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The Evolution of Redox Conditions and Groundwater Geochemistry in Recharge-Discharge Environments on the Canadian Shield

Évolution des conditions d'oxydoréduction et géochimie des eaux souterraines dans des zones d'alimentation-émergence sur le bouclier canadien

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ABSTRACT

Groundwater composition evolves along flow paths from recharge to discharge in response to interactions with bedrock and fracture-filling minerals, and dissolution of soluble (Cl-rich) salts in the rock matrix. The groundwater redox potential changes from oxidizing to reducing conditions due, initially, to rapid consumption of dissolved oxygen by organics in the upper ~100 m of bedrock and, subsequently, interaction with Fe (II)-containing minerals. Measured Eh values of groundwaters at depth in the granitic Lac du Bonnet batholith indicate that biotite and chlorite control groundwater redox potential. This is supported by other geochemical characteristics such as absence of CH_4, H_2S, H_2, NO_3, low concentrations of Fe (II), and abundance of SO_4.

Further evidence of evolution of redox conditions is given by variations in U concentration ranging from up to 1000 μg/L in dilute near-surface waters to <1 μg/L in some deep, saline groundwaters. Groundwaters at about 400 m depth in a recharge area on the Lac du Bonnet batholith contain significantly more U than groundwaters further along the flow path or near-surface in discharge areas. Uranium concentration is found to be a useful and sensitive indicator of redox conditions.

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ÉVOLUTION DES CONDITIONS D'OXYDORÉDUCTION ET GÉOCHIMIE DES EAUX SOUTERRAINES DANS DES ZONES D'ALIMENTATION-ÉMERGENCE SUR LE BOUCLIER CANADIEN

par

M. Gascoyne

RÉSUMÉ

La composition des eaux souterraines évolue le long des voies d'écoulement entre l'alimentation et l'émergence par suite des interactions avec le substratum et les minéraux de remplissage de fractures, et de la dissolution des sels solubles (riches en Cl) dans la matrice rocheuse. Le potentiel d'oxydoréduction des eaux souterraines passe des conditions oxydantes aux conditions réductrices en raison, au départ, de la consommation rapide d'oxygène dissous par les matières organiques dans la partie supérieure (~ 100 m) de substratum et, par la suite, de l'interaction avec les minéraux contenant du Fe (II). Les valeurs Eh mesurées des eaux souterraines en profondeur dans le batholite de Lac du Bonnet indiquent que la biotite et la chlorite régissent le potentiel d'oxydoréduction, ce qui est étayé par d'autres caractéristiques géochimiques comme l'absence de CH_4, H_2S, H_2, NO_3, les faibles concentration de Fe (II) et l'abondance de SO_4.

Une autre preuve de l'évolution des conditions d'oxydoréduction est donnée par les variations de la concentration d'U allant de 1 000 µg/L dans les eaux diluées près de la surface à <1 µg/L dans certaines eaux souterraines salines profondes. Les eaux souterraines situées à environ 400 m de profondeur dans une zone d'alimentation sur le batholite de Lac du Bonnet contiennent bien plus d'U que les eaux souterraines plus éloignées sur la voie d'écoulement ou près de la surface dans les zones d'émergence. On a trouvé que la concentration d'uranium était un indicateur utile et sensible des conditions d'oxydoréduction.

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AECL-11682
COG-96-500

CONTENTS

LIST OF TABLES

LIST OF FIGURES

continued...

LIST OF FIGURES (concluded)

1. INTRODUCTION

It is well known that the composition of groundwater in fractured, crystalline rock and its state of redox potential (Eh) changes as the groundwater flows from a recharge to a discharge environment. These changes are largely due to water-rock interactions and oxidation-reduction reactions that occur between dissolved species in the groundwater and minerals in the flow path (e.g., lining the walls of fractures in the bedrock) and are important in understanding the interactions between groundwater and materials used in a nuclear fuel waste vault located in a deep geologic environment. Canada, like several other countries, is investigating the concept of disposal of nuclear fuel waste in a stable crystalline rock formation on the Canadian Shield (AECL 1994). The rate of corrosion or dissolution of components of a waste vault (e.g. the UO_2 fuel elements, the metal containers and the surrounding buffer and backfill materials) and many of the sorption processes that may occur to retard radionuclides leaking from the vault, are controlled by groundwater composition and redox conditions.

In the Canadian disposal concept, the vault model (Johnson et al. 1994) assumes that groundwaters coming in contact with the used fuel containers will become reducing after several hundred years so that oxidative dissolution of the used fuel and subsequent release of fission products will therefore be negligible. Field studies (Ross and Gascoyne 1993) have suggested that groundwaters at disposal vault depths (500-1000 m) in Shield rocks are already reducing and need no additional conditioning. However, if the vault was situated in a location where oxidizing groundwaters could enter the vault, the reducing capacity of vault materials could eventually be neutralized and this would significantly affect the release of vault contaminants. Therefore, understanding the evolution of the redox condition and chemical composition of groundwaters with respect to location within the groundwater flow regime will help to determine the conditions that will develop within the disposal vault.

This paper describes the processes that cause the composition and redox state of groundwater to change along its flow path in crystalline rock formations and cites examples from AECL's research areas on the Canadian Shield. In particular, the extent to which oxygenated waters may penetrate the bedrock in a recharge area is examined to determine the potential for oxidizing groundwater to reach proposed disposal vault depths (500 m to 1000 m). Hydrogeochemical data from one of the research areas, the upland exposures of the granitic Lac du Bonnet batholith in southeastern Manitoba, are used to determine and trace the chemical and redox characteristics of groundwater recharging to depths of at least 400 m. Uranium concentration in the groundwater is found to be a useful indicator of redox conditions in these environments.

2. WATER-ROCK INTERACTIONS

2.1 SOURCE OF SALINITY

In most groundwater recharge environments in crystalline rock, near-surface groundwaters are typically dilute, slightly alkaline (pH 7-8) and Ca-(Na)-HCO_3 in composition. They evolve to higher pH (8-9), Na-(Ca)-HCO_3 waters as they move to greater depths or travel further along groundwater flow paths (Figure 1). Hydrolysis of plagioclase feldspars to liberate Na and Ca, coupled with Ca loss by calcite precipitation and/or ion exchange (for Na) on clay minerals in the flow paths, are believed to be the main chemical processes that cause this evolution. The controlling reactions are given below:

Feldspars are readily altered by CO_2-rich, low-pH recharge:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{1}$$

$$\underset{\text{(albite)}}{2NaAlSi_3O_8} + 2H^+ + H_2O \rightarrow 2Na^+ + \underset{\text{(kaolinite)}}{Al_2Si_2O_5(OH)_4} + 4SiO_2 \tag{2}$$

$$\underset{\text{(anorthite)}}{CaAl_2Si_2O_8} + 2H^+ + H_2O \rightarrow Ca^{2+} + \underset{\text{(kaolinite)}}{Al_2Si_2O_5(OH)_4} \tag{3}$$

Bicarbonate (and some Ca) is then lost from solution by calcite precipitation as pH increases:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2 \tag{4}$$

and Ca may also be removed from solution, preferentially over Na, by exchange with clays:

$$Ca^{2+} + 2M\text{-}R \rightarrow 2M^+ + Ca\text{-}R_2 \tag{5}$$

where M is H^+ or Na^+ and R is a clay mineral substrate.

Minor amounts of K and Mg are released to groundwater by attack of other minerals in the rock (e.g., biotite, hornblende, K-feldspar):

$$\begin{aligned}\underset{\text{(biotite)}}{2KMg_3AlSi_3O_{10}(OH)_2} + 14H^+ \rightarrow 2K^+ + 6Mg^{2+} &+ 7H_2O + 4SiO_2 \\ &+ \underset{\text{(kaolinite)}}{Al_2Si_2O_5(OH)_4}\end{aligned} \tag{6}$$

$$\underset{\text{(microcline)}}{3KAlSi_3O_8} + 2H^+ \rightarrow 2K^+ + 6SiO_2 + \underset{\text{(illite)}}{KAl_3Si_3O_{10}(OH)_2} \tag{7}$$

However, in dilute groundwaters, K and Mg are maintained at low concentrations (<10 mg/L) by the limited solubility of hydroxy and carbonate species at pH >7 and by ion exchange with clay minerals.

Other elements may be released to solution or precipitated depending on their solubility in the pH-Eh environment of the flow path. For instance, the release of Fe by pyrite oxidation,

$$FeS_2 + 7O_2 + 2H_2O \rightarrow Fe^{2+} + 4H^+ + 4SO_4^{2-} \qquad (8)$$

and the dissolution of slightly soluble fracture-infilling minerals,

$$\underset{\text{(gypsum)}}{CaSO_4 \cdot 2H_2O} \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O \qquad (9)$$

$$\underset{\text{(calcite)}}{CaCO_3} + H^+ \rightleftharpoons Ca^{2+} + HCO_3^- \qquad (10)$$

will modify the groundwater composition and may consume dissolved O_2 and H^+.

None of the above reactions, however, account for the most significant change that occurs in groundwater composition, especially for deeply circulating groundwaters: the increase in salinity due to uptake of Na, Ca and Cl ions. These ions may have been derived from several origins but have three modes of incorporation in the rock: 1) as residual fluids in fracture zones from previous hydrothermal or low-temperature alteration events, 2) as brines or crystalline salts of NaCl and $CaCl_2$ in the rock matrix (on grain boundaries, in pore spaces and in fluid inclusions in primary minerals); and, 3) as elements chemically bound in rock minerals, e.g. in halogen-bearing biotite or hornblende. The latter are released during weathering or low temperature alteration processes (Kamineni 1987):

$$\underset{\text{(biotite)}}{2KMg_3AlSi_3O_{10}(Cl)_2} + 10H^+ \rightarrow 2K^+ + 6Mg^{2+} + 3H_2O + 2Cl^- + 4SiO_2 + \underset{\text{(kaolinite)}}{Al_2Si_2O_5(OH)_4} \qquad (11)$$

If these ions are present in residual fluids in fracture zones or as salts in the rock matrix, they may be primary (as residual magmatic fluids), deuteric (from fluids involved in high-temperature alteration of the rock after emplacement), hydrothermal (from fluids associated with moderate temperature metamorphic events) or low temperature (as meteoric water, seawater or brine incursions, etc.). Possible origins of the saline fluids found in the Canadian Shield have been described elsewhere (e.g. Kelly et al. 1986, Frape and Fritz 1987, Gascoyne et al. 1989a,b) and will not be considered further here.

2.2 HYDROGEOLOGICAL CONTROLS

The processes of water-rock interaction described by equations 1 to 11 take place fairly rapidly after groundwater recharges at the surface and flows through permeable fractures and the porous rock matrix in near-surface weathered rocks. Groundwater composition will change, therefore, with distance along the flow path or, more generally (in areas with significant topography) with depth in the bedrock. This relationship is described schematically in Figure 1 and illustrated by the Cl-depth relationship observed for groundwaters in the Canadian Shield (Figure 2, after Gascoyne et al. 1987). These data were derived from groundwaters obtained from mines at Yellowknife, Thompson and Sudbury (Frape et al. 1984), well waters in the granitic Lac du Bonnet batholith in southeastern Manitoba (Gascoyne and Elliott 1985), and groundwaters in four unmineralized plutons across the Canadian Shield (Gascoyne et al. 1987). The Cl^- concentrations show an exponential increase with increasing depth and a change in slope, indicating a lower rate of increase, occurring in the depth range of 300-500 m. The rapid variation of Cl^- over shallow depths (area A in Figure 2) is interpreted as indicating advective groundwater flow and mixing of chemical compositions in the upper 300-500 m of rock. This changes to predominantly low- or no-flow conditions below this depth (area B) where dissolved salts move mainly by diffusive rather than advective processes. The depth to which advection occurs is largely controlled by local topography and the permeability and distribution of geological structures such as fracture zones.

Deep penetration of dilute groundwater may occur in upland recharge areas in plutonic rocks if permeable, steeply inclined fractures extend to considerable depth or connect with permeable, low-dipping fracture zones at depth. Groundwaters with Cl^- concentrations as low as 500 mg/L have been found in permeable fracture zones in gneissic and granitic terrains at depths of 800 m. Some examples of the penetration of dilute groundwaters to considerable depths are shown in Table 1 for boreholes that are located in upland areas on the Lac du Bonnet batholith and where hydraulic information from the packer-isolated borehole zones indicates groundwater recharge may be occurring to those depths. In most cases, however, saline groundwaters (Cl^- >1000 mg/L) predominate below depths of about 400 m, where fracturing is limited. In groundwater discharge areas, brackish or saline water may be found close to the surface because of the upward movement of water from deeper saline zones.

The hydrogeological influence on groundwater composition is best illustrated by the variation in compositions of groundwaters in permeable fracture zones in the area of Canada's Underground Research Laboratory (URL), situated in the Lac du Bonnet batholith (Figure 3). Near-surface groundwaters in Fracture Zone 3 (FZ3) and near-vertical fractures are typically $Ca-HCO_3$ in composition. They evolve to $Na-HCO_3$ in the deep recharging portion of the underlying FZ2 and, as they flow up the dip of the fault towards the surface, dissolved salt content increases and the waters become brackish. At greater depths in the area, and elsewhere in the batholith, brackish and saline (Ca-Na-Cl or Na-Ca-Cl) groundwaters predominate. These groundwaters often have isotopic (δ^2H - $\delta^{18}O$) characteristics that indicate they recharged under cold-climate conditions (at least 8000 years ago) or, in the case of deeper, highly saline groundwaters, under warm-climate conditions that are interpreted as being pre-glacial, i.e. $>10^6$ y old (Gascoyne and Chan, 1992; Gascoyne 1994). In some locations, these groundwaters exist in isolated fracture zones of limited extent, that are poorly connected to the near-surface fracture network. However, in other locations saline groundwaters can be found at depths of <100 m in highly permeable fractures and are clearly moving towards discharge at the surface. An example of this phenomenon can be seen on the left of Figure 3 where groundwaters in FZ2 have a salinity of 1.5 g/L but are only 40 m below the surface. Hydraulic head information clearly shows artesian conditions to exist in FZ2 at this location, indicating groundwater discharge is occurring at the base of the overburden above the subcrop of FZ2.

3. REDOX POTENTIAL

3.1 THE Eh MEASUREMENT

The redox potential (Eh) of groundwater is a measure of the relative amounts of oxidized to reduced species in solution. Redox potential is defined by the Nernst equation, which is derived from thermodynamic principles and applies to systems at equilibrium:

$$\mathrm{Eh} = \mathrm{E}^{\circ} + \frac{\mathrm{RT}}{\mathrm{nF}}\ \ln \left\{\frac{\mathrm{OXIDIZED}}{\mathrm{REDUCED}}\right\}\ \text{(volts)}, \qquad (12)$$

where Eh is the redox potential of the system relative to the standard hydrogen electrode (SHE), E° is the reference potential for the reaction at standard conditions, F is the Faraday constant, n is the number of moles of reacting oxidized and reduced species, R is the ideal gas constant, and T is temperature (K). For groundwaters, Eh is generally measured against a Ag/AgCl or calomel reference electrode and subsequently converted to the SHE. The Eh is usually determined with a Pt or Au electrode either in-situ (down-borehole) or in groundwater that is pumped through a flow-through cell at the surface which is sealed from penetration of atmospheric O_2. The use of more than one electrode or type of electrode is advisable to determine if a steady-state Eh can be reliably measured and to reduce problems such as sulphide poisoning or individual electrode malfunctioning. In the Canadian Nuclear Fuel Waste Management Program, multiple electrode measurements of Eh have been made in groundwaters at several research areas on the Canadian Shield (Ross and Gascoyne 1993) and, generally, agreement between electrodes is found if measurements are made over a long period.

3.2 CONTROLS ON GROUNDWATER REDOX POTENTIAL

At the surface, recharging groundwaters are oxidizing and have a positive Eh (~500 to 800 mV) governed largely by their dissolved O_2 content (up to ~10 mg/L). In the subsurface, a number of chemical and biological reactions quickly reduce the O_2 content to <1 mg/L and Eh decreases to lower, positive values. The O_2-consuming reactions that can occur rapidly are shown in the upper part of Table 2. Once the O_2 has been consumed, oxidation of organic matter that may either be dissolved in groundwater or present in the overlying soils will occur, but more slowly. This is represented by the half-reaction

$$CH_2O \rightarrow CO_2 + H^+ + e^- \qquad (13)$$

where CH_2O represents the organic compound (a carbohydrate, or similar). Other species are reduced in the balancing half-reaction. Examples of these other species that may undergo reduction in this process are shown in the lower part of Table 2. In a groundwater environment that is closed to addition of O_2, the oxidation of organic matter, usually with the assistance of microbial activity, results in reduction of major and minor dissolved species in the order NO_3^-, Mn(IV), Fe(III), SO_4^{2-}, HCO_3^- and N_2. These dissolved species, if present in sufficient abundance ($>10^{-5}$ mol/L, Stumm and Morgan, 1981) are capable of controlling the Eh of a groundwater. In a recent laboratory study to determine the threshold concentration at which a reduced species in solution may control Eh, Grenthe et al. (1992) concluded that a lower concentration of Fe^{2+} ($\geq 10^{-6}$ mol/L) was sufficient. This finding agrees with general observations (Wikberg et al., 1987, Ross and Gascoyne 1993) that groundwaters containing low concentrations of Fe^{2+} (typically <0.5 mg/L) have stable and reproducible Eh values, that broadly indicate control by the Fe(II)-Fe(III) couple.

The thermodynamic Eh values, calculated by the Nernst equation (1), are shown for each reaction in Table 3. As each of these oxidizing agents is consumed, the Eh of the groundwater decreases to more negative values. Generally, the Eh of groundwater in uncontaminated crystalline rock environments ranges from +100 to -200 mV and reactions such as reduction of inorganic C or N_2 gas are seldom significant.

Several examples have been presented in the literature in which the Eh of groundwater in natural flow systems decreases along the flow path as a result of this sequence of reactions (these examples are summarized by Champ et al. 1979). For instance, Back and Barnes (1965) observed a decrease of Eh from +700 mV in the recharge area to +150 mV in the discharge area of the Patapsco formation in the Maryland coastal plain, USA. A corresponding increase in dissolved Fe(II) (from 10^{-6} to 10^{-3} mol/L) was seen. Similarly, Edmunds (1973) noted a decrease in Eh, from +400 to -100 mV along the groundwater flow path in the Lincolnshire Limestone, UK, with the occurrence of a redox 'barrier' where dissolved O_2 and NO_3^- decreased below detection limits, Fe^{2+} increased and HS^- appeared. Champ et al. (1979) described a groundwater flow system in sand deposits at the Chalk River Laboratories, Ontario, in which Eh decreased from +600 mV at recharge to +50 mV over a 1 km flow path. Correspondingly, dissolved O_2, NO_3^- and SO_4^{2-} concentrations decreased while HS^- and dissolved inorganic carbon increased (CO_2 released by oxidation of organic carbon during redox reactions dissolved calcareous material causing HCO_3^- to increase).

Recently, the presence of dissolved O_2 has been observed in many groundwaters sampled from depths of up to 450 m in permeable sandstones overlying the Cigar Lake uranium ore deposit in northern Saskatchewan (Cramer and Smellie 1994). At depths of ~430 m in the groundwater recharge area of the flow system dissolved O_2 concentrations of ~100 µg/L were measured on two separate occasions. Further along the flow path and at depth in the altered basement, concentrations were lower, in the range 0-65 µg/L. Measurements of Eh in these groundwaters gave values ranging from -300 to +170 mV and showed no relationship to the dissolved O_2 levels (Figure 4).

The extent to which Eh decreases as groundwater travels along a flow system is largely determined by the mineralogy of the flow system, the type and concentration of dissolved redox-sensitive species in the groundwater and the presence of essential microorganisms to catalyze the reactions. For instance, Eh reactions may not progress far enough to completely consume all dissolved O_2 in the groundwater. Winograd and Robertson (1982) document examples from several large aquifers in the USA in which dissolved O_2 levels of 2-8 mg/L have been measured in deep, ^3H-free groundwaters. They ascribe the persistence of measurable O_2 at depth in these aquifers to the lack of organic compounds and other reduced species present either in solution or in the bedrock, which would otherwise consume the O_2. In contrast, Nordstrom and Puigdomenech (1986) have shown that the Eh of deep groundwaters in crystalline rocks in Sweden is controlled by the S/HS^- couple although Wikberg et al. (1987) subsequently proposed that the Fe(II)/Fe(III) couple (as magnetite-hematite in the rock) exerts the dominant redox control if down-borehole Eh measurements are used in the thermodynamic calculation of Eh.

In a study of the change in composition and Eh of groundwaters entering a recently excavated tunnel in the Hard Rock Laboratory, Aspö, Sweden, Banwart et al. (1994) found that although breakthrough of surface water was detected after three weeks of inflow to the tunnel, the water remained continuously anoxic since this time. Banwart et al. propose that microbially mediated oxidation of dissolved organics in the upper ~70 m of rock is consuming dissolved O_2 in the recharging waters and maintaining negative Eh values in groundwaters entering the tunnel. It is believed this process will continue indefinitely because of the constant input to surface waters of organic carbon.

3.3 REDOX INDICATORS

Many researchers have attempted to relate measured Eh to concentrations of the more abundant redox-controlling elements in the groundwater (e.g., Lindberg and Runnells 1984, Thorstenson 1985). Relatively little work has been done, however, in using concentrations of redox-sensitive trace elements as indicators rather than controllers of redox. This aspect is considered below, specifically in the case of uranium in crystalline rock formations.

Several dissolved, naturally occurring trace elements, which have multiple valence states, may be useful as indicators of redox potential of groundwaters. These include As (III, V), Se (II, IV, VI) and U (IV, VI). Because of their low solubility and low abundance in most geologic materials, they are unable to control groundwater Eh, but instead may adjust their relative abundances to reflect the prevailing Eh. Probably the most useful of these elements in studies of groundwaters in crystalline rocks is U, which is soluble in the oxidized (VI) state, but is practically insoluble in the reduced (IV) state. The uranyl ion (UO_2^{2+}) forms stable complexes in solution with carbonate and phosphate species over the pH range of 6 to 10 (Figure 5). It has, therefore, an appreciable solubility in most groundwaters. Similarly, variations in concentration can be readily detected because analytical methods are well developed and permit precise determination to levels as low as 1 ng/L (Brina and Miller 1992).

Various studies have shown that U is readily mobilized in oxidizing conditions and retarded in reducing conditions. For instance, a characteristic of most natural analogues of geochemical conditions that are expected in a nuclear fuel waste disposal vault is the presence of a redox front or barrier which either has caused a U ore deposit to form, or has protected it from being dissolved. Uranium in the Koongarra deposit, Australia, is currently being mobilized by penetration of oxidizing groundwater along fractures to depths of over 100 m (Snelling and Dickson 1979). In contrast, U in the Cigar Lake uranium ore deposit, Saskatchewan, remains immobile in a reducing environment at a depth of 450 m (Cramer and Smellie 1994) because oxidizing groundwaters are reduced by Fe (II)-rich host rocks before reaching the ore deposit.

Uranium is also found to be very mobile in unmineralized crystalline rocks around the world due to the presence of oxidizing groundwaters and high bicarbonate alkalinities (HCO_3^-). These occurrences have been summarized by Gascoyne (1989) and have been specifically described in Shield rocks and overlying sediments of southeastern Manitoba (Betcher et al. 1988, Gascoyne 1989, Gascoyne and Barber 1992).

The work described in this paper examines in detail the evolution of redox potential in crystalline rock environments in terms of variations in Eh and dissolved O_2 and U contents and uses data from groundwaters at several locations on the Canadian Shield to illustrate and identify the processes and controls on redox evolution.

4. METHODS

Groundwaters have been sampled from surface-collared, packer-isolated borehole zones using a variety of methods depending on borehole size and type of casing installation. For boreholes containing AQ drill-rod and temporary packers, groundwaters were flushed from the borehole using air-lifting or swabbing techniques and, subsequently, a down-hole bladder ('squeeze') pump was used to obtain final uncontaminated samples. For boreholes completed with Westbay plastic/steel casing systems, a bladder pump was used throughout. Boreholes installed with a multipacker-riser tube system were sampled using a peristaltic pump. These methods are described in detail by Ross and Gascoyne (1995).

Groundwaters in boreholes collared underground in the URL were sampled without pumps, by simply opening the valve on the short line of pressure-rated tubing that comes directly from the zone.

Samples of groundwaters were pressure-filtered (in-line with the down-hole pump) through a 0.45 μm filter and collected in pre-washed plastic bottles for major ion analysis using ion chromatographic, atomic absorption and inductively coupled plasma spectrometry techniques. Uranium concentration was determined using a Scintrex UA-3 analyzer. The pH, Eh and conductivity were determined at the borehole collar by passing the pumped groundwater through a plexiglas flow cell that was sealed from the atmosphere. Dissolved O_2 measurements were made using the appropriate range of CHEMetrics break-seal ampoule which have a detection limit as low as ~1 μg/L. Analytical procedures are described by Ross and Gascoyne (1995).

5. RESULTS AND DISCUSSION

5.1 DISSOLVED OXYGEN AND Eh

Dissolved O_2 measurements, when made occasionally in previous samplings of deep groundwaters at research areas on the Canadian Shield have generally shown that concentrations were below detection limits. It has not been not customary, therefore, to include routine dissolved O_2 measurements in the sampling procedures for most groundwaters. This is a common practice of other researchers performing sampling and analysis of deep groundwaters (as noted by Rose and Long, 1988, Winograd and Robertson, 1982, and Freeze and Cherry, 1979, p. 245). However, several studies at research areas on the Shield have examined groundwaters in more detail to verify this generalization.

In a study by AECL of groundwaters in a gabbroic pluton on the Canadian Shield near Sudbury, Ontario, Bottomley et al. (1990) determined dissolved O_2 and Eh as well as several other chemical and isotopic parameters. These data are shown in Figure 6. It can be seen that there is no clear correlation between Eh and dissolved O_2. This might be expected because Eh varies only slightly in the region where dissolved O_2 is measurable (0.01-10 mg/L). However, it is worth noting that 1) Eh is clearly not controlled by dissolved O_2 concentrations in most of the groundwaters because Eh is less than the values expected for O_2 control (+700 to +800 mV), and 2) Eh may also be quite low (<100 mV) for groundwaters where dissolved O_2 can be detected.

These data can also be used to determine if Eh and dissolved O_2 concentrations are related to the depth in bedrock and whether groundwater is recharging or discharging at those depths (Figure 7a, b). Many of the boreholes in the gabbroic pluton are shallow (<100 m deep) and most hydraulic head data from the boreholes indicate downward head gradients (recharging groundwater conditions). A few shallow boreholes and the deepest portions of two deep boreholes show upward heads (discharging conditions). In these cases, there is an indication (Figure 7b) that measurable dissolved O_2 concentrations occur in recharging groundwaters in the upper ~50 m of rock, but below this depth and in shallow discharging groundwaters, concentrations are very low or below the detection limits of the analytical technique used (<0.1 mg/L).

In a similar analysis of groundwaters from the granitic Lac du Bonnet batholith (Gascoyne and Kamineni, 1992) Eh has been routinely measured using Eh sensors sealed in a flow-through cell at the surface. The Eh was found to generally decrease with depth (Figure 8) to values close to those predicted by the Fe(II)/Fe(III) couple for biotite or chlorite (see below). Table 1 shows the Eh values measured for groundwaters from permeable zones in four boreholes drilled in upland areas of the Lac du Bonnet batholith. The hydraulic head measurements for these zones show strong recharging conditions. The Eh values range between -70 and +30 mV for depths between 330 m and 750 m, and all lie well within the range seen for other groundwaters in the batholith (Figure 8) indicating that their Eh is not significantly different from other groundwaters in the surrounding area.

To attempt to better understand the rate of change of dissolved O_2 concentrations and Eh with depth in groundwater recharge areas, studies have been conducted at three sites in the URL lease area on the Lac du Bonnet batholith. These sites include: 1) shallow bedrock and overburden piezometers in an upland area south of the URL; 2) vertical fractures in the upper 200 m of granitic rock that are accessed by horizontal or inclined boreholes from the URL shaft; and, 3) a free-draining vertical fracture in rooms 209 and 219 of the URL 240 m level. Groundwaters at all three locations were thought to be likely to contain dissolved O_2 and have high Eh values because of either their proximity to the surface or their rapid flow to depth caused by the large water table drawdown in the rock mass surrounding the URL.

Results of these measurements are given in Table 4. Most groundwaters sampled show low dissolved O_2 concentrations (µg/L levels) even in near-surface piezometers. Assuming the dissolved O_2 concentration in recharging groundwater at the surface is in equilibrium with atmospheric oxygen (ie. at a concentration of ~10 mg/L), over 99.98% of this O_2 is consumed by the time the groundwater near the URL shaft reaches a depth of ~60 m. Concentrations fall to ≤0.5 µg/L by a depth of 240 m. The dissolved O_2 concentration decreases exponentially with depth (Figure 9a) and can be approximated by a straight line on a log-log plot (Figure 9b).

The Eh measurements using a Pt electrode ranged between +70 and -190 mV in all locations except for the shallow piezometer O-111 (+200 mV) and in piezometers where H_2S was detected (~-200 mV). The variation in measured Eh with depth is shown in Figure 10. Again, a general trend of rapidly decreasing Eh with increasing depth, to a value of about -100 mV, can be seen.

These results collectively indicate the ability of reduced species in the overburden, bedrock and groundwater to consume dissolved O_2 and cause Eh to decrease in recharging groundwater in the URL area. They suggest that even in the case of deeply penetrating, rapid recharge, dissolved O_2 will be almost completely scavenged at shallow depths. It is difficult to say whether these conditions would be maintained over a 10^4-10^6 year period (as required to ensure the integrity of a nuclear fuel waste disposal vault). However, the results described above follow an 11-year period of strongly reduced head conditions around the URL and together with the shorter experience of monitoring redox conditions of groundwater inflow into the Hard Rock Laboratory at Aspö, Sweden (Banwart et al. 1994), suggest that O_2 will continue to be consumed at shallow depths indefinitely.

The most likely reaction controlling the consumption of dissolved O_2 in rapidly recharging groundwater is the microbially-mediated oxidation of dissolved organic carbon (DOC) represented as the carbohydrate, CH_2O:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

In this respiration process, approximately 2·7 mg O_2 are removed by 1 mg C. Surface waters typically contain 10-20 mg/L DOC (Thurman 1985) and, therefore, possess ample capacity to remove all dissolved O_2. At depth, DOC concentrations reduce to 0.5-2 mg/L, as found by

Vilks and Bachinski (1995) for groundwaters in the granitic Lac du Bonnet batholith of the Canadian Shield. If the surface environment is such that insufficient DOC is present in recharging waters (e.g. by direct recharge through exposed, fractured rock containing little soil or vegetation), then it is possible that significant dissolved O_2 concentrations (>5 μg/L) may persist to depth. All data from Canadian Shield environments that have been studied so far indicate that sufficient DOC will be present to consume dissolved O_2. If dissolved O_2 is able to penetrate to the interface with the excavation damaged zone around the vault, it is likely to be consumed by Fe (II) in unaltered minerals exposed in the zone and in crushed granite in the vault backfill.

5.2 REDOX COUPLES

The rapid decrease of dissolved O_2 and eventually, Eh in recharging groundwater in a crystalline rock environment described above is a result of oxidation of organics, reduced species and mineral phases in the groundwater and along the flow path in the bedrock. In particular, crystalline igneous rocks contain significant amounts of Fe (2 to 10%), part of which is in the reduced form, and magnetite and pyrite (up to 1%). Flow through permeable fractures or the porous, weathered rock matrix, near the surface, will cause oxidation of the Fe(II) minerals by dissolved O_2. At greater depths where flow is through much lower permeability cracks and pores, the Fe(II)-Fe(III) redox couple controls the Eh of groundwaters in most situations where the dissolved organic content of groundwaters is low.

Groundwaters in the granitic Lac du Bonnet batholith generally contain almost no H_2S, CH_4, H_2 or NO_3^- but they do contain abundant SO_4^{2-} (up to 1000 mg/L) and some Fe, mostly as Fe^{2+} (total Fe concentrations range from <0.1 mg/L to as high as 4 mg/L). The groundwaters containing >1 mg/L Fe have been generally obtained by pumping through steel drill rods and these samples are probably contaminated by the rods. Contamination by Fe from the drill bit or the earlier presence of drill rods in the borehole may also account for some of the Fe seen in the other groundwaters. In general, the saline groundwaters contain more Fe than dilute groundwater but this again may be partly due to a greater level of contamination (deeper saline zones are generally less permeable and are more difficult to flush). In fact, the higher Fe content of saline groundwaters may be due to their lower Eh because if such groundwaters come in contact with Fe metal or pipe rust, they will more readily dissolve the Fe than more oxidizing groundwaters.

Nevertheless the control by the Fe couple on the redox of deep groundwaters in the Lac du Bonnet granite can be shown from thermodynamic calculations for the dominant Fe-bearing minerals in the granite, biotite, in the rock matrix and chlorite in the fractures, as follows (H.W. Nesbitt, pers. comm.):

$$\underset{\text{(biotite)}}{KFe_3AlSi_3O_{10}(OH)_2} + H^+ + 8H_2O + \tfrac{3}{4}O_2 \rightarrow K^+ + 2H_4SiO_4 + 3Fe(OH)_3 + \tfrac{1}{2}Al_2Si_2O_5(OH)_4 \qquad (14)$$

For this reaction, the equilibrium constant (K_r) is determined by

$$\log (K_r) = \log [K^+] + 2 \log [H_4SiO_4] + pH - \tfrac{3}{4} \log [O_2] \qquad (15)$$

where [ ] indicates activities of dissolved species and log $(K_r) = 33.73$. From the composition of groundwater in the granite at 500 m depth (Gascoyne 1988), $K^+ = 10$ mg/L, Si = 5 mg/L, pH = 7.8 and the ionic strength, I = 0.27. From this, log $[O_2] = -49.5$ bars, which corresponds to a thermodynamic Eh of +39 mV.

Similarly for chlorite,

$$(FeII)_4\ (FeIII)\ Al_2Si_3O_{11}(OH)_7 + O_2 + 14H_2O = Al_2Si_2O_5(OH)_4 + 5Fe(OH)_3 + H_4SiO_4 \qquad (16)$$

for which log (K_r) = log $[H_4SiO_4]$-log $[PO_2]$ = 49.68. For the same groundwater condition, log $[O_2] = -53.4$ bars corresponding to an Eh of -18 mV.

These estimates are very close to the average Eh measured in groundwaters at this depth, -30 mV (Gascoyne, 1988), suggesting that the oxidation of biotite and chlorite to $Fe(OH)_3$ (ferrihydrite) is the dominant Eh control on these groundwaters. However, they rely on the assumption that the dissociation of molecular O_2 and interaction with H^+:

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \qquad (17)$$

is sufficiently rapid and at equilibrium at typical groundwater temperatures in order to be able to express a partial pressure of O_2 in solution as an Eh value. The agreement between measured and calculated Eh may be fortuitous or may be due to microbiological catalysis of reaction (17). Nevertheless, it would appear from these observations, the measured Eh range of O_2- free groundwaters, and the fact that species such as H_2S, NO_3^-, CH_4 and H_2 are largely absent from groundwaters in the Lac du Bonnet batholith, that groundwater redox is controlled by the Fe(II)/Fe(III) couple throughout most of the flow regime.

5.3 REACTION RATES

The rate of consumption of dissolved O_2 and subsequent decrease in Eh potential is difficult to quantify for the natural groundwater environment because several reactions may compete simultaneously (Table 2) and because concentrations of reacting species, surface-to volume ratios and the influence of microbial catalysis, all vary along the flow path.

Some indication of reaction rate for O_2 consumption by inorganic processes, without the influence of DOC and accompanying microbial processes, is given by the results of an experiment at the 420 m level in the URL, in which several boreholes in unfractured grey granite were filled with air-saturated, de-ionized water and isolated into zones by water-inflated packer systems. This experiment was initially performed to monitor the rate of influx of soluble salts from the rock matrix into the boreholes but it also served as a qualitative method of estimating the rate of dissolved-O_2 consumption by the unfractured, grey granite. In the experiment, the water in each zone was circulated to the borehole collar for sampling through two tubes that accessed the zone, using a peristaltic pump, without allowing contact of the water with the atmosphere. About 20 months after filling and isolating the borehole zones, a sealed flow cell containing Eh and pH electrodes, was connected into the circulation line for each zone and water was circulated until stable Eh and pH measurements were obtained (~1 hour). At this time, dissolved O_2 was measured using a CHEMetrics break-seal vial in the flow line. The results of this test, for each isolated zone, are shown in Table 5.

The presence of dissolved O_2 and a high Eh can be seen in all zone 1 waters, probably due to leakage of O_2 from the atmosphere past the first packer in the borehole, and diffusion of O_2 through the excavation-disturbed rock in which the zone is partly isolated. Borehole zone MB2-2 has a very low volume and, therefore, shows the effects of O_2 contamination during sampling more readily than the other larger-volume zones. Of note are the two zones GC2-2 and GC2-3 which are deeper in the rock and removed from the excavation-disturbed zone. In both zones, dissolved O_2 cannot be detected. These results indicate that dissolved O_2 has been completely consumed since filling the zones with oxygenated water and this is reflected in the relatively low Eh values. It is likely that the O_2 was used up by the rock minerals because only nylon tubing and the stainless steel central mandrel are present in each zone (in fact, there is no mandrel in GC2-3).

Based on these observations, the minimum rate of dissolved O_2 consumption may be calculated. Borehole GC2 shows the greatest O_2 depletion. It is a HQ-3 (96 mm diameter) borehole, and contains 7.25 L of water per metre length. Starting at initial O_2 saturation levels (~10 mg/L), 72.5 mg O_2 was consumed by 0.3 m^2 rock in 20 months. This gives a minimum O_2 consumption rate of 4.7×10^{-6} mg/m^2/s or 1.5×10^{-10} mol/m^2/s. If it can be assumed that oxidation of Fe(II) in biotite is the prime cause of O_2 depletion, then using the abundance of biotite in the granite (~5%, Stone et al. 1989), the minimum rate of O_2 consumption becomes 3×10^{-9} mol/m^2/s for biotite. This value is significantly greater than the rates calculated for reaction with Fe(II) released by dissolution of biotite (5.5×10^{-13} mol/m^2/s) or taken up by Fe(II) on biotite mineral surfaces (1.4×10^{-13} mol/m^2/s) in the results summarized by Malmström et al. (1995) determined on the basis of laboratory experiments.

These differences may be due to the influence of several other factors, for instance, microbiological activity may still be occurring to enhance O_2 consumption because the boreholes were not sterilized before filling with de-ionized water; alternatively, the influence of Fe(II) present in the pyrite and magnetite that is disseminated throughout the granite has not been accounted for.

5.4 URANIUM CONCENTRATION AS REDOX INDICATOR

As described in section 4.3, U concentration may be a useful indicator, but not controller, of groundwater redox conditions in unmineralized crystalline rock environments. Work done in research areas of the Canadian Shield shows that high U concentrations (>100 μg/L) are often found in near-surface groundwater in the Lac du Bonnet batholith (Betcher et al. 1988, Gascoyne 1989) and smaller amounts (<50 μg/L), less frequently, in the granitic rocks of the Eye-Dashwa Lakes pluton (Gascoyne, unpub. data). In a third area, the gabbroic pluton near Sudbury, U concentrations in all groundwaters were low (<5 μg/L, Bottomley et al. 1986), probably because the bedrock contains very little U (<1 mg/kg).

The granitic rocks of the Lac du Bonnet batholith are enriched in U (mean concentration of 6 mg/kg, Kamineni 1986) relative to the granite of the Eye-Dashwa Lakes pluton (~2.5 mg/kg, Kamineni et al. 1986) and both granites show further U enrichment (up to 20 mg/kg) in altered rock associated with fracture zones. Because of the greater number of bedrock and overburden boreholes in the Lac du Bonnet batholith, plus the large number of monitored private wells in the surrounding area, considerably more is known about U variations in groundwaters in this region than from other areas and these results are used here to examine U mobility and relation to redox conditions.

In the Lac du Bonnet batholith shallow groundwaters in both overburden and bedrock (<100 m depth) contain the highest U concentrations (up to 900 µg/L) while below depths of ~300 m, U concentrations are lower, generally <10 µg/L. This distribution is shown for 116 groundwaters sampled from permeable borehole zones and overburden piezometers in Figure 11 (Gascoyne and Barber 1992). Various correlations were made by Betcher et al. (1988) to try and determine the factors controlling U concentration in the groundwaters. The dominant factors appear to be Eh and HCO_3^- concentration of the groundwater. Higher U concentrations are associated with more oxidising, HCO_3^--rich groundwaters.

At the URL, U concentrations clearly bear a relation to depth below the surface and to the permeable fractures or fracture zones they are associated with (Figure 12). The control of Eh over U solubility is believed to be the main cause of the increase during 1992 in U concentration of groundwaters that drain into the ventilation raise (Figure 12) of the URL. This increase from about 20 µg/L to over 100 µg/L occurred despite the fact that the hydrogeological influence of excavation of the URL shaft 7 years before had essentially stabilized within a few months following completion of excavations and the major ion composition of inflowing groundwaters to the shaft had remained stable ever since. The increase can be attributed to gradual lowering of the depth of the U redox front in the granite around the URL shaft location (Figure 13). Prior to excavation of the URL shaft, the U redox front had existed as a boundary at about 100 to 200 m below the surface (Figure 13a). Dissolved U moving downwards in naturally recharging groundwaters would precipitate or sorb onto other solids as it crossed the redox front, resulting in significantly lower U concentrations in groundwater at depth. The excavation of the URL shaft altered the local hydrogeological conditions and caused drawdown of the water table. This, coupled with the induced higher rate of groundwater flow through the fractures, caused the U redox front to move slowly downwards as surfaces or minerals that could sorb or precipitate U were gradually consumed by oxidation. After about 7 years the front intersected the main groundwater inflow locations in the URL shaft (Figure 13b), causing rapid increases in U concentration in the inflow.

A localized lowering of the elevation of a redox front and an accompanying increase in U concentration in the inflowing groundwaters is probably a common feature of many large excavations at depth, such as mines, but the phenomenon is undetected because U concentration generally is not measured in the inflows.

Further indication of the redox-sensitivity of U is seen in the variations of U concentrations of groundwaters in the larger-scale flow regime in the area surrounding the URL (Figure 14).

This figure illustrates the complete flow system shown in Figure 3, from the groundwater recharge areas in the southeast and on the URL facility outcrop, through vertical fractures and deep low-dipping fracture zones, to the discharge area in the northwest, and includes U concentrations of groundwaters in specific borehole zones in the area. Data for the recharge area borehole zones (M2A-3, M8-3, URL 12-11) are listed in Table 1. All other U concentrations are taken from Gascoyne (1989) and Gascoyne and Barber (1992). High U concentrations (100-1000 µg/L) are seen in all parts of FZ3, the upper fracture zone, and recharge of these groundwaters to FZ2 is clearly seen by elevated U concentrations (17-46 µg/L) of FZ2 groundwaters in the recharge area. Lower U concentrations occur in the intermediate flow paths of FZ2 around the URL (0-20 µg/L) and low levels persist to the discharge area, near borehole B34, (7 to 12 µg/L). Only where local recharge enters FZ2 through steeply inclined fractures do the U levels increase somewhat (for instance, in the area of boreholes M11 and URL 11, where U concentrations of ~70 µg/L occur).

Based on these various lines of evidence, the concentration of U in groundwaters in the Lac du Bonnet batholith is believed to be a sensitive indicator of groundwater redox conditions, particularly in areas of recharge where dissolved O_2, Eh, Fe^{2+} and other indicators have concentrations too low to be measured or give conflicting results due to contamination.

For U to be useful as a redox indicator, the rates of its dissolution and retardation reactions must be fast compared to groundwater flow rate. An indication of the ease with which U is dissolved from altered rock in Fracture Zone 2 (FZ2) at the URL has been provided by the results of a geochemical tracer test performed in groundwater in this fracture zone (Gascoyne et al. in prep.). Uranium-free, oxygenated water was pumped through a 17 m section of FZ2 between two boreholes at the URL 240 m level. Dissolved U concentrations were found to rise soon after breakthrough of the oxygenated water and reach a steady-state within 6 d from the start of the test. These results indicate fast rates of reaction for the dissolution of U from the solid phase and rapid attainment of equilibrium with the host-rock. Under conditions of natural groundwater flow rates, therefore, U concentration in the groundwater is likely to be representative of chemical equilibrium attained between surrounding mineral phases and the groundwater. This concentration will be a direct indicator of the redox condition of the groundwater.

6. SUMMARY AND CONCLUSIONS

The evolution of the chemical composition of groundwater as it travels along a recharge to discharge flow path is controlled by rock-water interactions coupled with dissolution of soluble salts and pore fluids in the rock matrix. Redox potential varies along the groundwater flow path in response to contact with reduced mineral species and organics. In a crystalline rock environment on the Canadian Shield, dissolved O_2 is removed rapidly by the large organic content of recharge waters at the surface, and the presence of abundant Fe(II) and some sulphides in rock-matrix and fracture-infilling minerals. The Eh potential decreases to about -100 mV in this environment. The range of Eh of 0 to -100 mV for groundwaters in the granitic Lac du Bonnet batholith, measured by Eh electrodes, agrees well with calculated Eh from thermodynamic data for alteration of biotite and chlorite (the two main Fe-bearing minerals in the rock mass and fractures). Absence of CH_4, H_2S, H_2, NO_3^-, presence of low concentrations of Fe^{2+} (0.1-1 mg/L) and abundance of SO_4^{2-} (up to 1000 mg/L) support this estimate of redox conditions and indicate control by the Fe (II)/Fe (III) couple. The usefulness of U concentration as a sensitive indicator of redox has been shown from the variation of U concentration (up to 3 orders of magnitude) with depth in the Lac du Bonnet batholith.

Groundwaters in recharge areas clearly show evidence of recharge to considerable depths (up to ~400 m in the Lac du Bonnet batholith, deeper in areas with more topographic relief) by their low salinity and chemical characteristics. Uranium concentrations in these groundwaters are significantly higher (~20-50 μg/L) than further along the flow path and in the discharge area (0-20 μg/L).

These results indicate that U may be mobile at depths of at least 400 m in groundwater recharge areas of granitic rocks due to the slightly elevated redox conditions that may persist for some considerable distance along the flow path. The more intense weathering of rock that occurs in upland recharge areas lowers the amount of reduced (Fe (II)-rich) minerals that are available to cause Eh to decrease to reducing values (0 to -200 mV). As seen in the case of the granitic rocks at the URL excavation, groundwater drawdown during the operating period of a nuclear fuel waste vault may further lower the capacity of the rock and fracture-infilling minerals to reach and maintain a fully reducing environment at vault level. Short-term results of measurement of dissolved O_2 and Eh at the URL suggest that anoxic conditions could be maintained indefinitely if there was a continuous source of dissolved organic carbon in recharging waters. However, these observations indicate that a groundwater recharge area in a granitic rock terrain may not be a suitable location for a nuclear fuel waste vault. Siting in a less-weathered, more-reducing part of the groundwater flow field may be more suitable from a chemical perspective and would help to ensure the long-term integrity of the fuel waste.

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TABLE 1

THE COMPOSITION OF DEEP RECHARGE WATERS IN BOREHOLES IN THE WHITESHELL RESEARCH AREA

ROCK TYPE	DEPTH (m)	BOREHOLE/ ZONE	Na	Ca	Cl	SO_4	HCO_3	pH	TDS	Eh (mV)	U (μg/L)
Lac du Bonnet granite	335	M2A-3	100	13	35	23	210	8.3	390	-40	17
	355	M8-3	95	13	35	20	195	8.4	370	-15	25
	430	URL 12-11	102	22	74	63	140	7.9	410	+30	46
gneiss (south of Lac du Bonnet granite)	750	WJ 1-13	522	62	600	435	46	9.1	1672	-70	<1

concentrations are in mg/L unless indicated otherwise.

TABLE 2

REDOX REACTIONS THAT CONTROL Eh AND CONCENTRATIONS OF DISSOLVED SPECIES IN GROUNDWATERS

(after Champ et al. 1979, Freeze and Cherry 1982)

PROCESS	MECHANISM	REACTION
O_2 consumption	respiration	$CH_2O + O_2 \rightarrow CO_2 + H_2O$
	nitrification	$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$
	sulphide oxidation	$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+$
	Fe oxidation	$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+$
	Mn oxidation	$2Mn^{2+} + O_2 + 2H_2O \rightarrow 2MnO_2 + 4H^+$
Organics* consumption	respiration	$CH_2O + O_2 \rightarrow CO_2 + H_2O$
	denitrification	$5CH_2O + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O$
	Mn reduction	$CH_2O + 2MnO_2 + 4H^+ \rightarrow 2Mn^{2+} + 3H_2O + CO_2$
	Fe reduction	$CH_2O + 4Fe(OH)_3 + 8H^+ \rightarrow 4Fe^{2+} + 11H_2O + CO_2$
	SO_4 reduction	$2CH_2O + SO_4^{2-} + H^+ \rightarrow HS^- + 2H_2O + 2CO_2$
	CH_4 production	$2CH_2O + CO_2 \rightarrow CH_4 + 2CO_2$
	N_2 fixation	$3CH_2O + 3H_2O + 2N_2 + 4H^+ \rightarrow 4NH_4^+ + 3CO_2$

* organic compounds are represented here by the simple carbohydrate CH_2O, but may be phenols, esters, etc.

TABLE 3

REDUCTION REACTIONS IN GROUNDWATER THAT OCCUR IN SEQUENCE IF SUFFICIENT REACTANTS ARE PRESENT

(after Stumm and Morgan 1981)

REACTION			Eh (mV)*
$O_2 + 4H^+ + 4e^-$	→	$2H_2O$	+813
$NO_3^- + 6H^+ + 5e^-$	→	$\frac{1}{2}N_2 + 3H_2O$	+746
$MnO_2 + 4H^+ + 2e^-$	→	$Mn^{2+} + 2H_2O$	+396
$NO_3^- + 10H^+ + 8e^-$	→	$NH_4^+ + 3H_2O$	+363
$NO_3^- + 2H^+ + 2e^-$	→	$NO_2^- + H_2O$	+42
$CH_2O + 4H^+ + 4e^-$	→	$CH_4 + 2H_2O$	0
$Fe(OH)_3 + 3H^+ + e^-$	→	$Fe^{2+} + 3H_2O$	-185
$SO_4^{2-} + 9H^+ + 8e^-$	→	$HS^- + 4H_2O$	-214
$CO_2 + 8H^+ + 8e^-$	→	$CH_4 + 2H_2O$	-244
$N_2 + 8H^+ + 6e^-$	→	$2NH_4^+$	-277
$CO_2 + 4H^+ + 4e^-$	→	$CH_2O + H_2O$	-484

* The Eh values for these reactions are calculated from the Nernst equation:

$Eh = E_0 + (RT/nF) \ln [H^+]^n$ where $H^+ = 10^{-7}$ mol/L and n is number of moles of H^+.

TABLE 4

MEASURED DISSOLVED OXYGEN (dO_2) CONTENT AND Eh (Measured as Electrode Potential) FOR SHALLOW BEDROCK GROUNDWATERS IN O-SERIES PIEZOMETERS IN THE EAST SWAMP (URL Lease Area), THE URL MAIN SHAFT (HG-W5 Boreholes) AND BOREHOLES INTERSECTING THE FREE-DRAINING FRACTURE AT THE URL 240 LEVEL (JE-Series)

Borehole	Vertical Depth (m)	dO_2 (μg/L)	Eh (mV)
O-106-3	10	70	+55
O-106-4x	13	80	-75
O-107-1	4	200	+70
O-107-2	8	400	0
O-111-2	8	50	+200
O-112-2	9	300	-200*
O-112-3	16	4000	+70
228-HG-W5	62	2	-100
101-014-OC1 (4 zones)	130	2-4	-20 to -190
101-013-HG4-1	148	2	-10
101-013-HG4-2	176	4	-140
101-S07-MF1-3	165	4	-130
101-S07-MF1-5	176	2	-90
105-HG-W5	184	2	-90
JE-FZ (8 boreholes)	240	0-0.5	-35 to -130

* influenced by strong H_2S presence

TABLE 5

RESULTS OF Eh, pH AND DISSOLVED O_2 MEASUREMENTS IN BOREHOLE ZONES IN THE URL INITIALLY FILLED WITH DEIONIZED WATER

BOREHOLE-ZONE[1]	pH	Eh[2] (mV)	Dissolved O_2[3] (ppb)
MB2-1	7.4	210	>1000
MB2-2	7.1	240	>1000
GC1-1	9.3[4]	350	>1000
GC2-1	7.8	155	40-1000
GC2-2	7.9	90	<5
GC2-3	7.9	155	<5

---

[1] Zone 1 is nearest to the borehole collar.

[2] Corrected from $E_{(Pt)}$ measurements.

[3] Determined using two ranges of CHEMetrics tubes (0-40 and 100-1000 ppb).

[4] Near-floor collar; contamination by cement suspected.

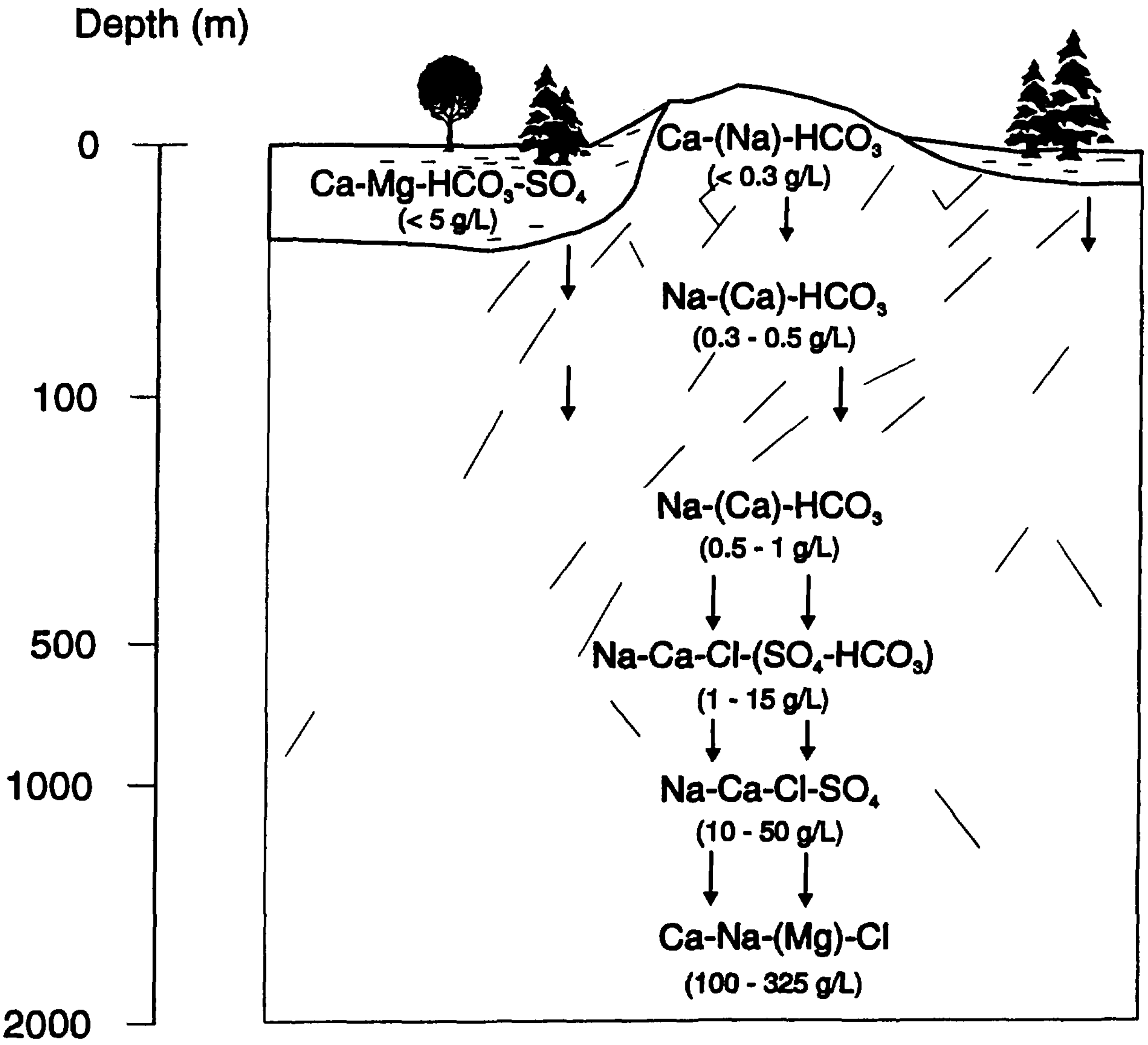

FIGURE 1: Schematic Diagram Showing the Evolution of Groundwater Composition with Depth or Distance Along Flow Field in a Crystalline Rock Formation on the Canadian Shield

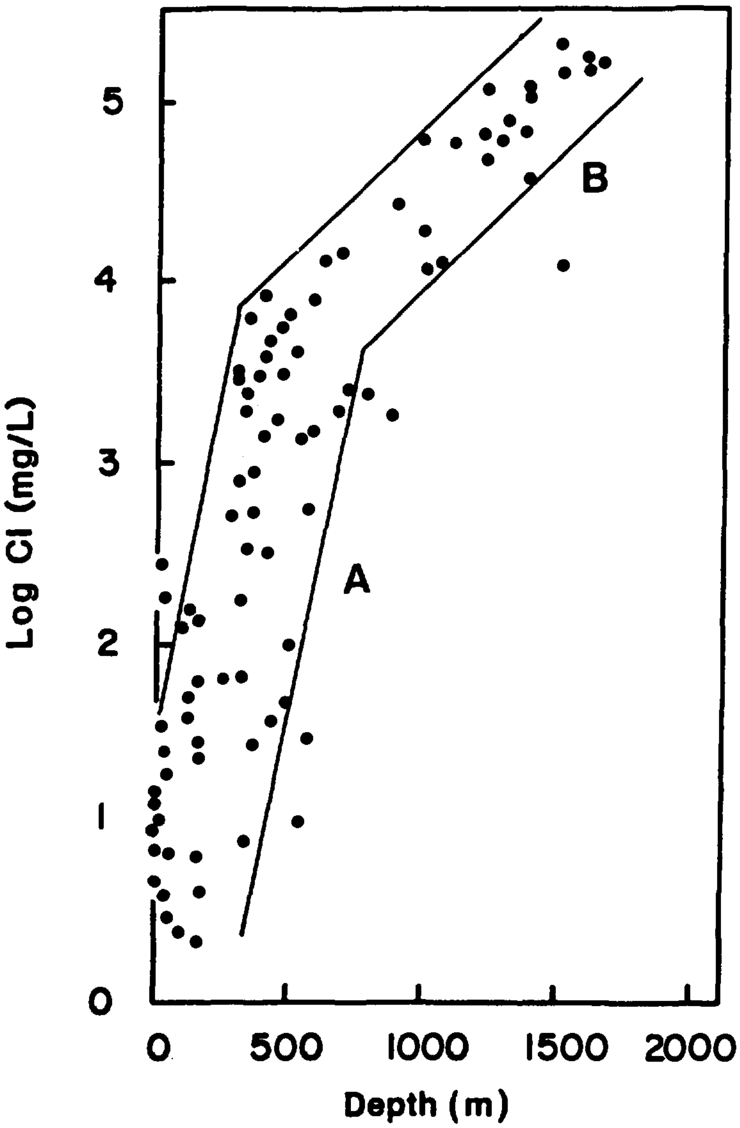

FIGURE 2: Variation of Cl⁻ Concentration with Depth of Sample for Groundwaters from Several Areas on the Canadian Shield (See Text). Lines represent envelope curves, fitted by eye, and areas A and B are discussed in the text.

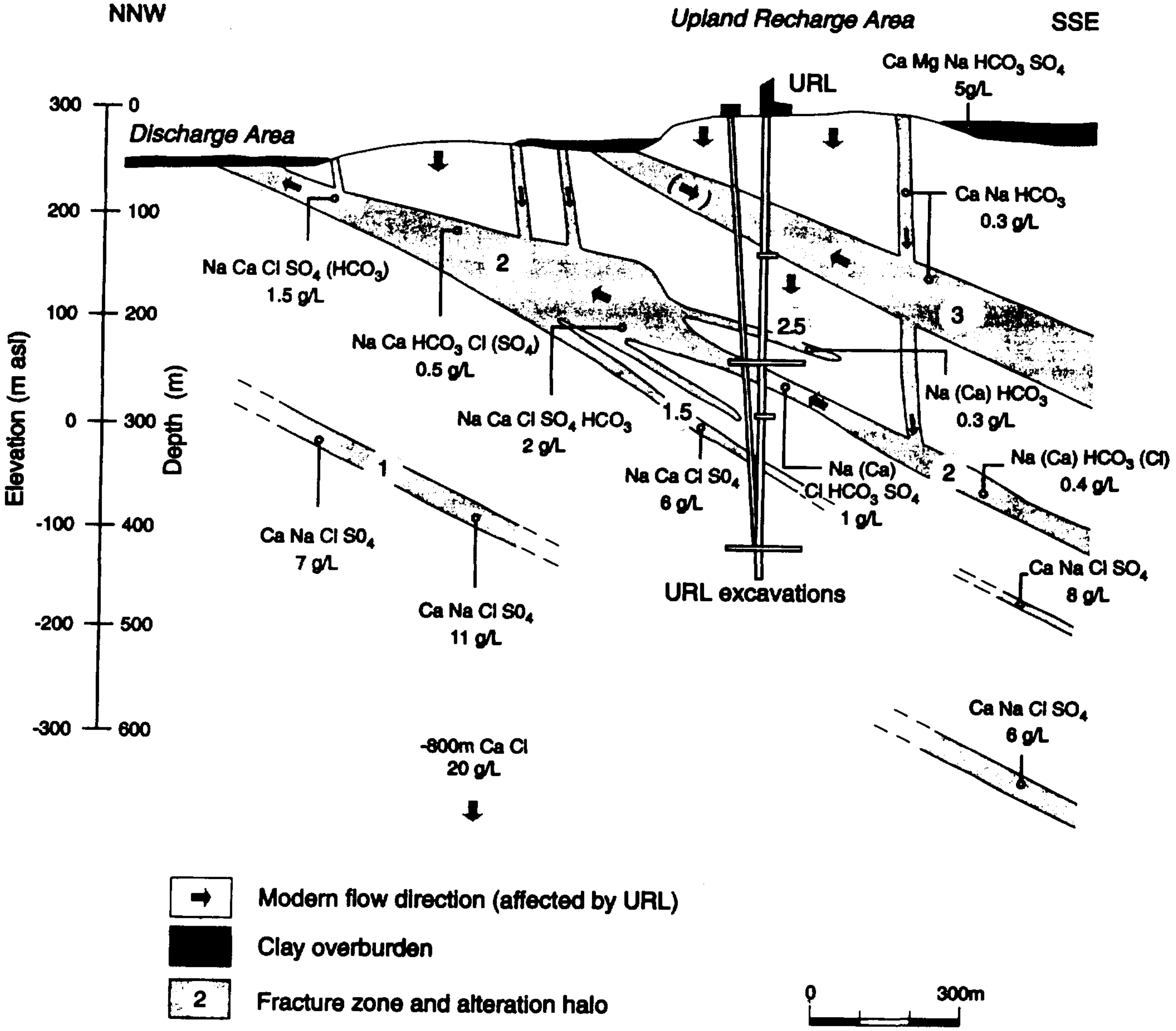

FIGURE 3: Schematic Cross-Section Through the URL Area Showing Locations of Inclined Fracture Zones (Numbered) and Groundwater Compositions and Salinities (TDS) in the Fracture Zones (Based on Pumping and Sampling from Numerous Boreholes in the Area). Flow directions are determined from pre- and post-excavation head distributions. Individual numbers are U concentrations (µg/L) in groundwaters at those locations.

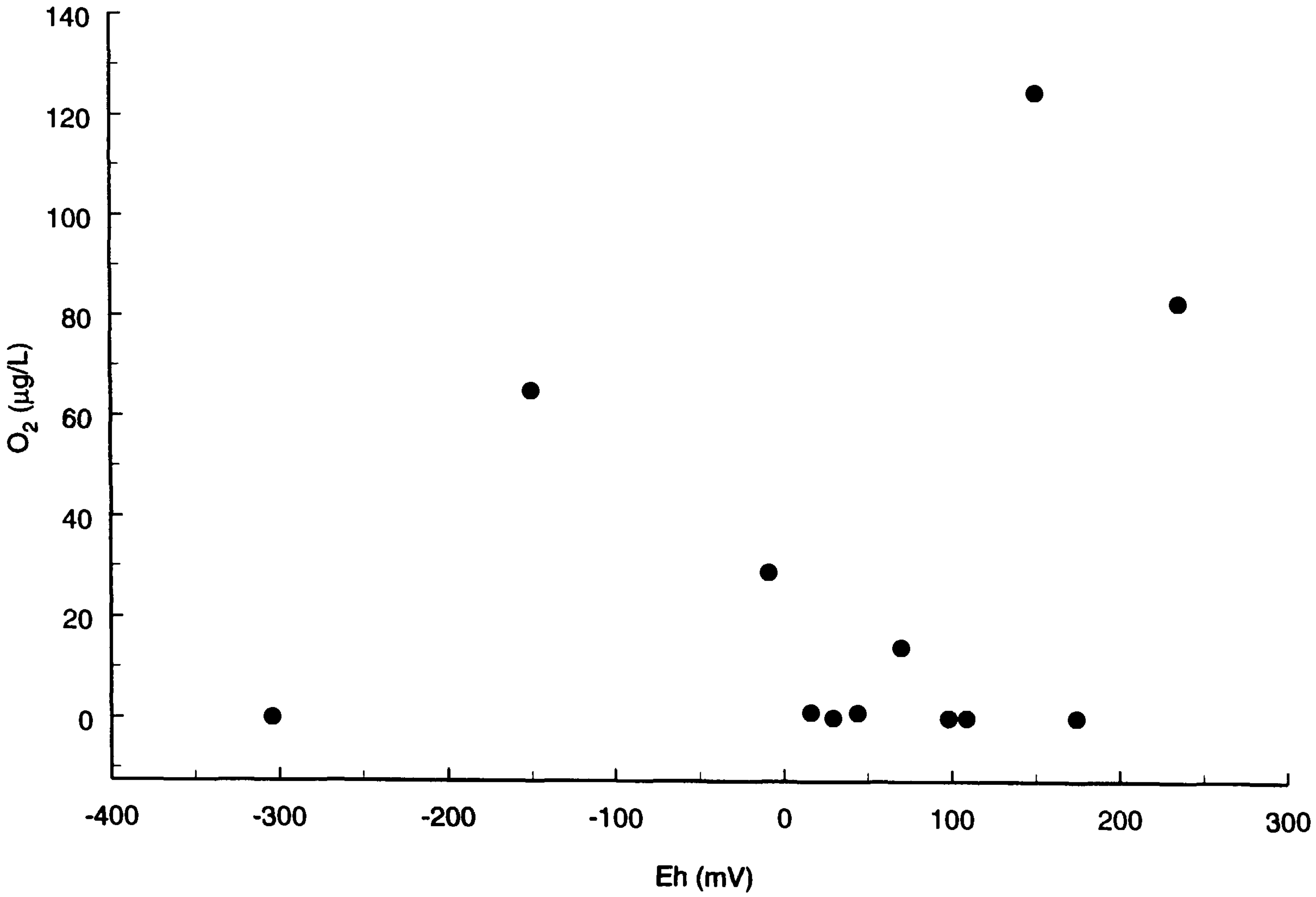

FIGURE 4: Variation of Dissolved O_2 with Electrode-Measured Eh for Groundwaters from Cigar Lake, Saskatchewan (after Cramer and Smellie, 1994)

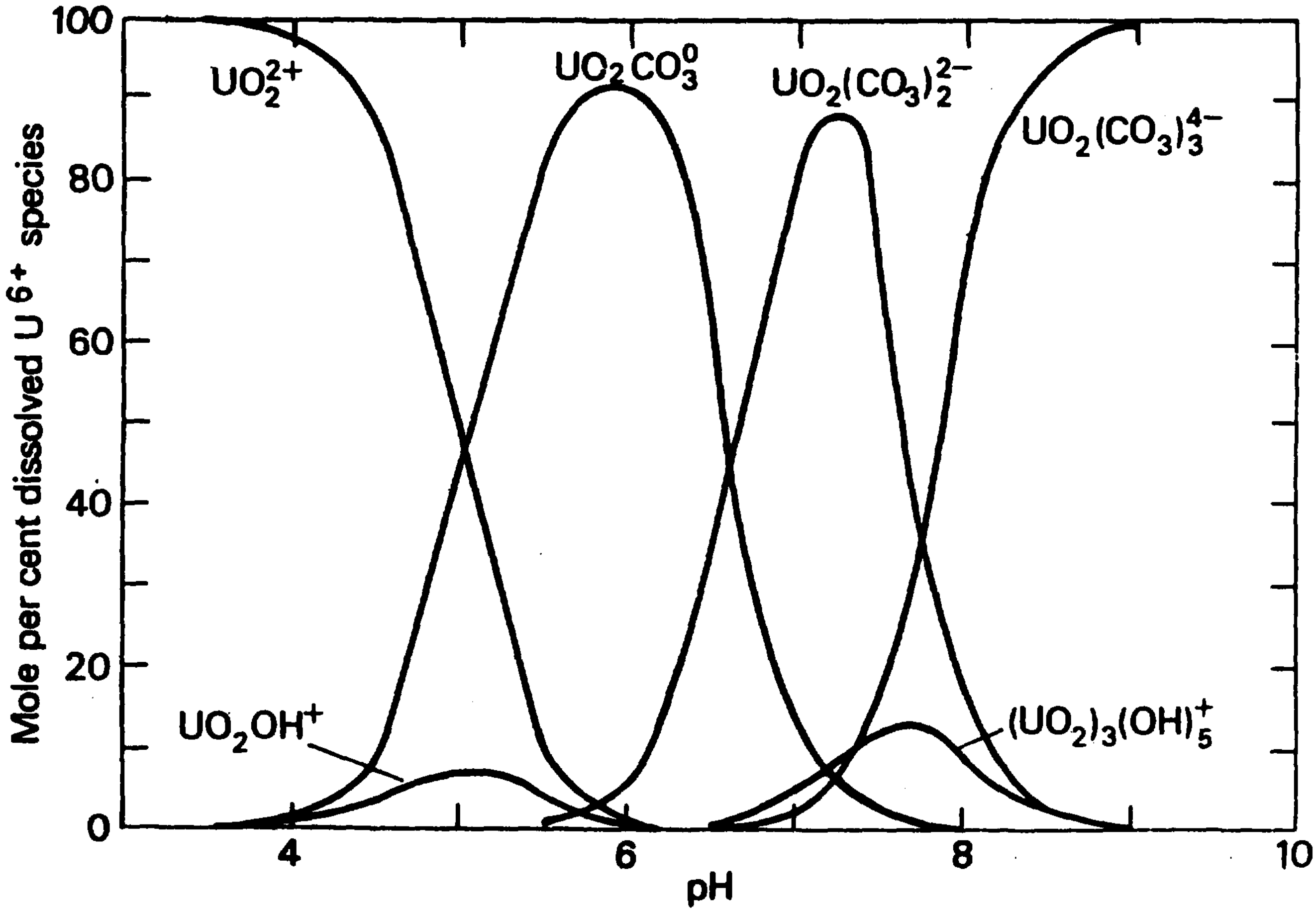

FIGURE 5: Distribution of Uranyl-Hydroxy and Carbonate Complexes with pH for $P(CO_2) = 10^{-2}$ atm. and a Total U Concentration of 10^{-8} mol. at 25°C (from Langmuir 1978)

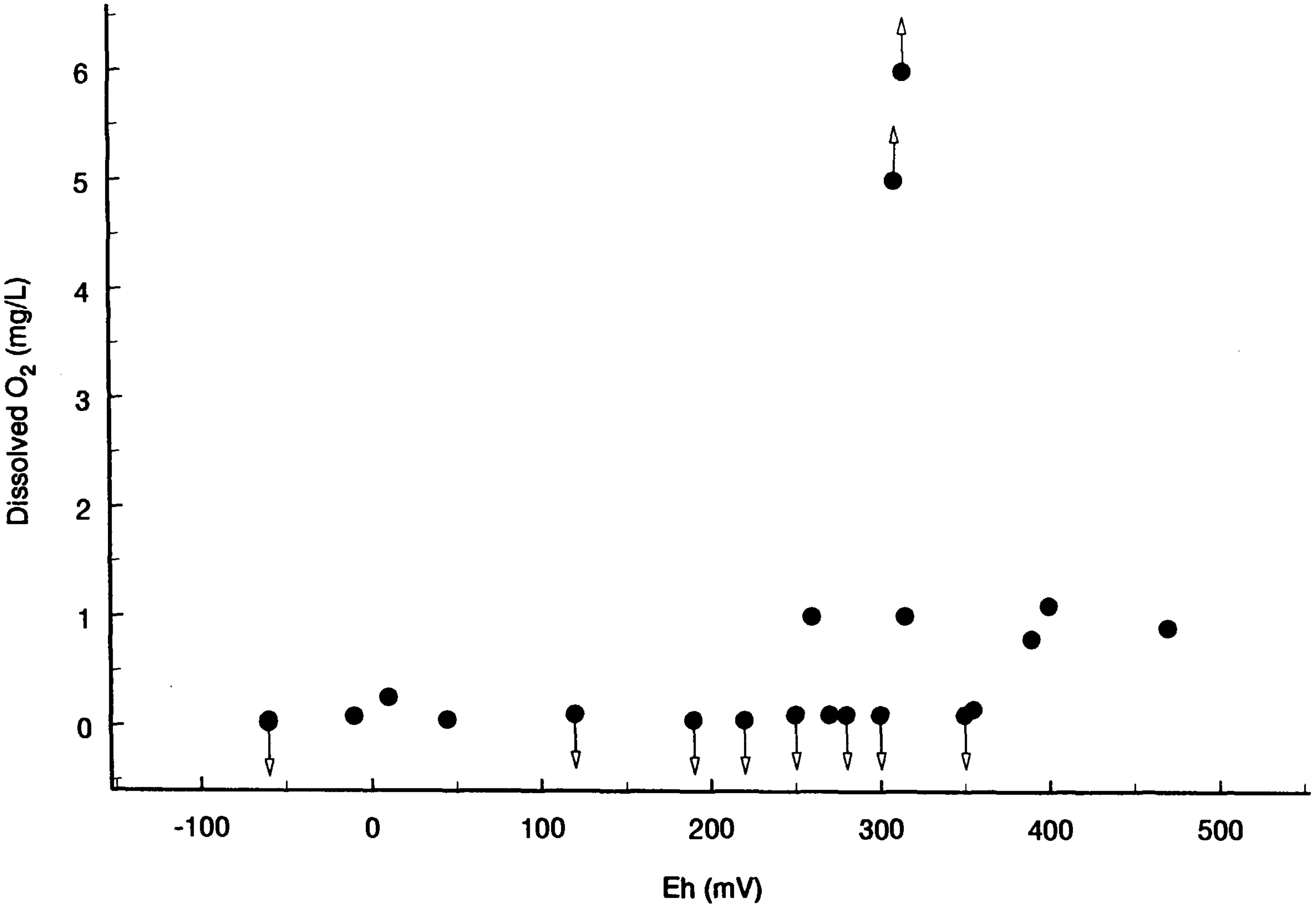

FIGURE 6: Variation of Eh with Dissolved O_2 Content of Groundwaters in a Gabbroic Pluton on the Canadian Shield. Down-Arrows Indicate Dissolved O_2 Concentrations <0.1 mg/L.

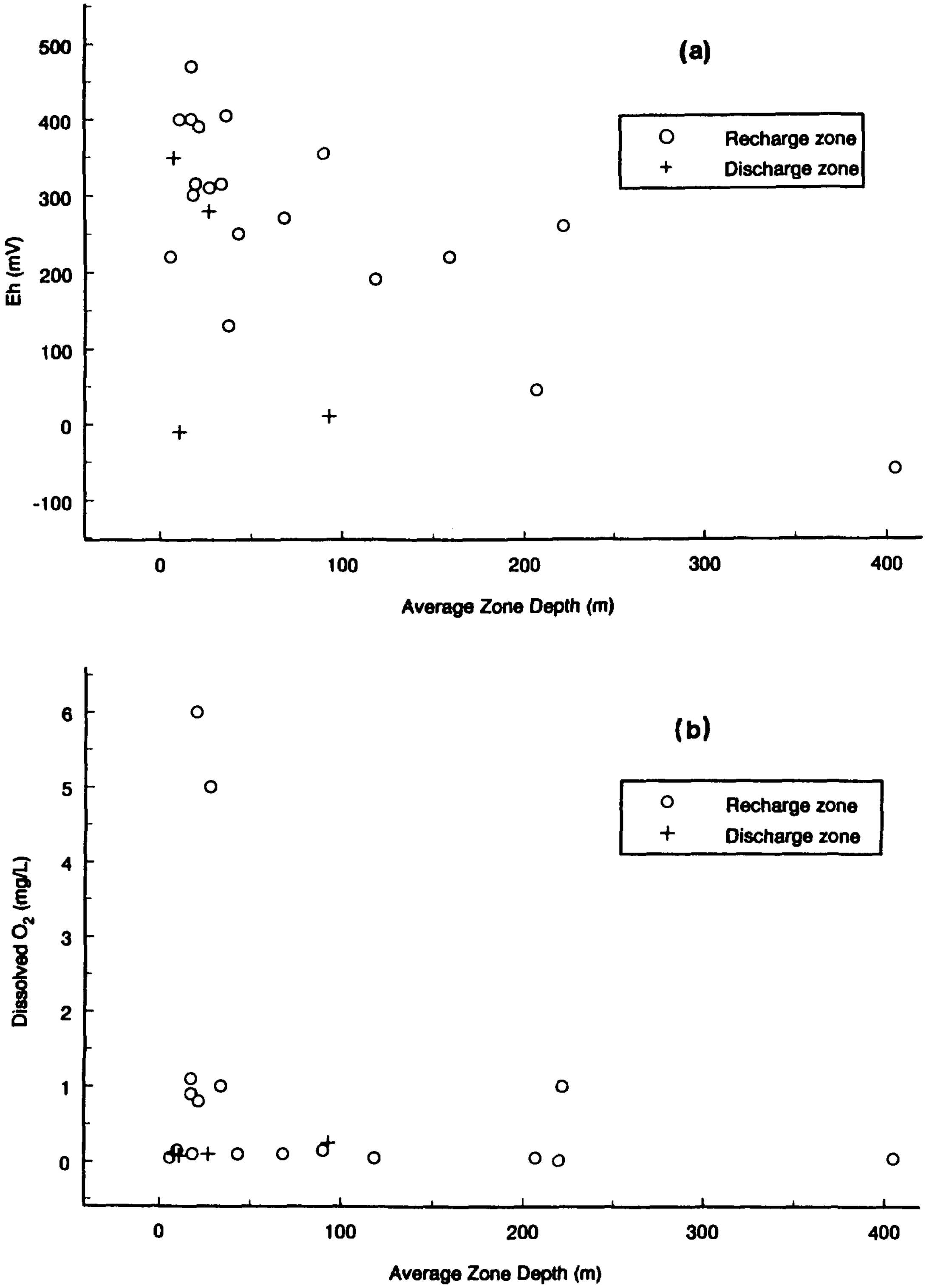

FIGURE 7: Variation of a) Eh and b) O_2 with Depth of Zone Sampled for Groundwater from a Gabbroic Pluton on the Canadian Shield

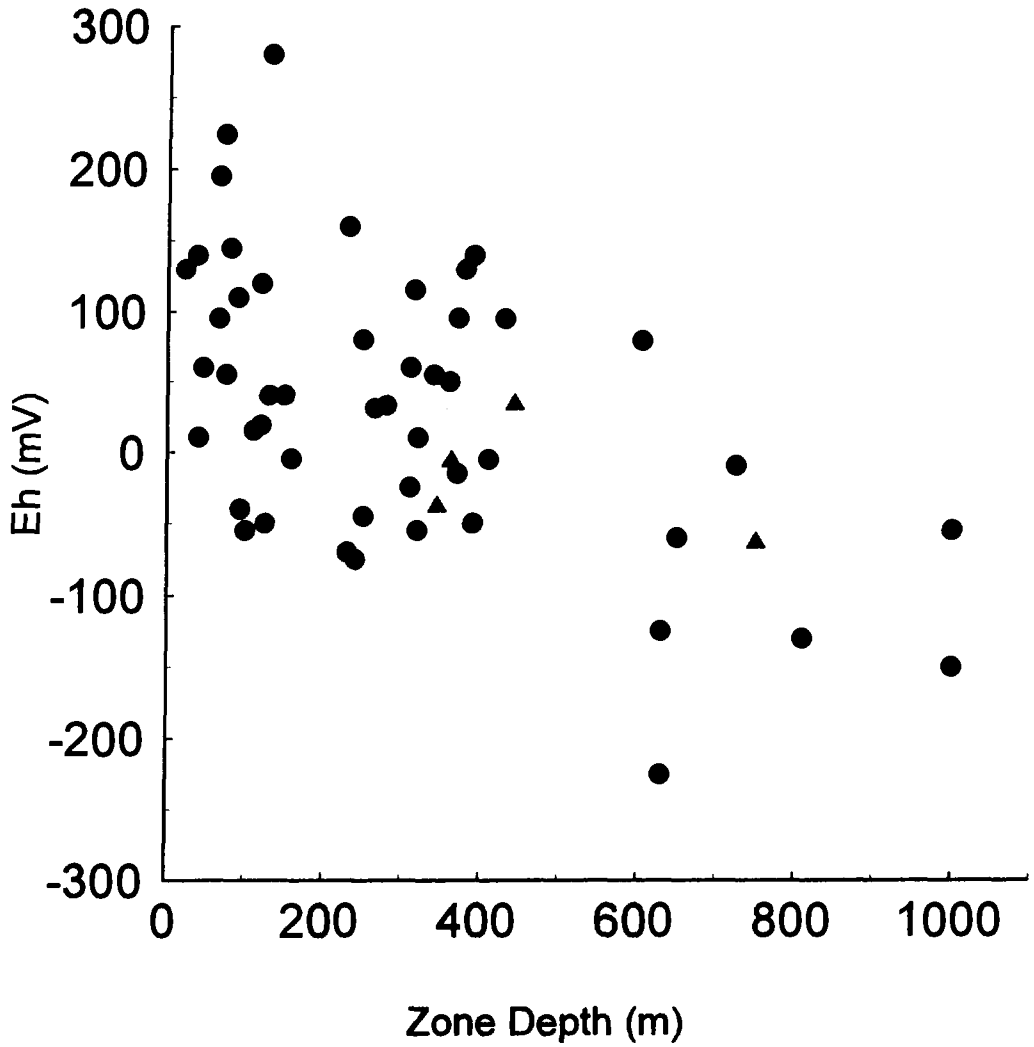

FIGURE 8: Variation of Redox Potential of Groundwaters in the Lac du Bonnet Batholith with Depth (after Gascoyne and Kamineni 1992). Triangles refer to samples in deeply penetrating recharge areas (Table 1).

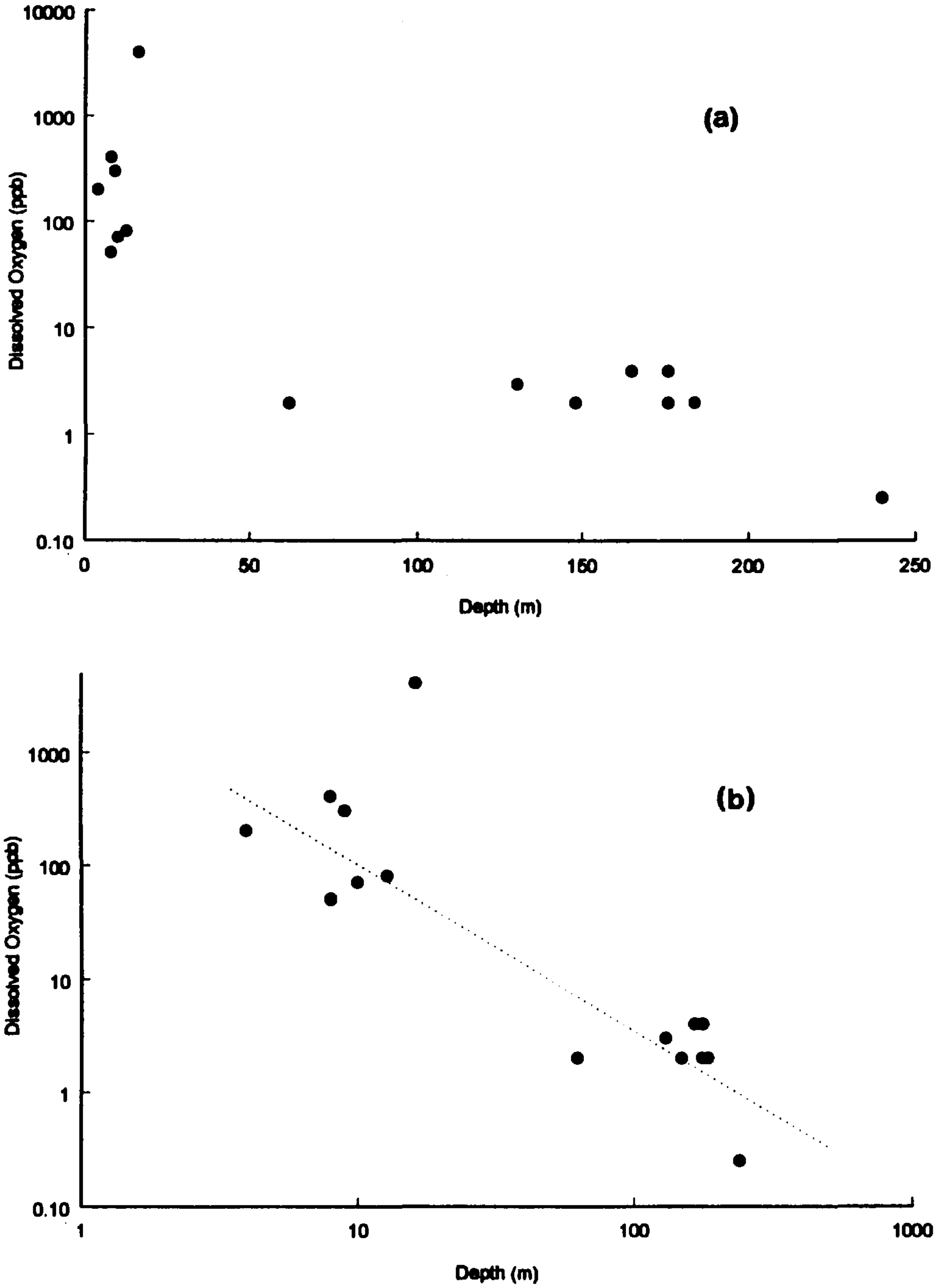

FIGURE 9: Variation of Dissolved O_2 with Depth for Recharging Groundwaters in the URL Lease Area on Log-Linear and Log-Log Axes (Line is Fitted by Eye)

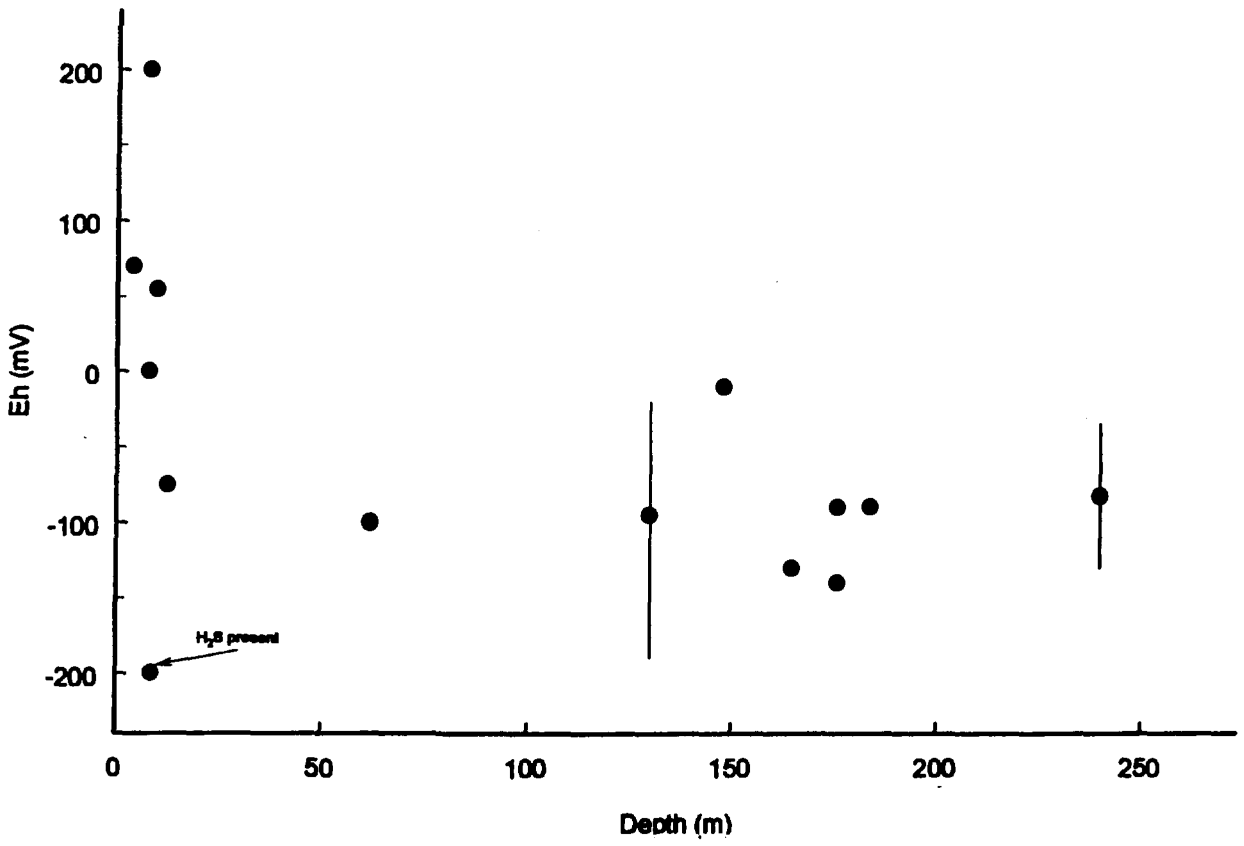

FIGURE 10: Variation of Eh with Depth for Recharging Groundwaters in the URL Lease Area

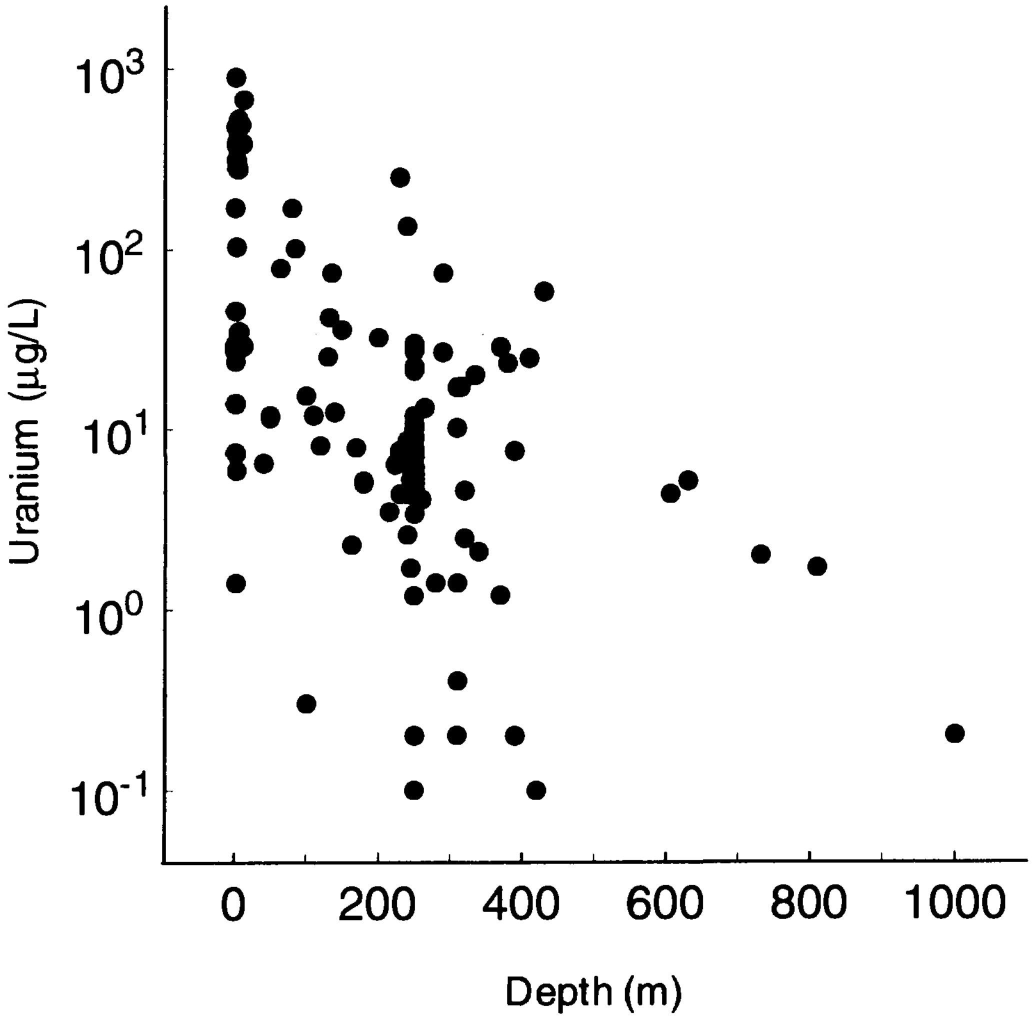

FIGURE 11: Variation of U Concentration with Depth for Groundwaters in the Lac du Bonnet Batholith (after Gascoyne and Barber, 1992)

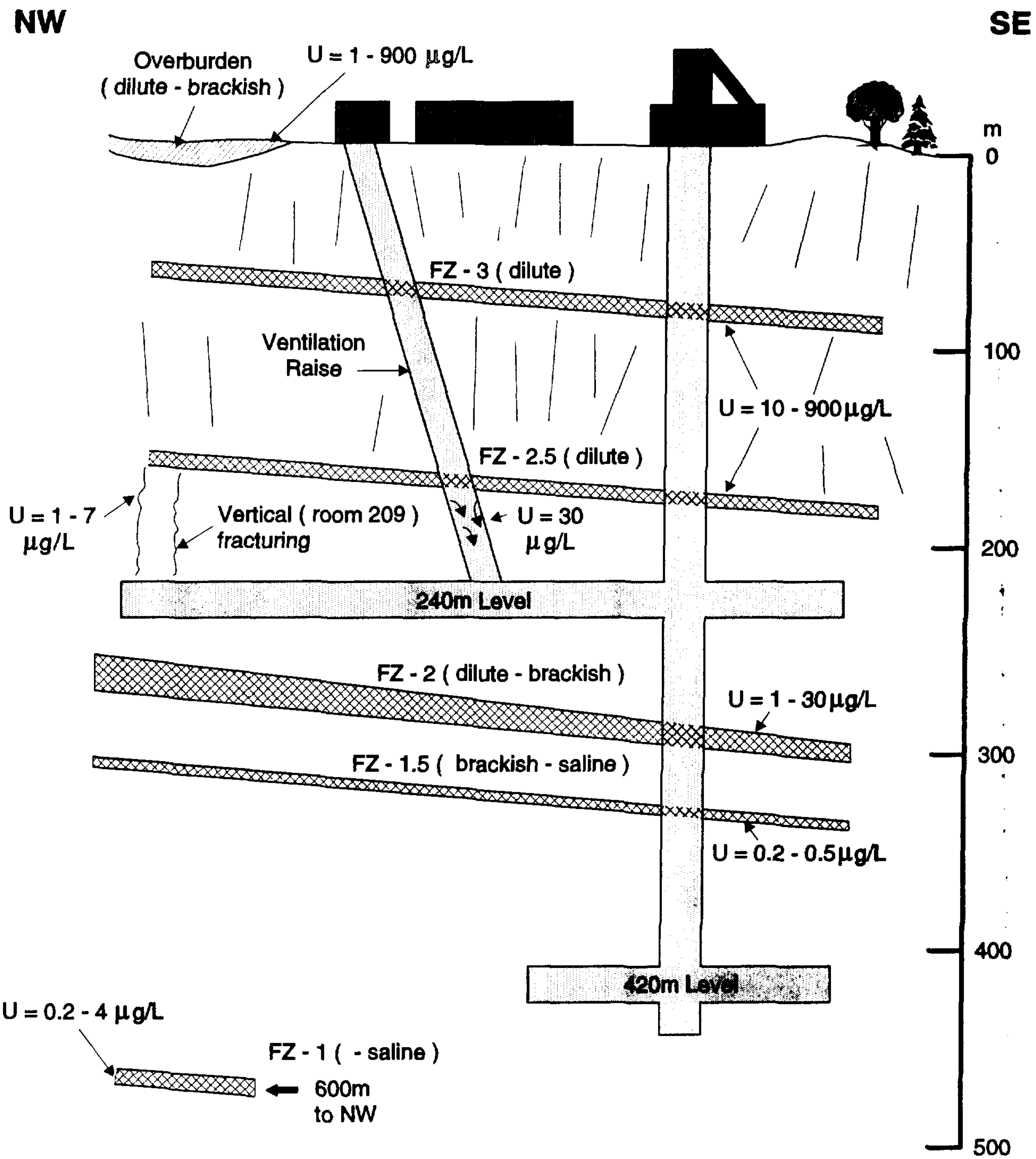

FIGURE 12: Schematic Diagram Showing the Measured Ranges of U Concentrations Typically Seen in Groundwaters Entering or Accessed from the URL

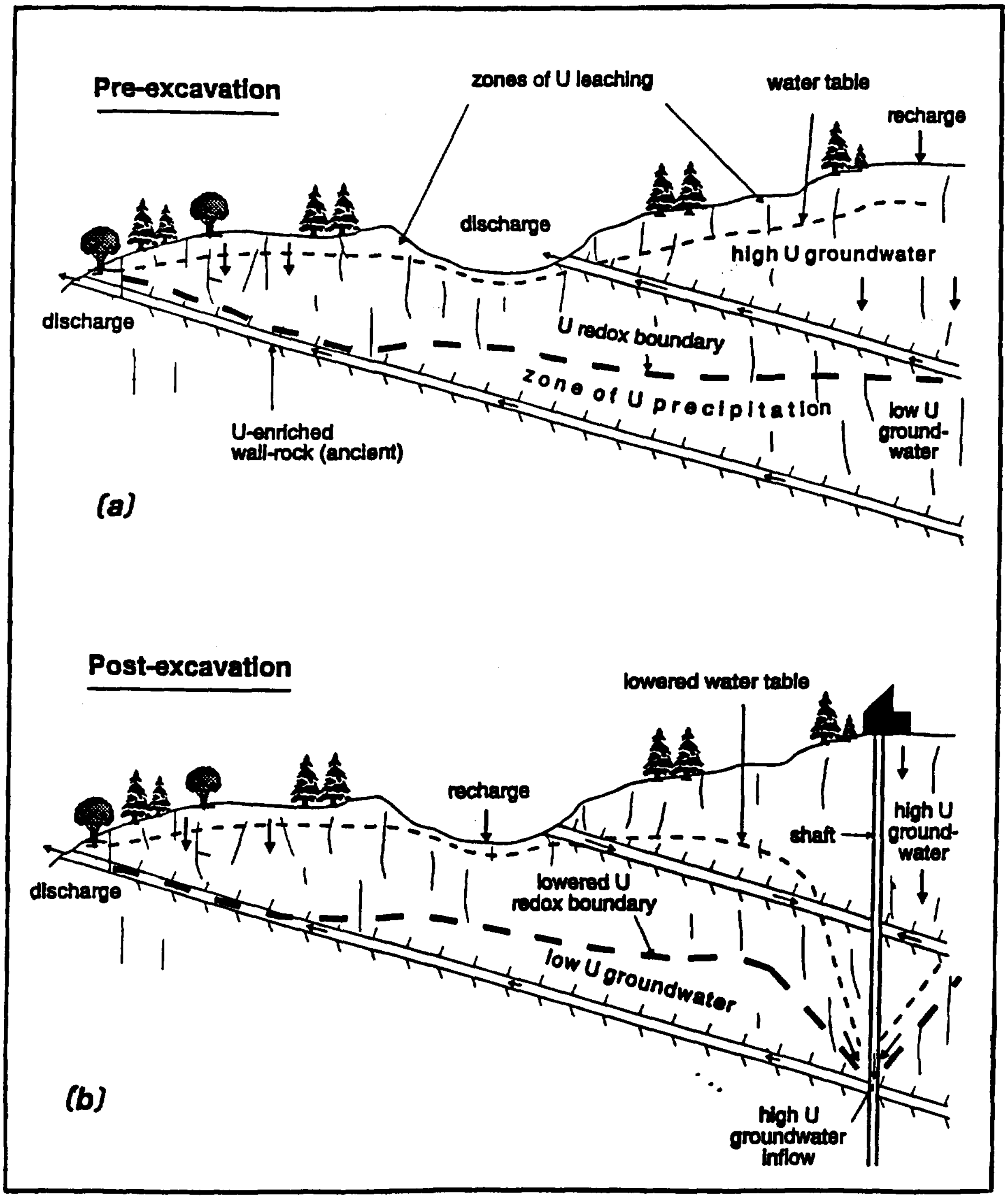

FIGURE 13: Schematic Diagram Showing Zones of U Mobility and Retardation in Groundwaters, a) Before Excavation and b) Following Excavation and Water Table Drawdown

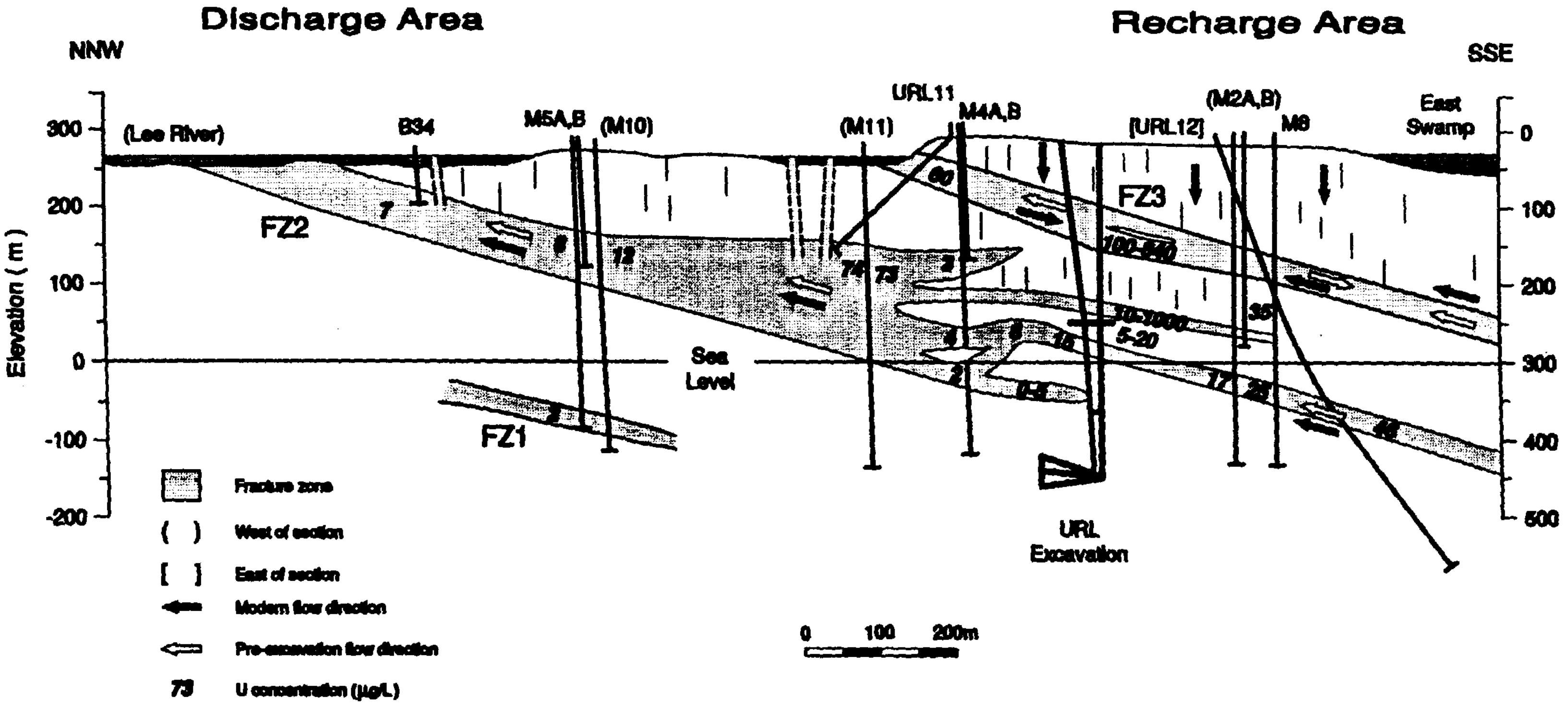

FIGURE 14: Cross-Section Through the URL Lease Area Showing Fracture Zones, Principal Groundwater Flow Directions, and U Concentrations of Groundwaters at Various Points Along the Flowpath

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