THE USE OF RADIOGENIC ELEMENTS, AND SELECTED TRACE ELEMENTS AND THEIR SOLUTION-MINERAL EQUILIBRIA IN GROUNDWATER AS EXPLORATION TOOLS FOR URANIUM DEPOSITS

By

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ABSTRACT

Groundwater from 96 wells was sampled from uraniferous aquifers in southwest Texas and Wyoming. Variations in concentrations of U, As, Mo, Se and V were compared with the saturation state of the groundwater with respect to mineral phases of these elements known or expected to occur in each area. The non-radiogenic trace elements exhibited strong redox dependence consistent with thermodynamic predictions, but their variations did not pinpoint existing uranium ore bodies, because of a shift in the groundwater flow regime since the time of ore emplacement. Saturation levels of trace element minerals such as realgar, native Se, and molybdenite showed broad anomalies around the ore-bearing areas, similar to patterns found for U minerals by Langmuir and Chatham (1980), and Chatham et al. (1981). The radiogenic elements Ra and Rn showed significant anomalies directly within the ore zones. Helium anomalies were displaced in the direction of groundwater flow, but by their magnitude and areal extent provided strong evidence for the existence of nearby uranium accumulations. Uranium isotope ratios showed no systematic variations within the two aquifers studied.
The optimum use of groundwater geochemical concepts for exploration should involve consideration of the hydrogeologic properties of the ore-bearing formation and potential sample site density. This approach works best in simple hydrologic systems where samples may be taken at an approximate density of one or more sample per square mile. When properly used, the approach can accurately pinpoint uranium mineralization at a fraction of the cost of conventional methods that involve test drilling and geophysical and core logging.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xii</td>
</tr>
<tr>
<td>LIST OF PLATES</td>
<td>xiii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>xiv</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>GEOCHEMICAL BACKGROUND FOR THE STUDY</td>
<td>3</td>
</tr>
<tr>
<td>Uranium</td>
<td>3</td>
</tr>
<tr>
<td>Uranium Isotopes</td>
<td>5</td>
</tr>
<tr>
<td>Radium and Radon</td>
<td>11</td>
</tr>
<tr>
<td>Helium</td>
<td>15</td>
</tr>
<tr>
<td>Non-Radiogenic Elements</td>
<td>19</td>
</tr>
<tr>
<td>FIELD METHODS</td>
<td>26</td>
</tr>
<tr>
<td>Computational Methods</td>
<td>26</td>
</tr>
<tr>
<td>THE TEXAS STUDY AREA</td>
<td>32</td>
</tr>
<tr>
<td>Geology and Physiography</td>
<td>32</td>
</tr>
<tr>
<td>Hydrogeology</td>
<td>37</td>
</tr>
<tr>
<td>Basic Groundwater Chemistry</td>
<td>41</td>
</tr>
<tr>
<td>Trace Elements in Groundwater</td>
<td>47</td>
</tr>
<tr>
<td>THE WYOMING STUDY AREA</td>
<td>80</td>
</tr>
<tr>
<td>Geology and Physiography</td>
<td>80</td>
</tr>
<tr>
<td>Hydrogeology</td>
<td>82</td>
</tr>
<tr>
<td>Basic Groundwater Chemistry</td>
<td>85</td>
</tr>
<tr>
<td>Trace Elements in Groundwater</td>
<td>95</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS (CON'T)

DISCUSSION .....................................................128
  Effectiveness of the Exploration Technique .......... 128
  The Solubility of Montroseite .......................... 131
  Age Dating of Groundwaters .............................. 136
  Logistics of the Exploration Program ................. 138

CONCLUSIONS ....................................................140

REFERENCES CITED ..............................................143
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Distribution of uranyl complexes vs. pH for typical ligand concentrations in groundwater.</td>
</tr>
<tr>
<td>2</td>
<td>The $^{238}$U decay series, neglecting all daughters with half-lives less than that of $^{222}$Rn.</td>
</tr>
<tr>
<td>3</td>
<td>Alpha activities of $^{235}$U vs. $^{238}$U, in pCi/l, in the groundwater samples from the upper and lower Oakville Formation.</td>
</tr>
<tr>
<td>4</td>
<td>The classification scheme proposed by Cowart and Osmond (1980) for variations in total U concentrations vs. the $^{234}$U/$^{238}$U alpha activity ratio.</td>
</tr>
<tr>
<td>5</td>
<td>Eh-pH diagram showing some mineral-solute boundaries for As, Mo, Se and U.</td>
</tr>
<tr>
<td>6</td>
<td>Eh-pH diagram for the system V-H$_2$O-O$_2$ at 25°C.</td>
</tr>
<tr>
<td>7</td>
<td>Regional geologic map of the south Texas coastal plain showing the location of the Oakville study area.</td>
</tr>
<tr>
<td>8</td>
<td>Generalized geologic cross-section of the Texas study area.</td>
</tr>
<tr>
<td>9</td>
<td>Piezometric map in the area of the Zamzow in-situ uranium mine.</td>
</tr>
<tr>
<td>10</td>
<td>Total dissolved solids concentration in the lower Oakville groundwater.</td>
</tr>
<tr>
<td>11</td>
<td>Prevalent chemical character of the Texas study area groundwater.</td>
</tr>
<tr>
<td>12</td>
<td>The position of the redox interface in the lower Oakville Formation.</td>
</tr>
</tbody>
</table>
13 pH variations in the lower Oakville Formation groundwater ..................................46

14 Uranium concentrations in the groundwater of the lower Oakville Formation .................48

15 Dissolved uranium levels along profile A-A' in Plate 2 ...................................50

16 Variations in AR in the lower Oakville Formation groundwater ..............................51

17 The Texas study area groundwater samples shown on a log U vs. AR plot as proposed by Cowart and Osmond (1980) .....................53

18 Radium concentrations in the lower Oakville Formation groundwater .................55

19 Radon concentrations in the lower Oakville Formation groundwater ......................56

20 Profile of log values of Ra and Rn concentrations in the lower Oakville Formation groundwater .............................57

21 Helium concentrations in the lower Oakville Formation groundwater ............................59

22 Arsenic concentrations in the lower Oakville Formation groundwater ..................60

23 Molybdenum concentrations in the lower Oakville Formation groundwater ...........61

24 Selenium concentrations in the lower Oakville Formation groundwater ............62

25 The concentration cliff of As, Mo, and Se in the lower Oakville Formation groundwater...64

26 SI values for realgar in the lower Oakville Formation groundwater ..................67

27 SI values for arsenopyrite in the lower Oakville Formation groundwater ..............68

28 SI values for As metal in the lower Oakville Formation groundwater .................69
SI values for ferrimolybdite in the lower Oakville Formation groundwater.................71
SI values for molybdenite in the lower Oakville Formation groundwater................72
SI values for native Se in the lower Oakville Formation groundwater................73
SI values for ferroselite in the lower Oakville Formation groundwater...............74
Vanadium concentrations in the lower Oakville Formation groundwater................76
Montroseite SI values in the lower Oakville Formation groundwater....................77
Paramontroseite SI values in the lower Oakville Formation groundwater..............78
Generalized geologic cross section of the Wyoming study area..........................81
Regional piezometric map in the Wyoming study area....................................84
Total dissolved solids concentration in the upper aquifer systems of the Lance Formation.................................86
Total dissolved solids concentration in the lower aquifer systems of the Lance Formation........................................87
Prevalent chemical character of the upper aquifer systems of the Lance Formation........................................89
Prevalent chemical character of the lower aquifer systems of the Lance Formation........................................90
Eh variations in the upper Lance Formation groundwaters...............................91
Eh variations in the lower Lance Formation groundwaters................................92

ix
Variations in pH in the upper Lance Formation groundwaters..........................93

Variations in pH in the lower Lance Formation groundwaters..........................94

Uranium concentrations in upper Lance Formation groundwaters..........................96

Uranium concentrations in lower Lance Formation groundwaters..........................97

The Wyoming study area groundwater samples plotted on a log U vs. AR plot as proposed by Cowart and Osmond (1980)............................98

Variations in AR in upper Lance Formation groundwater.................................99

Variations in AR in lower Lance Formation groundwater.................................100

Radium concentrations in upper Lance Formation groundwater.......................102

Radium concentrations in lower Lance Formation groundwater.......................103

Radon concentrations in upper Lance Formation groundwater.......................104

Radon concentrations in lower Lance Formation groundwater.......................105

Helium concentrations in upper Lance Formation groundwater.......................106

Helium concentrations in lower Lance Formation groundwater.......................107

Arsenic concentrations in upper Lance Formation groundwater.......................109

Arsenic concentrations in lower Lance Formation groundwater.......................110

Molybdenum concentrations in upper Lance Formation groundwater...................111
Molybdenum concentrations in lower Lance Formation groundwater .................. 112
Selenium concentrations in upper Lance Formation groundwater .................. 113
Selenium concentrations in lower Lance Formation groundwater .................. 114
Native As SI values in the upper aquifer systems of the Lance Formation .......... 115
Native As SI values in the lower aquifer systems of the Lance Formation .......... 116
Realgar SI values in the upper aquifer systems of the Lance Formation .......... 117
Realgar SI values in the lower aquifer systems of the Lance Formation .......... 118
Arsenopyrite SI values in the upper aquifer systems of the Lance Formation ........ 119
Arsenopyrite SI values in the lower aquifer systems of the Lance Formation ........ 120
Molybdenite SI values in the upper aquifer systems of the Lance Formation ....... 121
Molybdenite SI values in the lower aquifer systems of the Lance Formation ....... 122
Se metal SI values in the upper aquifer systems of the Lance Formation .......... 123
Se metal SI values in the lower aquifer systems of the Lance Formation .......... 124
Ferroselite SI values in the upper aquifer systems of the Lance Formation ........ 125
Ferroselite SI values in the lower aquifer systems of the Lance Formation ........ 126
Goethite SI values in the lower Oakville Formation groundwater ................. 134

xi
## LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>29</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>39</td>
</tr>
</tbody>
</table>

1. The theoretical migration distance of Rn in an aquifer..............................14
2. Matrices of linear correlation coefficients for He vs. Ra and Rn....................18
3. A summary of field analytical methods........................................27
4. A summary of sample collection methods........................................29
5. Tabulation of analytical methods with detection limits and accuracies.............30
6. Hydrologic characteristics of the lower Oakville aquifer...........................39
LIST OF PLATES

<table>
<thead>
<tr>
<th>PLATE</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Geologic map of the south Texas study site, showing ore zone locations and sample sites.</td>
</tr>
<tr>
<td>2</td>
<td>Base map of the south Texas study site and the location of profile A-A'.</td>
</tr>
<tr>
<td>3</td>
<td>Geologic map of the Wyoming study site, showing ore zones and sample sites.</td>
</tr>
<tr>
<td>4</td>
<td>Chemical analysis data for the south Texas study area groundwater samples.</td>
</tr>
<tr>
<td>5</td>
<td>Continued listing of south Texas study area groundwater chemical analyses.</td>
</tr>
<tr>
<td>6</td>
<td>Chemical analysis data for the Wyoming study area groundwater samples.</td>
</tr>
<tr>
<td>7</td>
<td>Continued listing of the Wyoming study area groundwater chemical analyses.</td>
</tr>
</tbody>
</table>
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Dedicated to my mother and dad.

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INTRODUCTION

The use of groundwater geochemical methods in prospecting for ores of economic interest has long been overlooked. In fact, only in the last few years have solution-mineral equilibrium concepts been recognized as a valid approach in the exploration for uranium ores (cf. McNally and Langmuir (1977); Applin and Langmuir (1978); Langmuir (1978); Lueck (1978); Langmuir and Chatham (1980); Runnells et al. (1980)). Most recently, Langmuir and Chatham have demonstrated that the state of saturation of a groundwater with respect to various uranium minerals may be more indicative of the location of ores than variations in the individual concentrations of the so-called pathfinder elements (As, Mo, Se, V, U, Ra, Rn, etc.). This study concentrated not only on the pathfinder elements as such, but also on the solution-mineral equilibria they are involved in within the groundwater regime. To date, no one has evaluated the effectiveness of these trace element mineral-solution equilibria in pinpointing uranium ore deposits.

The purpose of the study is to compare the accuracy of using variations in the concentrations of individual trace elements (excluding uranium) with variations in the solution-mineral equilibria of these elements in groundwater to
locate known uranium ore bodies. Towards that end two dis-
tinct field locations were chosen. Both areas contain sig-
nificant uranium mineralization. Existing domestic, stock,
and other wells were sampled in and around the ore zones,
and chemical analyses of the groundwater were performed for
a variety of major and trace elements. Computer calcula-
tions were performed on the groundwater chemical analyses
using an expanded version of the program WATEQF (Plummer et
al., 1976) to determine the aqueous speciation of the ele-
ments and the status of solution-mineral equilibria. Loca-
tions of anomalous elemental concentrations or saturation
levels were compared to the position of the ore to determine
which is the more reliable prospecting tool.
GEOCHEMICAL BACKGROUND FOR THE STUDY

Uranium

Uranium dissolved in surface or groundwaters is the most frequently used of the "pathfinder" elements (Dyck, 1975; Langmuir and Chatham, 1980). High concentrations of U (> 10 ppb) are common in oxidized groundwaters in uraniferous areas, but the concentration of U in groundwaters in an orebody may not be anomalously high (DeVoto, 1978a; Childers, 1979; this study).

The behavior of U in the groundwater regime can often be explained with reference to its geochemical properties. Earlier studies of U geochemistry (cf. Hostetler and Garrels, 1962), although sketchy, adequately explained the observed behavior of U in groundwater, and the formation of sedimentary U orebodies. The thermodynamic data for uranium and its implications have since been expanded upon by Langmuir (1978). Consequently, the behavior of U in inorganic complexes is now fairly well known.

Although organic complexing of U is less well understood, it is certain that U-organic bonds are fairly strong (Dyck, 1975; Schmidt-Collerus, 1967). The solubility of these complexes may be a function of the molecular weight (MW) of the organic ligand. Uranium organic complexes with
low MW ligands such as fulvic acids should be more soluble than those formed with high MW ligands such as humic acids. Furthermore, U is strongly sorbed on organic material in sediments, as evidenced by the widespread occurrence of uraniferous organic matter in ore bodies (cf. Hostetler and Garrels, 1962; Jensen, 1958; Breger, 1974). Riese et al. (1979) have clearly shown the association of organic matter with uranium ore minerals, and based upon SEM microphotography, have attributed this association to the sorption of uranyl-organic complexes onto clay minerals. Aside from recognizing the existence of such U-organic associations, they will not be dealt with further in this study.

The following discussion of uranium geochemistry is based largely on the work of Langmuir (1978). It has long been known that the principal control on U solubility is its oxidation state (cf. Hostetler and Garrels, 1962; Dyck, 1978). Uranium is relatively soluble as the oxidized $\text{UO}_2^{2+}$ (uranyl) ion or one of its complexes, and precipitates from groundwater upon reduction as $\text{UO}_2$, $\text{U}_3\text{O}_8$, or more often as a non-stoichiometric, relatively amorphous, intermediate (pitchblende). The mobility of uranyl ion is severely reduced in the presence of vanadate ($\text{VO}_4^{3-}$) due to the extreme insolubility of the uranyl vanadate minerals, carnotite and
tyuyamunite, which fact explains the common association of U and V in oxidized U ores. Uranyl complexes with sulfate, fluoride and biphosphate, and the di- and tri-carbonate complexes will dominate the aqueous speciation of U under most natural conditions of pH and ligand concentrations (Fig. 1). Uranyl chloride complexes are seldom important, but hydroxy and silicate complexes may be significant under slightly acid to neutral pH conditions, respectively. One can expect that the groundwater uranium concentration may be relatively high (> 10 ppb) in oxidizing recharge zones, and that it will decrease significantly (< 0.1 ppb) beyond the oxidation-reduction interface (where Eh < 0 volts). The concentration of U may be very high at the updip edge of a roll front (the "alteration envelope" of Granger and Warren, 1974; see also, Dyck, 1975; Cowart and Osmond, 1980). The fortuitous location of a sample well in or near this zone may lead to the accurate location of a uranium ore body based on a high U concentration.

Uranium Isotopes

Uranium isotope geochemistry is founded on the principle of isotopic secular equilibrium. When a decay series is at secular equilibrium, the rate of production of any daughter in that series will be equal to its rate of decay. In
Figure 1. Distribution of uranyl complexes vs. pH for typical ligand concentrations in groundwater. \( P_{CO_2} = 10^{-2.5} \) atm, \( \xi F = 0.3 \) ppm, \( \xi Cl = 10 \) ppm, \( \xi SO_4 = 100 \) ppm, \( \xi PO_4 = 0.1 \) ppm, \( \xi SiO_2 = 30 \) ppm (modified from Langmuir, 1978).
the case of U isotopes, the parent is $^{238}\text{U}$ and the daughter of interest is $^{234}\text{U}$. The two are separated in the decay series by the short-lived elements, $^{234}\text{Th}$ and $^{234}\text{Pa}$ (Fig. 2), whose significance on a geologic time scale is trivial when compared to the half lives of the above U isotopes. The $^{234}\text{U}/^{238}\text{U}$ alpha activity ratio (AR) has been recognized as the most convenient way of evaluating U isotopic data. At AR values other than unity, the U isotopes are not at secular equilibrium. Excellent summaries of the ways in which U isotopes may be fractionated can be found in Rosholt et al. (1963), Osmond and Cowart (1976), and Levinson and Coetzee (1978). The principal mechanism of isotopic fractionation is alpha recoil (Fleischer, 1980), in which a $^{238}\text{U}$ atom undergoes alpha decay and recoils like a shotgun. This can position it in a more readily leachable site near the solid-solution interface, or expel it directly into the surrounding solution. Fleischer (1980) has shown that following the alpha decay of $^{238}\text{U}$, the daughter, $^{234}\text{Th}$, may "carve" a wide track in the crystal lattice, leaving the crystal surface more susceptible to leaching along that track. When $^{234}\text{U}$ is produced by the beta decay of $^{234}\text{Pa}$, it will be more easily leached from the solid. Compounding this effect, the alpha particle escaping from $^{238}\text{U}$ may "pick up" two of the parent atom valence electrons as it escapes,
Figure 2. The $^{238}\text{U}$ decay series, neglecting all daughters with half-lives less than that of $^{222}\text{Rn}$.
to balance its divalent charge and become a neutral helium atom. This process leaves the daughter ($^{234}$Th) with two less valence electrons. When $^{234}$U is produced, it will then be present in the hexavalent state, the more soluble form of U (Rosholt et al., 1963). The result will be a liquid phase enriched in $^{234}$U and a solid phase depleted in $^{234}$U.

The possibility of geochemical fractionation of U isotopes exists, but is considered unimportant. Correlation tests have been run of AR versus all the major complex-forming anionic species in our study groundwaters, including carbonate, sulfate, fluoride, and phosphate. No significant correlation ($r$) was found for AR versus any of the anionic species in the 96 Texas and Wyoming groundwater samples. Fractionation due to mass action or biological processes should not be significant because there is less than a 2% mass difference between the isotopes, and U is not absorbed by the biota to any extent. Further evidence against the possibility of geochemical or biological fractionation is the observation that $^{238}$U and $^{235}$U are not fractionated. This is shown by the excellent correlation between $^{238}$U and $^{235}$U alpha activity (Fig. 3) found in the Texas well waters collected for this study.

Cowart and Osmond (1980), and Osmond and Cowart (1977) have presented the most thorough studies of the use of U
Figure 3. Alpha activities of $^{235}\text{U}$ vs. $^{238}\text{U}$, in pCl/l, in the groundwater samples from the upper and lower Oakville aquifers. Correlation coefficient (r) = 0.99.
isotopic composition as applied to exploration for sandstone U ores. By making plots of AR versus total U concentration, they claim they can uniquely characterize groundwaters in terms of proximity to U accumulations. Their generalized fence diagram for this purpose is shown in Fig. 4. Assumptions implicit in the theory leading to this figure are: first, that U concentration and AR act as independent variables; second, that the samples are collected in a potentially uraniferous area; and third, that dissolved uranium concentrations in stable and forming accumulations of uranium ore exceed 1 ppb. The study results as described here indicate that the first two assumptions are often valid. However, the third assumption is generally wrong when applied to reduced groundwaters in uraniferous formations, where dissolved uranium concentrations are usually below 1 ppb.

Radium and Radon

Radium and radon are two relatively short-lived daughters of uranium. Specifically, $^{238}\text{U}$, the most abundant of the uranium isotopes, decays to form $^{226}\text{Ra}$ and $^{222}\text{Rn}$ (Fig. 2). An alkaline earth element, radium is the first element of the $^{238}\text{U}$ decay series that varies significantly in chemical properties from its parents. Radium usually occurs in the groundwater regime as the mobile, free $\text{Ra}^{2+}$ ion. Radium
Figure 4. The classification scheme proposed by Cowart and Osmond (1980) for variations in total U concentrations (ppb) vs. the $^{234}\text{U}/^{238}\text{U}$ alpha activity ratio (AR).
may precipitate in pure phases as a sulfate or carbonate, but this must be extremely rare due to the very low natural abundance of Ra\(^{2+}\) ion in waters. More likely, the solubility of radium is controlled by cocrystallization with barium in barite, or with the alkali metals or alkaline earths in gypsum, jarosites or alunites, or by its adsorption on the surface of silica (Riese, 1980; verbal communication) and of Mn and Fe oxyhydroxides. Uptake of radium by plants may be significant in near-surface waters, but will not be a factor in deep aquifers such as those studied here (Levinson and Coetzee, 1978).

Radon-222 is a noble gas produced by the alpha decay of \(^{226}\)Ra. It has a very short half life (3.82 days), and therefore, is rapidly attenuated in the environment. Using the following equation given by Tanner (1964), approximate migration distances for \(^{222}\)Rn in the groundwater can be calculated as a function of Rn attenuation by alpha decay and radial dispersion and diffusion from a point source:

\[
\ln \frac{C}{C_0} = Z \left( \frac{V}{2D} - \frac{V^2}{4D^2} + \frac{\lambda}{D} \right)^{1/2}
\]

(I).

In this equation, \(C/C_0\) is the ratio of present to original concentration for Rn of decay constant \(\lambda\) migrating in the \(Z\) direction in a groundwater of velocity \(V\) and diffusion coef-
Table 1 shows the migration distances calculated as a function of $C/C_0$ by this equation, for a groundwater flow rate of about 1 m/yr, a reasonable value for an artesian sandstone aquifer. As can be seen from the table, the distances of migration are very small compared to the extensive dimensions of the uranium bearing aquifers in the two study areas. Dyck (1975) states that the range of Rn migration will not significantly exceed that of radium, in excellent agreement with the calculations in Table 1. In addition, a linear correlation coefficient ($r$) of dissolved radon versus radium was calculated for all 96 wells sampled in this study and found to be 0.67, a statistically significant result (Young, 1962). Radon is extremely soluble in water and so is less likely to degas, as does helium. Thus, the information obtained by either Rn or Ra analyses will be sufficient, and analyses of both seems unnecessary.

Table 1. The theoretical migration distance, $Z$, of ${}^{222}$Rn in an aquifer as a function of concentration attenuation fraction ($C/C_0$) by decay and dispersion for a groundwater flow rate of 1 m/yr., calculated using equation 1. $C_0$ and $C$ are the concentrations of ${}^{222}$Rn initially and at distance $Z$.

<table>
<thead>
<tr>
<th>$C/C_0$</th>
<th>1.0</th>
<th>0.1</th>
<th>0.01</th>
<th>0.001</th>
<th>0.0001</th>
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<tbody>
<tr>
<td>$Z$ (cm)</td>
<td>0.0</td>
<td>7.16</td>
<td>14.33</td>
<td>21.49</td>
<td>28.65</td>
</tr>
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</table>
Now that the major controls on radium and radon in the groundwater have been reviewed, the potential of these two radiogenic elements as indicators of uranium mineralization must be evaluated. The applicability of either element to prospecting will be determined by their chemical behavior, cost, speed and ease of their measurement. Radon can be measured semi-quantitatively in the field in about 30 minutes using a portable alpha counter, such as the MERAC IV (Miniature Electronic Radon Alpha Counter) manufactured by Western Systems, Inc. Radium analyses, although much more accurate, are also much more costly and time-consuming and cannot be made in the field. It is apparent from the data collected in this study that radium analyses will not yield any more information than radon measurements. Thus, radon is the preferred radiogenic tracer of the pair.

**Helium**

Helium is the most mobile of all radiogenic elements. It does not decay, and has a limited solubility in water. Eight He atoms are produced from alpha emission in the decay chain of $^{238}_{\text{U}}$ to $^{206}_{\text{Pb}}$. Seven He atoms result from the decay of $^{235}_{\text{U}}$ to $^{207}_{\text{Pb}}$, and six are generated in the decay of $^{232}_{\text{Th}}$ to $^{208}_{\text{Pb}}$ (Dyck, 1978). Since He is constantly produced from these alpha particles, anomalous He values are
expected in or near accumulations of radioactive elements. Clarke and Kugler (1973) were among the earlier researchers to suggest that He dissolved in groundwater could be used to accurately locate uranium mineralization. In fact, significant anomalies in dissolved He (compared to the average of 5.24 ± .10 ppm in the atmosphere) have been found in groundwaters from ore-bearing aquifers by Mead (1980), Reimer (1977), and Dyck (1975), among others. The use of regional variations of He in groundwater to locate mineralized areas may be limited to simple (or at least relatively homogeneous) hydrologic systems. In other words, the migration of He is in part structurally controlled, and lateral variations in groundwater He content cannot be expected to be systematic in highly faulted and fractured geologic terrains. Dyck (1976) has noted that He may accumulate in underground traps, especially in association with natural gas pockets. If the He then migrates upward to the surface, soil-gas or shallow groundwater He anomalies may result. Thus, He may either be indicative of structure, or of radioactive mineralization. If a He anomaly is structurally-related, this is also useful information in that faults and fractures may localize U deposits (Dyck, 1976) as in the case of the fault-controlled ore bodies of the Texas coastal plain.
Groundwater He surveys have been conducted by a number of researchers (cf. Clarke and Kugler, 1973; Reimer, 1977; Mead, 1980) under different geologic and hydrologic conditions, and in the vicinity of known mineralization. All of the three studies cited found significantly anomalous values of dissolved He in the groundwaters near U ores. Clarke and Kugler (1973) only collected samples in or very near to ore, so that regional variations in He were unknown. The other two studies (op. cit.) were performed over larger areas, with samples in, and peripheral to, known deposits. Interestingly, both studies located He anomalies offset from the exact position of the ore in the direction of groundwater flow. This is supported by the findings of this study; that the greatest He values are not located in the ore, but are nevertheless genetically related to the mineralization.

Since He is produced by many elements in the decay series of $^{238}\text{U}$, $^{235}\text{U}$, and $^{232}\text{Th}$, the location of He highs need not be correlated with the concentration of a particular radioactive element. Although He anomalies are caused by U accumulations, due to the great mobility of He (even in the groundwater regime) and to the finite mobility of some of the radioactive elements producing He, the anomalies are often "smeared out" over a region, making it difficult to pinpoint ore zones on the basis of He analyses alone. To
demonstrate the fact that the concentration of He in groundwater does not correlate with any of the radioactive elements, linear correlation coefficients (r) were calculated for He vs. Rn and He vs. Ra in groundwaters of the Texas and Wyoming study areas. The results are shown in Table 2.

Table 2. Matrices of linear correlation coefficients (r values) for He vs. Ra and Rn in groundwaters from the Texas and Wyoming study areas. Calculations based on 50 samples in Wyoming and 46 in Texas.

<table>
<thead>
<tr>
<th></th>
<th>Wyoming</th>
<th>Texas</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.00</td>
<td>He</td>
</tr>
<tr>
<td>Rn</td>
<td>-0.02</td>
<td>Rn 0.06</td>
</tr>
<tr>
<td>Ra</td>
<td>0.09 0.68</td>
<td>Ra 0.11 0.67</td>
</tr>
</tbody>
</table>

Various sampling techniques are employed prior to the determination of dissolved He. Most involve "scrubbing" the dissolved He with local atmospheric gas (Dyck, 1976). The greatest uncertainty in such determinations lies in the method of sample storage. Clarke and Kugler (1973) used annealed copper tubing with special rubber clamps at the ends. Others have used heavy soft-drink type bottles (Dyck and Tan, 1978), or stainless steel cartridges to store the water and/or gas samples for later laboratory analysis (this study, see Methods section). Reimer et al. (1979) and Mead
(1980) used mass spectrometers mounted in field vehicles so that analyses could be performed immediately or shortly after collection. Because of the gas scrubbing step, dissolved He analyses must be considered semi-quantitative at best (see discussion by Barretto in Smith et al., 1976). The development and refinement of He exploration techniques may be a slow and tedious process, as they have not been given much attention by exploration geologists.

**Non-Radiogenic Trace Elements**

The association of the elements As, Mo, Se, and V with U mineralization has long been known (cf. Ries, 1930; Rackley et al., 1968; Harshman, 1974; and others). Despite this fact, the use of variations in these elements in groundwaters to prospect for U deposits has only recently been proposed (Nichols et al., 1977; Arendt et al., 1978). Nichols et al. (1977) showed the most convincing correlations between dissolved V, Mo, As, and Se and known U mineralization in the South Texas coastal plain. Langmuir and Chatham (1980) found that concentration variations of these elements were sometimes useful in locating oxidized deposits, but that their concentrations were often below analytical detection in reduced deposits. A rigorous explanation for the behavior of As, Mo, and Se requires that we under-
stand the solution behavior and mineralogic controls on these elements.

Arsenic exists in groundwaters primarily in the 5+ and 3+ valence states. The predominant species of As are the hydrolysis products As(OH)$_3^+$, As(OH)$_4^-$, and the arsenates, H$_n$AsO$_4^{n-3}$(n=0-3). Fluoroarsenate (HAsO$_3$F$^-$ and AsO$_3$F$^2-$) and arsenous sulfide (HAsS$_2^+$ and AsS$_2^-$) complexes may be important, but will not dominate except under extremely high concentrations of F and dissolved sulfide, respectively. The most important controls on As solubility are sorption and desorption by amorphous ferric oxyhydroxides from acid to neutral waters (Pierce and Moore, 1980), sorption and desorption by aluminum hydroxides (Anderson et al., 1976) and clays, and the solubility of the reduced As minerals: native As, realgar (AsS) and arsenopyrite (FeAsS). Metal arsenate minerals such as erythrite and annabergite are too soluble to limit As levels in groundwater. Highest As levels would be expected in oxidizing or mildly reducing conditions (Ferguson and Gavis, 1972). Arsenic will precipitate as realgar or arsenopyrite under strongly reducing conditions and in the presence of sulfide. Arsenic levels in groundwater are generally below analytical detection limits (< 2 µg/l) in reduced groundwaters. Therefore, As is
a sensitive indicator of the oxidation state of groundwaters.

Molybdenum is often associated with reduced uranium ores as the Mo sulfides molybdenite (MoS$_2$(c)) and jordisite (MoS$_2$(am)?) (Vlek and Lindsay, 1977; DeVoto, 1978b). Molybdenum exists in aqueous solution in the 3+, 5+, and 6+ oxidation states (Kaback and Runnells, 1980), and may have formal charges of 4+ and 6+ in solid phases. The principal species of Mo in solution is the molybdate dianion, MoO$_4^{2-}$ (Kaback and Runnells, 1980). Major controls on Mo solubility are its sorption on organic matter (Davis et al., 1974) or ferric oxyhydroxides at an acid pH (Pokalov and Orlov, 1974), and the solubility of powellite (CaMoO$_4$) and the Mo-sulfides. As with arsenic, the highest concentrations of Mo can be expected in oxidized and moderately reduced waters in the absence of dissolved sulfide. Under very strongly reducing conditions, Mo-sulfides will precipitate. The precipitation of Mo as a sulfide phase will occur at lower Eh's than are required for the precipitation of uraninite from the aqueous uranyl carbonate complexes, due to the great stability of the molybdate anion. Hence, accumulations of Mo are often observed downdip of U ore bodies (Harshman, 1974).
Like As and Mo, selenium is commonly associated with U in reduced ores (Coleman and Delevaux, 1957; Howard, 1977). As with the other trace metals, this association reflects the redox behavior of Se, and the precipitation of Se minerals as Eh decreases. The primary valence states of Se in solution are $2^-$, $1^-$, $4^+$, and $6^+$. Se may have formal charges of $2^-$, $1^-$, $0$, $4^+$ and $6^+$ in solid phases. Howard (1977) has shown the close association of Se with Fe in mineral phases and natural waters. Under oxidizing conditions, the solubility of Se (as selenite ion, $H_nSeO_3^{n-2}$, $n=0-2$) is controlled by sorption on the surface of ferric oxyhydroxides; in reduced waters, ferroselite ($FeSe_2(c)$) may control Se levels. Native Se (Se(c)) is also important, and will control Se solubility in reduced groundwaters of low iron content. Selenium metal will precipitate at a higher Eh than will molybdenite or arsenopyrite (Fig. 5). Its presence also indicates the redox conditions in an aquifer.

In a dipping sedimentary aquifer the groundwater Eh typically varies from high values in the recharge zone to lower values downdip. As the Eh decreases, trace metals will theoretically precipitate from solution in the order Se, U, Mo, As. This prediction, based on thermodynamics, is in good agreement with the findings of Harshman (1974), who
Figure 5. Eh-pH diagram showing some mineral-solute boundaries as labelled. (UBP = uranyl bis-biphosphate, UDC = uranyl dicarbonate, UTC = uranyl tricarbonate; see text).
studied the trace metal zonations of a number of uranium deposits in the western United States.

The association of vanadium with uranium ore is a well known phenomenon (cf. Hostetler and Garrels, 1962; Langmuir, 1978). In oxidized deposits, uranyl vanadate minerals such as carnotite and tyuyamunite are common and extremely insoluble, and will effectively limit both the vanadium and uranium levels. In reduced deposits, the minerals uraninite and coffinite are commonly associated with montroseite (VOOH (?); Weeks et al., 1953).

A brief discussion of the solution chemistry of vanadium can be found in Langmuir (1978). In oxidized waters, the vanadate species \( H_nVO_4^{n-3} \), \( n = 0-4 \) predominate (Fig. 6). At \( pH < 6 \) and intermediate \( Eh \), the \( VO^{2+} \) species is important, while at very low \( Eh \) and \( pH \), the \( V(III) \) species \( (V(OH))_n^{3-n}, \( n = 0-2 \) prevail. The solids alpha-\( V_2O_4 \) and montroseite have an appreciable combined field of stability at low \( Eh \). As \( Eh \) decreases along the flow path of an artesian aquifer, these solids should precipitate from solution at about the same time as uraninite, molybdenite, and arsenopyrite (see Fig. 5). The saturation index values for these solids should increase as \( Eh \) decreases, and may be indicative of the location of ore.
Figure 6. Eh-pH diagram for the system V-H₂O-O₂ at 25°C. Solid solute boundaries are drawn at 100 ppb total V.
FIELD METHODS

Water quality analyses performed in the field are listed in Table 3 along with their methods of analysis. Each well was pumped until the water had attained a constant temperature and specific conductance prior to sampling to insure that formation water was being sampled. Some samples were preserved in the field for later laboratory analysis. Sample collection and preservation methods are listed in Table 4. Analytical techniques used to measure each parameter are listed in Table 5. The results of the chemical analyses are tabulated in Plates 4, 5, 6, and 7.

Computational Methods

The chemical environment leading to the precipitation of uranium in a reduced deposit is also favorable for the precipitation of many trace element phases (cf. Ferguson and Gavis, 1972; Harshman, 1974; Howard, 1977; Langmuir, 1978). The saturation state of groundwaters near a U ore body with respect to various trace element minerals would therefore be expected to vary in a similar manner to that of uranium minerals. Langmuir and Chatham (1980) and Chatham (1981) have shown distinctive patterns in saturation indices (SI values) for uraninite and coffinite around U ore bodies. An
Table 3. A summary of field analytical methods. All measurements made in non-flowing water at the discharge point of the well unless otherwise noted.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Analytical Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Corning Model 610A pH-Millivolt Meter, Corning standard combination pH electrode. Apparatus calibrated with three NBS primary standard buffers (pH 4.01, 6.86 and 9.18) and corrected for temperature effects.</td>
</tr>
<tr>
<td>Eh (mv)</td>
<td>Corning Model 610A pH-Millivolt meter, Corning asbestos fiber junction saturated calomel electrode, homemade platinum electrode. Calibrated with ZoBell's solution and corrected for temperature (Nordstrom, 1977). Readings monitored as sample flowed past electrodes. When stabilized, flow was stopped and final reading recorded.</td>
</tr>
<tr>
<td>temperature</td>
<td>Standard mercury thermometer, calibrated from -20°C to +120°C in 0.5°C increments.</td>
</tr>
<tr>
<td>(T°C)</td>
<td></td>
</tr>
<tr>
<td>specific conductivity</td>
<td>Yellow Springs Instruments Model 33 Salinity-Conductivity-Temperature Meter. Reading recorded when steady.</td>
</tr>
<tr>
<td>(umhos/cm)</td>
<td></td>
</tr>
<tr>
<td>dissolved oxygen (DO)</td>
<td>Yellow Springs Instruments Model 57 Oxygen Meter. Probe placed in flowing sample at well discharge point and allowed to equilibrate with sample before final reading was recorded.</td>
</tr>
<tr>
<td>(mg/l)</td>
<td></td>
</tr>
</tbody>
</table>
Table 3. Continued

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Analytical Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen sulfide</td>
<td>Corning Model 610A pH-Millivolt Meter, Corning asbestos fiber junction saturated calomel reference electrode, Orion solid state silver-sulfide specific ion electrode. Meter calibrated to zero millivolts with shorting strap. Reading recorded when steady.</td>
</tr>
<tr>
<td>bicarbonate, carbonate</td>
<td>Fresh sample 0.45 mm Millipore filtered, immediately packed in ice for analysis each evening. All samples were titrated to pH 4.5 with 0.01658 N sulfuric acid (Brown, Skougstad, and Fishman, 1970).</td>
</tr>
<tr>
<td>Radon (pCi/l)</td>
<td>Western Systems Merac IV (miniature electronic radon alpha counter). 500 ml glass bottle filled about 85% full with fresh sample and shaken vigorously for about 45 seconds. The MERAC IV was fit tightly over the mouth of the bottle and counted for 30 minutes. The number of counts per hour is roughly equal to pCi/l Rn.</td>
</tr>
</tbody>
</table>
Table 4. A summary of sample collection methods.

<table>
<thead>
<tr>
<th>Parameter(s)</th>
<th>Sampling Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca, Mg, Na, K</td>
<td>0.45 ( \mu m ) Millipore® filtered, acidified to pH 1 with concentrated nitric acid. 125 ml collected.</td>
</tr>
<tr>
<td>Ra</td>
<td>0.45 ( \mu m ) Millipore® filtered, acidified to pH 1 with concentrated nitric acid. 1 liter collected.</td>
</tr>
<tr>
<td>U, V, Fe, Mn, Mo, As, Se</td>
<td>0.45 ( \mu m ) Millipore® filtered, acidified to pH 1 with concentrated nitric acid. 500 ml collected.</td>
</tr>
<tr>
<td>Si(_2), SO(_4)</td>
<td>0.45 ( \mu m ) Millipore® filtered, not acidified. 500 ml collected.</td>
</tr>
<tr>
<td>PO(_4)</td>
<td>0.45 ( \mu m ) Millipore® filtered, treated with 40 mg/l mercuric chloride (HgCl(_2)). 125 ml collected.</td>
</tr>
<tr>
<td>U-234, U-235, U-238</td>
<td>0.45 ( \mu m ) Millipore® filtered, acidified to pH 1 with concentrated nitric acid. 4 liters collected.</td>
</tr>
<tr>
<td>F, Cl, NO(_3)</td>
<td>0.45 ( \mu m ) Selas® silver metal membrane filtered. Unacidified, stored in glass bottles. 125 ml collected.</td>
</tr>
<tr>
<td>He</td>
<td>500 ml bottle with Swagelock® cap fitted with rubber septum. Bottle filled about 85% full, shaken vigorously for 30 seconds. 20 cm(^3) of air was withdrawn from the bottle with a graduated syringe and introduced into an evacuated stainless steel canister. A lead-lined cap was then screwed onto the canister.</td>
</tr>
</tbody>
</table>
Table 5. Tabulation of analytical methods and their respective detection limits and accuracies.

<table>
<thead>
<tr>
<th>Species</th>
<th>Detection Limit</th>
<th>Accuracy</th>
<th>Analytical Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.1 mg/l</td>
<td>2 significant figures</td>
<td>Spectrophotometric with Molybdate blue</td>
</tr>
<tr>
<td>Ca</td>
<td>0.1 mg/l</td>
<td>±10%</td>
<td>Atomic Absorption Spectrophotometry(AAS)</td>
</tr>
<tr>
<td>Mg</td>
<td>0.1 mg/l</td>
<td>±10%</td>
<td>AAS</td>
</tr>
<tr>
<td>Na</td>
<td>0.1 mg/l</td>
<td>±10%</td>
<td>AAS</td>
</tr>
<tr>
<td>K</td>
<td>0.1 mg/l</td>
<td>±10%</td>
<td>AAS</td>
</tr>
<tr>
<td>HCO₃</td>
<td>10 mg/l</td>
<td>±0.5%</td>
<td>Potentiometric Titration</td>
</tr>
<tr>
<td>Cl</td>
<td>2 mg/l</td>
<td>±5%</td>
<td>Mohr Titration</td>
</tr>
<tr>
<td>SO₄</td>
<td>5 mg/l</td>
<td>--</td>
<td>Gravimetric - BaSO₄ Method</td>
</tr>
<tr>
<td>F</td>
<td>0.1 mg/l</td>
<td>--</td>
<td>Specific Ion Electrode</td>
</tr>
<tr>
<td>PO₄</td>
<td>0.01 mg/l</td>
<td>--</td>
<td>Spectrophotometric-phosphomolydate</td>
</tr>
<tr>
<td>NO₃</td>
<td>0.3 mg/l</td>
<td>--</td>
<td>Specific Ion Electrode</td>
</tr>
<tr>
<td>H₂S</td>
<td>1.0 mg/l</td>
<td>--</td>
<td>Specific Ion Electrode</td>
</tr>
<tr>
<td>Eh</td>
<td>--</td>
<td>±10mv</td>
<td>Platinum Electrode</td>
</tr>
<tr>
<td>DO</td>
<td>0.1 mg/l</td>
<td>--</td>
<td>DO Probe</td>
</tr>
<tr>
<td>Rn</td>
<td>1 pCi/l</td>
<td>--</td>
<td>Portable Alpha Counter</td>
</tr>
<tr>
<td>pH</td>
<td>--</td>
<td>±.05 units</td>
<td>Field pH Meter, Combination Electrode</td>
</tr>
<tr>
<td>SpC</td>
<td>--</td>
<td>±10 μmhos</td>
<td>Conductivity Probe &amp; Meter</td>
</tr>
<tr>
<td>T°C</td>
<td>--</td>
<td>±0.2°C</td>
<td>Thermometer</td>
</tr>
<tr>
<td>U</td>
<td>0.1 μg/l</td>
<td>--</td>
<td>Fluorimetric</td>
</tr>
<tr>
<td>V</td>
<td>1 μg/l</td>
<td>--</td>
<td>Spectrophotometric-Gallic Acid Method</td>
</tr>
<tr>
<td>Fe</td>
<td>0.01 mg/l</td>
<td>--</td>
<td>AAS</td>
</tr>
<tr>
<td>Mn</td>
<td>0.01 mg/l</td>
<td>--</td>
<td>Graphite Furnace AAS</td>
</tr>
<tr>
<td>Ra-226</td>
<td>0.1 pCi/l</td>
<td>±10%</td>
<td>Radon Emanation, Alpha Scintillation</td>
</tr>
<tr>
<td>As</td>
<td>2 μg/l</td>
<td>--</td>
<td>Hydride Generation,AAS</td>
</tr>
<tr>
<td>Mo</td>
<td>2 μg/l</td>
<td>--</td>
<td>Spectrophotometric, Thiocyanide Method</td>
</tr>
<tr>
<td>Se</td>
<td>2 μg/l</td>
<td>--</td>
<td>Same as for As</td>
</tr>
<tr>
<td>He</td>
<td>--</td>
<td>±0.01 mg/l</td>
<td>Mass Spectrometry</td>
</tr>
</tbody>
</table>
SI value is calculated by comparing the ion activity product expression with the solubility product ($K_{sp}$) expression for a particular mineral written in the same form. For the hypothetical case where a salt AB dissolves to form the aqueous ions $A^+$ and $B^-$, the SI expression is as follows:

$$SI = \log_{10} \frac{[A^+][B^-]}{K_{sp,AB}}$$  \hspace{1cm} (II),

where square brackets denote the activity of each species in the water sample, and $K_{sp}$ has the usual chemical definition. If a water is oversaturated with respect to AB, it will have a positive SI; a zero SI value denotes equilibrium; and a negative SI value indicates undersaturation.

To facilitate calculation of SI values for a variety of trace element minerals in each of the 96 water samples collected in this study, a revised and expanded version of WATEQF (Plummer et al., 1976) was further modified to include aqueous species and minerals of the elements arsenic, molybdenum, selenium and vanadium. SI values for reduced and oxidized minerals of these elements were calculated for each water sample and plotted on base maps to determine the areas where the various phases may control trace element levels.
THE TEXAS STUDY AREA

Geology and Physiography

The geology of the Oakville study area in south Texas (see Fig. 7) is characterized by a series of beds ranging in age from Eocene to Recent. The beds generally strike northeast, sub-parallel to the Gulf Coast, and dip one degree or less towards the coast. Varying erosion rates of the different strata have formed the gently rolling hills characteristic of the gulf coastal plain in the study area. The area is of low local relief, with elevations between 50 and 170m above mean sea level. Sediments older than the Miocene Catahoula Tuff were deposited by cyclic marine transgressions and regressions. The Oligocene(?) Frio Clay is a terrestrial deposit consisting of montmorillonite, zeolites, and some tuffaceous material, and is cut by occasional fluvial sandstone paleochannels. The tuffaceous material found in the Oligocene(?) Frio and Eocene Whitsett Formations probably originated from volcanic activity associated with the Big Bend volcanic region to the west. This volcanic activity peaked in early Miocene time, resulting in the deposition of the fluvial, tuffaceous Catahoula Formation. The Catahoula is postulated to be the source of the uranium in the area. Although it now contains about three parts per
Figure 7. Regional geologic map of the south Texas coastal plain showing the location of the Oakville study area.
million (ppm) equivalent uranium (Dickinson and Duval, 1977), it may originally have contained up to 45 ppm uranium, the maximum quoted value for alkalic, igneous rocks of western Texas (Gottfried et al., 1962).

The Balcones uplift from middle to late Miocene time marked the end of Catahoula deposition and the beginning of Oakville and Fleming deposition. The late Miocene Oakville and Fleming Formations lie conformably on the Catahoula Formation. These formations, which are not separately mapped in this area, consist of tuffaceous sands with some very coarse-grained, cross-bedded fluvial channels. The channel sands are generally lacking in carbon content, but locally contain pockets of carbonaceous materials and up to a few percent secondary pyrite.

The Pliocene Goliad Formation overlies the Fleming/Oakville Formation. It consists of clays and sandstones, with some caliche and limestone, and conglomerates with calcareous cement (Barnes, 1976). The Goliad was deposited in an arid climate and caliche caps were developed which now represent hydrologic barriers within the system. Since the deposition of the Goliad, the climate has shifted to more humid conditions. Later strata are subsequently more organic-rich, and little or no caliche has developed (Weeks and Eargle, 1963).
Quaternary alluvial deposits are interspersed throughout the area and were deposited by perennial and ephemeral rivers and streams. Figure 8 shows a generalized stratigraphic section of the study area.

In the report area, the Oakville Formation consists of coarse, fluvially deposited sand. The contact with the blue clay of the upper Catahoula is sharp and well defined. Two major sandstone strata exist in the Oakville, separated by a mudstone which is 10 to 15m thick. The lower sand is coarse with some isolated clay lenses, and is 15 to 25m thick. The upper sand is unsaturated with water and is about 15m thick. Groundwaters of the lower Oakville Formation are typically Ca- and Na-HCO₃ types updip, grading into Na- and Ca-Cl type waters further downdip.

A series of down-to-the-coast normal faults are present in the area. These structures extend into petrolierous beds at depth and have probably served as conduits for the upward migration of reducing fluids (Goldhaber et al., 1979). In the area of these faults, groundwaters are typically of the Na-Cl type, due to the upward migration of brines from depth. Pyrite was precipitated along the faults where the chemically reduced fluids were present providing a strong reductant for uranium deposition. Uranium minerali-
Figure 8. Generalized geologic cross-section of the Texas study area.
zation eventually produced ore bodies which occupy the sand units of the Oakville Formation adjacent to these faults.

**Hydrogeology**

There is strong evidence that the present day hydrogeology of the Oakville Formation (see Fig. 9) differs significantly from that at the time of ore genesis. The morphology of the Lamprecht orebody indicates that ore deposition occurred prior to the development of nearby growth faults shown in Plate 1. The deposit is shaped like a classic roll-type ore body and is oriented such that the principal groundwater flow direction must have been parallel to the dip of the aquifer. An attempt will be made in later sections of this paper to reconstruct the paleohydrogeology as it existed at the time of uranium accumulation.

The lower sandstone member of the Oakville Formation is the major water-producing stratum in the Texas study area, although some wells tap fluvial sandstone channels within the Catahoula Tuff. Despite the fact that good yields are realized from the lower Oakville aquifer, the presence of \( \text{H}_2\text{S} \) gas and locally high salinities near the faults gives the groundwater poor overall quality. Most people living in the area depend on community water supplies for domestic use.
Figure 9. Piezometric map in the area of the Zamzow in-situ uranium mine. Contours are in meters above mean sea level at 0.5 m intervals (from Anonymous, 1978b).
The Catahoula Tuff represents an impermeable lower boundary to the Oakville aquifer. A clay layer above the Oakville constitutes an effective upper barrier to groundwater flow. The lower Oakville aquifer is therefore confined, and artesian.

This aquifer ranges in thickness from 6 to 20 m (Anonymous, 1978a), and is the major uranium host rock in the area. Other aquifer characteristics reported elsewhere (Anonymous, 1978a), are listed in Table 6. These data were gathered by Wyoming Minerals Corporation for a permit for an in-situ uranium mine in the study area.

Table 6. Hydrologic characteristics of the lower Oakville aquifer. The number of pump tests was not specified.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmissivity (T)</td>
<td>$3 \times 10^{-4} - 4 \times 10^{-3}$ m²/sec</td>
</tr>
<tr>
<td>Direction of maximum T</td>
<td>N22°E - S82°E</td>
</tr>
<tr>
<td>Storage Coefficient</td>
<td>$&lt; 10^{-5}$</td>
</tr>
<tr>
<td>Pumping rates for tests</td>
<td>$5 \times 10^{-4} - 2 \times 10^{-3}$ m³/sec</td>
</tr>
<tr>
<td>Hydraulic Conductivity (K)</td>
<td>$5 \times 10^{-5} - 7 \times 10^{-4}$ m/sec</td>
</tr>
</tbody>
</table>

The regional groundwater flow direction in the Oakville aquifer is coastward, although faults locally disrupt the flow. This is illustrated by the piezometric map of an area straddling the Oakville Fault, which was prepared by the Intercontinental Energy Corporation (IEC) for an in-situ mine permit (Anonymous, 1978b; Fig. 9). Groundwater flow vectors show the influence of the Oakville Fault on the
local hydrology, with flow primarily eastward north of the fault, and southeastward south of the fault. Figure 9, provided by IEC (Anonymous, 1978b), shows that the Oakville Fault is an impermeable barrier to groundwater flow, in that piezometric contours are not continuous across the fault zone. Pumping tests performed across the fault by IEC also indicated that the fault was impermeable to groundwater flow, although the duration of their test seemed too short to convincingly draw this conclusion (Anonymous, 1978b).

The upper sandstone stratum of the Oakville Formation is unsaturated with water updip, but may be saturated down-dip. Its thickness ranges between 3 and 10m, and 10-32m of clay and calcite-cemented sandstone separate it from the lower aquifer (Anononymout, 1978a). Other characteristics of this aquifer are unavailable, and an attempt was made to avoid sampling wells which were screened within the upper Oakville.

At the time that the groundwater samples were taken, for this study, only the Zamzow, Lamprecht, and Benham ore bodies were undisturbed. The rest of the deposits shown in Plate 1 and following figures have been or are currently being open pit mined. Except for the wells adjacent to the Felder pit, all other sample sites used in this study were
sufficiently far removed from the abandoned (or presently active) mines so that hydrologic perturbation of the groundwater was minimal.

**Basic Groundwater Chemistry**

Groundwaters of the lower Oakville Formation were characterized by high dissolved solids (Fig. 10) and the presence of hydrogen sulfide in downdip wells. Salinities in some wells exceeded 3 parts per thousand (ppt), and one well (#16) had over 12 ppt salinity. These high levels of dissolved solids are caused by the upward migration of deep brines (Goldhaber et al., 1979) along the many growth faults in the area. These migrant fluids have also carried much of the hydrogen sulfide. The prevalent chemical character (PCC) of the Oakville waters is dominantly NaCl type, with a wide tongue of Na-HCO₃ type in the recharge area, and a broad band of Ca-Na-SO₄ type sub-parallel to the strike of the Oakville Formation (Fig. 11). The broad zone of Na-HCO₃ type water updip was postulated by Chatham (1981) to be an area of relatively high permeability through which greater volumes of recharging groundwaters have flowed than through adjacent sediments. This tongue, which occupies coarse fluvial channel sediments, may be a remnant of the paleohydrologic conditions in the Oakville Formation. The
Figure 10. Total dissolved solids concentration (ppm) in the lower Oakville groundwaters. Stippling denotes ore locations. Contours are at irregular intervals.
Figure 11. Prevalent chemical character (PCC) of the Texas study area groundwaters. PCC is determined by calculating equivalents per million of the dominant cations and anions.
location of the McLean, Felder, Zamzow, Lamprecht and Kopplin ore bodies suggests that uranium was precipitated from waters flowing along this channel, while the absence of ore bodies to the northeast is consistent with lower groundwater flow rates in these lower permeability sediments and hence, lower rates and amounts of uranium accumulation. The band of high sulfate waters was interpreted by Chatham et al. (1981) to be due to oxidation of sulfide aqueous species and minerals along the redox interface (where $E_h = 0$ volts; see Fig. 12). Corresponding to the high sulfate band is a zone of low pH caused by the sulfide oxidation (Fig. 13). Uranium ore bodies occur along the Oakville Fault (Plate 1) and slightly downdip of the redox interface, indicating that the position of the interface has changed since the time of ore accumulation (about 5 million years ago). When the growth faults were formed, chemically reducing fluids began to migrate upward from depth, displacing the redox front updip, and simultaneously stabilizing the reduced ore. Goldhaber et al. (1979) have identified at least three distinct episodes of sulfide migration upwards along the Oakville Fault, including a post-ore resulfidization event which led to the updip displacement of the redox interface to a position close to what is presently observed.
Figure 12. The position of the redox interface (Eh = 0 volts) in the lower Oakville aquifer. Stippling denotes ore locations.
Figure 13. pH variations in the lower Oakville Formation groundwater. Contours are at 0.2 pH intervals.
Based on the salinity and other data, the existence of faults at positions A, B, C, and D on Plate 1 has been postulated. Anomalies in Rn and temperature further support the existence of a fault at A, which may simply be an unmapped extension of the fault at the Oakville-Catahoula contact. Anomalies in TDS, Cl, SO₄ and He suggest the existence of faults at B and C. The inference of a fault at D is based on the observation that well #31 is chemically reducing despite the fact that it is only 1.6 km downdip from the outcrop and recharge area of the lower Oakville aquifer. In addition, high Cl and Rn values were recorded at sample site 31, indicating upward migration of brines and gases from deeper formations. The Rn anomaly at sample 31 may also be due to the close proximity of the Benham uranium deposit (Wyoming Mineral Corp.) in the lower Oakville aquifer which is now being mined by in-situ leaching methods (Anonymous, 1979).

**Trace Elements in Groundwater**

**Radiogenic Trace Elements**

The distribution of U in groundwaters of the Oakville Formation lower aquifer is shown in Fig. 14. Uranium varies from values in excess of 10 ppb in the recharge zone to below analytical detection (0.1 ppb) in reduced waters down-
Figure 14. Uranium concentrations (ppb) in the groundwater of the lower Oakville aquifer. Contours are at irregular intervals. Stippling denotes ore locations.
dip. This pattern is consistent with the redox properties of U. Except for one well (#36), which contains 100 ppb U, dissolved uranium is not a good indicator of the position of the ore bodies in this area. Sample number 36 is artificially high in U due to the infiltration of oxidized waters from the adjacent Felder open pit mine (Exxon). The levels of U in the other ore zone wells are only slightly higher than in the surrounding wells. Ignoring well #36, variations in U concentrations along profile A-A' in Plate 2 shown in Fig. 15 do not indicate the position of ore. U in groundwater is still a useful parameter for measurement, in that SI values for U minerals cannot be computed without a dissolved uranium analysis (see Chatham et al., 1981).

Figure 16 shows regional variations in the uranium isotope activity ratio (AR) in the lower Oakville aquifer. Values of AR range from 0.2 to 4.0, with most of the well waters having AR's between 1.0 and 2.0 — within the "normal" classification range of Cowart and Osmond (1980). However, results of our study do not agree with theirs. We attribute this to the fact that their water samples were not filtered. Thus, total U concentrations measured by Cowart and Osmond must have included dissolved plus suspended uranium minerals, and U adsorbed on suspended clays and ferric oxyhydroxides. In all nine of the sample locations common
Figure 15. Dissolved uranium levels (ppb) along profile A-A' in Plate 2.
Figure 16. Variations in AR in the lower Oakville aquifer groundwater. Contours are at unit intervals. Stippling denotes ore locations.
to both studies, our total U values are lower than theirs, reflecting the contribution of the uranium associated with suspended solids in their samples. AR's given in Table 7 do not vary systematically between our samples and theirs. This probably reflects the random variation in proportions of sorbed and suspended U in their samples. Sorbed U would be expected to have AR > 1, in that most solutions have AR > 1. Suspended U minerals would have AR < 1, in that alpha recoil effects would lead to solid phases deficient in $^{234}$U (Osmond and Cowart, 1976). In recent studies by Hussain and Krishnaswami (1980) and Asikainen (1981), the authors also neglected to filter their samples before collection. Because U may be strongly sorbed by ferric oxyhydroxides (Hsi and Langmuir, 1980) and other suspended colloidal-sized materials, it is extremely important that samples be filtered in the field before acidification to remove the suspended solids which carry the sorbed U (cf. Methods section).

Figure 17 shows the AR versus total U plot of the Texas area data on the fence diagram proposed by Cowart and Osmond (1980). With but a few exceptions, the reduced waters contain less than 1 or 2 ppb uranium, in agreement with Cowart and Osmond's "normal" classifications. Samples supersaturated with respect to uraninite are shown as solid circles. Samples which are near or within ore are generally supersat-
Figure 17. The Texas study area groundwater samples shown on a log U vs. AR plot as proposed by Cowart and Osmond (1980). The saturation indices are for uraninite (UO₂, see text.)
urated with respect to uraninite, but are not coincident with any one classification of the diagram. Only one sample near (or in) an ore zone plots in the area labelled "STABLE ACCUMULATION". This sample is number 36, which has an artificially high uranium concentration for reasons discussed previously. Therefore, although the classification scheme of Cowart and Osmond (1980) (Fig. 4) has some theoretical foundation, it is not considered applicable to natural systems due to their great complexity. In particular, the classifications "FORMING and STABLE ACCUMULATION" are unjustified, since waters in contact with reduced ore bodies generally have very low uranium concentrations (< 1 ppb).

Radium and Radon variations in lower aquifer groundwaters are shown in Figs. 18 and 19, respectively. Both species show pronounced anomalies in the ore zone, so that both are considered excellent pathfinders of U mineralization. Profiles for the two elements in Fig. 20 demonstrate this point, in that concentrations of both elements in the ore zone are approximately two to three orders of magnitude above their background levels up- and downdip from the ore. Because both elements are equally good indicators of the existence of ore, for reasons discussed previously, Rn is the preferred tracer of the two.
Figure 18. Radium concentrations (pCi/1) in the lower Oakville Formation groundwaters. Contours are in order-of-magnitude intervals. Stippling denotes ore locations.
Figure 19. Radon concentrations (counts per hour) in the lower Oakville Formation groundwaters. Contours are in order-of-magnitude intervals. Stippling denotes ore locations.
Figure 20. Profile of log values of Ra and Rn concentrations (pCi/l and cph, respectively) in the lower Oakville Formation groundwaters (see Plate 2).
Helium is everywhere higher than atmospheric values in the Texas study area groundwaters (Fig. 21). Although He anomalies do not accurately pinpoint the location of ore zones, extremely high He values (up to 5x atmospheric) are locally present in the groundwater, and reflect the presence of nearby uranium mineralization. The distribution of He in Oakville Formation groundwaters is consistent with the findings of Mead (1980) and Reimer (1977) who also noted that the greatest dissolved He values are displaced from the ore in the direction of groundwater flow. Despite the fact that He does not accurately pinpoint ore bodies, its presence in groundwaters at concentrations much greater than 5 or 6 ppm (the average atmospheric value) suggests that a given area has a high potential of containing economic uranium mineralization. Therefore, it is recommended that groundwater He analyses be included in any groundwater exploration program.

Non Radiogenic Trace Elements

Arsenic, molybdenum, and selenium concentrations in groundwater of the lower Oakville aquifer are plotted in Figs. 22, 23, and 24, respectively. None of these elements occur in anomalous concentrations in the ore body, nevertheless some useful information may be gleaned from the maps. Concentrations of all three elements are generally controll-
Figure 21. Helium concentrations (ppm) in the lower Oakville Formation groundwater. Contours are at irregular intervals. Stippling denotes ore locations.
Figure 22. Arsenic concentrations (ppb) in the lower Oakville Formation groundwater. Contours are at irregular intervals. Stippling denotes ore locations.
Figure 23. Molybdenum concentrations (ppb) in the lower Oakville Formation groundwater. Contours are at irregular intervals. Stippling denotes ore locations.
Figure 24. Selenium concentrations (ppb) in the lower Oakville Formation groundwater. Contours are at irregular intervals. Stippling denotes ore locations.
ed by redox conditions in the aquifer. As a group, they vary from highs of as much as 200 ppb to <2 ppb (the analytical detection limit) downdip. The levels of all three drop to values below analytical detection along a relatively narrow band coincident with the ore locations (Fig. 25). This band, hereafter referred to as the concentration cliff, is in turn closely related to the present redox interface. Figure 5 shows the Eh-pH conditions for which dissolved As, Mo, and Se are stable in solution relative to the mineral forms arsenopyrite, molybdenite and native Se, respectively. As Eh rapidly decreases near the redox interface, Se, then Mo or As are expected to precipitate in the solid phases mentioned. At pH values greater than approximately 7.8, As is expected to precipitate before Mo (see Fig. 5). Along some portions of the concentration cliff, arsenic levels drop to below analytical detection updip of Mo or Se, contrary to the thermodynamic predictions of Fig. 5. This early disappearance of dissolved As is attributed to the probable sorption of arsenite species \((\text{As(OH)}_n^{3-n})\) on iron oxyhydroxides following reduction from the more weakly sorbed arsenate species. Therefore, although the low levels of As in some updip well waters are not a result of low solubility, they are still related to redox processes. U should precipitate (as \(\text{UO}_2\) or coffinite) after
Figure 25. The concentration cliff of As, Mo, and Se in the lower Oakville Formation groundwater (see text).
Se, but before Mo and As as Eh drops. Thus, the concentration cliff should coincide with ore locations. The ore bodies of the Zamzow, Lamprecht and Benham sites all occur in, or slightly downdip of this band. The fact that the U ore bodies are positioned somewhat downdip of the concentration cliff is a further indication that the redox interface has been displaced updip since the time of ore formation. Considerable caution should be exercised when plotting concentration cliffs in other areas. If the ore-stage hydrogeology differs significantly from present conditions, the position of the concentration cliff may be misleading. Since As, Mo, and Se are commonly associated with U mineralization (Finch, 1967), the presence of a concentration cliff for these elements can be a strong indication of the position of ore. Conversely, the similar redox dependence of the trace elements and U explains why these four so often occur together (Harshman, 1974). Therefore, although the individual concentrations of As, Mo, and Se may not help locate ore bodies, their combined analyses shown on a base map such as in Fig. 25 should define a band of possible U accumulations, as long as the present day hydrogeology is sufficiently similar to that at the time of ore deposition. In addition, if the individual elemental concentrations drop abruptly along a concentration
cliff, the possibility of economic deposits of these metals themselves may be inferred.

None of the trace elements pinpoint ore locations. Also, the concentration cliff at best indicates the position of a broad band of the formation that might contain uranium mineralization. It is therefore desirable to inspect the saturation state of the groundwaters with respect to the mineral phases which may control the elemental concentrations. Saturation index (SI) maps have therefore been plotted for these controlling mineral phases.

Arsenic levels in oxidized groundwaters are only controlled by sorption equilibria. It has already been shown that ferric oxyhydroxides and other sorbent phases may severely limit As levels in partially oxidized waters. In reduced waters (Eh < 0 mV) the precipitation of mineral phases such as realgar (AsS), arsenopyrite (FeAsS), and metallic As will cause a sharp drop in dissolved As levels. SI maps for these three phases are shown in Figs. 26, 27 and 28. All three are seen to exhibit strong anomalies in the ore zone, but realgar SI values show the broadest overall anomaly. No waters were oversaturated with respect to As metal. Apparently FeAsS and AsS are the mineral phases which limit dissolved As levels. Orpiment (As$_2$S$_3$) SI values are very similar to those for realgar,
Figure 26. SI values for realgar in the lower Oakville Formation groundwater. Contours are at irregular intervals. Stippling denotes ore locations.
Figure 27. SI values for arsenopyrite in the lower Oakville Formation groundwater. Contours are at irregular intervals. Stippling denotes ore locations.
Figure 28. SI values for As metal in the lower Oakville Formation groundwater. Contours are at irregular intervals. Stippling denotes ore locations.
owing to their similar stoichiometry, and a plot of SI values for orpiment would therefore be redundant.

Molybdenum levels in oxidized waters may be limited by sorption or solubility effects. An SI map in Fig. 29 for ferrimolybdite \((\text{Fe}_2\text{(MoO}_4)_3\)) shows a general decrease in SI values as the groundwater becomes more reducing. In the reduced waters, Mo levels are strongly controlled by the Mo-sulfide phases molybdenite \((\text{MoS}_2)\) or the more amorphous jordisite \(\text{MoS}_2(?)\), (DeVoto, 1978b). SI values for molybdenite (Fig. 30) increase dramatically as the groundwater becomes more reducing. An area of MoS\(_2\) oversaturation is seen to form a pronounced anomaly directly over the major ore zone. If jordisite is of the same stoichiometry, SI contours would be in exactly the same position, except a few SI units lower, because of the greater solubility of an amorphous phase.

Groundwater selenium levels are probably limited by sorption phenomena in oxidized waters. In reduced waters Se metal or ferroselite \((\text{FeSe}_2)\) may limit dissolved selenium levels (Howard, 1977). SI maps for Se metal and ferroselite are shown in Figs. 31 and 32. Both show a dramatic increase in SI as the ore zone is approached from an updip direction, but only Se metal shows a distinct halo of saturated values around the ore zones. As lower Eh values occur farther
Figure 29. SI values for ferrimolybdite in the lower Oakville Formation groundwater. Contours are at intervals of 10 SI units. Stippling denotes ore locations.
Figure 30. SI values for molybdenite in the lower Oakville Formation groundwater. Contours are at irregular intervals. Stippling denotes ore locations.
Figure 31. SI values for native Se in the lower Oakville Formation groundwater. Contours are at irregular intervals. Stippling denotes ore locations.
Figure 32. SI values for ferroselite in the lower Oakville Formation groundwater. Contours are at irregular intervals. Stippling denotes ore locations.
downdip, the stability of Se metal is reduced because of its reductive dissolution to H₂Se or HSe⁻, which explains why SI values decrease directly up- and downdip of the ore zone. The two wells farthest downdip are slightly oversaturated with respect to Se metal (SI values of 0.8 and 0.9). This may be due to a slight rise in Eh as a result of mixing with oxygenated waters from the Pliocene Goliad Formation at the wellhead.

The distribution of dissolved vanadium in groundwaters of the Texas study area is shown in Fig. 33. Vanadium levels range from 140 ppb updip to values between 3 and 9 ppb in most downdip wells, with only two wells having less than 1 ppb. This relatively narrow range of concentrations in the reduced waters suggests that V levels are being controlled by the solubility of a reduced solid such as montroseite (VOOH) or paramontroseite (α-V₂O₄). As seen in Fig. 34, the saturation index of montroseite increases downdip, and levels off in the reduced waters to a value of -1.5 or -1.6. Since the SI's for α-V₂O₄ do not level off to such a uniform value (Fig. 35), I have concluded that a solid of similar stoichiometry to montroseite, but of somewhat greater stability, exists in the aquifer and limits V levels. Although the actual stability and stoichiometry of montroseite is poorly known, the possibility exists that montroseite is actually a solid-solution, with coupled substitu-
Figure 33. Vanadium concentrations (ppb) in the lower Oakville Formation groundwater. Contours are at irregular intervals. Stippling denotes ore locations.
Figure 34. Montroseite SI values in the lower Oakville Formation groundwater. Contours are at irregular intervals. Stippling denotes ore location.
Figure 35. Paramontroseite SI values in the lower Oakville Formation groundwater. Contours are at 10 SI unit intervals. Stippling denotes ore location.
tion of Fe$^{2+}$ and V$^{4+}$ for the V$^{3+}$ ions in the crystal lattice (Weeks et al., 1953; Evans and Block, 1953; Evans and Mrose, 1955). Such a solid solution series might be expected to decrease the apparent solubility of the pure VOOH phase, while the dissolution reaction would still be approximately represented by:

$$\text{VOOH}(c) = \text{VOOH}^+ + e^- \quad \text{(III),}$$

the equation which has been used in the WATEQ program to compute montroseite SI values. A change in the free energy of reaction (III) by approximately +2.1 kcals (equivalent to 1.5 SI units) may then be attributed to the effects of solid solution, or to errors in thermochemical data (see Discussion).
THE WYOMING STUDY AREA

Geology and Physiography

The Wyoming study area is located on the eastern flank of the Powder River Basin in northeastern Wyoming (Plate 3). Sediments in the area strike northward and dip gently westward (1°-2½°), producing a series of low, rolling hills and grassy plains (Raines et al., 1978). Local relief is generally less than 100m, with elevations ranging from 1500m to 2000m above mean sea level. The Belle Fourche River flows northeastward through the study area, and drains the eastern portions of the basin.

The Cretaceous Pierre Shale, and Fox Hills and Lance Formations, and the Tertiary Fort Union Formation outcrop in the study area, and total about 1000-1500m thick (Fig. 36). These formations document the final episode of a major marine transgressive-regressive sequence which resulted in deposition of most of the basin fill (Glaze and Keller, 1965). The early Cretaceous marine Pierre Shale averages 700m thick, although it may be as much as 830m thick. Deposition of the marginal marine Fox Hills sandstone began as the inland seas retreated.

The Lance Formation was deposited gradationally above the Fox Hills. It consists of a series of point bar sequen-
Figure 36. Generalized geologic cross-section of the Wyoming study area.
ces with organic-rich silt- and mudstone strata interspersed throughout (Dodge, 1978). Medium to fine-grained arkosic fluvial channel sands and accompanying organic-rich overbank deposits also are contained in the Lance Formation. The organic-rich sections of the Lance have locally produced strongly reducing groundwater environments. Uranium deposits occur in sandstone in the Lance adjacent to these organic lenses.

In-situ solution mining of uranium ore in the basal Lance is in progress in the study area, and plans are underway for developing further areas nearby (Stoick, 1979). Uranium mineralization is also known to occur in the surrounding Fox Hills and Fort Union Formations, but this study was limited to the middle and lower portions of the Lance Formation only.

**Hydrogeology**

Producing aquifers important to this study include the Fox Hills and Lance Formations, and the Belle Fourche River alluvium. Although an attempt was made to sample only Lance Formation groundwaters, there is undoubtedly leakage between the formations, and some wells may draw water from more than one formation.
The regional groundwater flow direction is to the north and northwest in the Lance and Fox Hills aquifers (Fig. 37), but to the east in the Belle Fourche Alluvium (Whitcomb and Morris, 1964).

Aquifer constants for the Lance Formation were given by Whitcomb and Morris (1964). Well discharges were reported in the range $1 \times 10^{-4}$ to $6 \times 10^{-4}$ m$^3$/s; specific capacities varied from $1 \times 10^{-4}$ to $4 \times 10^{-4}$ m$^3$/m; and hydraulic conductivities ranged from $3 \times 10^{-6}$ to $2 \times 10^{-5}$ m/s. Hodson et al. (1973) state that wells which are screened over a greater thickness of the Lance aquifer may produce several cubic meters per second. Such is the case in the town of Moorcroft, which draws its municipal supply from approximately 100m of saturated Lance aquifer.

In general, the hydrogeology of the Wyoming study area is much more complex than that of the Texas area, with isolated fluvial channels separated by zones of lower permeability and hydraulic conductivity. In areas of hydrologic inhomogeneity, it becomes much more difficult to model subtle changes in groundwater chemistry. Often one must rely on closely spaced wells along a profile which are thought to be screened in the same fluvial paleochannel. In order to simplify these problems the area has been divided into two sections, each having a "lower" and "upper" system. The
Figure 37. Regional piezometric map in the Wyoming study area. Contours are in meters above mean sea level at irregular intervals (modified from Cooley, 1979).
wells have been classified as being in the "lower" or "upper" system based on their depth and distance from the outcrop, and on cluster analysis of the chemical data (see Chatham et al., 1981).

**Basic Groundwater Chemistry**

The quality of the Lance Formation waters is generally good, with low total dissolved solids. Only a few of the wells sampled in this study had the odor or taste associated with hydrogen sulfide. Groundwaters in the area typically have a prevalent chemical character (PCC) of the Na-HCO$_3$ or Na-SO$_4$ type.

Groundwaters of the Lance aquifer are much more dilute than those of the Oakville. Total dissolved solids concentrations rarely exceed 1000 ppm (Figs. 38 and 39). The better overall quality and low trace element levels (as compared to the Oakville aquifer) may be the result of a lack of growth faults or adjacent tuffaceous beds. Growth faults in the Texas study area have permitted the upward migration of sulfide-rich brines, and devitrification of the Catahoula Tuff has added silica and trace elements to the groundwater. Because these two features are lacking in Wyoming, the groundwater quality is considerably better.
Figure 3.8. The total dissolved solids (TDS) concentration (ppm) in the upper aquifer systems of the Lance Formation. Contours are at 500 ppm intervals.
Figure 39. Total dissolved solids (TDS) concentration (ppm) in the lower aquifer systems of the Lance Formation. Contours are at 500 ppm intervals.
The Lance groundwaters are predominantly of the Na-HCO₃ type, as shown in the PCC maps in Figs. 40 and 41. Some downdip areas are of the Na-SO₄ type, reflecting the normal anion progression, HCO₃-SO₄-Cl, in a downdip flow direction (Freeze and Cherry, 1979).

Sulfide and organic matter are largely lacking in the Lance waters, either in aqueous or solid phases. The redox interface is therefore displaced further downdip than in the Texas study area (Figs. 42 and 43). Some wells which tap the base of the Lance (and probably the upper Fox Hills) are in reduced zones and may be near local accumulations of organic matter such as are found in fluvial-overbank sequences (cf. Geology section).

Groundwaters in the Wyoming study area are neutral to alkaline, with pH values in the range 7.4 to approximately 9.0 (Figs. 44 and 45). The alkaline pH's are due to the high amounts of dissolved carbonate in Na-HCO₃ type waters downdip. The generally low levels of trace metals may also be due to the elevated pH values, in that most minor and trace metals such as Fe and Mn are less soluble in alkaline solutions.
Figure 40. Prevalent chemical character (PCC) of the upper aquifer systems of the Lance Formation, as determined by cation-anion concentrations as epm.
Figure 41. Prevalent chemical character (PCC) of the lower aquifer systems of the Lance Formation.
Figure 42. Eh variations in the upper Lance Formation groundwaters.
Figure 43. $E_n$ variations in the lower Lance Formation groundwaters.
Figure 44. Variations in pH in the upper Lance Formation groundwaters. Contours are at irregular intervals.
Figure 45. Variations in pH in the lower Lance Formation groundwaters. Contours are at irregular intervals.
Trace Elements in Groundwater
Radiogenic Trace Elements

The distribution of uranium in groundwaters of the lower and upper aquifers of the Lance Formation is shown in Figs. 46 and 47, respectively. A few well waters exhibit high U levels (> 10 ppb), demonstrating the uranium potential of the area. However, the great complexity of the hydrologic system makes it difficult to relate regional variations of U and of other dissolved elements. Thus, variations in individual elemental concentrations are not always systematic (cf. sample #19 as compared to adjacent sample #26), and such groundwater chemical data are not reliable indicators of ore unless the well being sampled is cased in or very near to an accumulation of ore minerals.

AR values are shown in Fig. 48 on a plot such as was used by Cowart and Osmond (1980). Of interest in the Wyoming area is the wide range of observed AR values from 1.0 to 14.0. Samples with the highest AR values are low in total U. These high AR's are attributed to alpha recoil phenomena. Regional variations in AR for the lower and upper aquifer systems are shown in Figs. 49 and 50.

As in the Texas study area, there is no systematic variation in AR and total U values. Again, the fence diagram proposed by Cowart and Osmond fails to adequately ex-
Figure 46. Uranium concentrations (ppb) in upper Lance Formation groundwaters. Contours are at irregular intervals.
Figure 47. Uranium concentrations (ppb) in lower Lance Formation groundwaters. Contours are at 0.1 and 0.2 ppb.
Figure 48. The Wyoming study area groundwater samples plotted on a log U vs. AR plot as proposed by Cowart and Osmond (1980, see text). The saturation indices are for uraninite (AR = 0 denotes 234U is below detection).
Figure 49. Variations in AR in upper Lance Formation groundwater. Contours are at irregular intervals.
Figure 5.0. Variations in AR in lower Lance Formation groundwater. Contours are at irregular intervals.
plain these variations. It is recommended, therefore, that such diagrams be used with considerable caution if at all in uranium exploration programs.

Ranges of concentration of Ra and Rn in the lower and upper aquifers (Figs. 51 through 54) are not as wide as those observed in the Texas study site. One well (#19) exhibited anomalously high values of both elements (as well as U) and may be near a zone of remobilization of an ore body. This is further supported by the relatively low AR (1.1) which indicates a contribution to the total U concentration from a solid phase. Based on Ra and Rn analyses alone (which were excellent ore pathfinders in the Texas study area) #19 is the only water sample that suggests the local occurrence of uranium mineralization.

Helium varies from 4.4 to 11.2 ppm in Lance Formation groundwaters (Figs. 55 and 56). Values of less than 5.24 ppm (the atmospheric average) were found near the recharge zone in waters that contained measurable dissolved oxygen. According to Dyck (1975), above-atmospheric levels of He are not expected in highly oxygenated recharge waters. That He values increase downdip is indicative of the presence of mineralization in the aquifer, but as in the Texas location, dissolved He does not exactly pinpoint ore locations. Nevertheless, He serves as a useful parameter for indicating the uranium potential of an aquifer.
Figure 51. Radium concentrations (pCi/l) in upper Lance Formation groundwaters. Contours are at irregular intervals.
Figure 52. Radium concentrations (pCi/l) in lower Lance Formation groundwaters. Contours are at 0.1 (pCi/l) intervals.
Figure 53. Radon concentrations (counts per hour, cph) in upper Lance Formation groundwaters. Contours are at 100 cph.
Figure 54. Radon concentrations (cph) in lower Lance Formation groundwaters. Contours are at 100 cph.
Figure 55. Helium concentrations (ppm) in upper Lance Formation groundwaters. Contours are at irregular intervals.
Figure 56. Helium concentrations (ppm) in lower Lance Formation groundwaters. Contours are at irregular intervals.
Non-Radiogenic Trace Elements

The levels of As, Mo, and Se in Lance Formation groundwaters are shown in Figs. 57 through 62. The elements behave exactly as predicted thermodynamically, in that they are present in measurable concentrations when Eh > 0 volts and drop below analytical detection (< 2 ppb) as Eh drops below zero volts. The levels of these elements are generally much lower than in the Texas study site, owing to the more dilute water quality. Most of the samples were below detection in As, and many had less than 2 ppb Mo and Se as well. Consequently, no pronounced concentration cliff exists in the Wyoming study area. The absence of a concentration cliff may also reflect the more complex hydrogeology of the Wyoming study area, as discussed previously. However, there is a local concentration cliff near sample 19, further suggesting the possible proximity of an ore body.

Saturation index maps for As metal, realgar and arseno-pyrite are shown in Figs. 63 through 68. In general, SI values for all the trace element minerals increase downdip as Eh decreases. SI maps of molybdenite, Se metal, and ferroselite show similar patterns and appear in Figs. 69 through 74. Because of low sample density around the two known ore locations (Plate 3), little can be said about the effectiveness of SI maps of minerals of As, Se, Mo, and V in locating ore within the Lance aquifer.
Figure 5. Arsenic concentrations (ppb) in the upper Lance Formation groundwaters. Contours are at 2 and 5 ppb.
Figure 58. Arsenic concentrations (ppb) in lower Lance Formation groundwaters. Contours are at 2, 5 and 10 ppb.
Figure 59. Molybdenum concentrations (ppb) in upper Lance Formation groundwaters. Contours are at 2 ppb.
Figure 60. Molybdenum concentrations (ppb) in upper Lance Formation groundwaters. Contours are at 2, 4, and 10 ppb.
Figure 6. Selenium concentrations (ppb) in upper Lance Formation groundwaters. Contours are at irregular intervals.
Figure 62. Selenium concentrations (ppb) in lower Lance Formation groundwaters. Contours are at irregular intervals.
Figure 63. Native As SI values in the upper aquifer systems of the Lance Formation. Contours are at irregular intervals.
Figure 64. Native As SI values in the lower aquifer systems of the Lance Formation. Contours are at irregular intervals.
Figure 65. Realgar SI values in the upper aquifer systems of the Lance Formation. Contours are at irregular intervals.
Figure 66. Realgar SI values in the lower aquifer systems of the Lance Formation. Contours are at irregular intervals.
Figure 67. Arsenopyrite SI values in the upper aquifer systems of the Lance Formation. Contours are at irregular intervals.
Figure 68. Arsenopyrite SI values in the lower aquifer systems of the Lance Formation. Contours are at irregular intervals.
Figure 69. Molybdenite SI values in the upper aquifer systems of the Lance Formation. Contours are at 50 SI unit intervals.
Figure 70. Molybdenite SI values in the lower aquifer systems of the Lance Formation. Contours are at 50 SI unit intervals.
Figure 71. Se metal SI values in the upper aquifer systems of the Lance Formation. Contours are at 5 SI unit intervals.
Figure 7.2. Se metal SI values in the lower aquifer systems of the Lance Formation. Contours are at 5 SI unit intervals.
Figure 73. Ferracellite SI values in the upper aquifer systems of the Lance Formation. Contours are at irregular intervals.
Figure 74. Ferroselite SI values in the lower aquifer systems of the Lance Formation. Contours are at irregular intervals.
All but three of the Wyoming groundwater samples contained less than 1.0 ppb V. For this reason, it is difficult to model V behavior in the Lance groundwaters.
DISCUSSION

Effectiveness of the Exploration Technique

The solution-mineral equilibrium calculations proved to be quite effective as an exploration method for locating uranium mineralization in the Texas study area, but less effective in Wyoming. Several important factors help explain this difference in effectiveness. These include differences in the geologic and hydrologic settings, and in the available sampling density. Such factors can usually be determined before going into the field by inspecting topographic maps for isolated wells and houses, and by researching the geology and hydrogeology of the area. The sample site density in the Texas study area was approximately $1^{1/2} - 2$ samples per square mile overall, with nearly 5 samples per square mile around the Zamzow and Lamprecht ore bodies. The sample density for the Powder River basin was considerably lower, with slightly less than 1 sample per two square miles because of the more sparse population.

Dyck (1972, 1975) found that a sample density of 1 per 12 square miles was sufficient for dissolved uranium in surface and lake waters, but trends in Ra and Rn lost coherency at sample densities of less than 1 per square
mile. Groundwaters in artesian aquifers are not as well mixed as are lake and other impounded surface waters and rivers, so a greater sample density is required to pinpoint ore locations. It appears from the results presented here that an average of at least 1 sample per square mile is needed to produce unambiguous results. If the hydrogeology is simpler, fewer samples will be necessary. Conversely, more are required to characterize highly anisotropic and inhomogeneous hydrologic systems. The sample density needed to produce meaningful results will be dictated by the areal homogeneity of the aquifer, the groundwater flow rate, and the areal density of available wells. The exploration strategy for each specific target area will change based on these factors, as certain parameters (Ra, Rn) pinpoint ore from close range, while others (He, and some mineral SI values) display broader anomalies in the vicinity of ore deposits.

The Lance aquifer is very complex, with fluvial channels separated by less permeable overbank deposits and clay and organic-rich lenses. Results of a cluster analysis study showed a poor correlation between wells which were not closely spaced. Even some closely spaced wells were poorly correlated with one another because they were screened at varying depths. There is undoubtedly a considerable amount
of mixing with Fox Hills Formation groundwaters at the basal Lance sandstone which adds greater complexity to the system. In summary, one should use the mineral saturation approach for exploration with caution in areas of low sample density and/or complex hydrogeology.

The overall usefulness of this exploration technique may be seriously affected by differences between the present hydrologic system and that at the time of ore emplacement. As was noted for the south Texas study site, the development of growth faults following ore deposition led to an updip displacement of the redox interface. Concentration cliffs of As, Mo, and Se were similarly shifted updip. The ore deposits in the study area are not completely within the concentration cliff, contrary to the thermodynamic predictions depicted in Fig. 5.

Despite significant hydrogeologic changes in the Oakville aquifer since ore deposition, SI values for the minerals realgar, molybdenite, and arsenopyrite (Figs. 26, 27, and 30), and the minerals uraninite and coffinite (Chatham et al. 1981) still pinpointed the ore locations. Thus, there may have been enough time since the hydrologic system was altered for the water-rock reactions to approach equilibrium. Furthermore, the zero SI contours for uraninite and coffinite (Chatham et al. 1981) are slightly
updip from the known ore locations, suggesting that uranium ore may presently be forming updip from the established deposits, conforming with present hydrogeochemical conditions.

Gaseous pathfinder elements such as Rn and He are not subject to the redox controls which affect the dissolved metals. Thus, these elements should aid greatly in ore location regardless of hydrogeochemical constraints. This consideration may be particularly important when exploring for ores such as those which occur in the Grants district of New Mexico. These deeply buried tabular deposits were formed by lateral secretion (cf. W.C. Riese, 1980) and the groundwaters in the vicinity are everywhere reducing. Mead (1980) and DeVoto et al. (1980) showed that He has migrated upward through the stratigraphic section from the Grants deposits, resulting in dissolved He anomalies in the shallow aquifer systems above the ore. Because our data was limited to sampling within the Oakville Formation, we could not assess the possible existence of the anomalies from groundwaters of overlying formations.

**The Solubility of Montroseite**

The mineral montroseite (V, Fe)OOH was first described by Weeks et al. (1950; 1953) as a black, opaque vanadium
mineral which occurs with reduced ores of uranium in the Colorado Plateau. Because the groundwaters of the Oakville aquifer are highly vanadiferous, some vanadium minerals may be expected in association with the uranium ores. If the chief vanadium mineral is montroseite, then groundwaters within the orebody would be expected to be at or near saturation with respect to it. Instead, all the reduced groundwaters from the Texas study area have maximum montroseite SI values of either -1.5 or -1.6. The relatively narrow range of V concentrations in these waters (3-9 ppb) is a further indication that V levels are being controlled by a discrete phase. Evans and Block (1953) noted from x-ray analyses and structure factor calculations that some iron substitutes for vanadium in the montroseite lattice. Weeks et al. (1953) reported chemical analyses of hand-picked grains that showed up to 8.8 weight percent ferrous iron substitution. Because the V in montroseite is in a 3+ valence state, one atom of V\(^{4+}\) must also substitute in the lattice for each ferrous ion. This coupled substitution must alter the stability of the mineral. Kern and Weisbrod (1967) state that the enthalpy of mixing (\(\Delta H_m\)) should equal zero for ideal solid solutions. Brownlow (1979) noted that deviations from ideality are expected when the substituting ion has a different size or charge, causing disruption of the crystal lattice. This is particularly to be expected for coupled
substitution such as presented here. It is difficult, if not impossible, to estimate thermodynamic properties for irregular solid solutions, particularly when the magnitude of their deviation from ideality is unknown. Because the montroseite SI values do not approach zero, it can be assumed that a solid of different composition or stability must control vanadium levels in reduced waters. If a vanadium-iron solid solution mineral is considered to be closer to the iron end member, it is then necessary to calculate the effects of V$^{3+}$ substitution into the goethite (FeOOH) lattice. Goethite SI values in the lower Oakville aquifer groundwaters are shown in Fig. 75. SI values for goethite with 1 mole percent V$^{3+}$ ions were calculated assuming ideal solid solution conditions. Neither the position nor magnitude of the SI contours for this phase were significantly different from those of pure end-member goethite. Furthermore, goethite SI values did not level off as did the end member montroseite SI values.

Therefore, the phase which controls vanadium solubility is postulated to be more vanadium rich, as opposed to the opposite situation where V substitutes in a lattice in trace amounts. This phase is also thought to consist primarily of V$^{3+}$, rather than V$^{4+}$ because paramontroseite ($\alpha$-V$_2$O$_4$) SI values did not level off and were consistently lower in the
Figure 75. Goethite SI values in the lower Oakville Formation groundwater. Contours are at irregular intervals.
downdip waters. The thermochemical data for vanadium tabulated by Langmuir (1979) and used in the expanded WATEQF program (Plummer et al., 1976) was compiled from a variety of sources. Poor agreement between studies is common, and may account for some of the error. Another source of error is the Eh measurements. A great deal of controversy clouds the issue of Eh measurement (cf. Stumm and Morgan, 1970; Langmuir, 1971; and Whitfield, 1974), and error bars of ± 50 millivolts are likely in the measurement. Regardless of the Eh value used in the calculations, the vanadium solids may not be in equilibrium with the aqueous system. Wilson and Weber (1979), in an electron paramagnetic resonance (EPR) study of the reduction of vanadium (V) to vanadium (IV), found that only a small fraction of the quinquevalent vanadium was reduced by fulvic acids. Skogerboe and Wilson (1981) reported that the reaction:

$$\text{VO}^{2+} + 2\text{H}^+ + e^- = \text{V}^{3+} + \text{H}_2\text{O} \quad \text{(IV)}$$

did not occur in the presence of fulvic acid. C.G. Warren (1981) has pointed out that the redox equilibrium between V(III) and V(IV) is extremely slow in both directions. It is therefore possible that the vanadium system is not at equilibrium and that the solubility of vanadium is controll-
ed by kinetic factors, with slow reaction rates and limited availability of oxidizing agents controlling V levels.

**Age dating of groundwaters**

An attempt was made to determine groundwater ages using uranium isotope ratios and dissolved helium values. Both methods required approximations which led to considerable errors. Barr et al. (1979) and Fritz et al. (1979) presented a method of age dating groundwaters using uranium isotope data. The underlying principle of this method is that $^{234}\text{U}$ decays faster than $^{238}\text{U}$, and that the amount of $^{238}\text{U}$ decay for time periods of interest are negligible. Approximate ages for downdip groundwater samples are obtained by comparing the AR value of an updip water (initial value) with that of the downdip sample according to the equation:

$$t(\text{years}) = \ln\left[\frac{\text{AR}_S}{\text{AR}_O} - 1\right] \cdot (\lambda_{234})^{-1}$$

where $\text{AR}_S$ and $\text{AR}_O$ are the isotope ratios in the downdip and updip samples, respectively, and $\lambda_{234}$ equals $2.806 \times 10^{-6}$ yr$^{-1}$, the $^{234}\text{U}$ decay constant. For a positive age to result, AR must decrease along the groundwater flow path, which is frequently not the case. Ages computed by this method for the Oakville Formation groundwaters were unreas-
sonably high, and point out the oversimplification of this method. Spurious ages will result from mixing of groundwaters, such as the upward migration of deep brines, and from solid-solute interactions. Therefore, this method of age dating is considered unreliable for such complex hydrologic systems as the lower Oakville aquifer.

In order to compute groundwater ages from helium data, a variety of simplifying assumptions are made. Using the equation presented by Fritz et al. (1979), groundwater ages may be calculated as follows:

\[
t = \frac{^4\text{He} \cdot n}{(U \cdot Pu + Th \cdot P_{Th}) \cdot \rho_{\text{rock}}}
\]  

(VI),

where \(^4\text{He}\) is the volume fraction of dissolved He, \(n\) is the bulk porosity, \(U\) and \(Th\) are the gram fractions of those elements in the rock, \(Pu\) and \(P_{Th}\) are the rate of He production by each element and its daughters, and \(\rho_{\text{rock}}\) is the bulk density. In order for equation VI to be valid, \(U\) and \(Th\) in the rock must be in secular equilibrium with its daughters. This is frequently not the case in the Oakville aquifer, as witnessed by AR values other than unity. Also, because the Oakville is highly uraniferous, the rate of He production by Th and its daughters was assumed negligible. Using the equation, assuming an average ore tenor of 0.1\%,
and following a groundwater flow line across the Zamzow ore body (Plate 1), unreasonably high ages result for a 0.25 km flow path. This result was anticipated due to the probable input of He to the Oakville aquifer from depth along the Oakville fault. In a simpler geologic setting, the method may be more reliable. One interesting sidelight to equation VI is that if the groundwater age is already known, the average tenor of an ore body may be estimated. Unfortunately, upward leakage of brines along the Oakville fault has caused a great perturbation on the system, rendering virtually all age dating methods inaccurate. In addition, He input from depth prevents an accurate calculation of ore tenor if an average age is calculated based on groundwater flow rates.

Logistics of the Exploration Program

Compared to conventionally used exploration methods such as radiometric surveys (air- and carborne), and test drilling with logging, the exploration method described herein can be much less time consuming and costly. Approximately 2½ weeks was required for two people to collect the samples from each site. With topographic and geologic maps of the area under study, sample sites can be selected rapidly, and three to five samples per day may be collected. The
method is also more accurate than soil-gas and radiometric surveys, particularly for deeply buried deposits. By sampling existing domestic and stock wells, the drilling costs for pre-development stages are reduced to zero. As long as the well owner can provide a reasonably good figure for the depth of the well, it can be determined which formation or part thereof the water is being drawn from. Also, statistical programs such as cluster analysis may help to classify water samples. Assuming current prices from independent laboratories, a water sample may be analyzed for the elements Ca, Mg, Na, K, U, As, Mo, Se, V, He, SO₄, Fe, P, Cl, PO₄, and SiO₂ at a total cost of approximately one hundred dollars. If field analyses are performed for the species listed in Table 3, there will then be sufficient data to adequately model the general groundwater system as well as the speciation of uranium and the other trace elements. Once the WATEQF program is adapted to the specific computer system to be used, computer costs will amount to approximately one to two dollars per sample, and less if lower rates are available for off-peak hours. The costs presented here may change from one laboratory or computer system to another, and will certainly be subject to inflationary pressures. Nevertheless, implementation of a groundwater sampling program may be significantly cheaper than the older methods listed above.
CONCLUSIONS

The results of this study show that levels of certain trace metals in groundwater are effective indicators of the position of uranium ore, and that solution-mineral equilibrium calculations also aid in ore location.

The individual trace elements which best pinpoint the exact location of ore are the radiogenic elements Rn and Ra. Both showed high anomalies in known ore zones. Values of Ra and Rn in groundwaters from immediately outside ore zones were at background levels, demonstrating the extremely short migration distances of the two elements. For this reason, a significant high (two or more orders of magnitude above background) in dissolved Ra or Rn is considered to be an excellent indication of immediate proximity to ore.

Uranium and uranium isotopes do not effectively pinpoint ore, but high U values in updip waters (> 10 ppb) suggest that an aquifer may contain U ore downdip if a sharp redox interface has been established. Uranium isotopes are not effective as exploration tools; as no distinct patterns in isotope ratios were noted over known ore zones.

High He values in groundwater usually occur downdip (along the hydrologic gradient) from U accumulations (cf. Reimer, 1977; Mead, 1980). Helium travels with the ground-
water or is released by faults from structural traps at depth. Helium anomalies of two times background or greater are considered significant. Despite the fact that dissolved He does not pinpoint U ore, anomalous downdip values support the probable presence of ore updip. Helium in groundwater may well be the most useful single element tracer in a regional reconnaissance exploration program.

The elements As, Mo, Se, and V exhibit strong redox control. Their behavior in the groundwater regime is therefore similar to that of uranium in that high concentrations are observed in oxygenated waters and low or below detection levels are found in reduced waters. Concentration contours of these elements parallel those of U, and do not pinpoint ore locations. However, if a sharp redox interface exists, a concentration cliff in these element concentrations may be established which defines a band of possible U accumulation.

The best regional indicator of uranium ore derives from calculation of SI values and maps of uranium minerals (Chatham, 1981; Chatham et al., 1981) or of associated trace element minerals. SI maps of the arsenic minerals realgar, orpiment, and arsenopyrite and the minerals molybdenite and Se metal showed strong anomalies surrounding the Lamprecht and Zamzow ore bodies in south Texas. These phases have Eh-pH stability fields similar to those of uraninite and cof-
finite, which fact explains the similar patterns of SI maps for the trace element and U minerals.

Modelling of a potentially uraniferous aquifer by sampling existing domestic and stock wells may significantly reduce exploration costs when compared to currently employed methods such as drilling/logging, and airborne radiometric surveys. Saturation index maps are an excellent and relatively inexpensive exploration method, and may effectively replace other methods in areas where there is an adequate well water sampling density and the geohydrology is fairly well known. The mineral saturation approach also has the advantage of optimizing the use of groundwater as a prospecting tool. Such a use of groundwater affords a means of exploring for deeply buried uraniferous zones; zones inaccessible if one uses surface geophysical, geological and geochemical exploration methods.
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