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# GEOPHYSICS AND GEOCHEMISTRY IN THE SEARCH FOR METALLIC ORES

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Projet d'exploitation éventuelle d'une  
mine et d'une usine de niobium à Oka

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1979

W. Dyck  
Geological Survey of Canada

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#### Abstract

As the world's surficial mineral deposits become depleted new methods of search for subsurface deposits will have to be developed. The hydrogeochemical technique can be applied to groundwaters but the interpretation of the results is more difficult than for surface waters because of the addition of another dimension.

For the successful application of the hydrogeochemical method of prospecting a thorough knowledge of the chemistry of the elements, the composition of the rocks and the movement of the water are essential. At the surface this information is acquired relatively easily, below the surface with some difficulty.

A literature search reveals that by far the greatest amount of work on hydrogeochemical prospecting is published in Russian journals. While few prospectors can use these publications directly, several translation services have translated numerous major works.

The development of rapid and accurate methods of detection of uranium and its decay products in natural waters at very low concentrations has made the hydrogeochemical method a powerful tool in the search for U ore deposits.

The elements of interest in hydrogeochemical exploration for uranium are uranium and its decay products—radium, radon, and helium. Each element has specific radiochemical and/or geochemical properties which make it a useful tracer for uranium ore deposits. Recent studies indicate that isotopic data of these elements are useful in the interpretation of simple abundance anomalies and the estimation of ore potential.

Uranium is easily oxidized to the hexavalent state in the presence of oxygen in natural waters. Its mobility in surface and near surface waters is greatly enhanced by the complexing action of carbonates and humates in neutral and basic waters, of sulphates in acid waters, and of phosphates and silicates in neutral waters. Organic matter adsorbs uranium strongly and is responsible for decreasing migration of the uranyl ion in surface waters. The great abundance of bicarbonates in groundwaters of sedimentary rocks results in intensive leaching and wide dispersion of uranium in the ground in the zone of oxidation.

The hydrogeochemical techniques employing radium and/or radon are best suited to detailed or semi-detailed investigations of radioactive occurrences. Their ease of detection and short range make them good tracers for pinpointing uranium occurrences or outlining radioactivity too weak for the gamma-ray spectrometer or the fluorimeter.

Helium, because of its inertness and great mobility has the potential of revealing uranium orebodies through much greater thickness of cover than any other geochemical or geophysical technique, but the exact same factors can also cause false anomalies.

#### Résumé

Au fur et à mesure de l'épuisement des gîtes minéraux superficiels dans le monde entier, il faudra mettre au point de nouvelles méthodes d'exploration des gîtes de subsurface. On peut appliquer les techniques hydrogéochimiques aux eaux souterraines, mais l'interprétation des résultats est plus ardue que dans le cas des eaux de surface, en raison de l'introduction d'une autre dimension.

Pour pouvoir appliquer avec succès la méthode hydrogéochimique de prospection, il est essentiel de connaître parfaitement la chimie des éléments, la composition des roches et le mouvement des eaux. A la surface, il est relativement facile d'obtenir cette information, par contre, en profondeur, la situation est moins facile.

Un examen de la documentation montre que jusque-là, la majorité des travaux relatifs à la prospection hydrogéochimique ont paru dans des revues scientifiques soviétiques. Comme peu de prospecteurs sont capables de lire le texte original, des services de traduction ont été chargés de traduire un grand nombre des principales publications à ce sujet.

La mise au point de méthodes rapides et précises de détection de l'uranium et de ses produits de désintégration dans les eaux naturelles à des concentrations minimales, explique que la méthode hydrogéochimique soit devenue un instrument précieux pour l'exploration des gîtes uranifères.

Les éléments considérés au cours de l'exploration hydrogéochimique de l'uranium sont l'uranium et ses produits de désintégration — le radium, le radon, et l'hélium. Chaque élément a des propriétés radiochimiques et ou géochimiques spécifiques, qui en font un traceur utile pour la recherche des gîtes uranifères. Des études récentes indiquent que les données isotopiques relatives à ces éléments facilitent l'interprétation des anomalies simples, et l'évaluation du potentiel minier.

*L'uranium s'oxyde facilement à l'état hexavalent en présence d'oxygène dans les eaux naturelles. Sa mobilité dans les eaux de surface et peu profondes est nettement renforcée par la faculté des carbonates et humates à former des complexes avec l'uranium dans les eaux neutres et basiques, ou des sulfates dans les eaux acides, et la faculté des phosphates et silicates à former des complexes dans les eaux neutres. La matière organique absorbe fortement l'uranium, et réduit la migration de l'ion uranyle dans les eaux de surface. La grande abondance des bicarbonates dans les eaux souterraines qui traversent les roches sédimentaires favorise une dispersion et un lessivage importants et étendus de l'uranium dans le sol, dans la zone d'oxydation.*

*Les techniques hydrogéochimiques où l'on utilise le radium ou le radon, ou les deux à la fois, sont celles qui conviennent le mieux à une exploration détaillée ou semi-détaillée des venues radioactives. La facilité avec laquelle on les détecte et leur faible domaine d'influence en font de bons traceurs, pour localiser les gîtes uranifères ou délimiter toute radioactivité trop faible pour le spectromètre gamma ou le fluorimètre.*

*En raison de son inactivité chimique et de sa grande mobilité, l'hélium permet de détecter les corps uranifères à travers une couverture beaucoup plus épaisse, mieux que toute autre technique géochimique ou géophysique, mais ces mêmes caractères peuvent aussi donner lieu à de fausses anomalies.*

## INTRODUCTION

Hydrogeochemical prospecting is still in its infancy, but mankind has used it since the dawn of history with the aid of human senses, sight, taste and smell (Boyle, 1967; Boyle and Garrett, 1970). Modern ultrasensitive methods of detecting trace elements are partly responsible for the increased use of hydrogeochemistry in exploration. Perhaps equally important in the development of hydrogeochemical methods of exploration is the ever increasing demand for minerals and the need to detect buried deposits. The element uranium, more than any other, has become an important metal and presently receives more exploration attention than gold.

This paper describes the state of the art of hydrogeochemical exploration methods for uranium ore deposits. Because of the great wealth of published information, references with a few exceptions will be limited to the last ten years; and even then the bibliography will be incomplete because of lack of time and access to certain publications. The state of the art of a prospecting method for a certain element reflects current demand for that element, present knowledge of the geochemistry of the element, and technological advancements. The demand for uranium and technological advancements have increased greatly in the last decade. While our knowledge of uranium geochemistry is steadily increasing, certain aspects of its chemical behaviour in the natural environment have been known for sometime (Rankama and Sahama, 1950; Baranov, 1961; Hawkes and Webb, 1962; Vinogradov, 1963; Krauskopf, 1967; Levinson, 1974). The essential features of the geochemistry and methods of search for uranium in the hydrosphere are summarized in the following pages.

## PRINCIPAL RADIOCHEMICAL AND GEOCHEMICAL PROPERTIES OF URANIUM

Geological models play a vital role in pointing to regions of high ore potential. But one must be on guard against the tendency to let established principles negate yet undiscovered geological settings. As important as analogous settings are, the actual location of a U deposit is carried out by means of instruments and techniques that respond to the inherent radiochemical and geochemical properties of U and its decay products. It is therefore important that the prospector be familiar with them.

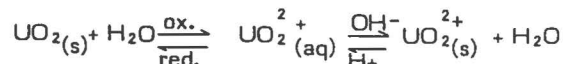
The ultimate origin of U remains a mystery, but isotope work suggests that there were periodic injections of U into the crust from the mantle (Cherdyn'tsev, 1971). Pure U metal comprises essentially two isotopes  $^{238}\text{U}$  (99.3%) and  $^{235}\text{U}$  (0.7%). A 3rd isotope,  $^{234}\text{U}$ , results from the decay of  $^{238}\text{U}$  but its isotopic abundance is only 0.006%. Even so, it plays

an important role in studies of the geochemistry of U, particularly in disequilibrium studies (Cherdyn'tsev, 1971; Osmond and Cowart, 1976; Cowart and Osmond, 1977). These U isotopes have nearly identical physicochemical properties and hence are never found separate in the natural state. But it is actually the  $^{235}\text{U}$  that is used in nuclear reactors. Fortunately the isotopic abundance is quite constant except one ore deposit in Gabon, reportedly has only 0.4%  $^{235}\text{U}$  in a small section of high grade ore and there is evidence that this orebody was a natural reactor at one time (Nicolli, 1973).

The principal decay products of  $^{238}\text{U}$  and main radioactive emissions are shown in Figure 21B.1. The elements of interest to the exploration geochemist are U, Ra, Rn, and He. Several methods are available for the determination of U in sub-ppb amounts in waters, the Ra-Rn couple is relatively easily measured and is quite specific for U, and mass spectrometric techniques are now available that will measure natural levels of He with relative ease. Some of the other elements in the series are either difficult to detect or have too short a half life, or are not specific for U. The various characteristic gamma rays emitted by the decay products and the branching decay modes are not shown in Figure 21B.1. For a classic account on nuclear and radiochemistry, the reader is referred to Friedlander et al. (1964).

Geochemically U is a strongly lithophile and oxyphile element; it has never been observed in the native state in nature. The most important mineral of U is  $\text{UO}_2$  in uraninite and pitchblende. Some other uranium minerals found in nature include hydroxides such as bequerelite, uranomicas e.g.  $(2\text{UO}_2 \cdot 3\text{H}_2\text{O})\text{K}[\text{UO}_2/\text{VO}_4] \cdot 1/2 \text{H}_2\text{O}$ , arsenates, vanadates, uranates, carbonates, silicates, phosphates, and sulphates. Its close association with Th in crystalline rocks is believed to be due to the fact that the ionic radii and simple chemistry of  $\text{U}^{\text{IV}}$  and  $\text{Th}^{\text{IV}}$  are quite similar (.97 and .95 respectively).

What makes hydrogeochemical prospecting possible are chemical processes which can be presented symbolically by the following interactive steps:



Not shown in these processes is the importance of  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  in the leaching and complexing of U in the natural environment. In fact Tugarinov (1975) claims that the  $\text{CO}_2$  regime is the main factor in dissolving, transporting, and depositing U. At  $\text{CO}_2$  concentrations of the order of 80 g/L and elevated temperatures U is leached from rocks at great depth and deposited from ascending solutions at  $\text{CO}_2$  concentrations of 5 g/L or less;  $\text{CO}_2$  is lost by degassing or reactions with enclosing rocks.

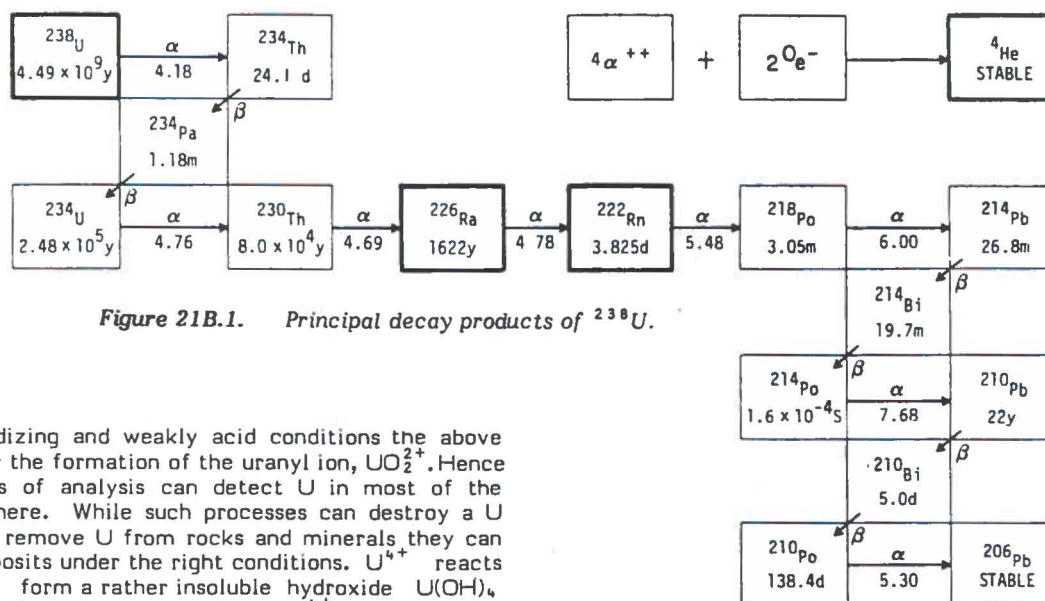


Figure 21B.1. Principal decay products of  $^{238}\text{U}$ .

Under oxidizing and weakly acid conditions the above processes favour the formation of the uranyl ion,  $\text{UO}_2^{2+}$ . Hence modern methods of analysis can detect U in most of the natural hydrosphere. While such processes can destroy a U ore deposit and remove U from rocks and minerals they can also produce deposits under the right conditions.  $\text{U}^{4+}$  reacts with bases to form a rather insoluble hydroxide  $\text{U}(\text{OH})_4$  ( $K_i = 10^{-46}$  at  $25^\circ\text{C}$ ). This corresponds to a  $\text{U}^{4+}$  concentration of about 0.02 ppb at a pH of 5. Because the hydroxide is unstable and dehydrates,  $\text{U}(\text{OH})_4 \cdot \text{UO}_2 + 2\text{H}_2\text{O}$ , actual concentrations of  $\text{U}^{4+}$  are even smaller than that. Some of the pH-Eh relationships of U have been described in some detail by Hostetler and Garrels (1962) and Langmuir and Applin (1977). Under appropriate conditions of pH and Eh water samples in the midst of a U deposit can be void of detectable amounts of U. Fortunately for the prospector  $\text{U}^{4+}$  has a strong affinity for  $\text{O}_2$ . Hence in the zone of oxidation, which can be from several tens to several hundred metres thick,  $\text{U}^{4+}$  is oxidized to the rather soluble  $\text{UO}_2^{2+}$  ion. This oxygen is supplied mainly by air dissolved in water during the hydrologic cycle, although auto-oxidation of uraninite also takes place. This latter process is believed to be partly responsible for the occurrence of pitchblende, the mineral with a varying composition of  $\text{UO}_2$  and  $\text{UO}_3$ , depending on the age and preservation of the mineral. As oxygen-bearing water finds its way through microfissures, made more abundant in the vicinity of U minerals as a result of radiation damage, it oxidizes and hydrolyses the  $\text{U}^{4+}$ . This process of solution of  $\text{U}^{4+}$  is aided even further by the formation of soluble complexes such as bicarbonate, carbonate, sulphate, fluoride, phosphate and silicate. A prominent role in the complexing of U species is played by organic matter particularly humic acids. In basic waters more of the humic acids dissolve and hence keep U in solution. In neutral or lightly acidic waters U is complexed by soluble fulvic acids or absorbs on the solid phase of organic matter and falls to the bottom of lakes and streams. For details of our present state of knowledge on the geochemistry of U the reader is referred to Krauskopf (1967), Vinogradov (1967), Yermolayev et al. (1968), Mann (1974a, 1974b), Roylance (1973) and Langmuir and Applin (1977).

Before describing field and analytical methods and results of the hydrogeochemical technique the problem of radioactive and chemical disequilibrium should be discussed. There are several pitfalls in the use of radiometric techniques in the search for surficial U deposits. These pitfalls result from the weathering of geologic materials which causes fractionation of U from its decay products. In the zone of oxidation the mobility of U is generally greater than that of its decay products. This means that the surface and near-surface waters will contain relatively more U than decay products according to decay chain predictions. Much of this U reacts chemically and partitions between soluble complexes, such as humic acids and carbonates, and the organic matter and clays in the bottom of lakes and streams.

Conversely, the soils and rocks from which this U is leached contain an excess of U-decay products. Under reducing conditions U is not mobile, in fact, it precipitates from solution. The greater apparent mobility of Ra under reducing conditions comes about in an indirect way. Although relatively insoluble, in natural waters, Ra will go into solution particularly in the presence of chlorides. However, actual R concentrations are, as a rule, much lower than those calculated from solubilities of its most insoluble salts, sulphates and carbonates. Most likely Ra coprecipitates with its more abundant group members Ba and Ca and freshly forming hydrous oxides of  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$ . Fe and Mn in their lower oxidation states will remain in solution so that salts of Ra, Ba and Ca in concentrations lower than their solubilities have no host to coprecipitate on. Conversely, under reducing conditions the soils and rocks retain U and become depleted in Fe and Mn and certain decay products of U, particularly Ra.

In order to avoid pitfalls it is therefore essential to measure not only U and Ra or Rn but also such parameters as salinity and alkalinity and oxidation-reduction couples such as  $\text{Fe}^{3+} - \text{Fe}^{2+}$ . In prospecting, relatively inexpensive approximations of the above parameters can be obtained by measuring conductivity, dissolved  $\text{O}_2$  Eh and pH. The reader who wishes to acquaint himself in more detail with the problem of radioactive disequilibrium may consult Dooley et al. (1966), Starik et al. (1967), Cherdyntsev (1971), Cowart and Osmond (1974, 1976, 1977), Osmond and Cowart (1977). For details on laboratory leaching experiments see Starik et al. (1967), Szalay (1967), Szalay and Samsoni (1970), Gavshin et al. (1973), Roylance (1973).

Recently Cowart and Osmond (1977) measuring radioactivity ratios of  $^{234}\text{U}$  and  $^{238}\text{U}$ , found a sharp rise in this ratio in groundwater aquifers down dip from sandstone-type uranium deposits, even though the total uranium content in these waters decreased. The reasons for this rise in activity ratio is not quite clear. One possible explanation may be the fact that  $^{234}\text{U}$  is bound more loosely than  $^{238}\text{U}$  because recoil during the two decay steps from  $^{238}\text{U}$  to  $^{234}\text{U}$  and hence is easier oxidized and mobilized during auto-oxidation in U ore zones where radiation damage is more pronounced than in country rock.

Seasonal variations will also affect the size and intensity of an anomaly. When precipitation varies during a season the amount of water in lakes and streams varies correspondingly resulting in inverse relationship between U content and rate of discharge (Ridgley and Wenrich-Verbeek, 1978) or size of lake or stream (Dyck et al., 1970). In lakes and streams ionic species vary less than dissolved gases. During the course of a season Dyck and Smith (1969) found that Rn levels increased considerably in lakes and streams covered with ice whereas U concentrations remained the same in lakes but decreased in streams during the winter months. Lake bottom waters from the Key Lake, Saskatchewan area contained only 25% less U in early summer than in the winter but the average Rn content was lower by a factor of 3 and the average He content by a factor of 8 (Dyck and Tan, 1978). Korner and Rose (1977) and Rose and Keith (1976) found large fluctuations in the U and Rn content of streams with time but were unable to relate them clearly to seasonal variations but rather ascribed them to fluctuations in proportion of groundwater to surface water and to amount of precipitation. Germanov et al. (1958) illustrate clearly the effect atmospheric precipitation has on the U content of spring waters, dropping from 10 ppb to about 1 ppb with a rise in precipitation from 200 mm to 500 mm.

The relative change in concentration of U and Ra (Rn) with depth is illustrated in Figure 21B.2, and observed concentration levels and ratios for various environments are given in Table 21B.1. The variations with depth are rather generalized and exceptions will occur depending on the groundwater flow pattern in a particular region. Smith et al. (1961) found an increase in Rn content with depth of well when areas of several square miles were considered but over

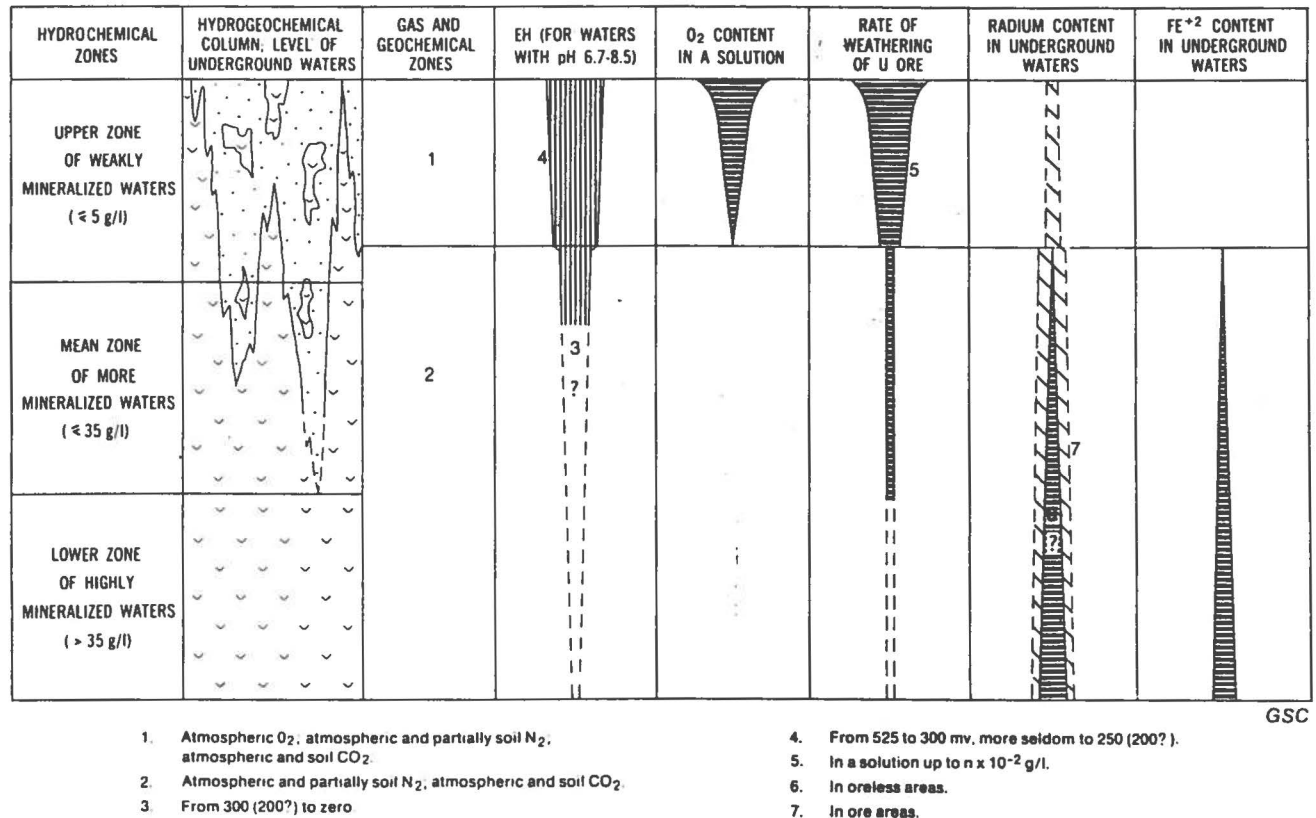
large areas, the depth of a well did not influence the Rn content noticeably. In Eastern Maritime Canada U, Rn, and He in well waters increased with depth as indicated by positive, though weak, correlation coefficients (Dyck, Chatterjee et al., 1976). In the Cypress Hills, Saskatchewan area (Dyck et al., 1977) by contrast both U and Rn levels decreased with depth. Obviously to explain such observations requires a great amount of effort and knowledge about the variables responsible for such changes. These factors are: Geography and topography, geology, type of U mineralization and location, atmospheric precipitation, groundwater movement, and rock type.

**ADVANCES IN ANALYTICAL TECHNIQUES**

The four elements (U, Ra, Rn, and He) of interest to the uranium hydrogeochemist vary greatly in their properties. Hence each requires specific modes of preservation and analysis. Advances in sample handling and analysis are therefore described below for each element separately.

**Uranium Analysis**

The collection and storage of water samples for U analysis is less of a problem than for other trace elements because it forms stable complexes with the ever present bicarbonates, carbonates and sulphates in natural waters. Even so, when U concentrations drop to 0.1 ppb or lower, loss of U to the walls of the containers in which samples are stored and labware used during analysis becomes appreciable. Hence, it is advisable that such samples be treated with a complexing agent or acidified prior to analysis to a pH of 1.



**Figure 21B.2.** Hydrogeochemical zonality in rocks void of organic matter (after Germanov et al., 1958).

Table 21B.1

Types, conditions of formation, and chemical and radioactive constituents of natural waters  
(After Novikov and Kapkov, 1965)

Radiological type of water	Genetic type of water	Hydrogeological type of water	Conditions of formation			Gas composition	Chemical composition	$\frac{^{234}\text{U}}{^{238}\text{U}}$	Radioactivity				
			Lithological	Structural	Hydrodynamic				Rn pCi/L	Ra g/L	U g/L	$\frac{\text{Rn}}{\text{Ra}}$	$\frac{\text{Ra}}{\text{U}}$
Radon (bearing)	weathering joints	Fracture and ground	massifs of acid magmatic rocks	Open structures (foothills)	Intensive water exchange	O <sub>2</sub> , CO <sub>2</sub>	HCO <sub>3</sub> <sup>-</sup>		>10 <sup>4</sup>	10 <sup>-12</sup> -10 <sup>-13</sup>	10 <sup>-6</sup> -10 <sup>-7</sup>	>>1	<1
	emanating collectors	Ground and head			Various	CO <sub>2</sub> , N <sub>2</sub>			<10 <sup>5</sup>	10 <sup>-12</sup>	10 <sup>-6</sup>	>>1	1-3
	Tectonic joints in granites	Head-fracture and vein			Intensive water exchange	CO <sub>2</sub> N <sub>2</sub>	Ca, Mg t to 100°C		<10 <sup>4</sup>	10 <sup>-12</sup>	10 <sup>-6</sup>	>>1	2-3
Radium (bearing)	Sedimentary and metamorphic rocks	Stratal and fracture head	Sedim. and metamorphic rocks	Closed structures (basins)	Very restricted exchange	H <sub>2</sub> S CH <sub>4</sub>	Na, Ca, I, Br, Cl		<10 <sup>4</sup>	10 <sup>-9</sup> -10 <sup>-10</sup>	10 <sup>-7</sup> -10 <sup>-8</sup>	<1	>>1
Uranium (bearing)	Surface water reservoirs	Closed reservoirs and streams	Considerable evaporation from reservoirs without outlets			O <sub>2</sub>			<10 <sup>3</sup>	10 <sup>-11</sup> -10 <sup>-12</sup>	10 <sup>-2</sup> -10 <sup>-4</sup>	-1	<1
Uranium Radium (bearing)	Sedimentary and metamorphic rocks rich in disseminated U	Stratal and fracture, ground and head	Sedimentary and metamorphic rocks	Open structures	Intensive exchange	O <sub>2</sub>	Various	1.5-2.5	<10 <sup>3</sup>	10 <sup>-10</sup> -10 <sup>-12</sup>	10 <sup>-3</sup> -10 <sup>-5</sup>	-1	-1
				Semi-open structures	Restricted exchange	CH <sub>4</sub>	"	1.5-2.5	<10 <sup>3</sup>	10 <sup>-9</sup> -10 <sup>-10</sup>	10 <sup>-5</sup>	-1	>1
Uranium Radon (bearing)	Fracture zones of magmatic rocks; oxidation of ore deposits	Fracture and/or stratal	Acid magmatic rocks	Fully open Structures	Intensive exchange	O <sub>2</sub>	"	2-5	10 <sup>4</sup>	10 <sup>-11</sup> -10 <sup>-13</sup>	10 <sup>-4</sup> -10 <sup>-5</sup>	>1	<1
			U ore deposits			CO <sub>2</sub>	-1	10 <sup>-10</sup> -10 <sup>-12</sup>	10 <sup>-2</sup> -10 <sup>-5</sup>	>1	<1		
Uranium Radon Radium (bearing)	Zone of oxidation of U ore deposits	As above	Ores with rich U inclusions	Open and semi-open structures	As above	O <sub>2</sub> CH <sub>4</sub> CO <sub>2</sub>	"	-1	10 <sup>4</sup> -10 <sup>6</sup>	10 <sup>-8</sup> -10 <sup>-10</sup>	10 <sup>-1</sup> -10 <sup>-4</sup>	>1	<1
			Ores with disseminated U			1-10	10 <sup>4</sup> -10 <sup>6</sup>	10 <sup>-8</sup> -10 <sup>-11</sup>	10 <sup>-1</sup> -10 <sup>-5</sup>	>1	-1		
Radon Radium (bearing)	Primary ore and U ore reduction zones	Fracture-stratal-head	As above	As above	Restricted exchange	H <sub>2</sub> S CO <sub>2</sub>	"		10 <sup>4</sup>	10 <sup>-8</sup> -10 <sup>-10</sup>	10 <sup>-6</sup> -10 <sup>-7</sup>	>1	>>1

This acidification can lead to false anomalies if suspended matter is present in the water (Wenrich-Verbeek, 1977). In surface waters this is usually a fluffy organic substance which has U adsorbed on it. Filtering such samples prior to acidification removes not only the suspended matter but also some of the dissolved U by adsorption on the filters. There is therefore no real satisfactory way of treating such samples short of analyzing *in situ*. Recently Parslow (1977) has worked out an attractive method which involves dropping a tea bag filled with ion exchange resin into a freshly collected water sample. NURE uses a similar method. This not only circumvents the acid-suspended matter problems and minimizes the adsorption on labware but also preconcentrates the sample, making it possible to determine very low concentrations of U (0.05 ppb) with good precision.

Surface waters in arid regions and groundwaters in sedimentary basins usually contain sufficient dissolved solids and U (> 0.1 ppb) so that adsorption on walls of bottles is no problem. However, acidification is still advisable, for groundwaters usually contain enough Fe and Mn in the lower valence states to form precipitates on exposure to air which then carry U down by adsorption. Frequently carbonates precipitate upon loss of CO<sub>2</sub>.

By far the largest number of U analyses in waters have been carried out by the fluorimetric technique. There are probably as many variations on this method as there are laboratories. In low conductivity surface waters it can detect about 0.2 ppb U using a 5 ml sample with sample pretreatment (Thatcher and Barker, 1957; Samsoni, 1967; Smith and Lynch, 1969). However, in the presence of Fe, Mn, and other dissolved salts the U fluorescence is quenched resulting in poor analytical precision and loss of sensitivity. For surface waters in humid zones this presents no problem but waters from arid regions, or groundwaters may be affected. To get around this, various solvent extraction and ion exchange techniques are employed (Centanni et al., 1957; Danielson et al., 1973; Parslow, 1977).

More recently nuclear reactors are being employed for U analysis. The two methods, delayed neutron counting analysis and fission track counting are providing quantitative U determinations although the DNC method requires preconcentration of U in natural waters, for its detection limit is about 1 microgram (Ostle et al., 1972). The fission track method can detect 0.01 ppb U in a drop of water, (Reimer, 1975; Fleischer and Delany, 1976), and indicate the proportion of U in true solution and in suspended solids. However, fission track counting is still tedious when done manually and rather expensive by image analysis. A novel innovation of the fluorimetric method, employing laser excitation is presently undergoing evaluation as a rapid technique for U in natural waters (Robbins, 1977). This instrument has the potential of analyzing for U *in situ* at the 0.1 ppb level.

For U concentrations greater than 1 ppb a colorimetric technique can be used (Hunt, 1958; Smith and Chandler, 1958), and for concentrations of > 0.01% even a spot test can be employed to identify U in minerals (Goldstein and Liebergoot, 1973).

#### **'Radon-222 and Ra-226 Analysis**

Because <sup>222</sup>Rn has a rather short half life ( $t_{1/2} = 3.8$  days) it depends greatly on the presence of Ra for its continued existence. Hence, methods suitable for Rn determinations will usually also measure Ra. There are a great many methods (based on the ionization chamber principle, - the ZnS (silver activated) scintillation phosphors, charged electrode collection method, alpha track etching, nuclear diode alpha counting) for measuring Rn in atmospheric air and soil emanations. For Rn in water determinations, the ZnS counter is used mostly, although the ionization chamber technique can

also be employed; but the latter is more cumbersome for comparable sensitivity. With care the ZnS method can detect 1 pCi/L Rn and hence 1 pCi/L Ra (Lucas, 1957; Baranov, 1961; Higgins et al., 1961; Rushing, et al. 1964; Novikov and Kapkov, 1965; Sedlet, 1966; Dyck, 1969; Allen, 1976; Naguchi and Wakita, 1977). The classical method of coprecipitation of Ra with BaSO<sub>4</sub>, while more sensitive than the Rn-Ra method requires very large samples and is therefore too cumbersome for prospecting. Although the ZnS method is relatively simple to use it does require somewhat more skill than that required for a scintillometer. Three factors require special attention for high quality data. 1) Selection of sample site; very turbulent streams and lakes will contain less radon than quiet ones. Samples more than 5 to 10 metres from the bottom of a lake or stream will seldom contain measurable concentrations of Rn. 2) Loss of Rn during collection and storage. When domestic wells are sampled the aerator on kitchen sink taps should be removed. Glass bottles filled completely and closed tightly with screw caps or bottle caps will avoid Rn escape during transport and storage. 3) Stray light can easily introduce false counts into the instrument. Hence regular background checks and two successive sample counts are advised.

#### **Helium Determinations**

The predominant technique of measuring He employs a mass spectrometer. It is specific in that it identifies the element and determines the amount simultaneously. Without some form of enrichment most mass spectrometers can detect He in the ppm range only. By condensing the major gas components into activated charcoal cooled with liquid nitrogen, and operating the mass spectrometer in the static mode, fractions of ppm may be measured. A portable battery operated instrument based on the mass spectrometer principle and suitable for the detection of 50 ppm or more He has been described by Eremeev et al. (1973). This instrument is capable of analyzing up to 30 samples per hour but lacks the sensitivity required for near-surface samples. A portable He analyzer capable of measuring 1% or more has been described by Sonnek et al. (1965). It works on the principles of chromatography and thermistor response.

He analyses were carried out before the days of the mass spectrometer with the aid of a manometer, liquid nitrogen and activated charcoal. This method is still being used today by some scientists (Penchev, 1969). More recently He leak detectors have been modified for field work (Goldak, 1974; DeVoto et al., 1976; Reimer, 1976; Dyck and Pelchat, 1977). There is also on the market a chromatographic technique using a He ionization detector with sufficient sensitivity for natural samples (Carlo Erba, 1976).

One of the most difficult steps in the He method is the retention of the He in the sample until it is analyzed. For gases, high-vacuum valves and containers are required which make the sampling of large numbers of samples expensive. Clarke and Kugler (1973) have adapted a method involving annealed copper tubing and special pinch clamps for the collection of water samples. At the Geological Survey of Canada water samples are collected in 300 ml soft drink-type glass bottles. Filled completely and capped properly these samples will retain He for a long time (about 10% loss per month) (Dyke et al., 1976). The determination of the isotope ratio of <sup>4</sup>He/<sup>3</sup>He is much more difficult than total He determination and can only be carried out with a high-sensitivity and high-resolution mass spectrometer. Since there is only about 1 ppm <sup>3</sup>He in natural He, a mass spectrometer has to measure precisely 1 part of less in 10<sup>12</sup> parts of air. To achieve such a low detection limit, special procedures and apparatus such as preconcentration of sample, operation of mass spectrometer in the static mode, high-gain multipliers, etc., are employed. A resolution of 600 or more

is required in order to separate the  $^3\text{He}$  peak from the mass 3 peaks produced by ( $^1\text{H}^2\text{D}$ ) and  $^3\text{H}$ . Details of two such analytical facilities have been described by Mamyrin et al. (1970) and by Kugler and Clarke (1972). Such complex instruments and procedures make He isotope determination very expensive.

#### APPLICATION OF PRINCIPLES AND TECHNIQUES TO U PROSPECTING

The action of water on soils, rocks, and minerals is the basis for hydrogeochemical prospecting. The hydrologic cycle provides the continuity for this action. The moment rain touches the earth a series of chemical and physical forces come into play. One of the best summaries of the fate of U and Ra in the hydrologic cycle is given by Germanov et al. (1958). No prospector should venture forth without the knowledge contained in that report. Although 20 or more years old and dealing with eastern European settings mainly, its findings can be applied equally well everywhere to groundwater prospecting for U. Other noteworthy publications on the subject resulting from the U boom in the fifties are by Denson et al. (1956), Fin (1956), UN (1955, 1958), Phoenix (1960). In wilderness areas such as northern Canada surface waters are being used as a complement to lake and stream sediment surveys. To focus in some detail on past experiences the elements U, Ra and Rn, and He will be discussed separately. In a general way U is best suited for prospecting on a regional scale in the zone of oxidation; Ra and Rn are well suited for semidetached and detailed investigations in either the oxidizing or reducing environments and He, although not yet well understood, seems to be most suitable for detailed subsurface prospecting.

#### Uranium

Surface lake and stream waters have been used extensively for U exploration. In humid regions U concentrations are generally low and it is desirable to have a method that can detect 0.05 ppb U particularly in granitic terrane and terrane with extensive overburden (Chamberlain, 1964; MacDonald, 1969; Meyer, 1969; Dyck et al., 1970; Durham and Cameron, 1975; Dyck and Cameron, 1975; Cameron and Hornbrook, 1976; Jonasson, 1976; Cameron and Ballantyne, 1977; Coker and Jonasson, 1977). Because of its great mobility U in waters is an excellent regional tracer and sample densities of 1 sample/30 km<sup>2</sup> will outline significant U mineral zones (Dyck, 1975) see also Figure 21B.3. Since organic matter adsorbs U strongly and carries it to the bottom of lakes and streams, sediments are sometimes the preferred medium (Cameron and Hornbrook, 1976; Ferguson and Price, 1976), depending on the cost of sample collection and use of samples. However, the competition for the uranyl ion between soluble complexes and solid organic matter will distort the size and intensity of anomalies (Dyck, 1975; see also Maurice, 1977). It is therefore important that notice be taken of the organic matter in the sediment and the alkalinity of the water in a survey area. A simple approximation of alkalinity is obtained by measuring the conductivity of the water and of organic matter by measuring the volume of unit weight of sediment. Breger and Deul (1955) also recognized the ability of organic material to adsorb uranium from water. However, in alkaline waters U adsorption is weaker than in neutral waters (Doi et al., 1974; Lopatkina, 1970). Similarly there is evidence that in acidic waters U adsorption decreases. Salinity or conductivity were found to be useful in interpreting stream water U anomalies (Dall'Aglio, 1971) and in the searching of calcrete-type uranium deposits in arid regions (Premoli, 1976). A knowledge of the presence of carbonate rocks also helps in the interpretation of U anomalies. Sergeeva et al. (1972) have shown that  $\text{UO}_2\text{CO}_3$  is moderately soluble in neutral and alkaline waters.

Haglund et al. (1969) found that U in limestones is easily leached out. The effect of alkalinity and organic matter on the partition of uranium in stream water and sediment illustrated in Figure 21B.4.

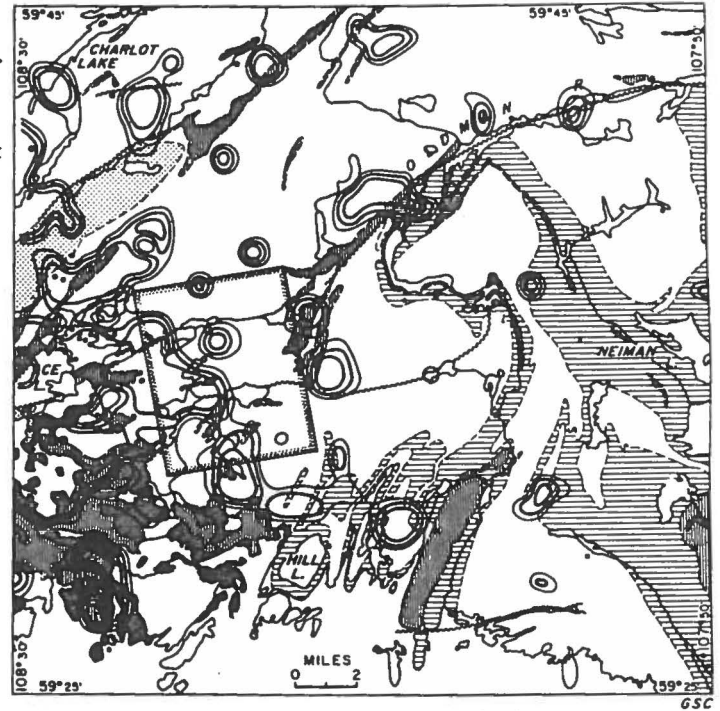
In areas where U mines are in operation U values in waters tend to rise to tens and even hundreds of ppb due to contamination attesting to the high mobility of U but confusing the prospector in terms of assigning significance to an anomaly in nearby virgin territory. A similar rise in U values is observed in streams in arid and semi-arid regions particularly in regions with radioactive coal seams (Boberg and Runnells, 1971). In mountainous terrain with carbonate rocks alkaline stream waters with ppb levels of U are common (Illsley, 1957; Ballantyne, 1976). In areas with known U mineralization alkaline lakes without outlets can attain several thousand ppb U (Culbert and Leighton, 1978). Similar results were obtained by Kyuregyan and Kochargan (1969) from less saline waters in the Caucasian district of Russia. Saline lakes and their deposits contain much less U in the absence of mineralization (Bell, 1955; 1960). Rose and Keith (1976) found large variability in Pennsylvania stream waters and hence opted for sediment as the preferred medium. Although stream and lake sediments cost more to collect they do have the advantage of averaging out seasonal fluctuation of U and other elements observed in waters (Rose and Keith, 1976).

As surface water becomes groundwater it picks up  $\text{CO}_2$  from decaying organic matter and carbonates and becomes a more effective leaching agent. Initially Ca and Mg dominate the population of cations but these are gradually replaced by Na and K as the water sinks and moves through clay minerals. Trace elements also go into solution during this leaching process, particularly the oxyphile elements such as U. The concentration of total dissolved solids is also a function of the annual precipitation and relief. Significant U concentration levels are usually greater than 1 ppb in groundwaters from sedimentary environments so that analytical requirements are less stringent, but interferences from quencher elements are more pronounced. The effect of rainfall, relief, and total dissolved solids is evident in the groundwater results obtained from two sedimentary environments, Eastern Maritime Canada and Cypress Hills, Saskatchewan. To see the effect of these parameters it is necessary to compare U and Rn patterns and concentrations. These are illustrated in Figures 21B.5, 21B.6, 21B.7, and 21B.8. In the Maritimes where the annual precipitation is 80 cm and relief is gentle the average conductivity, U and Rn concentrations of 1700 well waters from a 25 000 km<sup>2</sup> region were 301 micromhos/cm, 1.0 ppb and 857 pCi/L respectively (Dyck et al., 1976a). There is good spatial and mathematical correlation between these variables. It should be noted here that the positive association of uranium and fluorine in alkaline waters observed in this study and by others (Doi et al., 1975; Ballantyne, 1976; Boyle, 1976; Culbert and Leighton, 1978) suggests a common source such as radioactive pegmatites or minerals such as U-rich fluorapatite. Thermodynamic calculations by Langmuir and Applin (1977) show that fluorine complexes with U only in fairly acid media (pH < 4.5) and the phosphate ion forms stable U complexes in weakly acid and neutral waters (pH 4.0 to 7.5). Little is known about these complexes in natural waters and some research is in order. In the Cypress Hills, relief is pronounced and average annual precipitation about 25 cm. There, 900 well water samples from a 15 000 km<sup>2</sup> area gave 1460 micro mhos/cm, 11.5 ppb U, and 355 pCi/L on the average. We see here a significant drop in precipitation and Rn content and an even more significant rise in U and conductivity compared to Maritime data. Furthermore, in the Cypress Hills area the Rn highs cluster in the high country and the Cypress Hills Formation whereas U is concentrated on and down the slopes of the hills. Where relief becomes gentle, as in the north and

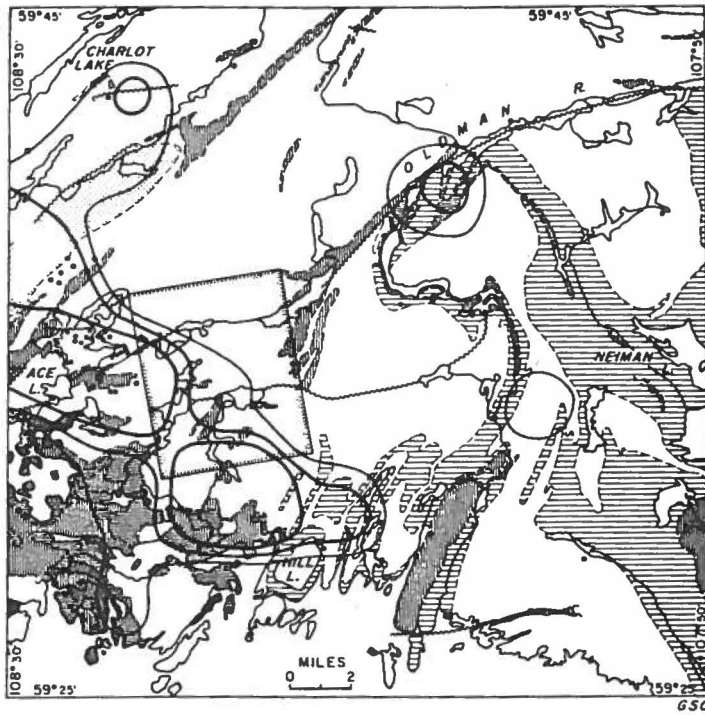
Figure 21B.3.

Uranium in surface lake waters,  
Beaverlodge, Saskatchewan, 1969;  
Effect of sample density.

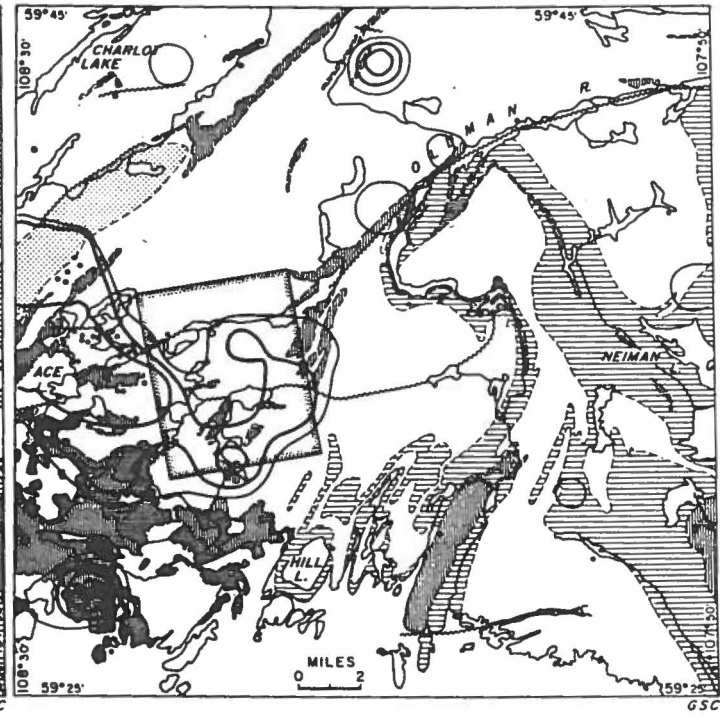
- BEAVERLODGE,  
SASK.
-  BASAL CONGLOMERATE
  -  GRANITE, GRANITE-GNEISS
  -  AMPHIBOLITE
  - METASEDIMENTS**
  -  QUARTZITE
  -  MIGMATITE
  -  LIMESTONE
  -  RADIOACTIVE MIN. OCC. ....



SAMPLE DENSITY = 1.31 SQ. MI.

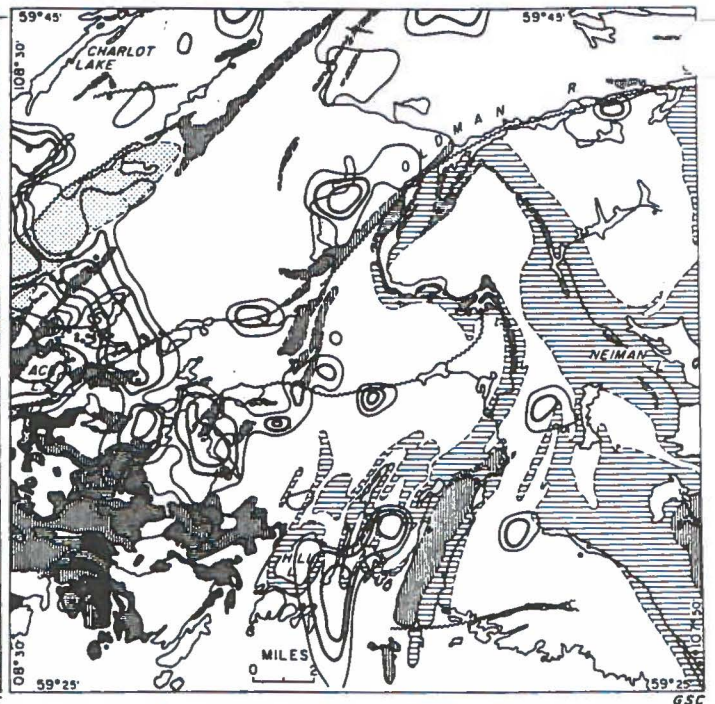
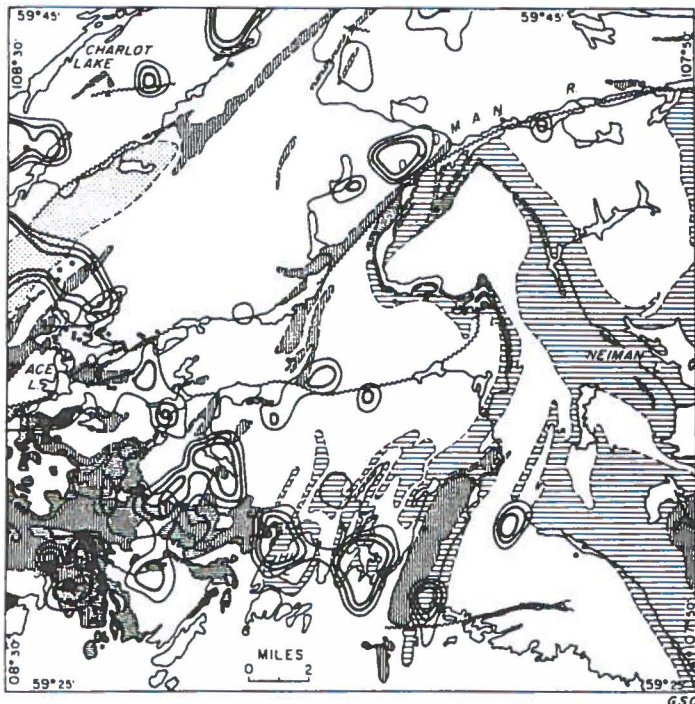
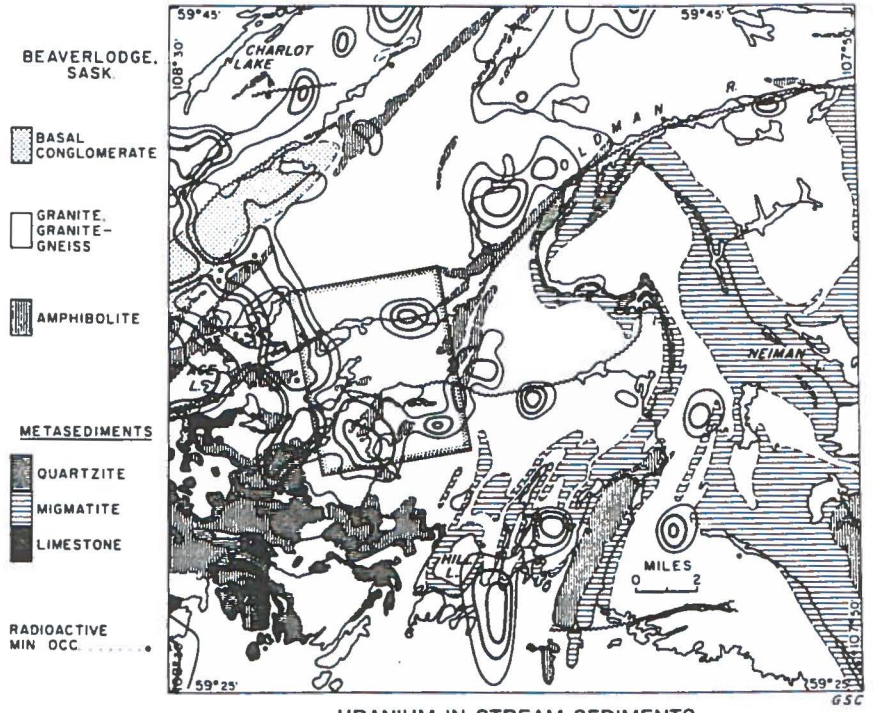


SAMPLE DENSITY 1/12 SQ. MI



SAMPLE DENSITY 1/5 SQ. MI

**Figure 21B.4.**  
 Effect of alkalinity and organic matter on the partition of U in stream water and sediment, Beaverlodge, Saskatchewan.



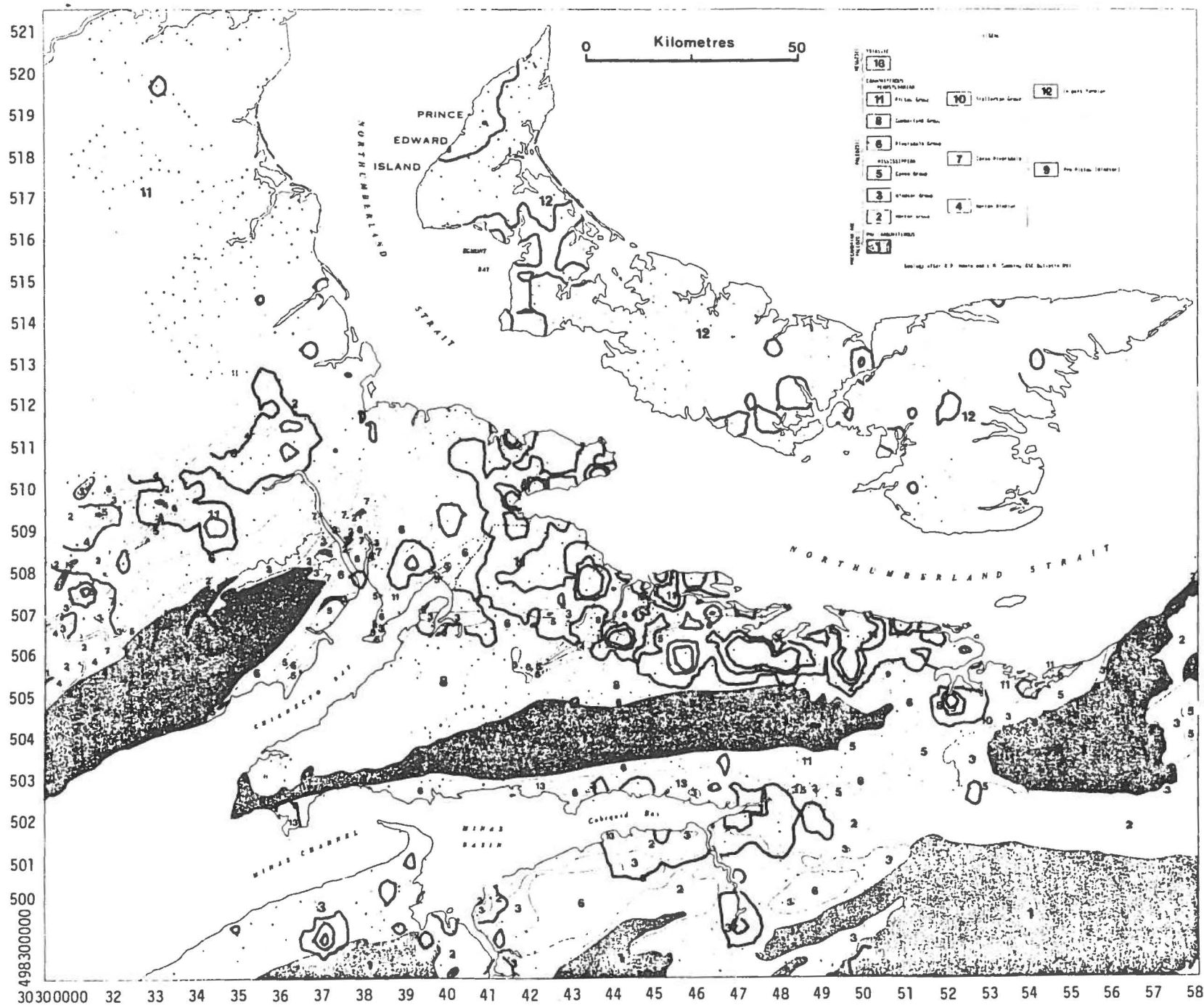


Figure 21B.5. Uranium in well waters in ppb, contours  $\bar{X} = 1.0$ ,  $\bar{X} + S = 4.0$ ,  $\bar{X} + 2S = 7.0$ , Eastern Maritime Canada.



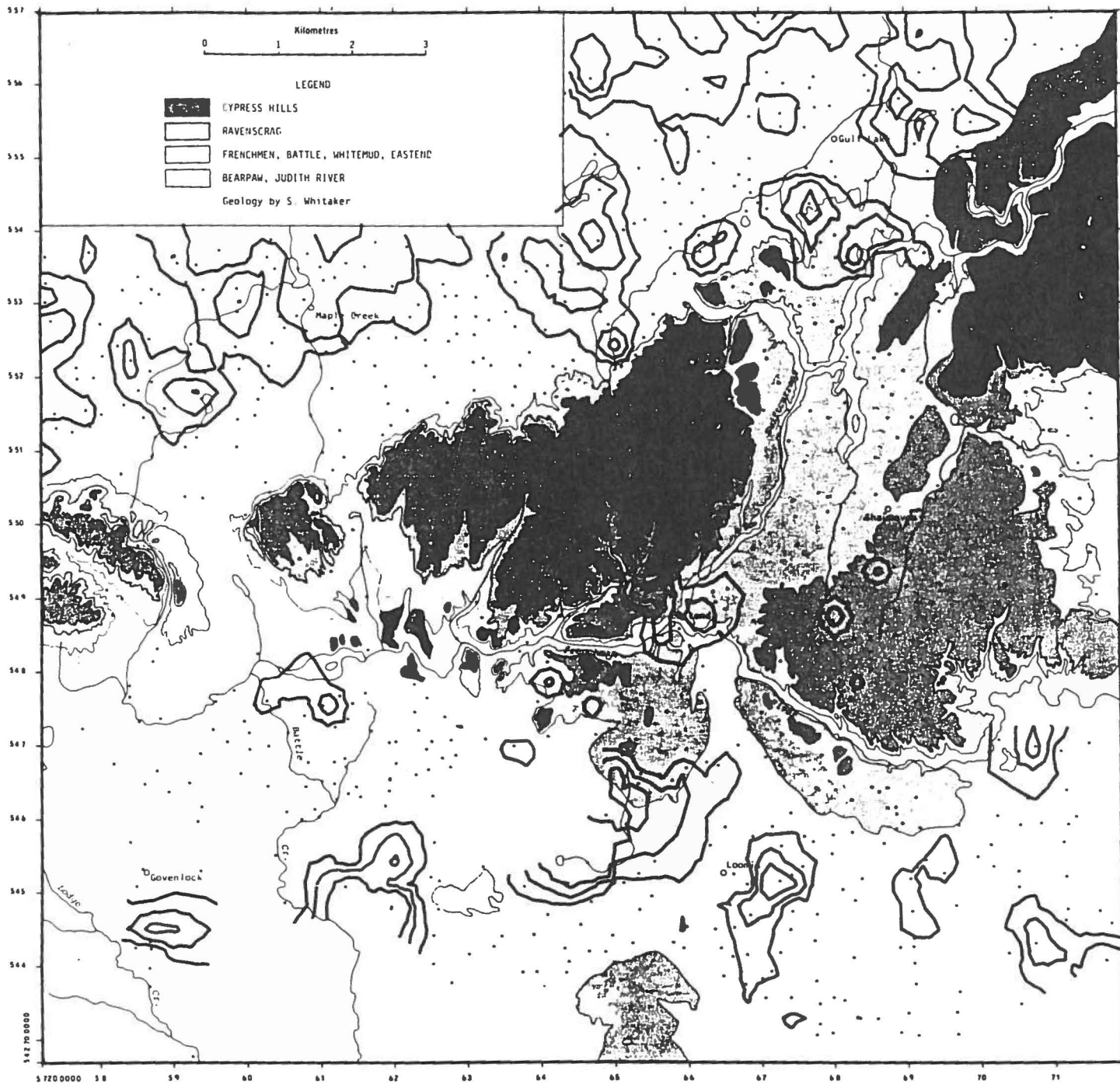
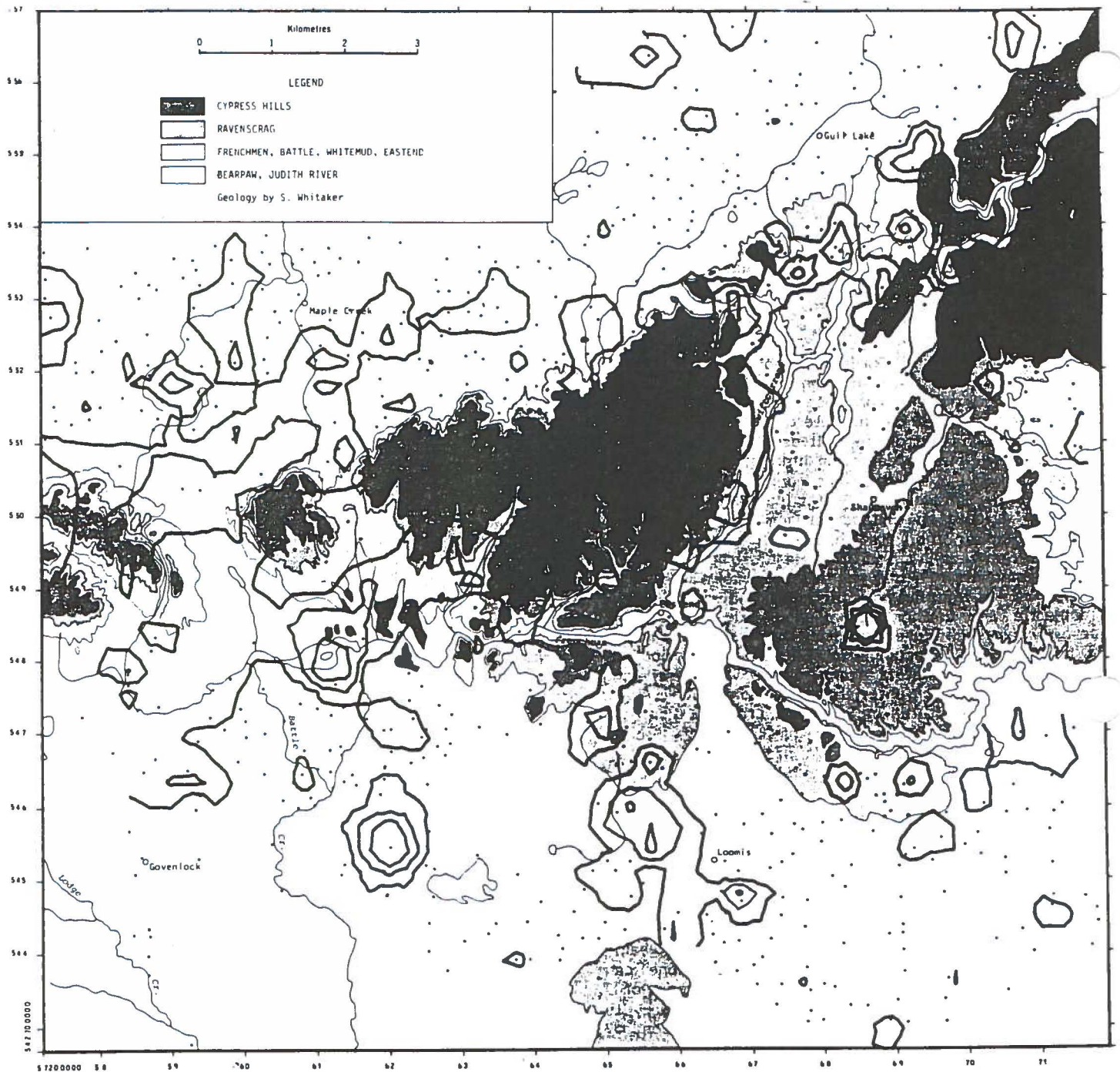


Figure 21B.7. Uranium in well waters in ppb, contours  $\bar{X} + .25S = 17$ ,  $\bar{X} + S = 32$ ,  $\bar{X} + 2S = 53$ , Cypress Hills, Saskatchewan.

north east of the area, U and Rn highs more or less overlap and coincide with the Cypress Hills Formation. The lower Rn values suggest lower Ra concentrations and hence less U mineralization in the Cypress Hills than in the Maritimes even though the absolute U concentrations suggest the opposite. Similarly Korner and Rose (1977) found that Rn in groundwaters was anomalous near U mineralization but U not. However, rate of water turnover is not the only factor, the porosity of the ground and the type of sediments also influence Rn and Ra release into the waters. Even so, the two elements U and Rn make a powerful team in the search for U mineralization at depth. But it is absolutely essential in the interpretation that the investigator have a good knowledge of the behaviour of these two elements. Even then, in order to know for a fact, drilling is ultimately required.

The present U boom has redirected industry and government funds to the search of U in an unprecedented scale and hydrogeochemistry is playing an important role in this search (King et al., 1976; ERDA, 1977; USGS, 1977; Darnley et al., 1975). Unfortunately a rather useful publication dealing with all aspects of U exploration is not available in English (Novikov and Kapkov, 1965). Hence the author feels obliged to summarize excerpts from this book. Table 21B.1 is a summary of a vast amount of information on the types, conditions of formation and chemical and radioactive constituents of natural waters. The hydrogeochemical method has been used extensively and profitably in Russia. Under favourable conditions this method can detect U deposits at considerable depth. In mountainous terrain deposits buried 300 to 400 m, and in foothill regions 50 to



**Figure 21B.8.** Radon in well waters in pCi/L, contours  $\bar{X} + .25S = 439$ ,  $\bar{X} + S = 689$ ,  $\bar{X} + 2S = 1023$ , Cypress Hills, Saskatchewan.

70 m have been detected. The interpretation of hydrogeochemical results are rather difficult because they depend on so many environmental factors, including climate, chemistry of the elements, geology, mineralogy, hydrodynamics, etc. of a region. Of utmost importance is the background concentration of an element in an area. In mountainous regions, a U concentration of  $10^{-6}$  g/L may be anomalous, whereas in arid regions evaporation of water can give backgrounds of the order of  $10^{-4}$  g/L. Therefore a rise in the uranium content is of greater interest if it is corrected for total dissolved solids or conductivity in the water.

#### Radon-222 and Radium-226

To treat U separately from its decay products, as is being attempted in this discussion, is not really the best way to carry out a hydrogeochemical exploration program. Each element in the U decay series is unique in some respects and hence is suited best for certain conditions and a certain phase in the exploration program. Radon-222, because of its short half life can never migrate far away from its immediate parent Ra-226, and since Ra is usually not found in detectable amounts ( $\sim 1 \times 10^{-12}$  g/L) in surface waters, the Rn in

waters in larger amounts must come from Ra in solids such as rocks, soils and sediments. Although the solubility product of Ra salts is seldom reached in natural waters, it invariably gets adsorbed as sulphates and carbonates on surfaces of rocks and minerals. In the zone of oxidation it is also coprecipitated by hydrous oxides of iron and manganese. Only in the vicinity of strong sources of very saline waters will the Ra concentration rise to  $10^{-10}$  g/L or even  $10^{-8}$  g/L. The link between Rn in water and Ra in sediments must be firmly implanted in the prospector's mind. For he could easily miss a deposit in the bottom of a large deep lake if he sampled the surface water for Rn only. Rn will not travel much beyond 6 m by true diffusion, although mechanical agitation by wind on lakes or a flowing stream can increase the Ra-Rn separation to 50 to 100 m. A second factor is the emanation efficiency of Rn of the solid through which the water moves. This seldom reaches 20% and is usually only a few percent. Even though Ra is so immobile in the surficial environment, the law of dynamic equilibrium demands that some of it go into solution and since it has a relatively long half life (1600 years), it can migrate considerable distances, perhaps several kilometres, in well established aquifers at concentrations below the detection limit of most analytical techniques, adsorbing and desorbing continually on the walls of the solids through which the water moves. While most of this Ra is adsorbed on surfaces at any one time, the Rn emitted by it enters the water phase easily. Thus it happens that water from taps in the town of Bancroft contains easily detectable amounts of Rn even though the lake water that this water comes from has no detectable Rn levels. Similarly old domestic well casings when logged with a gamma-ray probe can have much higher activities than fresh holes drilled right beside them. Accumulations of Ra are particularly prominent in groundwaters from depth, where reducing conditions prevail, which enter the zone of oxidation. As Fe and Mn oxides precipitate, Ra is coprecipitated. Also deep waters usually contain large amounts of  $\text{CO}_2$  which escape when the waters reach atmospheric pressure. Thus  $\text{CO}_2$  escape causes Ca and Mg carbonates to precipitate, again carrying Ra down with them. This phenomenon is particularly evident in mineral springs (Cadigan and Felmlee, 1977). Waters from acidic rocks are usually more radioactive than waters circulating in basic rocks. Waters with intensive circulation and intensive flow are weakly radioactive. Groundwaters with a limited circulation tend to become mineralized and may become strongly radioactive in acidic rocks enriched in uranium. In mountainous areas with rugged relief, waters near the peaks are commonly weakly radioactive but at the foot of the mountains one can encounter highly radioactive springs even in the absence of U ore, although usually, some mineralization is necessary to produce highly radioactive waters, such as secondary mineralization in fractures through which the water moves.

Several criteria are given below which will help in deciding on the significance of radioactive anomalies in groundwater:

- (i) A threefold or greater increase in the content of Rn or Ra compared to the background of a region.
- (ii) Occurrence of anomalous amounts of all four elements (Rn, Ra, U, and He).
- (iii) Increased content of indicators such as Mo, Pb, Cu, Zn, As, P, V, Ni, F.
- (iv) A sharp rise in the Rn concentration after a rain or thaw period of up to 10 times normal levels in the presence of U ore; not more than a fourfold rise above natural levels in the absence of U deposits.

The use of the radioactivity of waters in prospecting practiced in Eastern Europe extensively (Baranov, 1961; Novikov and Kapkov, 1965), has only recently found wider acceptance in North America. No doubt the complexity of the method and the large variations in Rn levels (largely due to its gaseous nature and short half life) have contributed to this reluctance (Rogers and Tanner, 1956; Rogers, 1958; Makkaveev, 1960; Smith et al., 1961).

With good equipment and operators, the method can be applied to surface lake and stream waters at sample densities of about one sample per  $3 \text{ km}^2$  or higher (Boyle et al., 1971). In sedimentary basins with well established groundwater regimes and gentle terrain this method outlines radioactive areas at sample densities of 1 sample/ $13 \text{ km}^2$  (Dyck et al., 1976a). The distribution of Rn in well waters in Eastern Manitoba Canada is shown in Figure 21B.6 and for the Cypress Hills area in Figure 21B.8. These results have already been discussed briefly in the previous section. Rn tests in a phased multi-method approach to U exploration has provided useful information in delineating drilling targets (King et al., 1976). Korner and Rose (1976) found Rn in wells in Pennsylvania useful in reconnaissance scale exploration, however Rn in stream waters was not considered as useful because of low erratic Rn levels. Wenrich-Verbeek et al. (1976) applied factor analysis to Ra data from radioactive springs and conclude that Ra in spring waters can be an indicator for deeply buried U deposits.

These varied experiences and seemingly conflicting reports on the effectiveness of Rn and Ra in hydrogeochemical prospecting confirm the complexity of their geochemistry, the lack of sufficient research, or careless application of the method. It is only through first hand experience and through understanding of the elements and the environment in which they are tested that a prospector will find ore using the hydrogeochemical technique.

### Helium

The fact that He is produced during the radioactive decay of U and Th makes it a potential tracer for U and Th ore deposits. Each time an alpha particle, from the many nuclear transformations in the decay series of U and Th, loses its charge it becomes a He atom. Thus, for this discussion, the decay schemes of the three naturally radioactive series can be represented by the simplified decay schemes:



Being inert and very small, He does not react chemically but has a great tendency to escape into fissures and thence into the groundwater regime. From there it may eventually be expelled into gas-tight underground pockets or into the atmosphere. Atmospheric air at the present time contains 5.2 ppm He by volume. Air dissolved in surface waters contains 2 ppm He. This surface water He background is quite stable in lakes, streams and shallow wells. Dissolved gases in groundwater can contain over 100 000 ppm He (Dyck, 1976).

There appears to be very little literature on the use of He for U prospecting, however, lately Clarke and Kugler (1973) have shown that the He content in groundwaters near U mineralization does rise. But, He escapes rapidly into the atmosphere or is carried away by circulating groundwaters in permeable soils. In stagnant groundwater or wet clays, a He gradient may be observed over a deposit.

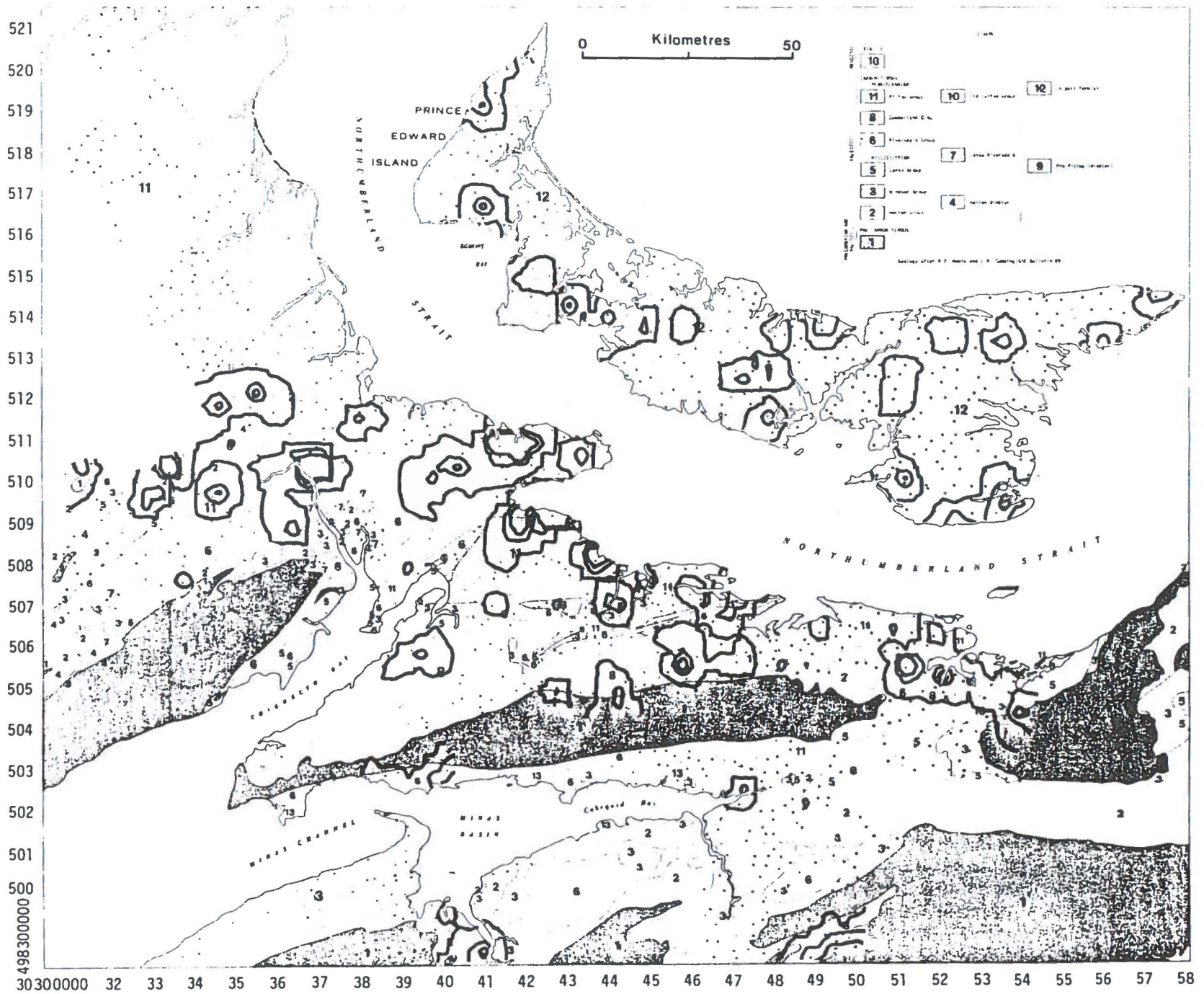
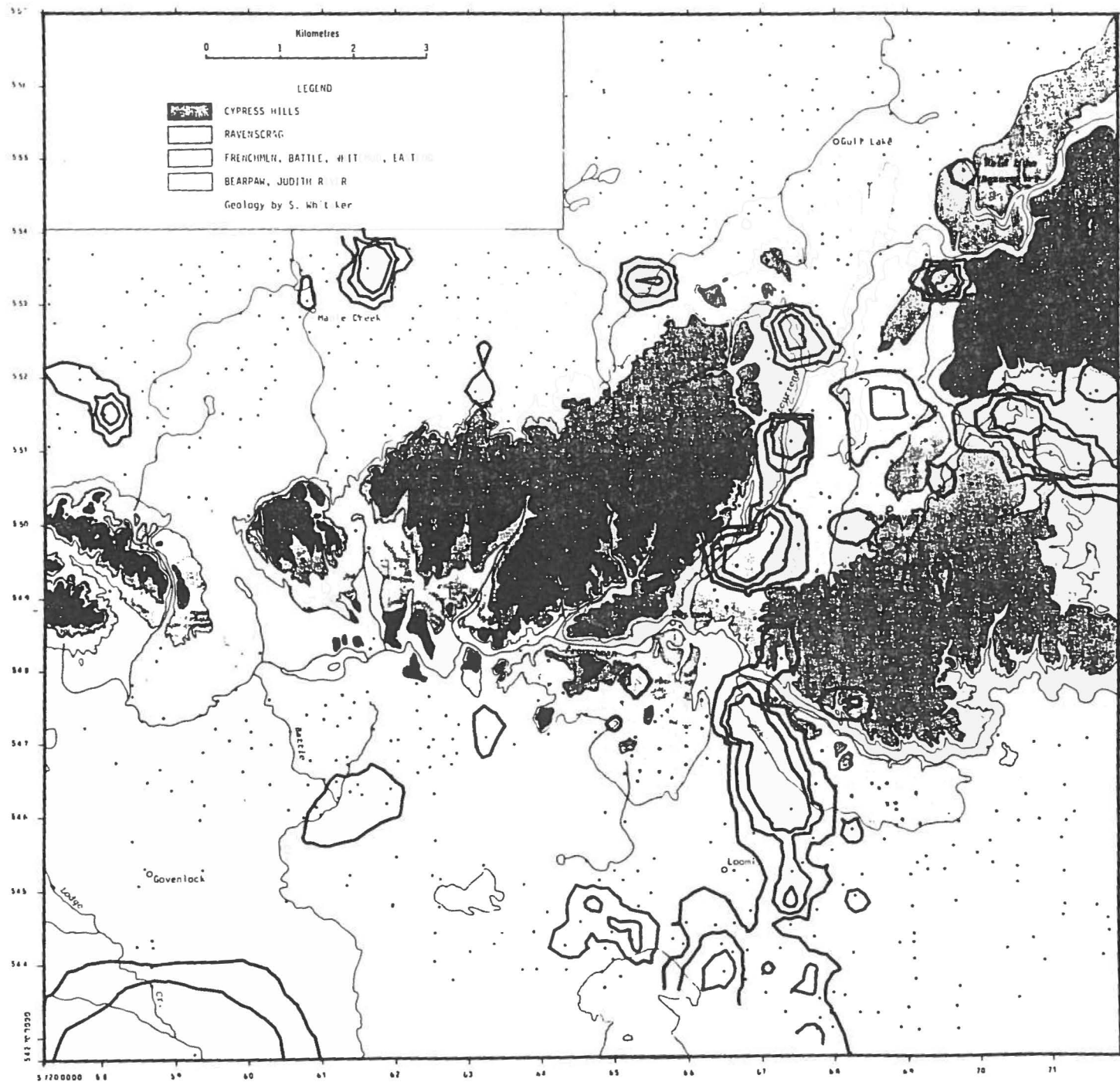


Figure 21B.9. Helium in well waters in microccs/L, contour = 550,  $\bar{X} + S = 4350$ ,  $\bar{X} + 2S = 8160$ , Eastern Maritime Canada.



A summary of He occurrences and its use in mineral exploration is given by Dyck (1976). Most of the He observed in groundwaters and springs has escaped into the water systems from rocks and minerals, particularly the U- and Th-rich basement rocks. Thus most regional He anomalies will reflect fault and fracture zones rather than U ore deposits (Ovchinnikov et al., 1973; Eremeev et al., 1973). However, in areas of high U potential, a He anomaly in groundwater or lake waters can point to a U deposit buried at depth. Recent tests by the author indicate that in the case of lakes, a thermal gradient is necessary to detect a He gradient. Such gradients exist in the winter in northern regions by virtue of an ice cover. While handling of water samples in subzero weather is a problem, particularly for He analysis, because rigid containers are required, the build up of He (and Rn) under the ice in bottom lake waters can be significant in the presence of U mineralization, relative to summer conditions. For example, the average net He content in 87 lake water samples from the vicinity of the Key Lake, Saskatchewan U ore deposits was 8 times higher in the winter than in the summer. Total Rn levels were 3 times higher in winter than in summer. Pogorski et al. (1976) found higher than average He concentrations in waters from the Bancroft area. Clarke et al. (1977) using  $^4\text{He}$ ,  $^3\text{He}$  and  $^3\text{H}$  determinations found positive correlation between U mineralization and He concentrations in central Labrador. Although both He isotopes are of radiogenic origin their mode of production differs and theoretical considerations suggest and experimental data confirm higher  $^4\text{He}/^3\text{He}$  ratios in gases from U rich rocks and U ore deposits (Gerling et al., 1971; Kamminsky et al., 1971; Tolstihlin et al., 1969). Since  $^3\text{H}$  decays to  $^3\text{He}$ ,  $^3\text{H}$  measurements are necessary to correct the  $^3\text{He}$  measurements.  $^3\text{H}$  is radioactive and is produced by cosmic rays, nuclear reactors and hydrogen bombs also release large amounts of  $^3\text{H}$  in the atmosphere continuously. Hence  $^3\text{He}$  can be used for estimating lake water residence times which permits the evaluation of relative intensities of He anomalies.

Groundwaters, easily obtained in inhabited areas from domestic wells, are not subject to the temperature gradient experienced by surface waters although seasonal fluctuations in precipitation will cause some fluctuation in water tables and flow rates. The He maps of the two Canadian environments discussed earlier under U and Rn are shown in Figures 21B.9 and 21B.10. The Maritime He pattern coincides well with the U and Rn patterns suggesting a common source such as U mineralization or U-rich acid volcanics or volcanic ash. The Saskatchewan He pattern on the other hand, while much stronger, follows the  $\text{CH}_4$  pattern very closely on the regional scale suggesting the known oil and gas accumulations at depth as the common source. Just from probability considerations alone, it is obvious that few if any of these He anomalies point to U ore directly but rather that they reveal regional geological and structural features at depth. However, structural mapping with the aid of gases is a powerful tool for prospecting for ore deposits in general (Ovchinnikov et al., 1973). Recently Reimer and Otton (1976) found that groundwaters and soil gases downstream from a roll-type U deposit gave anomalous He. The problem of discerning between He from basement rocks and He from U ore deposits will always be with the prospector, much in the same way as are the U and Rn-Ra anomalies in the hydrosphere. But combined, these elements increase the chances of detecting buried ore.

## CONCLUSIONS

A great deal of work on the geochemistry of uranium and decay products has been carried out to date. Much of this work is published in Russian journals but translations of several major papers are available in English. This geochemical knowledge has been applied successfully to the search of U deposits in many parts of the world.

The elements of interest in hydrogeochemical exploration for uranium are uranium and its decay products: radium, radon and helium. Each element has specific radiochemical and geochemical properties which make it a useful tracer for uranium ore deposits.

Uranium is easily oxidized to the hexavalent state. Its mobility in surface and near surface waters is enhanced by the complexing action of carbonates in neutral and basic waters, of sulphates and fluorides in acid waters, of phosphates in neutral and slightly acid waters, and of silicates in neutral waters. Solid organic matter adsorbs uranium strongly and is responsible for limiting migration of the uranyl ion in surface waters. However, dissolved organic matter is also an important complexing agent of uranium and can enhance its dispersion under appropriate conditions. The greater abundance of bicarbonates in groundwaters within certain sedimentary rocks results in intensive leaching and wide dispersion of uranium in the zone of oxidation.

The hydrogeochemical techniques employing radium, and radon or both are best suited to detailed or semi-detailed investigations of radioactive occurrences. Their ease of detection and short range of dispersion from source make them good tracers for pinpointing uranium occurrences or outlining radioactive zones too weak for direct detection by gamma-ray spectrometry or fluorimetry. Conflicting reports on the success of the Rn/Ra method of prospecting point the need for further research into the behaviour of these elements particularly that of Ra, since it controls its short-lived daughter, Rn.

Helium, because of its chemical inertness and great mobility, has the potential to reveal uranium orebodies through much greater thickness of cover than any other geochemical or geophysical technique, but exactly the same factors can also produce anomalies unrelated to mineralization. Tests of the usefulness of  $^3\text{He}/^4\text{He}$  ratios as a means of differentiating between He from U deposits and basement rocks and  $^3\text{H}$  measurements as a means of determining residence times of water reservoirs are urgently needed to evaluate the He method as a U prospecting tool for buried deposits.

Springs have served man as guides to buried minerals since the dawn of history. In inhabited areas wells can do the same for 20th century man. In uninhabited areas systematic drilling and testing of aquifers will become one of the tools of search in the future.

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