

INVESTIGATION OF REGIONAL GEOHYDROLOGY SOUTH OF GREAT SLAVE LAKE, CANADA, UTILIZING NATURAL SULPHUR AND HYDROGEN ISOTOPE VARIATIONS

K.U. WEYER*, H.R. KROUSE**, W.C. HORWOOD*

*Hydrology Research Division,
Environment Canada,
Calgary, Alberta

**Physics Department,
University of Calgary,
Calgary, Alberta,
Canada

Abstract

INVESTIGATION OF REGIONAL GEOHYDROLOGY SOUTH OF GREAT SLAVE LAKE, CANADA, UTILIZING NATURAL SULPHUR AND HYDROGEN ISOTOPE VARIATIONS.

The well-defined topographic, geological, and orographic setting in the area south of Great Slave Lake, in Canada's North-West Territory (N.W.T.), is favourable for a meaningful investigation of the local and regional groundwater flow systems in the area of the Mississippi Valley type lead-zinc deposits at Pine Point. Chemical and isotope ($\delta^{34}\text{S}$, δD) investigations have provided supporting evidence for conceptual models of groundwater flow. The range of the δD values encountered (-111 to -205‰ SMOW) indicates that the hydrodynamic systems convey meteoric waters. Differences in δD values of water samples were used to elucidate the hydrological relationship between groundwater and a major river in a karst area. The ore bodies at Pine Point are engulfed in a reducing hydrosphere. Sulphur species, derived from gypsum layers by regional groundwater flow, are instrumental in maintaining the reducing conditions. There is evidence that the reduction of sulphate to sulphide is caused by bacteria. Microbiological sulphate reduction, rather than isotopic exchange processes, is also responsible for shifts of measured $\delta^{34}\text{S}$ values in dissolved sulphates. After correction for those shifts, four different sources for dissolved sulphate were identified. In addition to supporting the conceptual model of regional groundwater flow in this area, the isotopic data also help to delineate hydrological features on a more local scale.

INTRODUCTION

There exists a large body of literature relating the occurrence of Mississippi Valley type lead-zinc deposits to ground water conditions at the time of the ore genesis. Less emphasis seems to have been placed, however, on investigations of current hydrogeology in the wider region of known ore bodies and how these conditions relate to the situation close to the ore bodies. Investigations of this kind are of interest to the economics of the

dewatering of a mine and also facilitate the assessment of environmental impact of the dewatering operation itself, which under certain circumstances can be very extensive.

In response to the occurrence of such a situation in Pine Point, N.W.T., the Calgary office of the Hydrology Research Division of the Canadian Federal Department of Fisheries and Environment and the large Canadian mineral producing company, Cominco Limited, the operator of Pine Point Mines Limited, in 1977 originated and planned a four-year joint research project on the regional geohydrology south of Great Slave Lake. The area covered extends about 200 km in north-south and east-west directions. As it is not easily accessible by normal means of transportation, extensive use must be made of helicopters, fixed wing float planes and boats during the investigation. Severe winter conditions prevail from October to well into April with temperatures dropping down to lower than -40°C . However, because of the karstic nature of some of the ground water bearing rocks (limestone, dolomite, evaporites) we find even under these extreme temperatures that springs and also former exploration boreholes flow all winter.

From the viewpoint of hydrogeochemistry, the ore bodies at Pine Point are engulfed in a reducing hydrosphere. Otherwise the main ore minerals, galena (PbS) and sphalerite (ZnS), would have been oxidized during recent geologic times. The reduced state of the hydrosphere in the Pine Point area is caused and maintained by bacterial sulphate reduction into HS^- and H_2S . The sulphate itself, to a large extent, is derived from Devonian gypsum layers in the vicinity of the Pine Point ore bodies. To date no gypsum is known to exist close to the ore bodies. Also, other evaporitic layers exist in the environs but not near the ore bodies.

This geological setting and its reflection in the chemistry of flowing groundwater permits the use of hydrogeochemical techniques to assess the validity of conceptual hydrodynamic models of regional and local groundwater flow in this area. In addition to detailed major and minor ion chemical analyses, sulphur and hydrogen isotope analyses were also conducted on more than 200 water samples taken so far from lakes, rivers, springs and boreholes. It was felt that the hydrogen isotope data would relate to the origin of the water while the sulphur isotope data would identify strata through which the water had moved.

Sulphur and hydrogen isotope abundances are expressed by δ -values which represent deviations (in parts per thousand) of the abundance ratios in the sample from that of a standard. For sulphur isotopes,

$$\delta^{34}\text{S} \text{ (in } \text{‰}) = \left[\frac{[^{34}\text{S}/^{32}\text{S}]_{\text{sample}}}{[^{34}\text{S}/^{32}\text{S}]_{\text{meteorite}}} - 1 \right] \times 10^3$$

where meteoritic troilite (FeS) is selected as the standard. For hydrogen isotopes,

$$\delta\text{D} \text{ (in } \text{‰}) = \left[\frac{[\text{D}/\text{H}]_{\text{sample}}}{[\text{D}/\text{H}]_{\text{SMOW}}} - 1 \right] \times 10^3$$

where Standard Mean Ocean Water (SMOW) is the adopted mean value for ocean water.

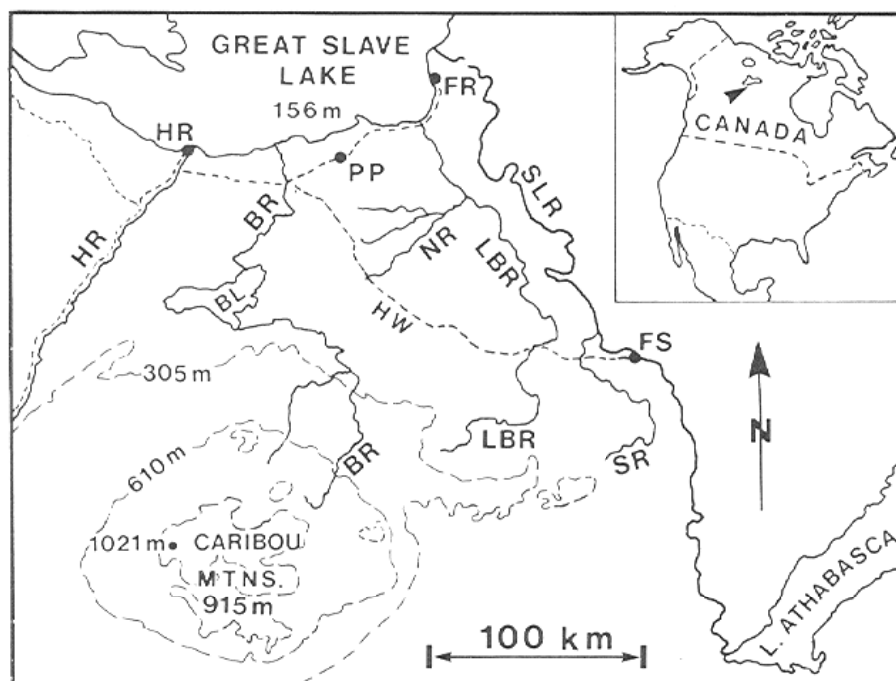


FIG.1. Geographical and topographical features south of Great Slave Lake. BL = Buffalo Lake; BR = Buffalo River; FS = Fort Smith; FR = Fort Resolution; HW = Highway; HR = Hay River (river and town); LBR = Little Buffalo River; NR = Nyarling River; PP = Pine Point; SLR = Slave River; SR = Salt River.

Concerning sulphur isotopes, it was known from former investigations in this area [1,2] that the $\delta^{34}\text{S}$ values in SO_4^{2-} of Cretaceous layers (negative values down to -20‰) are distinctly different from the $\delta^{34}\text{S}$ values in SO_4^{2-} from Devonian layers (about $+20\text{‰}$). Since the major regional recharge area, the Caribou Mountains plateau is comprised of Cretaceous layers, and the surrounding lowlands to the east and north are composed of Upper and Middle Devonian strata, we speculated that sulphur isotope data should be useful in delineating groundwater flow patterns.

Unfortunately the scope of our investigation is too large and complex for a thorough discussion within the limitations of this report. Consequently, after a short description of the physiographic and geologic conditions we will only outline the results of our studies to date and present some interesting facets in more detail.

TOPOGRAPHICAL AND GEOLOGICAL FRAMEWORK

The investigated area extends over about 200 km from the Caribou Mountains plateau (Fig.1) in the south (elevation up to 1000 m) to the south shore of Great Slave Lake in the north (elevation 156 m). In the east-west direction, the area extends for about 200 km from the Hay River in the west (elevation ~ 250 m to 156 m) to Little Buffalo River and Slave River in the east (~ 200 to 156 m).

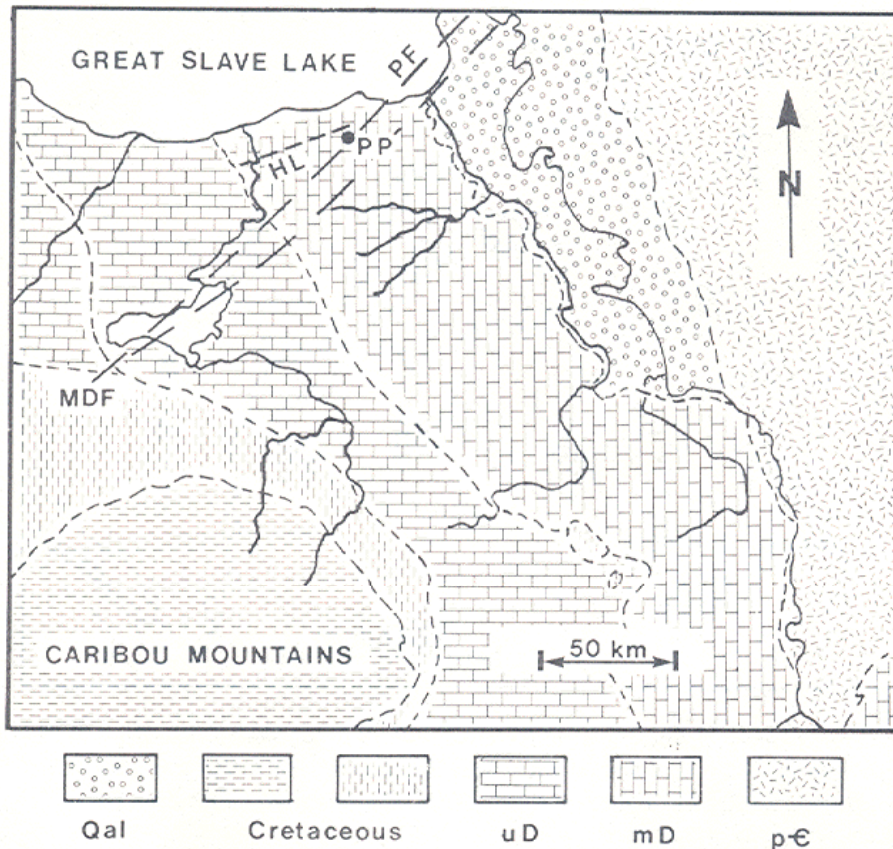


FIG.2. Geological map of the area investigated, after [3, 4, 5]. Qal = Quaternary; uD = upper Devonian; mD = middle Devonian; pC = Precambrian; HL = 'hinge line'; MDF = McDonald Fault; PF = Preble Fault; PP = Pine Point.

The Caribou Mountains consist mainly of clastic Cretaceous rocks (Fig.2), whereas the surrounding lowlands in the investigated area show mainly Upper and Middle Devonian calcareous, gypsiferous and other evaporitic rocks outcropping, often covered by quaternary sediments [3,4,5]. In the lowlands between the Caribou Mountains and Pine Point, there is also found the supposedly largest gypsum karst area in the world. All hard sedimentary layers dip gently to the west and they are underlain by Precambrian rocks. In the Precambrian rocks extended fault zones are known to exist, as for example the McDonald Fault stretching from NE to SW. Also major N-S fault zones are suspected to stretch from the Caribou Mountains plateau into the area of Pine Point.

CHEMISTRY OF WATERS

A comparison of the results of chemical analyses identified three different base types of water occurring in the lowlands (Fig.3):

- (1) a calcium-bicarbonate water, found locally in the glacial drifts, (sample 33);

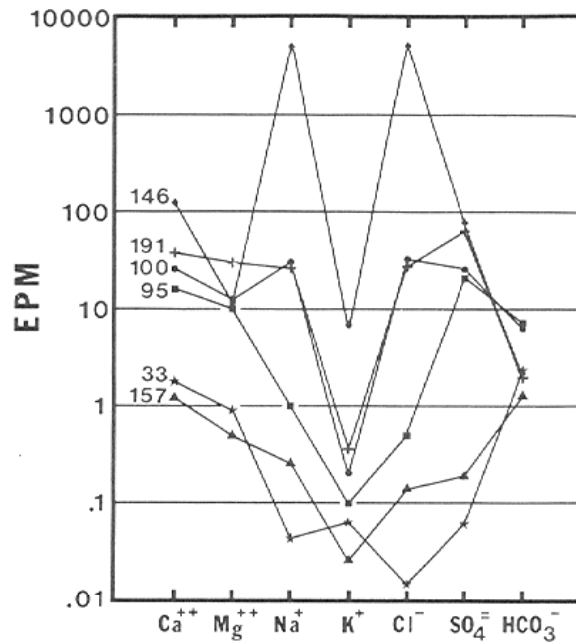


FIG.3. Semilog plot of chemical characteristics of selected water samples (EPM = equivalent per million).

- (2) a sulphate-bicarbonate water with Ca^{++} as the main cation (this water is probably derived from the Devonian gypsum layers, sample 95); and
- (3) sodium chloride brines as derived from Devonian evaporitic layers (sample 146 is a brine with $\sim 25\%$ TDS).

The chemistry of most of the other water samples seems to show mixing or evolution of these three basic types of water, as illustrated by samples 100 and 157. Sample 191, in addition, documents influence of magnesium sulphate.

CONCEPTUAL MODEL OF GROUNDWATER FLOW SOUTH OF GREAT SLAVE LAKE

It has been established to a reasonable degree of certainty that in the investigated area there exist large regional flow systems, some of which originate in the Caribou Mountains plateau. By means of comparison of chemical and isotope analyses of water samples as well as by measurements of the runoff of Salt River, Little Buffalo River and Buffalo River, major discharge areas were identified (Fig.4).

To the east of the investigated area discharges were located along Salt River, Slave River and Little Buffalo River. The increases of runoff at Salt River and Little Buffalo River (including Nyarling River) are shown in Fig.4; they were due to groundwater discharge. This was made obvious by the conductivity values of the river waters which increased downstream and reached 10 000 $\mu\text{mho/cm}$ in Salt River and reached 2000 $\mu\text{mho/cm}$ in Little Buffalo River (Nyarling River is $\sim 3000 \mu\text{mho/cm}$). In the area of Salt River, about 4 m^3/s are discharged and at springs discharges of 0.4 and

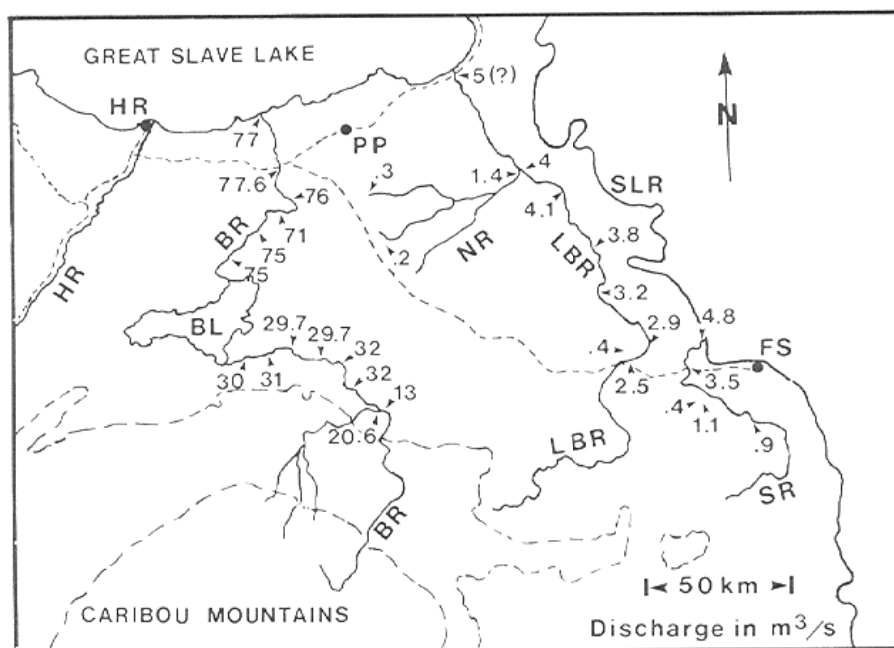


FIG.4. Results of runoff measurements in m^3/s (measurements taken at low flow conditions in September, 1977). For explanation of abbreviations, see Fig. 1 caption.

$1.1 m^3/s$ have been measured. In the same area brines of up to 25% TDS have been encountered. Along Little Buffalo River and Nyarling River, brines up to 14% TDS have been found frequently as well as sulphate-rich waters.

To the north of the area, major groundwater discharge occurs at the shoreline of Great Slave Lake and also along the lower reaches of Buffalo River downstream of the highway crossing. If groundwater discharge in this area increases during summer, its influence on the river water elevates the normal conductivity of $\sim 250 \mu mho/cm$ measured at the highway crossing over Buffalo River to $\sim 700 \mu mho/cm$ at the mouth [6]. At some discharge points, chloride formed a major chemical constituent while at others, sulphate formed the major constituent. The part of the Buffalo River which is close to the McDonald Fault, where the river turns to the north, also seems to be a groundwater discharge area. Runoff measurements showed an inflow of $\sim 4.5 m^3/s$.

Sulphate water and also salty water occur in discharges of the pumps of the open pits at Pine Point Mines. At one pit, salty water (sample 100) seems to be "upwelling" along geological structures aligned with the tectonical "hinge line," which controls the position of some of the known ore bodies.

Salty water also is discharged at a group of springs (sample 191) downslope of one open pit between the mining area and the shoreline of Great Slave Lake. This indicates that the regional flow system carrying the salty water under-flows the Pine Point ridge from the south in a northerly direction to Great Slave Lake. Also an extended area discharging salty water into Buffalo River is found close to the mouth of Buffalo River

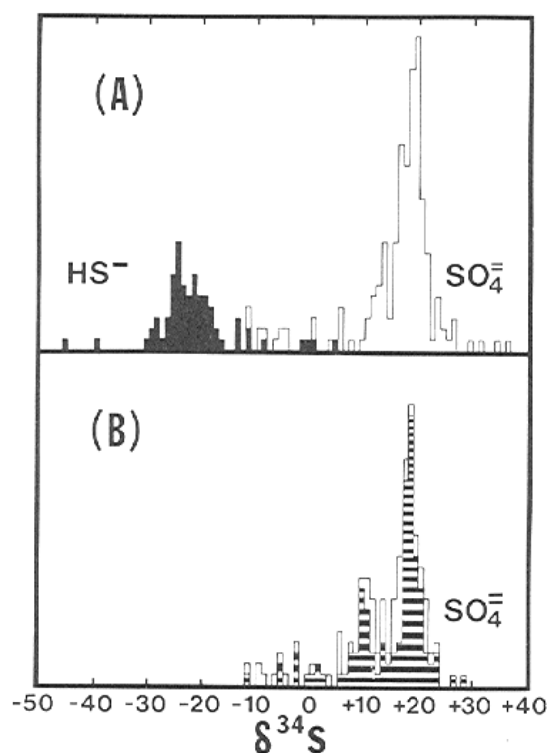


FIG.5. (A) Distribution of measured $\delta^{34}\text{S}$ values for dissolved sulphate and sulphide ions. (B) Distribution of corrected $\delta^{34}\text{S}$ values for soluble sulphur-containing ions. In areas with horizontal stripes, isotopic balances were obtained from $\delta^{34}\text{S}$ values and concentrations of sulphate and sulphide ions. In areas without stripes, measured $\delta^{34}\text{S}$ values of sulphates were used since sulphide data were lacking.

at Great Slave Lake. In general it is concluded that salty water as well as sulphate water is also discharged under the Great Slave Lake.

RESULTS OF ISOTOPE STUDIES

Sulphur Isotopes

The sulphur isotope data for dissolved sulphate and sulphide ions are summarized in Fig.5(A) and 7(A), as measured in the waters. In Fig.5(B) and 7(B) the isotopic compositions of the initial SO_4^{2-} are based upon isotopic balance calculations using measured SO_4^{2-} and H_2S concentrations and $\delta^{34}\text{S}$ values for sulphate and sulphide. These calculations used the following equations (F = Fraction of SO_4^{2-} reduced):

$$F = \frac{[\text{H}_2\text{S}] \times 0.941}{[\text{SO}_4^{2-}] \times 0.334 + [\text{H}_2\text{S}] \times 0.941} \quad (1)$$

$$\delta\text{S}_{\text{init}} = \delta\text{S}_{\text{SO}_4^{2-}} \times (1 - F) + \delta\text{S}_{\text{H}_2\text{S}} \times F \quad (2)$$

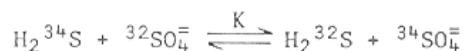
The constants in Eq.(1) are atomic weight ratios to convert concentrations to sulphur equivalents.

In these calculations we assume a closed system to exist. If all sulphides were derived by sulphate reduction, the calculated values correspond to the initial sulphate. This assumption may be questionable, as one of the calculated initial sulphate concentrations reaches 7000 ppm. On the other hand, 5000 ppm SO_4^{2-} were measured in some brines.

Based on the value of F determined in Eq.(1), the corrected sulphur isotope value δS_{init} is calculated in Eq.(2). The calculated initial concentrations of SO_4^{2-} and the apparent initial isotope values for SO_4^{2-} , δS_{init} , were then used to plot the figures 5(B) and 7(B).

In Fig.5(B) the areas lacking stripes summarize sites where $\delta^{34}\text{S}$ determinations of sulphide ions were not possible. Those entries are based on sulphate only and corrections for the presence of sulphide would shift the majority to lower $\delta^{34}\text{S}$ values. Such corrections would emphasize three peaks in the distribution with $\delta^{34}\text{S}$ values near +18.5, +9.5, and just below 0‰. Thus the isotopic balance calculations restructure the data and permit characterization of water groups as discussed later.

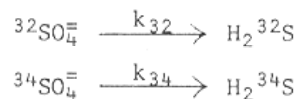
The question arises whether to identify the isotopic differences between soluble sulphate and sulphide with biological sulphate reduction or with isotopic exchange processes such as



We prefer the former interpretation for four reasons:

- (1) The $\delta^{34}\text{S}$ value of the sulphate increases with the increasing ratio of sulphide to sulphate concentration consistent with kinetic isotope effects during sulphate reduction;
- (2) Figure 6 shows that the isotopic fractionation is not a simple function of temperature as would be the case in an exchange reaction where the equilibrium constant usually has a temperature dependence of the form $K \propto \ln T^{-2}$;
- (3) measured E_h values, consistent with a reducing environment would seem to favour sulphate reduction;
- (4) generally environmental conditions would not preclude microbiological activity.

Many steps which are not completely understood are involved in the biological reduction of sulphate to sulphide. Therefore the simplified one-step competitive reactions



are often used to describe the reduction. Equations which relate the ratio of the isotopic rate constants k_{32}/k_{34} to the $\delta^{34}\text{S}$ values of sulphate and sulphide and the extent of reduction have been developed by a number of authors for this simplified approach (e.g. [7]) and for more complicated models [8]. Calculations in this paper are based on the simple one-step approximation.

Numerous laboratory experiments (e.g. [9]) have shown that microbiological isotopic selectivity during sulphate reduction varies widely with culturing conditions, but generally the ratio of the isotopic rate constants k_{32}/k_{34} decreases with increasing rate of reduction. If one examines waters in close proximity to each other and in similar environments in this study, trends are noted, but cannot be extended to all samples. For example, data in area II (Fig.6) suggests a decrease in k_{32}/k_{34} with increasing temperature, but this relationship does not apply to the majority of the data (triangles in plot).

Consistent with other studies, summarised in [10], most of the average k_{32}/k_{34} values are much higher than the value of 1.022 found in chemical reduction and identified with the initial S-O bond rupture during reduction [11]. There is always the problem of loss of gaseous sulphide in calculation of isotopic balance, but in our case the actual k_{32}/k_{34} value would be higher than the one calculated. We will not pursue the reasons for the higher isotopic selectivities in the present report but in this connection, three observations are noteworthy:

- (1) there are a number of k_{32}/k_{34} values higher than 1.05;
- (2) the most frequently encountered value in the histogram of Fig.6 is near 1.04 and by virtue of the number of samples examined in this study, it would seem that this value has significance;
- (3) there is not a peak in the histogram near 1.022 as one would expect, on the basis of its identification with S-O bond rupture.

Important for the present study is the fact that the high isotopic selectivities significantly alter the $\delta^{34}\text{S}$ values of SO_4^- in these waters even for relatively low percentages of reduction. Under these conditions, chemical determinations of dissolved sulphate, sulphides, and possibly sulphur compounds in intermediate valence states are necessary to identify the source of the sulphur species using $\delta^{34}\text{S}$ values.

The scatter diagrams in Fig.7 display the measured (A) and corrected (B) relationship between soluble SO_4^- contents of the water and the sulphur isotope values $\delta^{34}\text{S}$ in SO_4^- .

Figure 7(A) shows $\delta^{34}\text{S}$ values of -10‰ and lower for the Cretaceous as previously reported [1] (squares) and measured in this study (dots, and triangle). The triangle represents a value for a spring discharging at Fort Smith at the bank of the Slave River. This Cretaceous $\delta^{34}\text{S}$ -value is interesting since there are no Cretaceous layers known in this area and therefore the occurrence of this Cretaceous sulphur isotope value might be taken as an indication for discharge of water originating in the Caribou Mountains. Further investigations on this matter are being undertaken.

Devonian isotope values are clustered between $+15$ and $+25\text{‰}$. In Fig.7(A) the majority of the waters from three different open pits cluster at the number 50 (signifying 50 dots not plotted).

Surprising is the occurrence of the diamond-shaped single datum point near $\sim 0\text{‰}$. This value belongs to the sample 191. We found it difficult to explain its occurrence before we made the corrections for plot 7(B). In Fig.7(B) the position of sample 191 becomes explainable, since the corrections cause seven other data points to shift into its vicinity. These, interestingly, belong to the group of springs marked as "I" in Fig.6 and 8 as well as to some wells in one of the open pits. The probable reason that

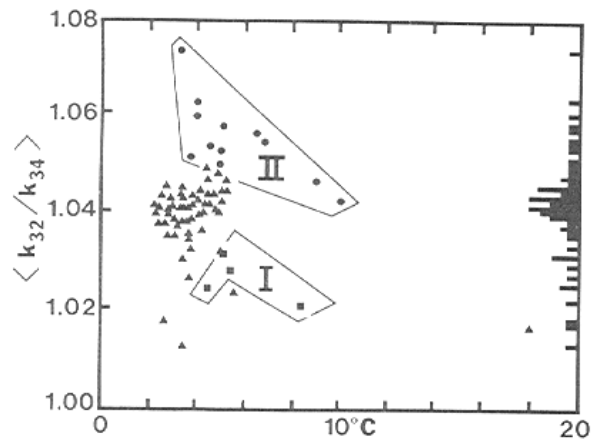


FIG. 6. Calculated values of the average ratio of isotopic rate constants k_{32}/k_{34} as a function of temperature of water measured in the field. The histogram to the right shows that the most frequently encountered value is slightly greater than 1.04. I and II refer to two areas discussed in the text (see also Fig. 8).

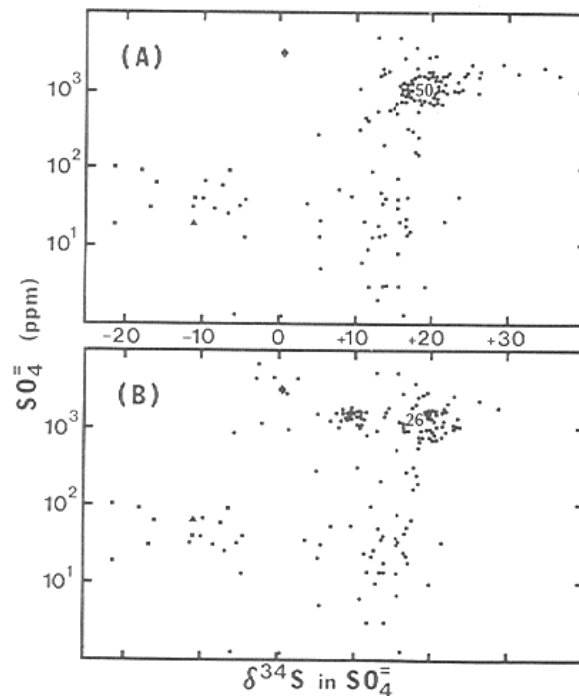


FIG. 7. Scatter diagrams of $\delta^{34}\text{S}$ in SO_4^{2-} versus sulphate concentrations in natural waters south of Great Slave Lake. The numbers 26 and 50 signify 26 or 50 data points not plotted in the area of the number.

(A) Measured distribution for dissolved sulphate.

(B) Distribution of corrected $\delta^{34}\text{S}$ values after the isotopic balance and the initial SO_4^{2-} content had been calculated using H_2S values.

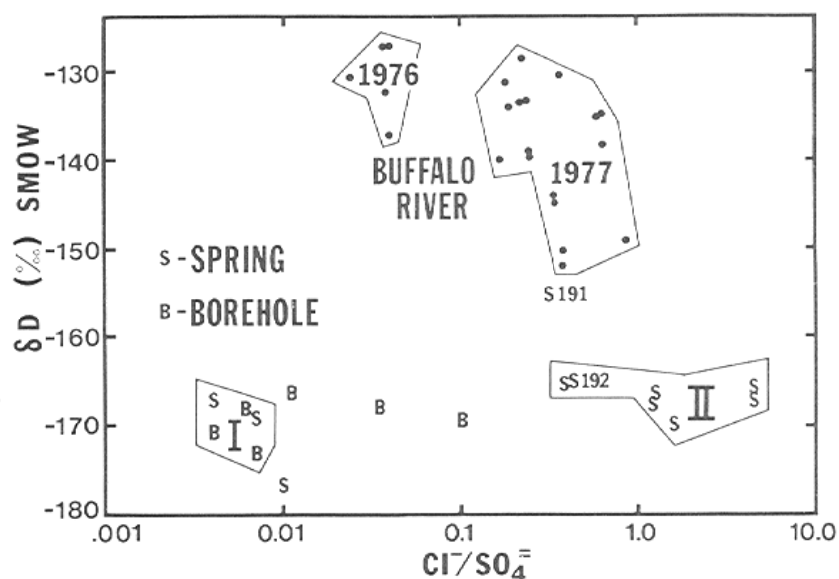


FIG.8. Plot of δD versus Cl^-/SO_4^{2-} ratios for river water and groundwater of the Buffalo River area. Corrected sulphate concentrations were used. I and II refer to the two areas similarly designated in Fig. 6.

the $\delta^{34}S$ value for sample 191 had not been shifted is that the relatively high Hg-content of the water curbed H_2S production.

In general, the massive "Devonian concentration" of data points at number 50 in Fig.7(A) has been divided into two groupings in Fig.7(B), one at number 26 (about $+18\text{‰}$) and the second one shifted to lower $\delta^{34}S$ values (about $+10\text{‰}$). One spring, sample 192, which is only some 20 m from sample 191, did not shift to the vicinity of sample 191 in Fig.7(B) after isotopic correction, but remained in the cluster near $+18\text{‰}$. These two springs will be discussed later with respect to hydrogen isotopic data.

After applying the corrections it appears that we are dealing with four different sources of sulphate with sulphur isotopes relating to the following values: -10 , 0 , $+10$, $+18\text{‰}$. The two extreme values are related to Cretaceous and Devonian rocks respectively. We suspect that the values of $\sim +10\text{‰}$ might also be derived from Devonian strata while the values near 0‰ are suggestive of Cretaceous strata or some other unknown source.

Hydrogen Isotopes

The range of the δD values encountered in this study (from -111 to -205‰ SMOW) indicates that the hydrodynamic systems in the area convey meteoric waters.

Hydrogen isotope data were also used in association with the water chemistry to characterize different water groups (Fig.8). The waters of Buffalo River are enriched in deuterium by 30 to 35‰ as compared to

springs and boreholes in discharge areas close to Great Slave Lake and near Buffalo River. Again, we will not pursue the reasons for the isotopic differences, but rather we will make use of them for hydrological reasoning. It seems evident that there is no direct connection between the river and the springs discharging nearby despite the high gradient in the river bed for about 30 km upstream and the occurrence of karstic systems.

On the basis of Cl^-/SO_4^{2-} ratios, two groupings of groundwaters (I and II on diagram) with similar δD values can be separated. These are identical to the two groups separated in Fig.6. This may suggest that the biological isotopic selectivity bears some relationship to the Cl^-/SO_4^{2-} content. Such a relationship may however depend on some other factor such as the availability of organic nutrients in waters of the two areas.

Sample 191 is from a spring enriched in deuterium by $\sim 10\text{‰}$ as compared to sample 192 from a spring closeby. As mentioned previously, the two springs also differ in their $\delta^{34}S$ values ($+0.6$ and $+17.6\text{‰}$ respectively). Other chemical and physical parameters as well as visual appearance differ significantly for these two springs. Apparently these two adjacent springs are discharging waters from different flow systems. It should be pointed out that these two springs are not close to Buffalo River but on the slope between an open pit and the shoreline of Great Slave Lake.

CONCLUSIONS

Hydrogen and sulphur isotope studies proved to be helpful tools in the investigation of groundwater flow south of Great Slave Lake, particularly when combined with other chemical and hydrological methods. Although sulphur isotope data from some of the past studies of the hydrosphere were ambiguous, in this study the use of isotopic balance calculations based on concentration and $\delta^{34}S$ data for soluble sulphides and sulphates greatly enhanced the interpretation. One might question the simplified model adopted for these calculations on the basis that it would not represent adequately the actual complex biophysicochemical system. Nevertheless the results proved useful and were consistent with findings from other techniques.

ACKNOWLEDGEMENTS

The stable isotope facilities at The University of Calgary received financial support for this study from the Natural Sciences and Engineering Research Council of Canada. We wish to thank Miss Laura Boreiko, Miss Jesusa Pontoy and Mrs. Nenita Lozano for technical assistance and Mrs. Elsie Pearn and Mrs. Berenice Delay for assistance in manuscript preparation. Thanks are also due to Mr. A. R. Wilson (Water Survey of Canada) for the discharge measurements.

REFERENCES

- [1] HITCHON, B., KROUSE, H.R., Hydrogeochemistry of the surface waters of the Mackenzie River drainage basin, Canada--III Stable isotopes of oxygen, carbon, and sulphur, *Geochim. Cosmochim. Acta* **36** (1972) 1337.
- [2] SASAKI, A., KROUSE, H.R., Sulfur isotopes and the Pine Point lead-zinc mineralisation, *Econ. Geol.* **64** (1969) 718.

- [3] DOUGLAS, R.J.W., NORRIS, A.W., Geology Great Slave, District of Mackenzie, Geological Surv. of Can. Map 1370A, Scale 1:500 000, Ottawa (1974).
- [4] Bedrock Geology of Northern Alberta, Research Council of Alberta Map 35, Scale 1:500 000, Edmonton (1970).
- [5] DOUGLAS, R.J.W., Geology Trout River, District of Mackenzie, Geological Surv. of Can. Map 1371A, Scale 1:500 000, Ottawa (1974).
- [6] STEIN, J.N., MILLER, M.D., "An investigation into the effects of a lead-zinc mine on the aquatic environment of Great Slave Lake," Environment Can., Fisheries Serv., Winnipeg (1972).
- [7] NAKAI, N., JENSEN, M.L., The kinetic isotope effect in the bacterial reduction and oxidation of sulfur, *Geochim. Cosmochim. Acta* 28 (1964) 1893.
- [8] REES, C.E., A steady-state model for sulphur isotope fractionation in bacterial reduction processes, *Geochim. Cosmochim. Acta* 37 (1973) 1141.
- [9] KAPLAN, I.R., RITTENBERG, S.C., Microbiological fractionation of sulphur isotopes, *J. Gen. Microbiol.* 34 (1964) 195.
- [10] KROUSE, H.R., Sulphur isotope variations in thermal and mineral waters, (Proc. Internat. Symp. Water-Rock Interaction, Czechoslovakia, 1974), *Ustredni Ustav Geologicky, Prague* (1974) 340.
- [11] HARRISON, A.G., THODE, H.G. Kinetic isotope effect in the chemical reduction of sulphate, *Trans. Faraday Soc.* 53 (1957) 1648.

DISCUSSION

H. HÜBNER: You have found a time dependence on your values for $\text{SO}_4^{=}$ content and $\delta^{34}\text{S}$. Could you apply the pool theory and get an idea of the reservoir of your system?

K.U. WEYER: We have observed a time dependence on $\text{SO}_4^{=}$ content and $\delta^{34}\text{S}$ values in some cases, especially in samples taken from rivers. The last slide shown during my oral presentation indicated that such a dependence was found for the Buffalo River. We prefer not to apply the pool theory, since it is basically a static model, whereas the system to be explained is, in hydrodynamic terms, fairly complex and variable. I believe one could apply the pool theory and obtain data on the reservoir of the system; an assessment of their validity would, however, be rather difficult. So far, we have not considered applying it.

P. FRITZ: A question of particular importance in Canada is that of the identification of underground flow systems; for example, one has to decide whether brines, which originate in deep basins, leak into shallow aquifers or not. Do you have any information in this connection, especially since you report a very large range of δD values for your waters?

K.U. WEYER: In the area investigated the chemistry of the water does not necessarily indicate the length of the flow system, and brines could have originated in shallow flow systems, as some of the evaporitic strata are not very deep-seated. The wide range of δD values has proved useful for the hydrological interpretation, as I indicated in my oral presentation in relation to Fig. 7. The reason for the

occurrence of such a wide range is not yet known for certain. It might be related to differences in precipitation and climate between the plateau of the Caribou Mountains (altitude ~1000 m) and the lowlands nearby (altitude ~200 m).