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REPORT

A Review of Theories on the Origins of Saline Waters and Brines in the Canadian Precambrian Shield

by

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Ottawa, Canada

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A REVIEW OF THEORIES ON THE ORIGINS OF SALINE WATERS AND BRINES IN THE CANADIAN PRECAMBRIAN SHIELD

A report prepared by D.J. Bottomley, Wastes and Impacts Division, Directorate of Fuel Cycle and Materials Regulation.

ABSTRACT

Groundwater at depths greater than 500 m in the Canadian Precambrian Shield is typically saline with a sodium-calcium/chloride chemical composition. Brines with dissolved solid concentrations exceeding 100 g/L have been encountered in several deep mines (>1000 m) on the Shield. Theories on the origins of these deep saline waters and brines can be grouped into two general categories: (1) autochthonous (*in situ*) origins attributable to silicate mineral hydrolysis over geologic time scales, leaching of fluid inclusions or radiolysis effects, and (2) allochthonous (external) sources caused by the infiltration of brine of modified seawater origins in the geologic past. Although the chemical and isotopic compositions of these waters clearly reflect the effects of reaction between the water and their silicate host rocks, it is unlikely that the high chlorinity of the brines is an autochthonous attribute. It is proposed that the compositions of these brines are most compatible with the Paleozoic residual brine hypothesis of Spencer (1987). This theory invokes deep infiltration of a high-density residual brine, formed by the evaporation of seawater during Devonian time, into underlying Precambrian basement rocks where subsequent chemical modifications occurred.

RÉSUMÉ

Les eaux souterraines à des profondeurs supérieures à 500 m dans le Bouclier canadien précambrien sont typiquement salines et se composent chimiquement de sodium et de chlorure de calcium. Des saumures comportant des concentrations solides dissoutes de plus de 100 g/L ont été retracées dans plusieurs mines profondes (>1000 m) du Bouclier. Les théories sur les origines de ces eaux salines et de ces saumures en profondeur se regroupent en deux catégories générales : (1) les origines autochtones (*in situ*) découlant de l'hydrolyse de silicate minéral échelonnée sur plusieurs périodes géologiques, de la lixiviation d'inclusions fluides ou des effets de la radiolyse; (2) les sources allochtones (externes) provoquées par l'infiltration de saumures provenant d'eau de mer à un moment donné dans les antécédents géologiques. Bien que la composition chimique et isotopique de ces eaux reflètent clairement les effets des réactions entre l'eau et leur roche encaissante de silicate, il est peu vraisemblable que la forte chlorinité de ces saumures soit une caractéristique autochtone. L'auteur suggère que la composition de ces saumures est très compatible avec l'hypothèse de Spencer au sujet des saumures résiduelles du

Paléozoïque (1987). Selon cette théorie, des saumures résiduelles à haute densité, formée par l'évaporation de l'eau de mer durant le Dévonien, se sont infiltrées dans les assises rocheuses précambriennes sous-jacentes où des modifications chimiques ultérieures se sont produites.

FOREWORD

In 1989 a Federal Environmental Assessment Review Panel was struck to review the Canadian concept for the disposal of nuclear fuel waste (NFW). After public consultation, they issued "Final Guidelines for the preparation of an environmental impact statement on the nuclear fuel waste management and disposal concept" in 1992. In October 1994, Atomic Energy of Canada Limited (AECL) released their "Environmental Impact Statement (EIS) on the Concept for Disposal of Canada's Nuclear Fuel Waste" for public review.

As the regulatory authority for the nuclear industry in Canada, the Atomic Energy Control Board (AECB) was expected to participate in the review of the EIS. To prepare for this review, beginning in 1989 AECB staff initiated research contracts and undertook independent calculations in-house, to obtain a better appreciation of the magnitude and complexity of the problems of NFW disposal. The intent of this work was to explore independently the types of calculations and reasoned arguments that AECB staff expected to find in the EIS, and to help identify sensitive and important aspects of the assessment of the disposal concept.

The in-house work resulted in a series of largely autonomous internal reports produced by AECB staff from 1991 through 1993, including this one. These reports, being published as AECB INFO documents, are:

An Overview of Potential Isotopic Techniques for Dating Groundwaters in Crystalline Rocks

D. Bottomley, 1991

A Review of Theories on the Origins of Saline Waters and Brines in the Canadian Precambrian Shield

D. Bottomley, 1991

The Geochemical Immobilization of Uranium in a Spent Fuel Repository in the Canadian Shield: Evidence from Natural Analogue Investigations

D. Bottomley, 1992

Regional-Scale Groundwater Flow Modelling of Generic High Level Waste Disposal Sites

D. Metcalfe, 1992

Reference Used Fuel for the Canadian Nuclear Fuel Waste Disposal Concept

P. Flavelle, 1993

Source Term for the Bounding Assessment of the Canadian Nuclear Fuel Waste Disposal Concept

P. Flavelle, 1993

Perspectives of the Scale of the Canadian Nuclear Fuel Waste Disposal Concept

P. Flavelle, 1993

Impacts of Disturbed Rock Zones and Backfill Material on Ground Water Flow Through a Generic HLW Repository

S. Lei and D. Metcalfe, 1993

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1. INTRODUCTION

Occurrences of saline groundwaters (dissolved solid concentrations of 10 to 100 g/L) and brines (dissolved solid concentrations > 100 g/L) have been reported from many sites on the Canadian Precambrian Shield, the Fennoscandian Shield (Blomqvist, 1990), Ukrainian Shield, and from a variety of crystalline rock plutons elsewhere (Frape and Fritz, 1987). These waters are of the sodium-calcium/chloride variety and typically occur at depths greater than about 300 m with concentrations of total dissolved solids (TDS) increasing to more than 300 g/L at depths greater than about 1000 m. Because crystalline rocks are comprised of sparingly soluble silicate minerals, the presence of saline waters in these rocks suggests that processes other than the dissolution of silicates may have been responsible for their chemistry, particularly for the most concentrated occurrences. The presence of saline groundwaters and brines in crystalline rocks has important implications for the Canadian Nuclear Fuel Waste Management Program which proposes disposal of spent nuclear fuel waste in a repository constructed at a depth of 500-1000 m in plutonic rock. Obviously the salinity of the water is an important factor in the corrosion of the spent fuel container, the dissolution rate of the waste form, and on the mobility of radionuclides which may leach into groundwater and be transported into and through the geosphere and to the biosphere. Understanding the origins of the salinity may also provide a better conceptual understanding of regional groundwater flow at depth in the Shield and of the capability of crystalline rock to isolate radionuclides from the biosphere.

Nordstrom et al. (1989a) have grouped existing theories on the sources of salinity in crystalline rock groundwaters into autochthonous or allochthonous origins. Autochthonous origins include geochemical reactions and processes between groundwater and the host rocks and include silicate mineral hydrolysis, fluid inclusion leakage, and radiolysis. Allochthonous saline origins and processes, on the other hand, are external to the host rock and include Holocene (< 10,000 years old) seawater, Paleozoic (245-570 Ma old) seawater or basinal brines, Paleozoic residual brines, dissolution and infiltration of Paleozoic marine evaporites, and Proterozoic (570-2,500 Ma old) seawater or basinal

brines. This classification is adopted in this overview to discuss possible origins for saline groundwaters in the Canadian Precambrian Shield. It will become clear during the course of this review that no single source can explain the chemical and isotopic compositions of all saline occurrences on the Precambrian Shield and that mixed autochthonous-allochthonous sources are likely. Nevertheless, brines from deep mines on the Canadian Shield (Frape et al., 1984 and Frape and Fritz, 1987) may be dominated by a single allochthonous source as discussed in a subsequent section. Before evaluating each of these potential sources, it is necessary to describe the general characteristics of saline groundwater and brine occurrences on the Canadian Shield.

2. SALINE GROUNDWATER AND BRINE OCCURRENCES ON THE CANADIAN SHIELD

The geochemistry of groundwaters at AECL research area plutons is summarized in Gascoyne et al. (1987) and Gascoyne and Kamineni (1992). Saline groundwaters occur in the Eye-Dashwa Lakes pluton near Atikokan in northwestern Ontario where TDS concentrations are as high as about 40 g/L at depths of approximately 1000 m. These waters are of the calcium /chloride variety with low concentrations of K^+ and Mg^{2+} (ie. < 10 mg/ L). Very deep (~ 1000 m) saline groundwater in the Lac du Bonnet batholith has TDS concentrations up to 50 g/L and is of the calcium-sodium/ chloride type with sulphate concentrations as high as 1200 mg/L. Brackish sodium/chloride groundwaters exist at depths greater than 300 to 400 m in the East Bull Lake and Chalk River plutons with maximum TDS concentrations of about 4 g/L and 0.7 g/L, respectively. Shallow groundwaters at all these sites are of the dilute calcium-sodium/ bicarbonate type with chloride concentrations as low as < 1 mg/L. Stable isotope analyses (^{18}O and 2H) of all groundwater samples from these plutons indicate that these waters are of meteoric origin, regardless of depth and composition, and have not exchanged isotopically with their host rocks (Bottomley et al., 1984a and b; Dicken et al., 1984; Bottomley et al., 1990). However, the true isotopic composition of some of the deep saline groundwaters at these sites may be at least partially masked by drilling water contamination (Gascoyne et al., 1987).

Brine samples from depths of up to 1800 m from mines on the Shield are exclusively of the calcium/chloride type with TDS concentrations of

up to 325 g/L at the Thompson mine (Frape and Fritz, 1987). Most brine samples contain relatively low concentrations of Mg^{2+} and K^+ but have unusually high concentrations of Sr^{2+} and Br^- (1000-2000 mg/L). Isotopic analyses of these waters indicate that they are relatively depleted in ^{18}O , or enriched in 2H , with respect to the global meteoric water line suggesting that they have exchanged oxygen isotopes with their host rocks. McNutt et al. (1987 and 1990) also concluded that the Sr isotopic compositions of these waters were controlled by exchange with silicate minerals. This indicates that extensive chemical as well as isotopic modifications occurred as the result of water/rock interactions, probably in a rock dominated environment (ie. a system with a relatively low water/rock ratio). This does not necessarily imply that the salinity is the result of autochthonous processes, only that initial elemental ratios, particularly for geochemically non-conservative cationic species, may have been drastically altered through water/rock interactions. Saline and brackish (dissolved solid concentrations of 1 to 10 g/L) waters are also present at these mine sites at intermediate depths and are the product of mixing between the deep brine end member and shallow fresh meteoric water.

The results of these investigations show that distinct hydrochemical zonation exists in the Canadian Shield. At depths of up to about 300 m, groundwater is relatively fresh and is of the sodium-calcium/bicarbonate variety. Brackish sodium/chloride water occurs at depths of about 300-500 m below which saline sodium-calcium/chloride waters are present. The salinity continues to increase with depth and to become more calcic such that calcium/chloride brines occur at depths greater than 1000-1500 m. The question arises as to whether the observed salinity-depth relationship is solely the result of autochthonous processes or whether it reflects the intrusion of saline water or brine into crystalline rocks from allochthonous sources in the geologic past. Potential saline sources are discussed in the following section with the objective of determining the origins of saline water and brine occurrences on the Canadian Shield.

3. POTENTIAL SALINE SOURCES

3.1 Autochthonous Sources

3.1.1 silicate mineral hydrolysis

The average chlorine concentration in granites and granodiorites is about 200 ppm (Fuge, 1974). Hydroxysilicate minerals, in which the hydroxyl ion may be substituted for by chlorine, are the major mineralogic sources of chlorine and include biotite, muscovite, hornblende, apatite and tourmaline. Plutons with unusual abundances of these minerals are likely to be enriched in chlorine relative to the "average" granite. For example, amphibole gabbro in the East Bull Lake pluton has a mean chlorine concentration of about 360 ppm (Kamineni, 1987). In contrast, the chlorine concentration in the Stripa granite is only 160 ppm and most of this is present in fluid inclusions rather than bound in silicate lattices (Nordstrom et al., 1989b).

Thermal saline groundwaters occur at depths of between 200 and 700 m in the 285 Ma old Carmenellis granite of southwest England (Edmunds et al., 1987) and are the only known saline groundwaters from igneous rocks in Britain. This mica-rich granite is significantly enriched in volatiles including chlorine and exhibits areas of extensive Sn-W-Cu mineralization. Saline groundwater in the pluton is of the sodium-calcium /chloride variety with TDS concentrations up to 20 g/L and temperatures as high as 55 °C. Edmunds et al. (1987) have convincingly shown that the salinity of these waters is largely controlled by the acid hydrolysis of oligoclase plagioclase and biotite in a semi-closed convective hydrothermal flow system. The relatively high heat flow in the Carmenellis granite is apparently related to radioelement heat production within the granite (Tammemagi and Wheildon, 1974).

Kay (1984) has compared the groundwater chemistry in the Carmenellis granite with that of groundwater at depths of less than 300 m in 640 Ma old granites of the Altnabreac area near Caithness, Scotland. Groundwater in the Altnabreac granites is non-thermal and has low chloride concentrations of less than about 25 mg/L indicating that little if any chloride has been leached from the granite despite groundwater residence times of 10,000-14,000 years. Kay (1984)

concluded that at normal groundwater temperatures chemical interactions between water and silicate minerals are so slow that groundwater chloride concentrations in "average" granites will remain low over time scales of at least 10⁴ years. Accordingly, it is likely that a minimum, but unspecified "threshold" temperature, must be reached before silicate hydrolysis can be a significant source of groundwater salinity. Similarly, Bottomley et al. (1990) concluded that, although silicate minerals (amphiboles and biotite) may have been an important source of chlorinity for ancient hydrothermal waters in the East Bull Lake pluton (Kamineni, 1987), an allochthonous salinity source is a more likely explanation for the low temperature sodium/chloride waters now present in the pluton.

3.1.2 fluid inclusion leakage

Fluid inclusions that are formed in minerals at the time of their crystallization are often abundant in granitic rocks. The composition of the aqueous phase in the inclusions can range from 0 to 70 wt. % NaCl (Roedder, 1984) with an average composition of perhaps 10 wt. % (Nordstrom and Olsson, 1987). Calculations by Nordstrom and Olsson (1987) suggest that leakage of fluid inclusions could produce groundwater chloride concentrations in granites ranging between about 50 and 20,000 mg/L in a static system. Consequently, leakage of fluid inclusions, possibly facilitated by micro-stresses from isostatic rebound, could produce the observed chloride concentrations associated with some saline occurrences on the Precambrian Shield.

Nordstrom et al. (1989b) favour the fluid inclusion hypothesis to explain the presence of brackish sodium-calcium/chloride groundwaters at the Stripa mine. These authors estimate that leakage of less than 1% of the fluid inclusions under static flow conditions could produce the maximum chloride concentrations (700 mg/L) observed at this site. Supporting evidence for this hypothesis is the similarity in Br/Cl ratios of fluid inclusion leachates (0.0101) to those of the deep groundwaters (0.0107), both of which are significantly greater than seawater (0.00347) and many, but not all, formation waters. Measured whole rock chloride concentrations in the Stripa granite (160 ppm) are similar to the average chloride concentration for the granite calculated on the basis of the salinity of the fluid inclusions and their volumetric abundance, suggesting that relatively little rock chloride is lattice-bound.

Accordingly, silicate hydrolysis is not likely a significant source of groundwater chlorinity at the Stripa site.

Although fluid inclusion leakage could produce saline groundwater, the actual importance of this process relative to other potential sources of chlorinity may be minor. For example, sulphur isotopic compositions of dissolved sulphate in deep Stripa groundwaters strongly suggest that the major source of salinity is allochthonous (Fontes et al., 1989). Furthermore, the use of Br/Cl ratios as generic tracers has been criticized because some formation waters do, in fact, have ratios similar to those determined for Stripa fluid inclusions and for Shield mine brines (Kelly et al., 1986; Spencer, 1987).

Fluid inclusion leakage would be most effective in generating saline groundwaters under "stagnant" groundwater flow conditions such as apparently exist in many deep mine environments on the Canadian Shield (Frape and Fritz, 1984). However, the chloride concentrations in these brines are up to a factor of 10 times greater than the maximum chlorinity likely to be produced by fluid inclusion leakage in a typical granitic rock (Nordstrom and Olsson, 1987). Considering that so little of the fluid inclusion needs to leak to increase the salinity of groundwater, it is perhaps surprising that concentrated saline waters or brines are not present at depth in the Stripa mine. It must be concluded that although fluid inclusion leakage may be a source of groundwater salinity, the geochemical evidence for its importance is not unequivocal. Moreover, it is most unlikely that fluid inclusions are the source of the highest chlorinity brines in the Shield.

3.1.3 radiolysis

Radiolytic salt enrichment is caused by the decomposition of water due to radiolysis by alpha, beta, and gamma rays mainly from uranium, thorium and their daughters. Vovk (1981 and 1987) has proposed that radiolysis may be primarily responsible for the generation of saline sodium-calcium/chloride waters and brines in the crystalline basement rocks of the East European Platform which have concentrations of total dissolved solids as high as 330 g/L. Radiation damage to the rock matrix is also associated with this process and this may promote water/rock interactions, further increasing the salinity of the residual water. A feature of radiolysis is the production and accumulation of molecular

hydrogen from the decomposition of the water molecule whereas molecular oxygen is largely consumed through oxidation of reduced carbon, sulfur, and iron compounds present in the water or aquifer materials. Hydrogen gas concentrations are often significant in Canadian Shield brines but the mechanism responsible for its generation is unclear (Fritz et al., 1987).

While it has been demonstrated on both theoretical and experimental grounds that radiolysis could produce highly saline waters in stagnant systems, its actual significance relative to other potential saline sources is difficult to quantify. In particular it is unclear how radiolysis, by itself, could produce the elemental and isotopic ratios that are characteristic of the most concentrated brines present on the Shield (Frape and Fritz, 1987).

3.2 Allochthonous Sources

3.2.1 Holocene seawater origins

Postglacial seawater transgressions in the coastal areas of the Baltic Sea in Finland and Sweden (Yoldia and Litorina Seas) resulted in the intrusion of seawater into Precambrian bedrock aquifers in areas having surface elevations lower than the highest elevations of these transgressions. Consequently, brackish and saline Na/Cl groundwaters are common in these areas at depths of less than about 200 m (Lindewald, 1981; Lahermo and Lampen, 1987; Nurmi et al., 1988; Nordstrom et al., 1989). Similarly, Bottomley et al. (1984a) suggested that the presence of dilute Na/Cl groundwater at depths of 300 to 400 m in Precambrian gneiss in the Chalk River area reflected a component of marine Champlain Sea water that occupied much of the St. Lawrence and Ottawa River Valleys about 10,000 years ago.

Generally, groundwaters containing a Holocene seawater component can be readily identified by their chemical and isotopic compositions. In many cases these Na/Cl waters are significantly less concentrated than seawater because of mixing with fresh, meteoric water at the time of recharge. Consequently, these waters have isotopic compositions (^{18}O and ^2H) that plot on or to the right of the Global Meteoric Water Line (Craig, 1961) depending on the relative size of the seawater component in the groundwater. Because these waters recharged after the last Wisconsin

deglaciation about 10,000 years ago it is possible to date these waters using the carbon-14 method and thus to show that these waters are of relatively recent origins (Bottomley et al., 1984a). Accordingly, these waters are not generically related to the Ca/Cl brines that are present at depths of greater than about 1000 m in the Precambrian Shield (Frape et al., 1984).

3.2.2 Paleozoic seawater/basinal brines

Although there is no evidence for the presence of unmodified Paleozoic or older seawater in the Shield, Kelly et al. (1986) have argued that Precambrian Shield brines originated from the basement penetration of Paleozoic basinal brines present in overlying sedimentary formations which have subsequently been eroded. According to this hypothesis, the chemical and isotopic composition of Shield brines can be explained by the following processes:

- (1) initial evolution of the waters as Paleozoic-hosted formation waters,
- (2) deep infiltration into basement rocks via fractures and chemical reaction with silicate minerals under conditions of relatively high temperatures and low water/rock ratios resulting in "self-sealing" of these brines,
- (3) erosion of the Paleozoic cover and back-reaction of the waters with fracture minerals under low temperatures and variable water/rock ratios, and
- (4) subsequent mixing with fresh meteoric waters.

Deep, Na/Cl brines in the Ukrainian Shield are also thought to have originated from the infiltration of Paleozoic seawater into crystalline basement rocks through regional fault zones (Vovk, 1987). Saline Na-Ca/Cl groundwaters in the Lac du Bonnet batholith (Manitoba) may have resulted from the vertical infiltration of basinal brines although it is also possible that they penetrated the batholith laterally from the adjacent Western Sedimentary Basin (Bottomley et al., 1984b; Gascoyne et al., 1989).

Kelly et al. (1986) have observed that the isotopic composition of both Precambrian Shield and Paleozoic basinal brines appear to show a latitudinal dependancy with the lighter waters occurring in more northerly regions. This has been interpreted not only as supporting

evidence for a basinal brine origin but also that both the water and the dissolved salts infiltrated into the basement rocks at the same time. If true, this has implications for groundwater age-dating methods which require, in most cases, that the age of the dated solute be similar to that of the water.

3.2.3 Paleozoic residual brines

This hypothesis is similar to the basinal brine model except that it involves substantial seawater evaporation within the basin prior to basement infiltration as the main process responsible for the high concentrations of dissolved salts present in the Precambrian Shield brines (Spencer, 1987). High salinity, Ca/Cl brines are common in Devonian age (360-408 Ma old) formations of the Western Canada Sedimentary Basin and it is believed that they represent modified residual brines from which large quantities of gypsum and halite precipitated. In contrast, most formation waters in strata within the basin that are younger than Devonian age are of the Na/Cl variety. It has been proposed that these residual brines were not retained in the evaporating system but were density-driven to depths of several kilometres into the underlying crystalline basement rocks in a convective groundwater flow system (Spencer, 1987). Further modifications to the chemistry of these waters, particularly the conversion from the Na/Cl to Ca/Cl type, resulted from relatively high temperature interactions with silicate minerals in the basement rocks at temperatures of 100-300°C.

The most widely distributed salt deposits in Canada occur in middle to upper Devonian age strata in the prairie provinces. Furthermore, significant thicknesses of salt deposits occur in slightly older upper Silurian (408-421 Ma old) formations in the Hudson Bay and Michigan sedimentary basins. Therefore, it is likely that Silurian and Devonian seas and their sediments covered much of the present day Precambrian Shield craton affording the opportunity for the deep vertical infiltration of evaporated residual basinal brines into underlying crystalline basement rocks where additional modifications to the chemical and isotopic compositions of the brines occurred. This is a particularly appealing origin for Precambrian Shield brines as it is capable of explaining their Ca/Cl composition, high salinity, unusual isotopic compositions, and high Br/Cl ratios. *The Br/Cl ratios of these waters are discussed further in a*

subsequent section.

3.2.4 Dissolution and infiltration of Paleozoic/Mesozoic evaporites

It is possible for readily soluble minerals (halite, gypsum, calcite) present in sedimentary rocks to be subsequently dissolved in meteoric water and to eventually infiltrate into Precambrian crystalline rocks. This hypothesis is conceptually different from the basinal brine model which does not preclude at least a connate component to the brine.

The dissolution/infiltration hypothesis, on the other hand, envisages that the water could be many millions of years younger than the strata from which the solutes are derived. For example, Michelot et al. (1984) have suggested, on the basis of sulphur isotope data, that sulphate in deep groundwaters at the Stripa site may be derived from Permian (245-286 Ma old) evaporites despite maximum groundwater ages of only 25,000 years. The nearest Permian evaporites to Stripa occur in the Zechstein deposits of Germany and Poland so it has been proposed that dissolved salts may have been transported to the Stripa site from these deposits by rivers draining into the pre-Baltic basin during the Pleistocene (10,000-1.6 Ma ago), when the basin was cut-off from the ocean. Alternatively, Permian evaporites may have been deposited on the Fennoscandian peninsula and subsequently eroded but not before salts were dissolved from these deposits and transported into basement rocks by infiltrating groundwaters (Fontes et al., 1989).

This hypothesis could explain the origin of relatively dilute saline groundwaters present at moderate depths in the East Bull Lake and Lac du Bonnet plutons and potentially at other plutons, particularly those adjacent to Phanerozoic sedimentary formations. However, dissolution of sedimentary rocks followed by infiltration seems an improbable source for the deep concentrated Shield brines because it is unlikely that such waters would approach halite saturation during this process.

3.2.5 Proterozoic seawater/basinal brines

This hypothesis is similar to the Paleozoic seawater/basinal brine alternative but proposes a significantly greater age for the origin of the brines in the Precambrian Shield (ie. > 570 Ma). Guha and Kanwar (1987)

have suggested that Na-Ca/Cl vug brines in the Copper Rand Mine (Chibougamau, Quebec) originated from infiltrated Proterozoic basinal brines. These vug brines have TDS concentrations as high as 407 g/L and isotopic compositions that plot above the meteoric water line in a fashion similar to other Shield brines (Frape et al., 1984). The inferred Proterozoic age for these brines is based on the known age of Cu-Au mineralization in this area and the apparently close genetic relationship that exists between the brines and the gold zones.

4. AN ALLOCHTHONOUS ORIGIN FOR CANADIAN SHIELD BRINES

The chemical and isotopic compositions of groundwaters in the Canadian Precambrian Shield have clearly evolved over time as the result of water/rock interactions (Frape et al., 1984; Frape and Fritz, 1987; McNutt et al., 1990). Given sufficient time within the host rock, perhaps a few hundred million years (Nordstrom et al., 1989a), allochthonous and autochthonous attributes tend to converge and it becomes increasingly difficult to distinguish a possible allochthonous component. Frape et al. (1984) have suggested that, because the chemical and isotopic compositions of deep brines in the Shield do not reflect primary compositions, it is not possible to determine the ultimate age of the water and, therefore, these brines should be considered "crustal fluids" of uncertain origin. Such a pessimistic conclusion, however, is not applicable to the less concentrated brackish and saline groundwaters that have been observed in several of the AECL Research Area plutons where sedimentary or marine components have clearly been identified (Bottomley et al., 1984; Gascoyne et al., 1987 and 1988; Bottomley et al., 1990). The remainder of this paper addresses the question of whether it is possible to identify an ancient allochthonous saline source component in the deep shield brines, through a process of elimination, that reconciles the first order chemical and isotopic properties of the brine end member (Frape and Fritz, 1987) with that of a potential source. The properties of these brines that must be considered are :

- (1) concentrations of total dissolved solids that are up to 10 times that of seawater,
- (2) chloride concentrations that are up to 14 times that of seawater,
- (3) Ca/Cl compositions for the most concentrated brines,
- (4) uniformly high Br/Cl ratios that frequently exceed those of most

formation waters, and (5) unusual ^{18}O and ^2H compositions that plot above the global meteoric water line.

4.1 Total Dissolved Solids

The high concentrations of dissolved solids preclude none of the potential allochthonous or autochthonous sources previously discussed except an unmodified seawater origin. Basinal brines are concentrated relative to seawater because of processes that are operative within the basin itself and include evaporation, membrane (shale) filtration, and/or evaporite dissolution (Hitchon et al., 1971). However, silicate hydrolysis and leaching of intragranular salts could also, theoretically, produce brine solutions if such reactions occurred under conditions of low water/rock ratios and given sufficient time ($\gg 10^4$ years). Therefore, TDS concentrations in themselves are not diagnostic of a unique salinity source.

4.2 Chlorinity

Proponents of autochthonous origins for Shield brines argue that the high chloride concentrations could have resulted either from the leaching of chloride-rich hydroxysilicate minerals or by the leaching of fluid inclusion salts. While in principle such processes may be possible there is no evidence that they are operative to the extent that is necessary to produce the observed chloride concentrations. For example, essentially all mineralogical sources of chloride in an average granite would have to be dissolved under stagnant flow conditions to create such concentrations. However, no data in the form of whole rock analyses of core samples demonstrating the required chloride depletion have been reported. Furthermore, Kelly et al. (1986) have noted that there appears to be no viable physical mechanism for collecting fluid inclusion brines into pockets of equally saline mine waters without simultaneously involving great dilution. Accordingly, autochthonous sources for brine chlorinity lack credibility until it is demonstrated that either the host rocks are depleted in chloride, in the case of the silicate mineral hydrolysis hypothesis, or until a feasible accumulation mechanism is presented in the case of the fluid inclusion hypothesis. This leaves basinal brines as

the most probable source of the chlorinity.

It may be feasible in the future to demonstrate an allochthonous or autochthonous origin for brine chlorinity through an analysis of the boron isotopic composition of the brines and their host rocks. Recent work has shown that boron of marine origins has a $^{11}\text{B}/^{10}\text{B}$ ratio that is clearly distinct from the ratio in igneous rocks and minerals (Swihart et al., 1986; Bassett, 1990). Shield brines have reported boron concentrations of up to 9 mg/L (Frape and Fritz, 1987), compared to 4.8 mg/L in seawater, but to date no boron isotopic measurements have been attempted.

4.3 Ca/Cl Compositions

The most concentrated brines in the Canadian Shield are of the Ca/Cl variety which is a relatively rare water-type in nature. Besides being present at depth in crystalline rocks, they are also found in oilfield groundwaters, fluid inclusions in some hydrothermal systems, some saline lakes, and in rift zone thermal waters. Frape and Fritz (1982) and Pearson (1987) have suggested that the predominance of calcium as the major cation may be the result of the incongruent dissolution of silicate minerals, particularly plagioclase albitization, over very long periods of time. However, Spencer (1987) proposed that these brines could be produced by evaporative concentration of an original seawater source within a sedimentary basin followed by infiltration of the residual brine into crystalline basement rocks where water/rock interactions (albitization) significantly altered the Ca/Na ratio and isotopic composition of the parent brine. This is an attractive hypothesis in that it can readily explain the high salinity, chlorinity, and Br/Cl ratios of these brines as primary allochthonous features whereas the Ca/Cl and the isotopic compositions are autochthonous characteristics. This proposition is discussed in further detail in the following sections. It is unlikely that alternative allochthonous sources could be responsible for the characteristic Ca/Cl composition of Shield brines.

4.4 Br/Cl Ratios

Bromide and chloride ions are generally considered to be conservative geochemical parameters in most groundwater flow systems

and Br/Cl ratios have been used to assist in the identification of the origins of saline waters and brines in crystalline rocks as previously discussed. Precambrian Shield brines have uniformly high Br/Cl weight ratios of about 0.01 which is approximately 3 times that of seawater. Any proposed allochthonous salinity source must be compatible with this observation.

Brines which have formed by the evaporation of seawater to the halite saturation stage and beyond will exhibit elevated Br/Cl ratios relative to the seawater precursor because the partitioning coefficient for bromide in halite is small, varying between 0.006 and 0.0032 depending on the Mg^{2+} concentration in the brine (Spencer, 1987). Bromide and chloride concentrations (moles/litre) in Canadian Shield mine waters from Thompson, Sudbury, Yellowknife, Matagami, and Norita (Frape and Fritz, 1987) are plotted in Figure 1 and have been grouped into brackish, saline, and brine waters. Line "A" shows the trend in chloride and bromide concentrations as seawater is progressively evaporated to gypsum and halite saturation. Halite precipitation buffers the chloride concentration (at about 6 molar) with progressive evaporation toward epsomite ($MgSO_4 \cdot 7H_2O$) saturation, but bromide concentrations continue to increase (Line "B"). It is in this fashion that elevated Br/Cl ratios are produced. For example, if evaporation proceeded as far as epsomite saturation, the bromide concentration and Br/Cl weight ratio would be approximately 0.05 molar and 0.02, respectively. At stages of evaporation intermediate between that of halite and epsomite saturation, bromide concentrations would plot at various points along Line "B". Subsequent infiltration into crystalline basement rocks and mixing with fresh meteoric water would result in dilution of chloride and bromide concentrations (e.g. Line "C"), but the elevated Br/Cl ratios of the residual brine would be preserved. Chloride and bromide concentrations in Canadian Shield mine waters may largely be the result of the dilution of a residual evaporite brine (Fig. 1) suggesting a possible Devonian origin for these brines. Other potential salinity sources appear incapable of producing brines with the observed Br/Cl ratios for reasons previously discussed.

4.5 Isotopic Compositions

The isotopic compositions of saline waters and brines from Canadian

Shield mines are unusual in that they follow a mixing trend that tracks to the left of the global meteoric water line (Fig. 2). In contrast, magmatic and metamorphic waters plot to the right of the meteoric water line. Similarly, most hydrothermal waters of meteoric origins and formation waters from major sedimentary basins plot to the right of the line because of oxygen isotopic exchange with relatively ^{18}O rich host rocks such as carbonates. Evaporation of surface waters can also result in relative ^{18}O enrichment as shown by the trend line in Figure 2. Clearly, the ^{18}O depletion (or ^2H enrichment) exhibited by these brines is not an isotopic signature of any potential allochthonous salinity source.

Kelly et al. (1986) and Pearson (1987) have shown that low temperature isotopic exchange with silicate minerals could theoretically produce ^{18}O depleted groundwaters under conditions of low water/rock ratios such as exist at depth in the Canadian Shield. At low temperatures, equilibrium isotopic fractionation factors strongly favour partitioning of the ^{18}O isotope into the mineral phase. However, these fractionation factors have largely been determined from the extrapolation of high temperature experimental results to low temperatures. Furthermore, the kinetics of isotopic exchange with the common rock forming silicate minerals are considered to be relatively slow. Nevertheless, the potentially great age of these brines may be sufficient to have allowed this process to control their isotopic compositions. An alternative explanation is that of ^{18}O exchange with fracture calcites which are common in many plutonic rocks and which can recrystallize (and exchange ^{18}O) at low temperatures. In any case, it must be concluded that the ^{18}O depleted signature of shield brines is the result of water/rock interactions, a process that also modified the chemistry of the postulated residual evaporite brine source through the removal of Na^+ , K^+ and Mg^{2+} into secondary minerals.

5. IMPLICATIONS FOR WASTE ISOLATION WITHIN THE GEOSPHERE

It appears that the chemical and isotopic attributes of Canadian Shield brines were derived from a combination of allochthonous and autochthonous processes. The high salinity, chlorinity and Br/Cl ratios probably reflect a residual evaporite origin for these brines of Devonian age, whereas the elemental ratios and isotopic compositions are the product of extensive autochthonous water/rock interactions. These brines

are unrelated to the brackish and saline waters found at shallower depths in the Shield for which other origins are possible as previously discussed. Mixing of groundwaters of different origins, either through natural or artificial (e.g. mines or boreholes) advection/diffusion processes, further complicates the unraveling of the geochemical processes operative in this complex hydrogeochemical system.

If a residual evaporate brine is the salinity source for the Shield mine brines then the permeability of the crystalline basement rocks must have been sufficient for the brines to penetrate to depths of several 10's of kilometres (Spencer, 1987). The time required for these basinal brines to infiltrate to these depths is unknown. Kelly et al. (1986) have observed that deep circulation of these brines seems contrary to the apparent present day isolation of the brines and attribute this to self-sealing of the fractures by their own reaction products with the host rocks. However, the Devonian age of these brines is much younger than the age of the crystalline basement rocks and it must be assumed that waters of different origins flowed through fractures in the basement, reacted with the rock and formed fracture minerals prior to Devonian time. If these fractures are presently sealed, why were they apparently not also sealed during the Devonian, thus preventing deep penetration of these brines into the basement? There appear to be five possible answers to this question:

- (1) the age of most of the basement fracturing in which the brine presently resides was, in fact, produced during the Devonian,
- (2) previously sealed fractures of Precambrian origins were reactivated in the Devonian in response to changing tectonic conditions,
- (3) the fractures at depth were sealed prior to the Devonian and have retained low hydraulic conductivities similar to the unfractured rock since then except for residual megascopic "fluid inclusions" within fracture zones which yield brine flows when intersected by boreholes or mine shafts,
- (4) the fractures are not sealed but the brines are hydraulically isolated because of the absence of a regional hydraulic gradient sufficient to displace these brines, or
- (5) the fractures are not sealed and the brines are flowing laterally in response to a regional hydraulic gradient and discharging to surface at regional groundwater discharge zones.

The first alternative can largely be discounted since most fractures

in crystalline plutonic rock on the Canadian Shield appear to have originated in the Precambrian, although subsequent reactivation has periodically occurred (Kamineni and Stone, 1983). Fracture reactivation during the Devonian (alternative 2) could explain the deep penetration of the brine into the Shield but not the fact that the brine still resides deep in these rocks, unless post-Devonian fracture reactivation at depth has been insignificant. The third alternative implies that fracturing at depths of several kilometres does not significantly increase the hydraulic conductivity of the rock mass, presumably because they are largely sealed with secondary minerals and are not as vulnerable to reactivation as shallower fracture systems. This also implies that brine infiltration into the basement may have been a relatively slow process. The time required for the brine to infiltrate to the depths now found could be constrained if secondary fracture minerals formed from brine/rock interactions could be unequivocally identified and dated. This would show whether the infiltration of the brines was a relatively rapid or slow process which is of considerable significance in the assessment of crystalline rock as a long term waste isolation medium.

There is currently insufficient information on the nature of regional groundwater flow systems deep in the Shield to assess whether these brines are presently migrating. Therefore, any discussion of alternatives (4) and (5) would be highly speculative. Regardless of the uncertainty in our understanding of the past and present hydrodynamics of these systems, the mere presence of these brines throughout the Shield indicates that the deep and shallow groundwater regimes were hydraulically connected at the time of brine infiltration some 300-400 Ma ago. Regional groundwater flow system studies on the Shield are necessary to determine whether this hydraulic connection presently exists.

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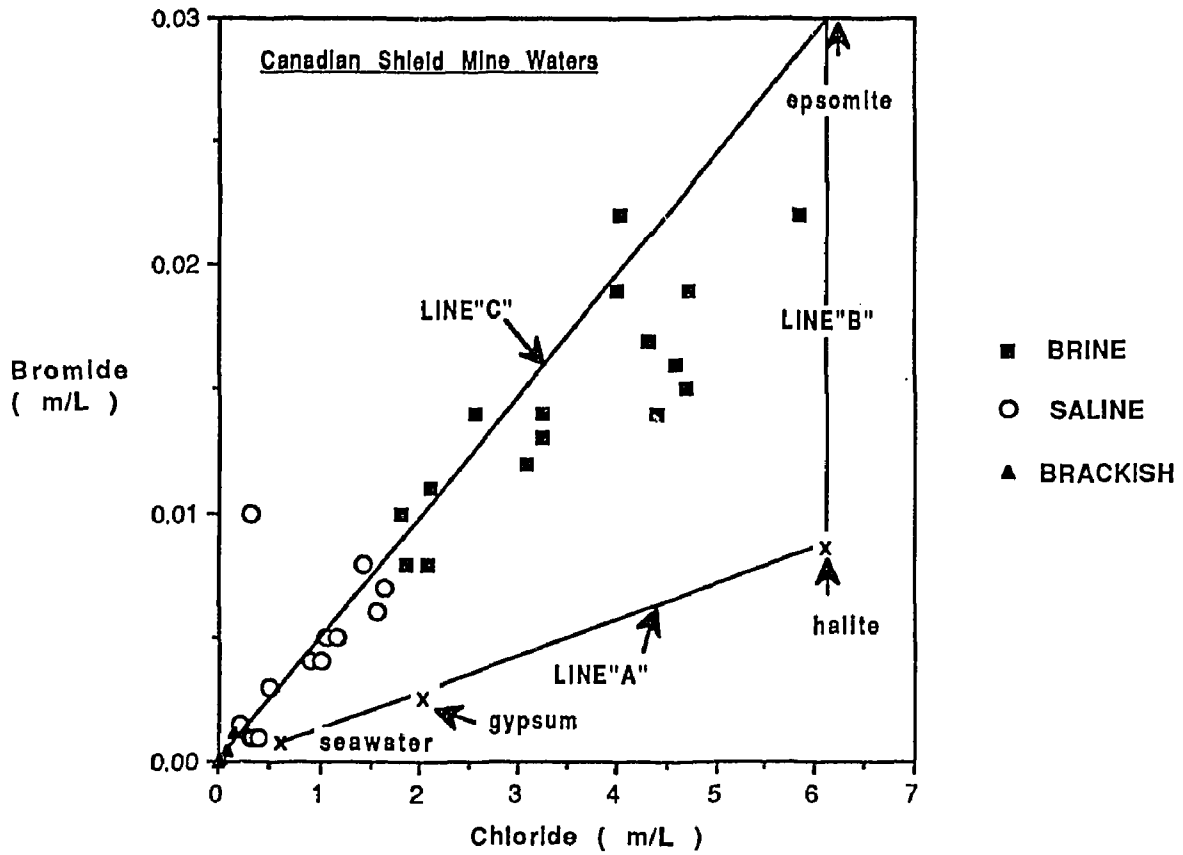


Fig.1 Plot of Cl and Br concentrations in Canadian Precambrian Shield mine waters (data from Frapce and Fritz, 1987).

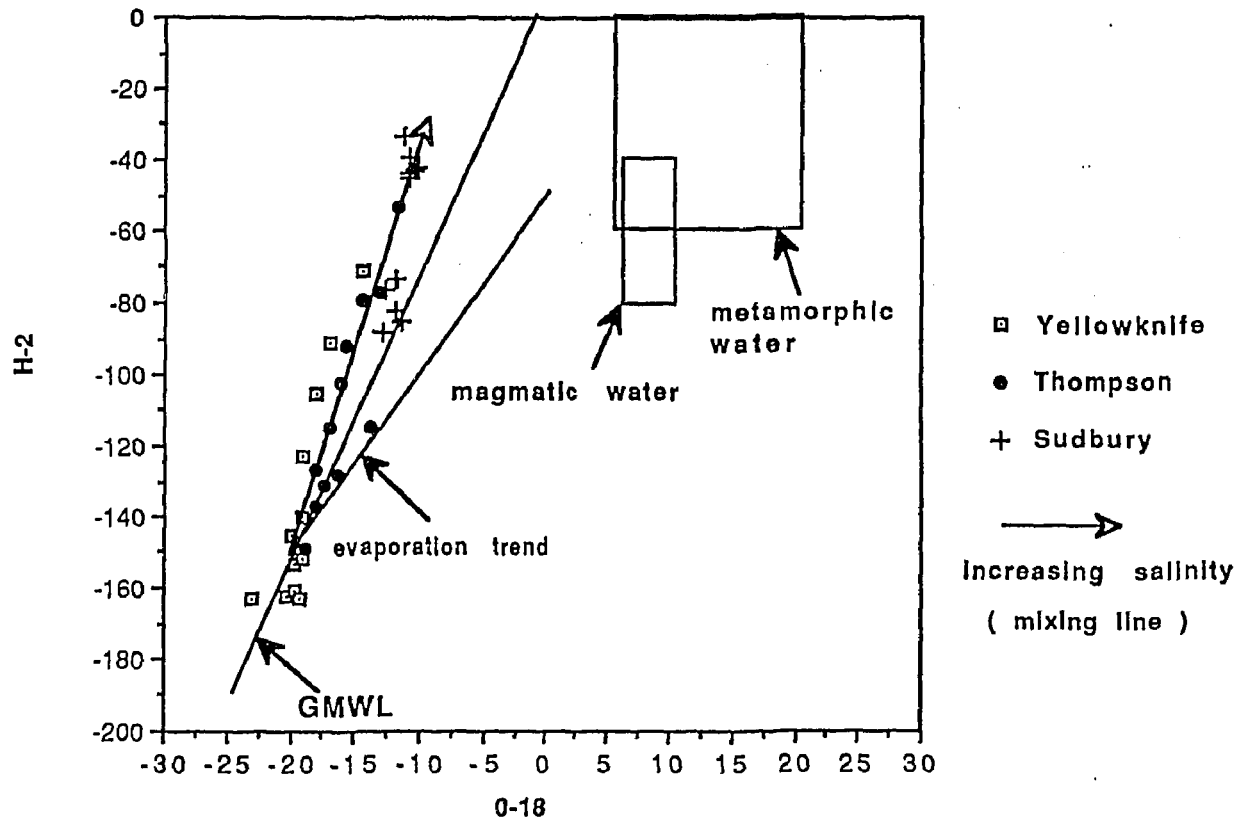


Fig.2 Isotopic composition of saline waters and brines from Canadian Precambrian Shield mines (Frape et al., 1984)