NO_3^-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	1.47	3.49	70.7	5.54
SiO_2	46.1	45.0	37.3	39.7	43.7	42.9	21.3	20.9	34.7	22.8
Fe	0.05	0.26	0.27	0.06	0.07	0.23	0.06	0.05	0.14	0.06
PO_4^{1-}	0.03	0.02	0.04	0.01	0.02	0.04	0.01	0.004	0.05	0.004
NH_1	0.08	0.07	0.04	0.47	0.04	0.04	0.15	0.15	0.17	0.13
Al	0.05	0.03	0.07	0.04	0.04	0.04	ND	0.03	0.13	ND
Mn	0.01	0.04	0.06	<0.01	0.01	<0.07	<0.01	0.01	0.01	<0.01
Mo (μg/L)	<0.1	9.3	12	9.2	3.6	2.6	3.7	120	1.1	0.9
U_3O_8 (μg/L)	<0.1	3.8	0.7	5.7	7.5	3.9	3.0	1.5	9.5	12
Se (μg/L)	<0.8	1.3	1.5	1.4	1.6	1.7	0.6	0.5	28	6.5
As (μg/L)	1.4	18	1.8	1.6	<1.0	8.6	1.0	98	30	2.1
Cu	0.007	0.006	0.007	0.007	0.011	0.007	0.016	0.009	0.030	0.009
TDS	970	770	860	790	880	990	680	840	6,830	2,010
Screened interval m	110 to 127	116 to 136	123 to 156	141 to 156	165 to 175	170 to 178	67+	49+	67+	91+
(ft)	(360 to 422)	(380 to 445)	(405 to 512)	(463 to 513)	(540 to 575)	(557 to 585)	(220+)	(160+)	(220+)	(300+)

* All in mg/L except where noted and for pH (standard units) and Eh (mV)
ND Not determined
DO Dissolved oxygen

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APPENDIX B: WELL CROSS SECTIONS

The following cross sections of the Oakville aquifer show the location and depth of sample wells. Well numbers correspond to numbers on figure 1 and in Appendix A. All wells are projected to the line of section. Total depth of each well is shown next to the well. The blacked-in area at or near the bottom of most wells is the screened interval; the precise depths of screened intervals are given in Appendix A. Wells without a blacked-in area are open at the bottom.
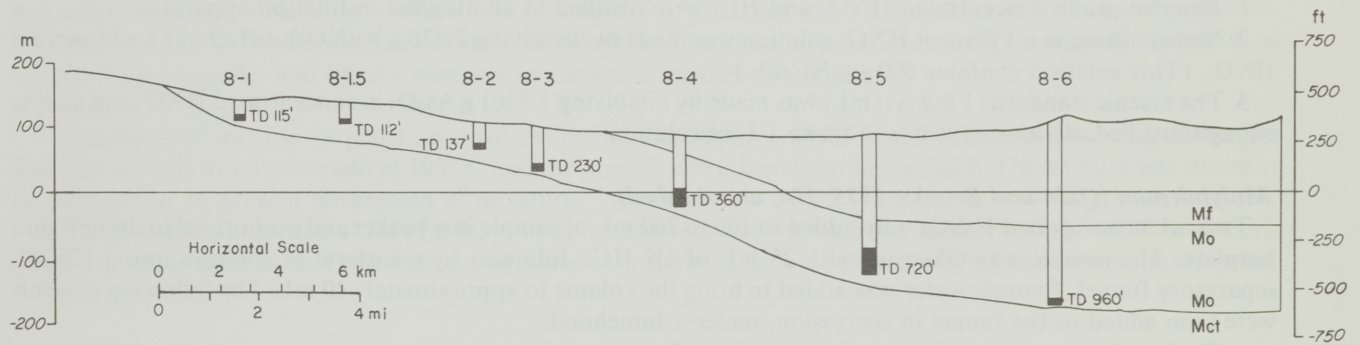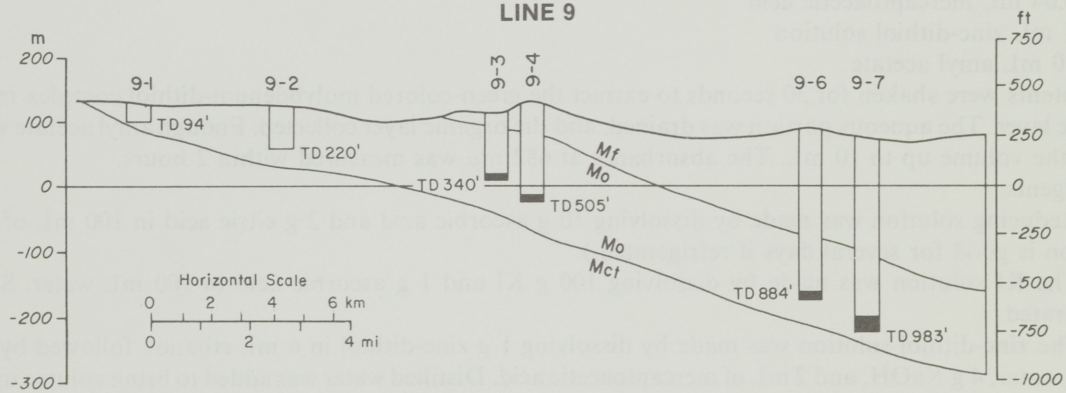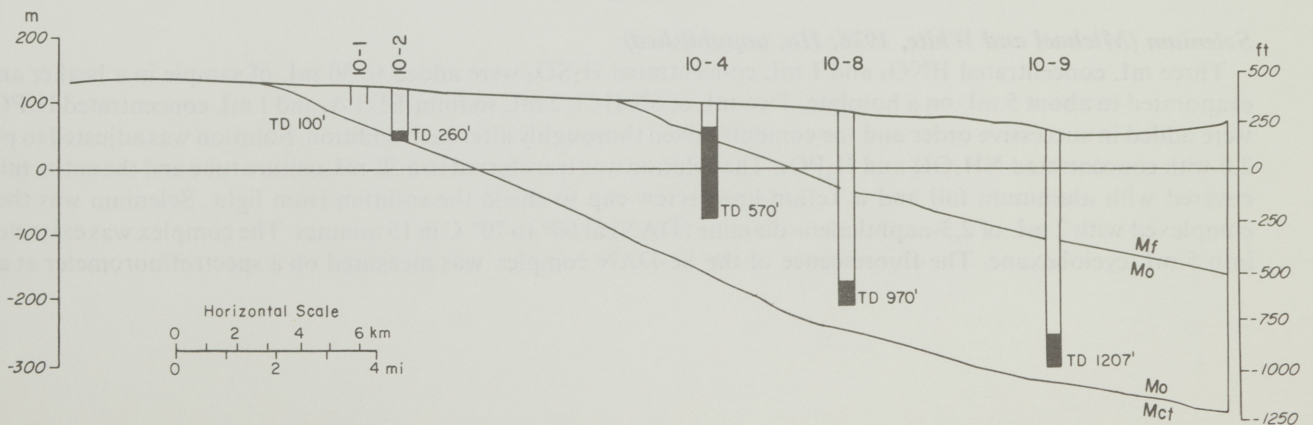

LINE 1

LINE 2

LINE 4

LINE 3

LINE 5

LINE 6

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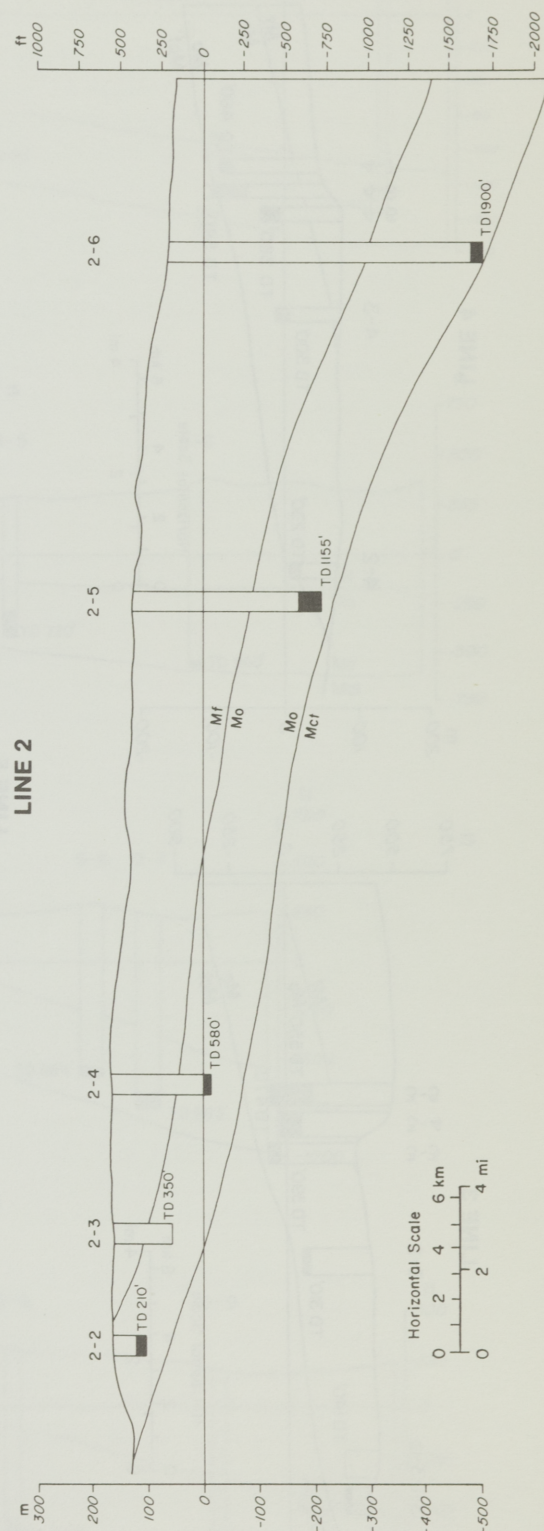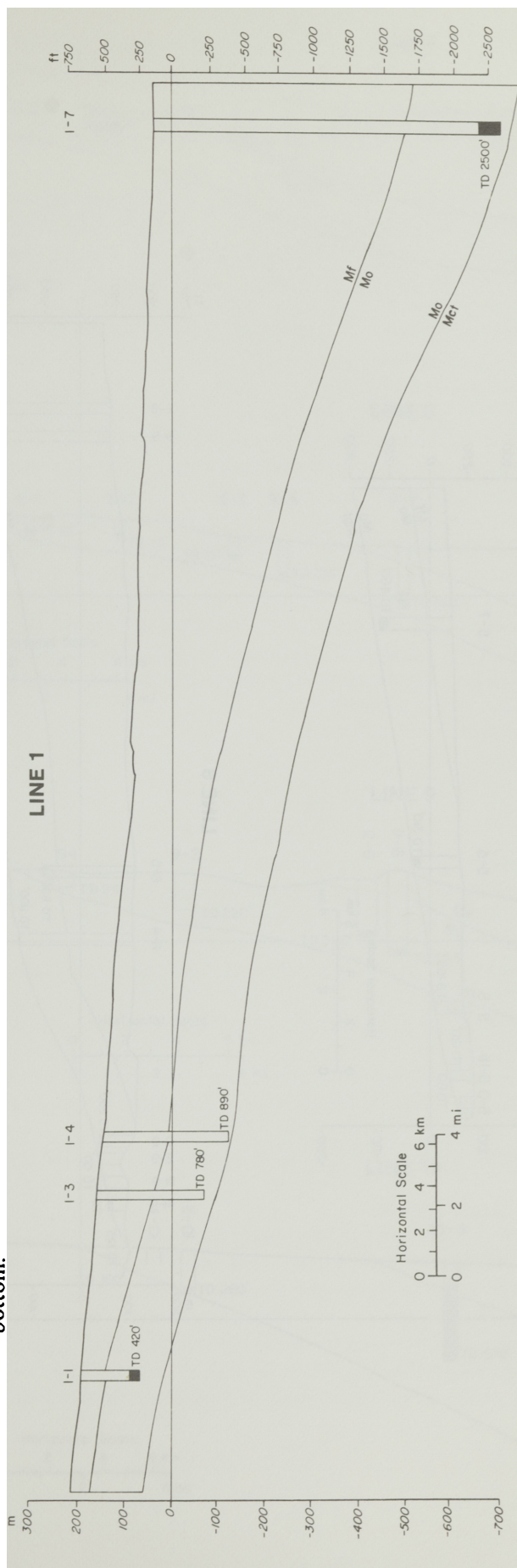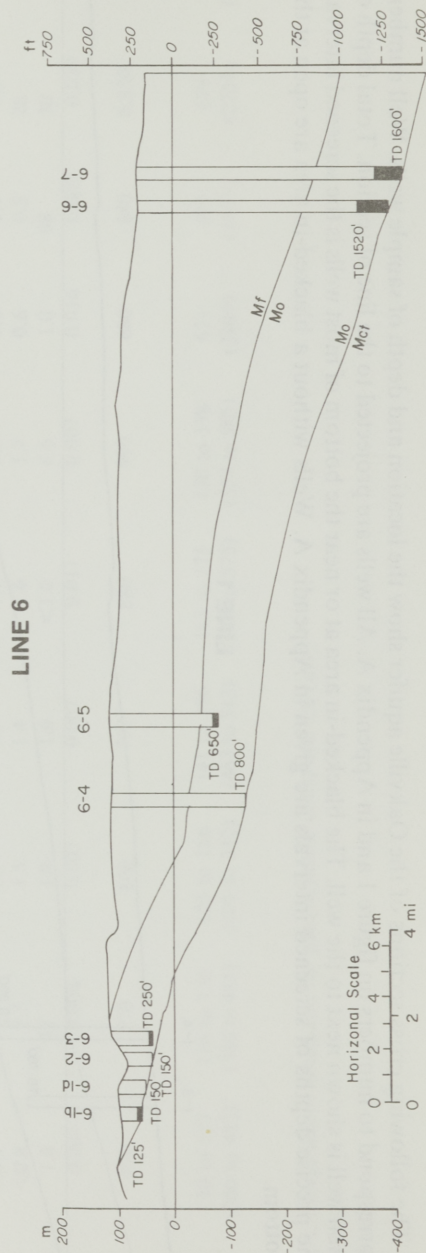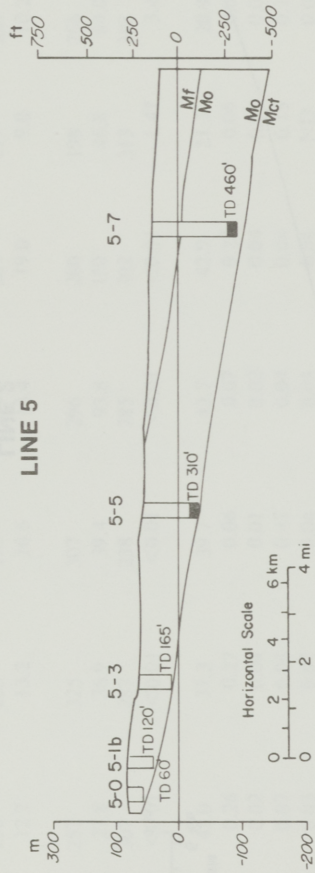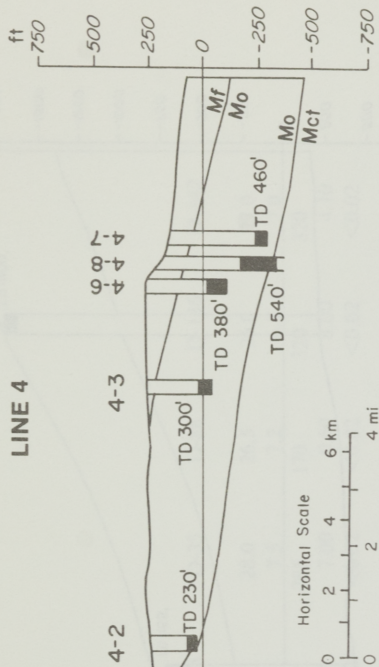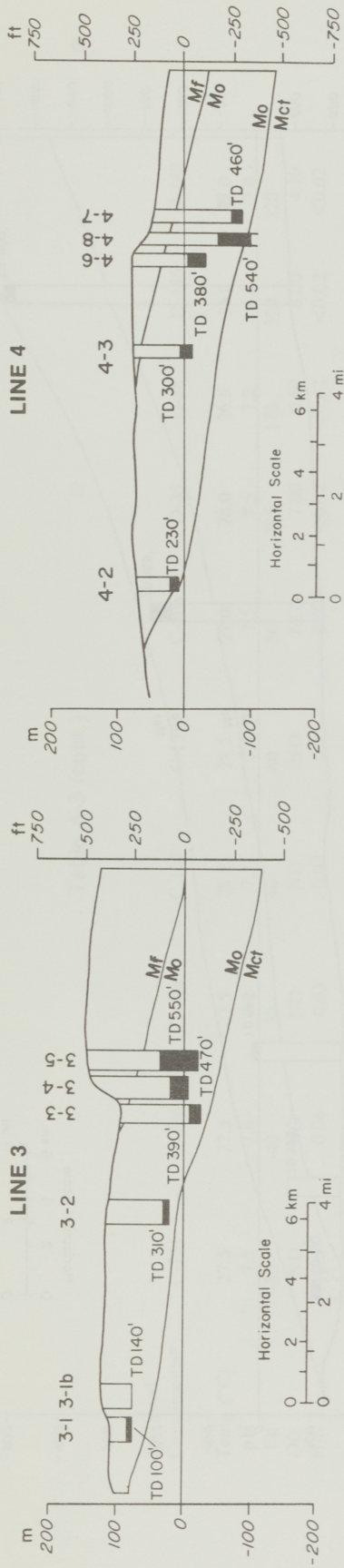
LINE 7
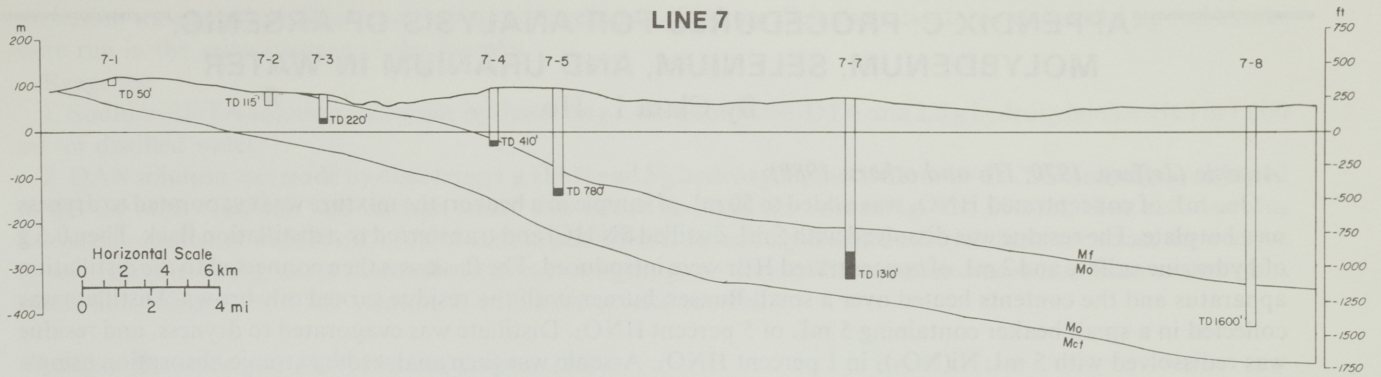
LINE 8

LINE 9

LINE 10

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APPENDIX C: PROCEDURES FOR ANALYSIS OF ARSENIC, MOLYBDENUM, SELENIUM, AND URANIUM IN WATER

By Clara L. Ho

Arsenic (Jeffery, 1970; Ho and others, 1980):

One mL of concentrated HNO_3 was added to 50 mL of sample in a beaker; the mixture was evaporated to dryness on a hotplate. The residue was dissolved with 5 mL distilled 6N HCl and transferred to a distillation flask. Then 0.5 g of hydrazine sulfate and 2 mL of concentrated HBr were introduced. The flask was then connected to the distillation apparatus and the contents heated over a small Bunsen burner until the residue turned oily brown. Distillate was collected in a small beaker containing 5 mL of 5 percent HNO_3. Distillate was evaporated to dryness, and residue was redissolved with 5 mL $Ni(NO_3)_2$ in 1 percent HNO_3. Arsenic was then analyzed by atomic absorption using a graphite furnace technique. Two blanks and two arsenic standards containing as much as 0.1 μg As/mL in the final solution were distilled and analyzed in the same manner as the samples.

Reagents:

1. Reagent-grade concentrated HNO_3 and HCl were distilled in an all-glass distillation apparatus.

2. Nickel nitrate in a 1 percent HNO_3 solution was made by dissolving 2.476 g $Ni(NO_3)_2 \cdot 6H_2O$ in 1 L of 1 percent HNO_3. (This solution contains 500 μg Ni/mL.)

3. The arsenic standard (1 mg As/mL) was made by dissolving 1.5361 g As_2O_3 in concentrated HNO_3 and adding enough distilled, de-ionized water to make 1 L of solution.

Molybdenum (Quin and Brooks, 1975; Ho, unpublished):

Two mL concentrated H_2SO_4 were added to 100 to 200 mL of sample in a beaker and evaporated to dryness on a hotplate. The residue was taken up with 25 mL of 4N HCl, followed by transferal of solution into a 125-mL separatory funnel. Enough water was added to bring the volume to approximately 40 mL. The following reagents were then added to the funnel in succession, under a fumehood:

a. 2 mL reducing agent (mixed and set aside for 5 minutes)

b. 3 mL KI solution

c. 0.04 mL mercaptoacetic acid

d. 1 mL zinc-dithiol solution

e. 10 mL amyl acetate

Contents were shaken for 30 seconds to extract the green-colored molybdenum-dithiol complex into the amyl acetate layer. The aqueous portion was drained, and the organic layer collected. Enough amyl acetate was added to bring the volume up to 10 mL. The absorbance at 682 mμ was measured within 2 hours.

Reagents:

1. Reducing solution was made by dissolving 10 g ascorbic acid and 2 g citric acid in 100 mL of water. (The solution is good for several days if refrigerated.)

2. The KI solution was made by dissolving 100 g KI and 1 g ascorbic acid in 100 mL water. Solution was refrigerated.

3. The zinc-dithiol solution was made by dissolving 1 g zinc-dithiol in 6 mL ethanol, followed by addition of 10 mL water, 4 g NaOH, and 2 mL of mercaptoacetic acid. Distilled water was added to bring volume up to 100 mL. Solution was stored in a refrigerator.

4. The 4N HCl solution was made by mixing 500 mL of distilled 50 percent HCl with 250 mL of distilled water.

Selenium (Michael and White, 1976; Ho, unpublished):

Three mL concentrated HNO_3 and 1 mL concentrated H_2SO_4 were added to 50 mL of sample in a beaker and evaporated to about 5 mL on a hotplate. Two mL of 6N HCl, 2 mL sodium-EDTA, and 1 mL concentrated H_3PO_4 were added in successive order and the contents mixed thoroughly after each addition. Solution was adjusted to pH 2.0 with concentrated NH_4OH and H_3PO_4. The solution was transferred to a 50-mL culture tube and the entire tube covered with aluminum foil and a Teflon-lined screw cap to shield the solution from light. Selenium was then complexed with 2 mL of 2,3-naphthalene diamine (DAN) at 60° to 70° C in 15 minutes. The complex was extracted into 5 mL cyclohexane. The fluorescence of the Se-DAN complex was measured on a spectrofluorometer at an

excitation wavelength of 374 mμ and emission wavelength of 517 mμ. Selenium standards of up to 0.1 μg and blanks were run in the same manner as the samples.

Reagents:

1. Sodium-EDTA solution was made by dissolving 1.489 g sodium-EDTA and 2.5 g hydroxylamine·HCl in 1,000 mL of distilled water.

2. DAN solution was made by dissolving 1 g DAN and 5 g hydroxylamine·HCL in 1 N HCl. Solution was adjusted to pH 2.0 with NH$_4$OH, and enough water was added to bring the volume up to 1,000 mL. The solution was extracted repeatedly with 20 mL cyclohexane in a 2,000-mL separatory funnel until cyclohexane extract showed the lowest constant background fluorescence at wavelengths given above. The solution was stored in an amber glass bottle in a refrigerator. (The solution is stable for several months.)

Uranium (Baltisberger, 1964; Ho and Dupre, 1980):

One hundred mL of sample in a beaker were evaporated to dryness on a hotplate. Organic substances in residue were oxidized with concentrated HNO$_3$. The residue was dissolved with 5 mL of 10 percent HNO$_3$ and transferred into a culture tube with a Teflon-lined screw cap. Uranium was complexed with trioctylphosphine oxide (TOPO) and extracted into cyclohexane in 16 seconds. Uranium-TOPO adduct in 0.1 mL cyclohexane was fused with NaF-KF to form a pellet. The fluorescence of the pellet was then measured on a fluorometer. Two uranium standards of up to 0.1 μg per pellet and blanks were run in the same manner as samples.

Reagents:

1. The NaF-KF mix for the pellet was made by combining 98 parts of NaF and 2 parts of KF (by weight) in a jar. The mixture was dried overnight at 105° C and the powder was mixed thoroughly again. The mixture was stored in an air-tight jar to prevent absorption of moisture.

2. The trioctylophosphine oxide (TOPO) - cyclohexane solution was made by dissolving 2 g TOPO in 100 mL reagent-grade cyclohexane. The solution was stored in an amber glass bottle fitted with a 5-mL automatic repipette.