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SALINE MINEWATERS OF THE KEWEENAW PENINSULA, NORTHERN MICHIGAN: THEIR NATURE, ORIGIN, AND RELATION TO SIMILAR DEEP WATERS IN PRECAMBRIAN CRYSTALLINE ROCKS OF THE CANADIAN SHIELD

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ABSTRACT. Known since early work by Lane (1908a and b), stagnant pockets of Ca–Na–Cl brine occur at depth in many, if not all, native copper mines of the Keweenaw Peninsula. Typically occurring below ~300 m depth, the brines are characterized by high salinities (200 g/l or more), high Ca/Na ratios (5:1-7:1), low K and Mg contents, and δD (−17 to −21 per mil) and $\delta^{18}O$ (−7.3 to −7.6 per mil) values which plot well above the global meteoric water line. Similar saline waters are now known to be widespread in the Canadian and other shields (for example, Frape, Fritz, and McNutt, 1984) and are probably the "rule" for deep groundwaters in Precambrian basement rock. In North America, these waters have latitude-dependent isotopic compositions with lighter waters occurring in more northerly regions, suggesting a related age and origin.

In the Keweenaw Peninsula, several origins can be precluded. The minewaters are isotopically different from the late Precambrian meteoric and burial metamorphic waters of the region (Livnat, ms) and could not reasonably have evolved therefrom. They are also distinctly different from, and surely older than, local Pleistocene waters. Fluid inclusions in the Keweenaw copper deposits are chemically similar to the minewaters, but their δD values increase systematically with sample depth, indicating contamination by surface waters, probably in Precambrian time. Furthermore, there is no viable mechanism for collecting these inclusion waters into large quantities of brine with salinities as high as 30 wt percent.

This paper advocates a basinal water model involving several stages: (1) initial evolution of the waters as Paleozoic-hosted formation waters, (2) deep infiltration, reaction, and "self-sealing" of these brines in basement rocks under conditions of relatively high temperature and W/R ratios, (3) removal of Paleozoic cover and back-reaction of the waters, chemically and isotopically, under new conditions of low temperature and W/R ratios, and (4) subsequent and variable mixing with fresh meteoric waters. In the Keweenaw Peninsula, stages (1) and (2) must have occurred by Late Jurassic time while a Paleozoic cover still existed. Viewed in this framework, the brine pockets are essentially large "fluid inclusions" in which the liquid phase is evolved basinal water and the host a grouted silicate rock. Like most inclusion liquids in oxygen-bearing minerals,

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these brines have, upon cooling, back-exchanged with their host over a prolonged period of time.

Geologically, this model provides a common denominator (Paleozoic cover) for the otherwise diverse settings in which the saline waters occur today. It accounts for the many similarities between Paleozoic formation waters and the basement brines, while explaining their significant differences. Implications of the model with respect to subsurface fluid waste disposal and to the genesis of Mississippi Valley-type ore deposits are briefly discussed.

INTRODUCTION

Widely scattered occurrences of deep, highly saline groundwaters in Precambrian crystalline rocks have been known in the mining community for many years (for example, Langford and Hancox, 1936; Bruce, 1941; Boyle, 1961). In fact, the term "connate water" was first coined by A. C. Lane to describe such saline minewaters in the native copper district of the Keweenaw Peninsula of northern Michigan (Lane, 1908a, b). In later years, D. E. White (1968) re-studied the Keweenaw minewaters, calling attention to their unusual chemical and isotopic properties, and suggesting that these could reflect geologically ancient residence of these waters in their late Precambrian host rocks. Numerous recent investigations have documented that saline waters of the Keweenaw type are actually widespread in occurrence and are probably the rule, rather than the exception, for deep groundwaters in silicate rocks of the Canadian and other Precambrian shields (Frape and Fritz, 1981, 1982; Fritz and Frape, 1982; Frape, Fritz, and McNutt, 1984; McNutt, Frape, and Fritz, 1984; Edmunds and others, 1985; Gascoyne and others, 1985; McNutt, 1985; Nordstrom, 1985; Pekdeger and Matthess, 1985; Vovk, 1985). The locations of the Keweenaw Peninsula and of some of the other Canadian Shield brine occurrences studied by Frape and Fritz are shown in figure 1.

Since 1973, the authors have been engaged in an investigation of the metamorphic petrology and stable isotope geochemistry of the Keweenaw Peninsula. In the course of this work, we and others (Crisman, ms) have gathered new data on the Keweenaw minewaters as well as on fluid inclusion waters trapped in gangue minerals of the Keweenaw copper deposits. The purposes of this paper are to consolidate all data now available for these "type locality" Keweenaw brines, to compare them to other waters of possibly kindred origin, and to interpret their history in the light of facts currently available.

MINEWATERS OF THE KEWEENAW PENINSULA

The geologic setting and copper deposits of the Keweenaw Peninsula are fully described by Ensign and others (1968) and W. S. White (1968). Lane studied the brines in a large number of the native copper mines where they occur in pockets in porous parts of tholeiitic basalt flows and interbedded conglomerates of the Portage Lake Lava Series (Lane, 1908a and b, 1909a and b, 1914, 1927). The amounts and depths of waters varied in the mines, but, according to Lane, the upper 300 m were typically wet

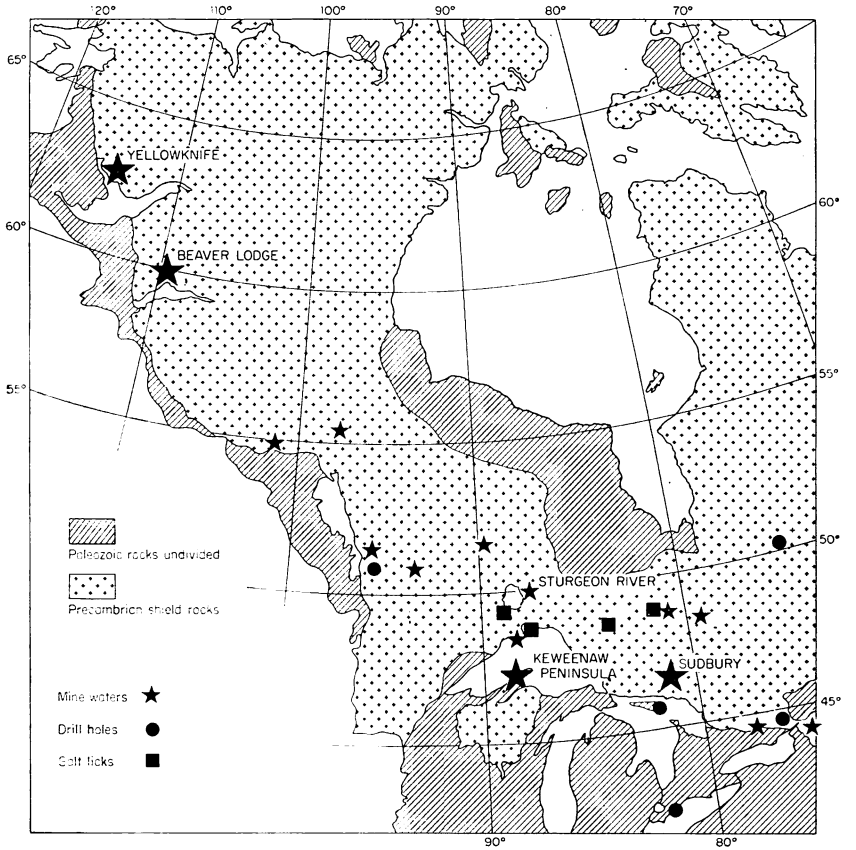

Fig. 1. Selected data of Frape and Fritz (1981) showing widespread distribution of known saline groundwater occurrences across the Canadian Shield and the location of hypersaline minewater localities cited in present paper. The "salt licks" are natural surface discharges of the saline groundwaters.

with fresh water that required much pumping. Below that, the mining entered relatively dry ground in which the rocks were damp but yielded no appreciable flow. The workings gradually became wetter again with increasing depth, and pockets of saline waters were locally breached in drilling or blasting. In some cases, the brines were encountered at shallower depths within as little as 100 m of the ground surface. When released, the brines first emerged as seeps or pressurized flows that gradually ebbed and ceased altogether in periods ranging from days to years.

The salinities of the deep minewaters tended to increase systematically with depth and, in some mines, reached values in excess of 30 wt percent total dissolved salts. These waters are no longer accessible for sampling, but the numerous partial analyses by Lane (1908a and b, 1909b), though old, provide an excellent record of the bulk compositional variation. This variation is depicted in figure 2, where all available analy-

ses are plotted in terms of total salinity versus Ca/Na ratios. Compositions of modern surface waters in the region are also shown in that diagram. In general, sample salinities increase with sample depth in figure 2, although the rate of salinity increase with depth varied greatly from mine-to-mine. The Keweenaw minewaters plot within a well-defined "main sequence" in which the deepest, most saline waters, having Ca/Na weight ratios in a restricted range of about 5:1 to 7:1, grade continuously into shallower, more dilute waters with highly variable Ca/Na ratios.

Brines of the type common in the native copper mines have been discovered recently at depths of 396 to 518 m in the White Pine mine located about 70 km southwest of the Keweenaw native copper district. Here, the brines occur in chalcocitic sediments within and near the base of the Upper Precambrian Nonesuch Shale. Recent analyses of these

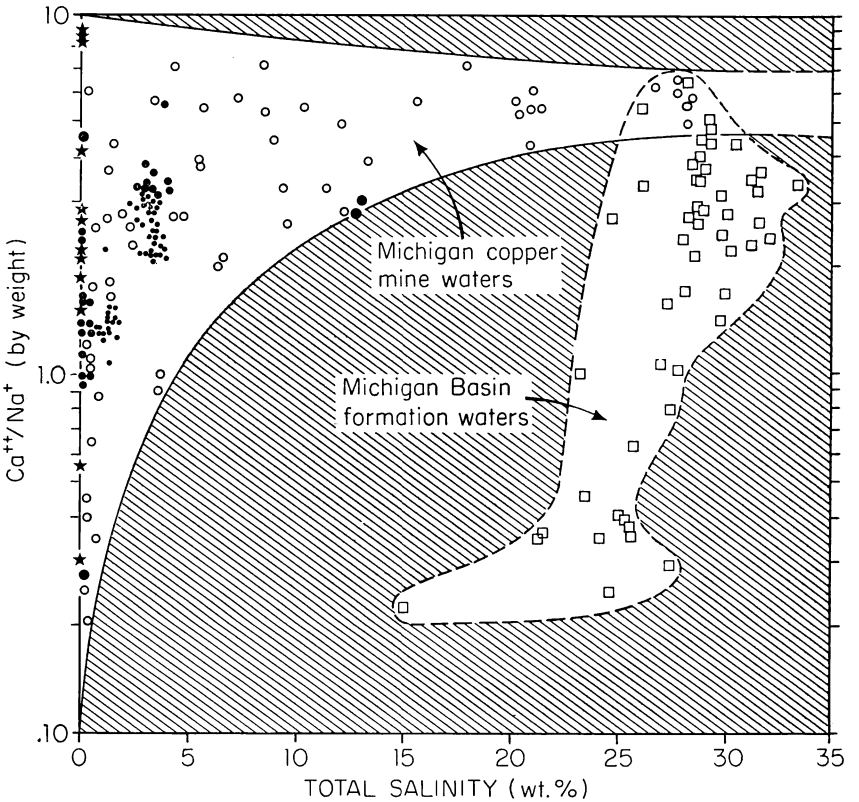

Fig. 2. Comparison of Michigan Basin formation waters with the "main sequence" of northern Michigan copper mine waters in terms of total salinities and dissolved Ca/Na ratios. Michigan Basin data [open squares] are from Sorenson and Segall (1974) and White, Hem, and Waring (1963). The copper minewaters include waters of the native copper mines (open circles: Lane, 1908a, b; White, Hem, and Waring, 1963); the present study) and of the White Pine mine (solid circles: Crisman (ms); White Pine Copper Company (personal commun., 1983). Data for fresh surface waters of northern Michigan (open stars) are those of Lane (1908a, b).

TABLE 1

	1 Centennial #6 Minewater (Keweenaw)	2 Centennial #6 Minewater (Keweenaw)	3 White Pine Minewater (Keweenaw)	4 Fluid Inclusion Brine (Keweenaw)	5 Yellowknife Minewater (N.W.T.)	6 Sudbury Minewater (Ontario)	7 Michigan Basin Formation Water	8 Deep Hole (N-2) Illinois Basin
Units	ppm	ppm	mg/l	ppm	mg/l	mg/l	mg/l	mg/l
Ca	47,500	62,900	91,780	60,480	57,300	65,000	94,900	22,400
Mg	7	179	1,373	50	920	12	14,700	2,840
Na	13,200	11,900	17,640	8,780	32,600	16,880	21,300	49,000
K	70	38	234	160	495	122	12,100	1,380
Sr	223	320	1,261	N.D.	1,640	1,390	N.D.	N.D.
Fe (Total)	<1	1	N.D.	N.D.	19	N.D.	N.D.	N.D.
Mn	<1	3	40	N.D.	22	N.D.	N.D.	N.D.
HCO_3	26	24	15	N.D.	<2	N.D.	261	116
Cl	102,171	128,000	156,500	134,080	142,000	156,000	256,000	125,000
SO_4	368	88	N.D.	N.D.	<1	138	44	508
Br	829	997	1,520	N.D.	1,520	1,090	N.D.	N.D.
I	N.D.	3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
SiO_2	<10	<10	N.D.	N.D.	8	N.D.	N.D.	N.D.
Total Dissolved Salts Reported	164,395	204,463	270,363	203,550	261,478	240,632	399,305	201,244
$\delta D(^{o}/oo)$	-17.1	-25.2	N.D.	-74	-73	-33	-43	+71
$\delta^{18}O(^{o}/oo)$	-7.6	-7.3	N.D.	N.D.	-14.4	-11.3	+4.3	-2.42

Abbreviation: N.D. = not determined. Data sources: 1, present study; 2, White (1968); 3, Crisman (1982); 4, present study; 5, Frape and Fritz, 1981; 6, Frape and Fritz (1982); 7-8, Graf et al. (1966). Analysis 2 of present study employed standard heating procedure to remove water of hydration from cations for δD analysis and prolonged CO_2–H_2O equilibration technique with corrections for salt content suggested by Sofer and Gat (1972) for $\delta^{18}O$ analysis.

White Pine waters by Crisman (ms) and by the White Pine Copper Company are also plotted in figure 2. In spite of the differences in their hostrocks, the White Pine and Keweenaw minewaters plot within the same main sequence, suggesting that both belong to the same mixing sequence.

Representative chemical analyses of the more concentrated White Pine and Keweenaw native copper minewaters are listed in table 1, along with analyses of other waters with which they will be compared in this paper. All the more saline minewaters are essentially calcium-dominated Ca–Na–Cl brines with notably low K and Mg contents.

Only two isotopic analyses of the deep Keweenaw brines are available, but the results, given in table 1 and plotted in figure 3, are unusual in that both waters plot well above the global meteoric water line (Craig, 1961) on familiar δD versus $\delta^{18}O$ diagrams. The anomalous isotopic composition of these Keweenaw waters is discussed in later pages.

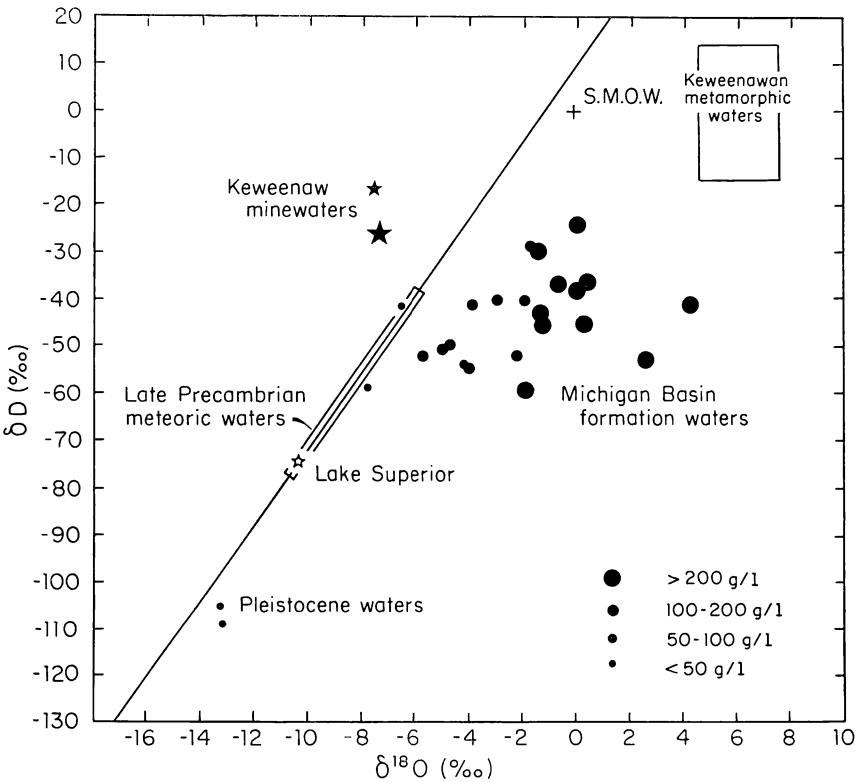

Fig. 3. Stable isotope (H,O) compositions of Centennial native copper mine waters, Keweenaw Peninsula, compared to those of Michigan Basin waters (Clayton and others, 1966), of late Precambrian Keweenaw burial metamorphic waters (Livnat, ms), of late Precambrian meteoric waters in the Keweenaw region (Livnat, ms; Kelly and others, 1985), and of subsurface Pleistocene water in the Michigan Basin (Clayton and others, 1966). GMWL = Global meteoric water line (Craig, 1961).

As cited above, independent studies, mainly those of S. K. Frape, P. Fritz, and their colleagues, have shown that brines of the Keweenaw type occur at depth in many mines and drill holes in the Canadian Shield. The most recent summary of the chemistry and isotopic compositions of these shield waters appears in Frape, Fritz, and McNutt (1984). All these waters are so similar in mode of occurrence, in dissolved salt chemistry (table 1), and in their unusual isotopic compositions as to suggest a related origin in spite of the fact that they occur in widely separated regions and in rocks of diverse ages, lithologies, and histories. Thus, while local interpretations can be devised for the Keweenaw brines, they must be integrated into this broader shield context. For this reason, we shall consider all these minewaters, including the Keweenaw brines, as being genetically related and will refer to them collectively as "Precambrian-hosted brines."

COMPARISON OF PALEOZOIC- AND PRECAMBRIAN-HOSTED BRINES

In terms of bulk chemistry, the Precambrian-hosted brines are very similar to deep formation waters in the Paleozoic sedimentary basins bordering the Shield. For Michigan, this similarity is evident in figure 2 where the compositions of 55 Michigan Basin waters are plotted on the salinity versus Ca/Na diagram. With increasing depth and salinity, the Michigan Basin waters approach and finally merge with compositions of the Keweenaw minewaters at the highly saline end of the "main sequence." Viewed in this simple context, the concentrated Keweenaw minewaters are indistinguishable from deep formation waters characteristic of the Michigan Basin.

It is informative to compare the dissolved Ca and Br contents of the Precambrian-hosted brines with those of typical basinal waters. Anderson, Graf, and Jones (1966), drawing chiefly upon data for the Michigan, Illinois, and Alberta Basins, pointed out the strong proportional co-variation of Ca and Br in formation waters of marine sedimentary basins. They discussed various basinal processes that could produce or contribute to this trend, emphasizing evaporation of an initial meteoric/seawater mixture coupled with Ca-enrichment by shale micropore filtration. In the log Ca-log Br diagram of figure 4, we have reproduced their bestfit line expressing this co-variation and have added lines to indicate the degree of scatter in their data. When plotted on the same diagram, all the more saline minewaters (containing more than 100 g/l TDS) fall in a distinct cluster within and at the highly saline end of the band of basinal water data. Although within this band, the Precambrian-hosted waters lie consistently to the right of Anderson, Graf, and Jones' (1966) best-fit line through the basinal data. The more dilute minewaters show much scatter due to admixture of meteoric waters of highly variable Ca and Br contents. While other explanations may be possible, the data of figure 4 support the view that the highly saline minewaters are infiltrated basinal brines which entered the basement and either retained their original Ca-Br signatures or, as seems more likely, underwent some exchange with basement rocks in which Br was enriched relative to Ca.

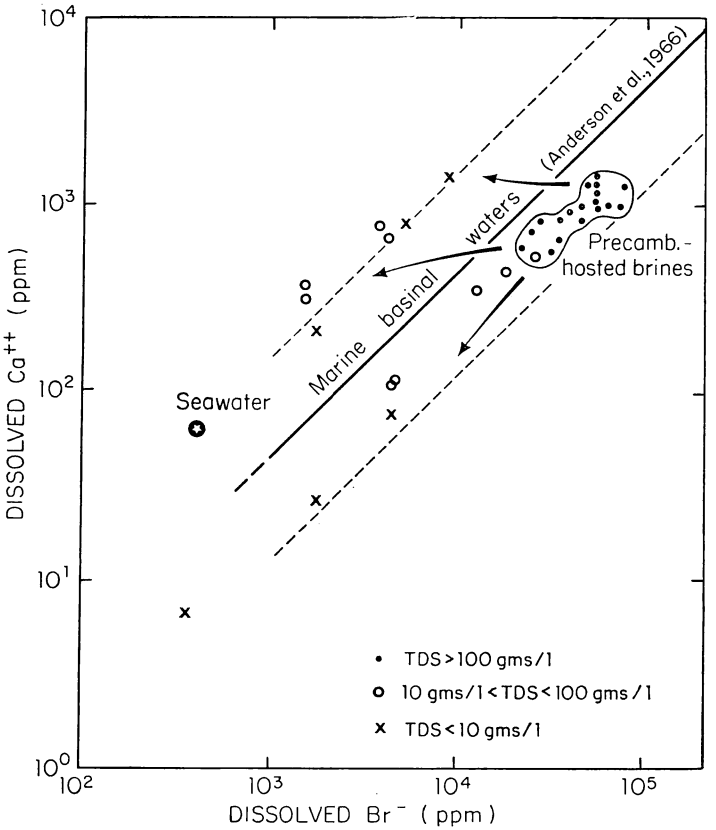

Fig. 4. Comparison of dissolved Br and Ca contents of Precambrian-hosted minewaters (data chiefly of Frape et al., 1984; also of White, Hem, and Waring, 1963, and the present study) with those of marine basinal waters (Anderson, Graf, and Jones, 1966). Solid line is Anderson, Graf, and Jones' best fit to their basinal water data; dashed lines indicate spread of their data. Arrows portray inferred contamination of highly saline minewaters by younger fresh waters.

The proportions of the "conservative" elements Cl and Br are commonly used as tracers in attempts to define the sources and evolution of natural waters (D. E. White, 1965), but this approach leads to inconclusive results in the case of the Precambrian-hosted brines. In view of their geographic dispersion and the diversity of their geologic settings, these brines have remarkably similar Cl/Br ratios, as is illustrated in figure 5. This similarity certainly suggests a related origin for these minewaters, whatever that origin may have been. If only the data for Michigan are considered, the close similarity between the Cl/Br ratios of the Keweenaw minewaters and those of the Michigan Basin formation waters, evident in figure 5, might be cited as evidence that the minewaters were derived from the basinal waters with little subsequent modification in the relative proportions of their dissolved Br and Cl. However, similar comparisons

in other regions might lead to different conclusions. For example, formation waters of the Alberta Basin, also plotted in figure 5, have Cl/Br ratios consistently higher than those of the Yellowknife minewaters or, for that matter, any of the saline minewaters. This could be taken, equivocally, to mean that the minewaters did not originate as basinal waters, or that they are basinal waters but that the Alberta Basin was not the recharge source,

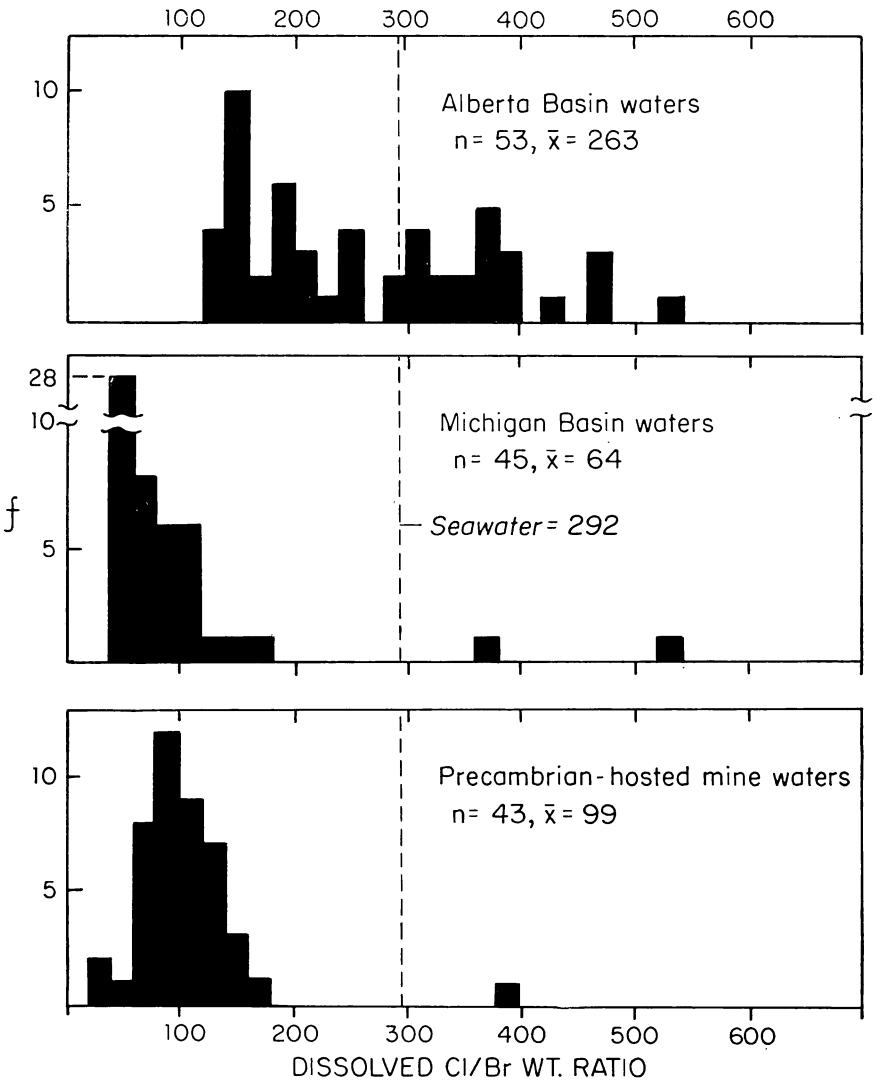

Fig. 5. Comparison of Cl/Br ratios of Precambrian-hosted minewaters (data chiefly of Frape et al., 1984 and of White, Hem, and Waring, 1963 and present study), of Michigan Basin formation waters (Graf and others, 1966), and of Alberta Basin formation waters (Hitchon et al., 1971).

or that they did start out as Alberta Basin waters which, after infiltration, were enriched in Br relative to Cl by basement exchange. As noted by McNutt, Frape, and Fritz (1984), one obstacle to using such Cl/Br ratios as genetic tracers is that we simply do not know enough about the directions and magnitude of Br and Cl exchange during basement silicate alteration.

One striking difference between the Paleozoic- and Precambrian-hosted brines is the conspicuously low K and Mg contents of the Shield minewaters (table 1). There are also systematic, though less obvious, differences in the proportions of Na, K, Ca, and Mg. These more subtle differences are brought out, if one attempts to apply the empirical Na–K–Ca thermometer of Fournier and Truesdell (1973) to the two types of brines. In so doing, the authors wish to stress that we *know* that the Na–K–Ca thermometer was *not* intended for application to Paleozoic-hosted basinal waters whose chemistry is not buffered by Na–K–Ca silicate exchange. Nevertheless, certain systematic relations emerge, if the thermometer is used to calculate *apparent* temperatures. These relations are illustrated in figure 6 where such apparent temperatures are plotted for 113 Michigan Basin and other Paleozoic-hosted formation waters and for 22 Precambrian-hosted minewaters. As expected, the basinal waters give anomalously high apparent temperatures, some as high as 300°C (actual *in situ* temperatures of these basinal waters are known to be in the range of about 15°-120°C). Application of the magnesium correction (Fournier and Potter, 1979) to the basinal waters brings their apparent temperatures into a lower, but still anomalously high range. When the same procedure is applied to the Precambrian-hosted brines (also plotted in fig. 6), their apparent temperatures fall in a distinctly lower range of about 23° to

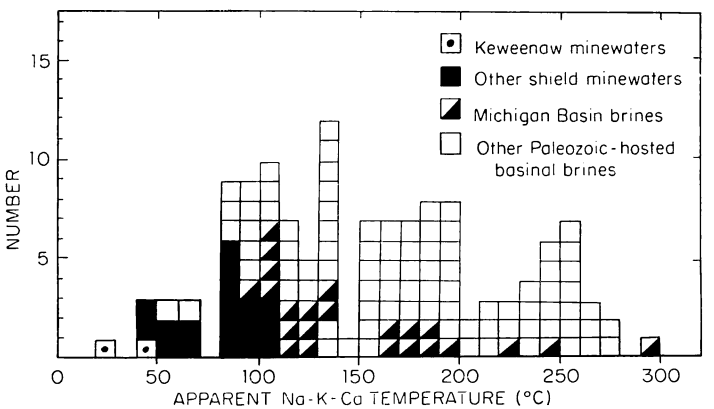

Fig. 6. "Apparent" Na–K–Ca temperatures of Precambrian- and Paleozoic-hosted subsurface waters (see text for discussion). Keweenaw minewater data are those of White, Hem, and Waring (1963) and the present study. Other shield minewater data are those of Frape and Fritz (1981, 1982) and Fritz and Frape (1982). Michigan Basin data are those of Graf and others (1966) and the other basinal water data (Illinois, Gulf Coast, and Alberta Basins) are those of Hitchon, Billings, and Klovan (1971) and of Graf and others (1966).

100°C with the two Keweenaw (Centennial mine) brine samples giving the lowest temperatures of all. The Centennial mine apparent temperatures are in or close to the modern-day range of temperatures in that mine (Lane, 1909a). As discussed later, we believe these differences in apparent temperatures between the two types of waters, though meaningless in terms of thermometry, are significant in terms of Na–K–Ca re-equilibration of basinal waters that infiltrated and reacted with basement silicate rocks.

The most outstanding difference between the Paleozoic- and Precambrian-hosted waters is in their stable isotope compositions. This was illustrated in figure 3 where the hydrogen and oxygen isotopic compositions of the Keweenaw minewaters can be compared with compositions of formation waters in the nearby Michigan Basin. Similar comparisons of Shield and basinal waters for other parts of North America are less direct because, in most cases, the close geographic proximity of the waters offered by the Michigan case is lacking. Nevertheless, such a comparison is attempted in figure 7, where the isotopic compositions of Precambrian-hosted brines of several widely scattered mining districts are plotted along with the compositions of formation waters in several Paleozoic basins. The lines drawn to represent formation waters of the Alberta, Michigan, and Illinois basins are taken from Clayton and others (1966); each basin, of course, shows much scatter of data around these lines. The "deep Illinois brine (N-2)" plotted in figure 7 is a special case discussed below. The analyses of the deep Yellowknife and Sudbury minewaters are those of Frape and Fritz (1982).

The chief difference between the two types of waters, whether compared only in Michigan (fig. 3) or on a North American scale (fig. 7), is that the Paleozoic-hosted waters plot (as do most evolved waters of the world) to right of the meteoric water line, whereas all the highly saline Precambrian-hosted minewaters plot to the left, or on the "wrong side," of that line. At the same time, both water types show a similar latitudinal shift with lighter waters occurring in more northerly regions. Where comparisons of δD values can be made for adjacent shield-basin regions, as in Michigan, the most saline Precambrian-hosted brines have δD values very similar to those of the most saline Paleozoic-hosted brines in the adjacent basin

In their studies of formation waters in the Illinois Basin, Graf and his co-workers (Graf, Friedman, and Meents, 1965) called attention to unusual brines occurring in the Mount Simon sandstone, where it lies directly on Precambrian basement rocks along the north flank of the basin. The composition of this brine is given in table 1. Isotopically, it plots well above the meteoric water line (point N-2 in fig. 7) and, in this respect, is more similar to the Precambrian-hosted minewaters than to formation waters typical of the Illinois Basin. Brines of similar chemical composition have been found in granite cores from deep drill holes which penetrated Precambrian bedrock in northern Illinois (Couture, Seitz, and Steindler, 1983).

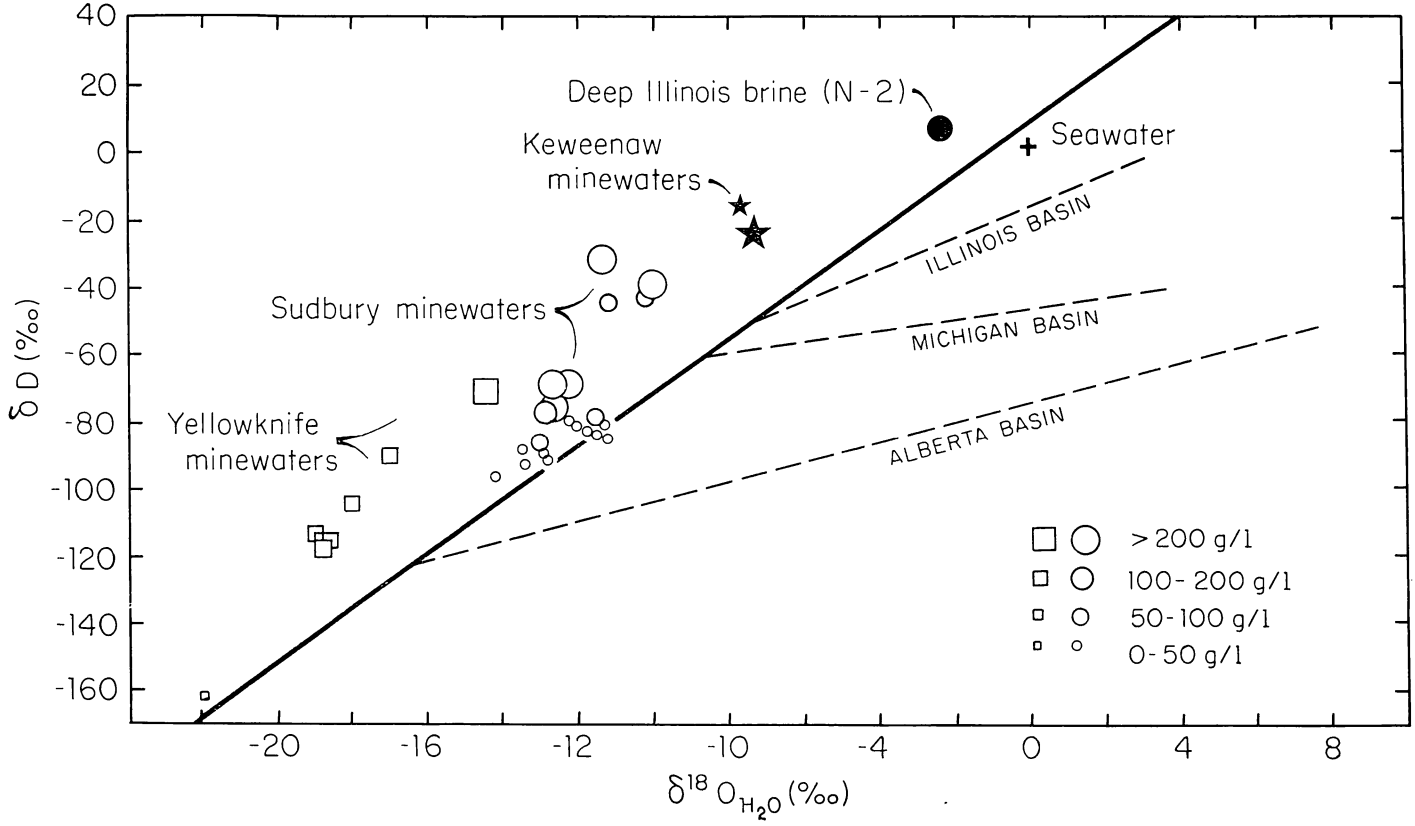

Fig. 7. Comparison of stable isotope (H,O) compositions of various Paleozoic-hosted and Precambrian-hosted subsurface waters. Regression lines drawn for Illinois, Alberta, and Michigan Basin waters are those of Clayton and others (1966). Keweenaw minewater data are from present study and D. E. White (1968). Data on Yellowknife and Sudbury minewaters are from Frape and Fritz (1981, 1982) and Fritz and Frape (1982). Deep Illinois basin water (N-2) analysis from Clayton and others (1966). GMWL = global meteoric water line (Craig, 1961).

COMPARISON WITH KEWEENAW FLUID INCLUSIONS

Studies of fluid inclusions in the Keweenaw copper deposits were undertaken in the hope that they would provide a set of pristine Precambrian fluids with which to compare the Keweenaw minewaters. Additionally, we wished to assess the idea that, whatever their age, the Precambrian-hosted minewaters may have derived their salts by leaching of fluid inclusions in the enclosing hostrocks.

The fluid inclusions were studied in several hundred polished plates of coarsely crystalline quartz, calcite, datolite, epidote, and other transparent gangue minerals in the native copper lodes. Unfortunately, although these crystals appear ideal for inclusion studies, their fluid inclusions tend to be extremely small and highly "necked down" (Roedder, 1979). Definite primary fluid inclusions are extremely rare. The great majority of inclusions occur along healed fractures, and, in many cases, it is even difficult to distinguish pseudosecondary from secondary inclusions. Many other inclusions appear chaotically dispersed in the host crystals and are simply difficult to interpret.

Partial chemical analyses of seven bulk inclusion leachates were performed, and results for the most concentrated leachate (199 gms/l TDS) are listed in table 1. These data, of course, represent the blend of fluids released in bulk crushing of the samples, not the composition of any single type or generation of inclusions. Also, the listed concentrations are probably minimal, because the leaching procedure is not highly efficient. As shown in figure 8, the leachate compositions plot more-or-less along

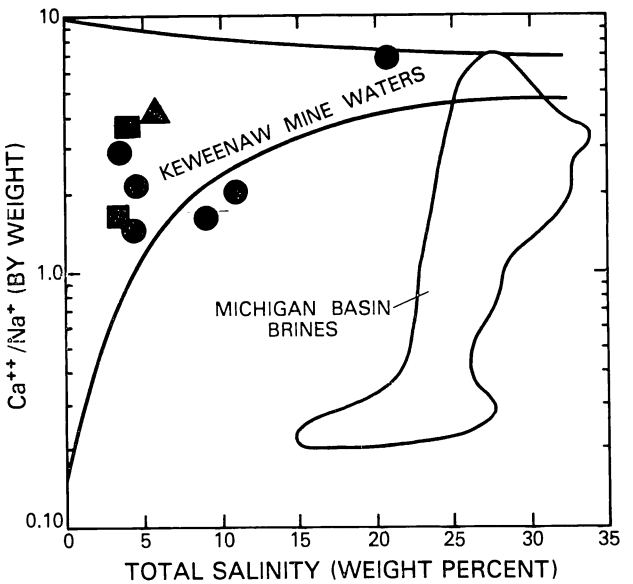

Fig. 8. Total salinities and dissolved Ca/Na ratios of inclusion fluids in Precambrian Keweenaw minerals as compared to Michigan Basin formation waters and the "main sequence" of Keweenaw minewaters. Fluid inclusion host minerals are quartz (circles), calcite (squares), and barite (triangle).

the same main sequence as that defined by salinities and Ca/Na ratios of the Keweenaw minewaters. Thus, these are chemically *similar* waters but not necessarily the *same* waters, as the two could have developed their similarities at different times and by different processes. Assuming the high Ca/Na ratios of the more saline inclusion leachates are primary fluid features, these are quite reasonable in that the primary waters would have been involved in basalt-seawater exchange during burial metamorphism of the Portage Lake lavas (Livnat, ms).

The δD values of 23 inclusion extracts are plotted in figure 9 along with the δD values of the Keweenaw minewaters of Michigan Basin Formation waters (Graf, Friedman, and Meents, 1965; Clayton and others, 1966) and of the Precambrian burial metamorphic waters as estimated by Livnat (ms). Livnat's estimates were based, not on the fluid inclusions themselves, but upon δD values of solid phases in the copper lodes coupled with temperatures estimated by isotope thermometry and study of the metamorphic phase equilibria. As evident in figure 9, the δD values of the fluid inclusions vary so widely that they overlap virtually all the other water types considered and, thus, are not diagnostically helpful. The δD data for inclusions in barite should probably be discarded, because this mineral is notoriously subject to inclusion leakage and contamination by

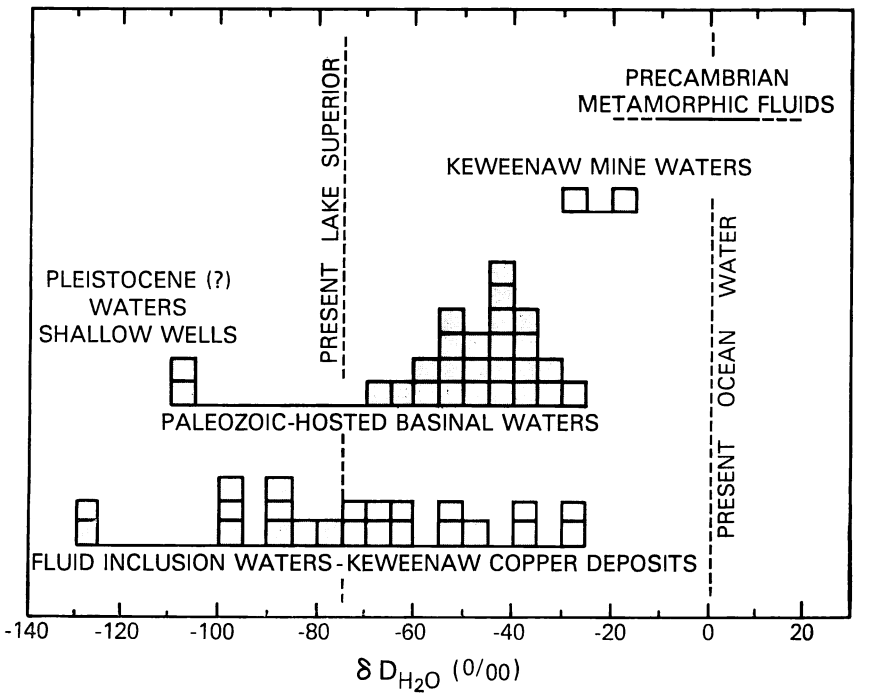

Fig. 9. Comparison of δD values of Keweenaw fluid inclusion waters (present study), of Keweenaw minewaters (D. E. White, 1968; present study), of Paleozoic-hosted waters of the Michigan Basin (Clayton and others, 1966), and of Precambrian burial metamorphic waters of the Keweenaw Peninsula as estimated by Livnat (ms).

late waters, but even if this is done, the range of inclusion water δD values remains so large as to be uninterpretable. The data indicate that the primary inclusion record has been obscured by low δD, secondary fluids of uncertain age. Such contamination is further indicated by the fact, as illustrated in figure 10, that δD values of the inclusion waters increase systematically with sample depth: presumably, the deeper samples contain higher proportions of the primary waters whose δD values are close to −20 per mil.

Given such a contaminated inclusion record, comparison of the minewaters and inclusion waters quickly degenerates into comparison of two equally problematic fluids. The Keweenaw minewaters may actually shed more light on the fluid inclusions than *vice versa*. That is if *both* the δD and $\delta^{18}O$ values of the minewaters are considered, it is clear that these waters are isotopically very different from the Precambrian metamorphic fluids (see fig. 3) and could not have isotopically evolved from those Precambrian waters in any reasonable way. Therefore, were it assumed that the minewaters and inclusion waters are the *same* waters, it follows that the inclusion waters, even the deepest most saline samples, could not be primary Precambrian waters. Alternatively, and we think more likely, the inclusion waters (both the primary and contaminating waters) are Precambrian, and the minewaters are younger. The two water types are

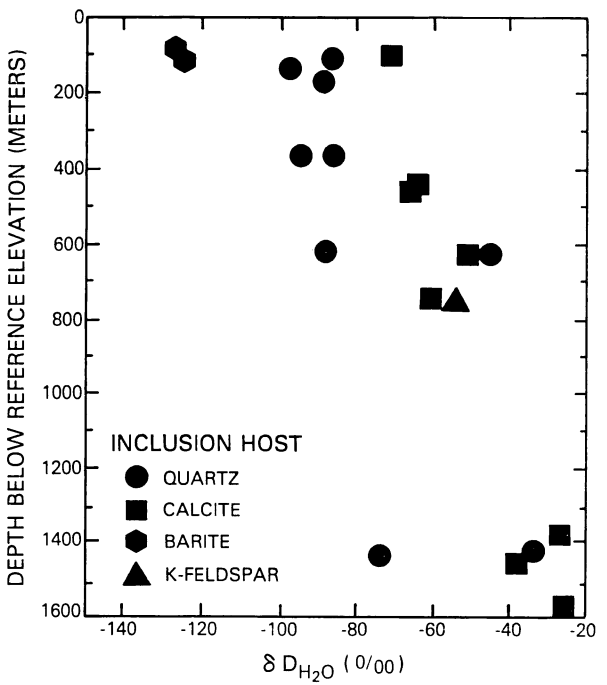

Fig. 10. Variation in αD values of fluid inclusions in Late Precambrian minerals of the Keweenaw copper deposits as a function of sample depth. Reference elevation is 462 m above mean present sea level.

chemically similar, because both have exchanged with the same basalt host rocks, the inclusion waters as seawater involved in the Late Precambrian burial metamorphism and the minewaters as infiltrated basinal brines which exchanged with the basement rocks during Paleozoic and later time.

There is the other question of whether or not the present-day minewaters, whatever their age, could have acquired their dissolved salts by the leaching of fluid inclusions in the silicate hostrocks. This possibility might at first seem feasible in the Keweenaw situation, where extensive fracturing and leakage of primary inclusions is commonplace, and where the minewater compositions are similar to inclusion compositions. But even in the Keweenaw case, it is difficult to imagine any physical mechanism for collecting the inclusion brines into pockets of equally saline minewaters. As stressed by Frape and Fritz (1982) and documented by Roedder (1979), fluid inclusions may be numerous, but they rarely comprise more than about 0.1 volume percent of their host minerals. Any leaching process of such sparse and dispersed fluids would involve great dilution. It is conceivable that salt contents of dilute inclusion leachates could be upgraded by subsurface evaporation and/or formation of hydrated basement alteration products, but then the saline Precambrian-hosted minewaters show no isotopic evaporative trend, and it seems unlikely that formation of mineral hydrates could produce residual brines containing as much or more than 30 wt percent dissolved salts. There are some cases, such as described by Nordstrom (1985), in which the minewaters have low salinities intermediate between fresh water and the most saline fluid inclusions where one might reasonably entertain the inclusion leaching mechanism. However, we believe it is totally inadequate as a general explanation of the deep Canadian Shield brines which *typically* contain in excess of 100 g/l total dissolved salts.

ORIGIN OF THE PRECAMBRIAN-HOSTED BRINES

Numerous possible sources of the Precambrian-hosted brines have been reviewed by Frape and Fritz (1982), including: (1) fossil seawater, (2) fluid inclusion brines, (3) sedimentary basin brines, (4) waters from evaporite beds, (5) hydrothermal ore fluids, and (6) magmatic waters. Among these numerous possibilities, we believe that a basinal water source is the best explanation, certainly for the Keweenaw brines, and probably for the similar saline minewaters elsewhere in the Canadian Shield. While providing a geological denominator common to the scattered brine localities and a ready source of chlorine, such an origin is also supported by strong similarities between the two kinds of waters, including their bulk salt contents, their Br/Ca ratios, and their similar δD ranges within any given region. Both water types also show a similar latitude-dependent shift in their isotopic compositions. Finally, as in Illinois, examples are known where the deepest sediment-hosted basinal waters are more similar isotopically to the basement waters than they are to formation waters in the overlying stratigraphic column, and where waters of similar dissolved

salt chemistry occur both in the sediments and underlying basement rocks recovered from deep holes in the same region.

There are, to be sure, conspicuous differences between the two water types, but they are differences to be expected for basinal waters that infiltrated and subsequently exchanged with silicate basement rocks. Notable among these are the low K and Mg contents of the Precambrian-hosted basement waters. If basinal waters infiltrated and reacted with basement silicates over a geologically prolonged time, then, as has been emphasized by others (Frape and Fritz, 1982; Frape, Fritz, and McNutt, 1984; McNutt, Frape, and Fritz, 1984), they would lose K and Mg in forming chlorite, clay minerals, and other silicate alteration products. For such exchange to have produced the Keweenaw and other saline minewaters, it must have occurred at low temperatures and under conditions of low water recharge (low W/R ratios) at some time after removal of the Paleozoic cover. In previous pages, the empirical Na–K–Ca thermometer (Fournier and Truesdell, 1973) was applied, not for purposes of thermometry, but instead to illustrate that the difference between the two water types is precisely the difference to be expected if typical basinal brines (which give erroneously high apparent temperatures) were to enter and equilibrate with basement silicates at low temperatures. As evident in figure 6, all the Precambrian-hosted minewaters show the expected shift toward low and valid Na–K–Ca temperatures, and, among them, the Keweenawan brines present the closest approach to complete low temperature chemical equilibration. By comparing the strontium isotopic compositions of the Precambrian-hosted brines and their enclosing rocks, McNutt, Frape, and Fritz (1984) provided additional evidence of the partial to complete chemical equilibration of these waters with their silicate host-rocks. If, as inferred here, basinal waters approached or attained *chemical* equilibrium with basement silicates at low temperature, this in turn implies that *isotopic* equilibration was also attained or approached between the brines and their silicate alteration products (O'Neil and Taylor, 1967).

The other striking difference between the Paleozoic- and Precambrian-hosted brines — the fact that the former plot to the right and the latter to the left of the global meteoric water line — is also consistent with the basinal water model. A few general points must be considered before turning to details of that model.

The final isotopic composition of a basinal brine that entered crystalline basement would depend both on its basement exchange history and on its earlier evolution in the sedimentary cover rocks. Processes involved in the early stage evolution of the minewaters as basinal brines are fully discussed by others (Clayton and others, 1966; Hitchon and Friedman, 1969; Hitchon, Billings, and Klovan, 1971). The strong latitudinal dependence of δD values in basinal brines indicates that the water molecules now present are dominantly meteoric and that they infiltrated the basins at some uncertain time in the past when regional temperature distributions were similar to those prevailing over North America today. The meteoric waters entering a basin are enriched in ^{18}O by exchange with

carbonates at elevated temperatures in the basinal aquifers at depth. Some deuterium enrichment also tends to occur, probably by micropore filtration, but this isotopic trend is subordinate. The relative importance of processes such as shale filtration, initial seawater evaporation, and evaporite dissolution is debatable, but the net effects are to produce chloride brines whose salinities, $\delta^{18}O$ values, and calcium contents tend to increase with basinal depth, and whose isotopic compositions retain the imprint of an initial meteoric source.

Evidence is mounting to show that such evolved basinal waters infiltrate basement rocks and there undergo significant isotopic and chemical exchange (Couture, Seitz, and Steindler, 1983; Shieh, 1983; Kombrink and Clayton, 1983; Doe, Stuckless, and Delevaux, 1983; Kyser, in press). Basinal brines circulating in basement rocks would initially form silicate alteration products under conditions of relatively high W/R ratios and elevated temperatures. These alteration products could be either enriched or depleted in ^{18}O depending upon the temperature and initial $\delta^{18}O$ values of the basinal brine and crystalline hostrocks. After uplift and removal of the sedimentary cover, brines left in the basement rocks would tend to "back-react" with their own earlier alteration products, undergoing retrograde ^{18}O depletion under the new conditions of reduced temperature and low W/R ratios. This depletion would result from the increase of ^{18}O mineral-water fractionation factors with decreasing temperature. The final $\delta^{18}O$ value of the brine would depend not only upon the lowest temperature at which equilibrium was attained between the brine and the alteration products but also upon initial ^{18}O contents of the alteration minerals. A subordinate, retrograde enrichment in deuterium might also occur because of the slight increase in deuterium mineral-water fractionation factors with decreasing temperatures.

Water-rock ratios are a key factor in this basinal water model. They must be *relatively* large in the early infiltration stage, so that the basinal waters dominate the exchange and impart their meteoric isotopic imprint on the basement alteration products. In the retrograde stage, W/R ratios must be low if these alteration products are then to dominate the retrograde exchange with a small volume of trapped water. The most likely geological factor favoring the change from high to low W/R ratios would be the tendency of basement alteration products to seal off small volumes of the brines that originally caused their formation. Recent experiments (Moore, Morrow, and Byerlee, 1983) have demonstrated that such "self-sealing" is rapid and effective, particularly at elevated temperatures and relatively low fluid flow rates such as those that should prevail in fractured crystalline basement rocks. In the model proposed here, such self-sealing is thought to have been most active in early stages when a Paleozoic cover existed.

The concept of geologically gradual ^{18}O depletion at low temperatures and low W/R ratios is certainly not new. In fact, it was specifically suggested by D. E. White (1968) as a possible explanation for the unusual isotopic composition as well as the low K, Br, and Li contents of the

Centennial mine (Keweenaw) minewaters. The process has also been documented by Rye and O'Neil (1968) who were the first to show that fluid inclusion waters trapped in oxygen-bearing host minerals at high temperatures undergo large post-entrapment ^{18}O depletions at lower temperatures. In the case they studied, fluid inclusions in quartz and calcite, initially trapped at 300°C, underwent extensive retrograde exchange with their host crystals upon cooling but did not fully equilibrate to surface temperatures in the 40 Ma after initial fluid entrapment. Full, or at least more complete, equilibration might be expected over longer periods of time such as is thought to be the case for the Precambrian-hosted minewaters. As noted before, the Ca, Na, and K contents of these minewaters suggest chemical equilibration between these waters and their basement alteration products, and such chemical equilibrium implies isotopic equilibration.

Knowing only the final isotopic composition of the Precambrian-hosted minewaters, we cannot fully quantify the basinal water model, but it can be developed schematically by making several arbitrary assumptions. This is done in figure 11, where the proposed evolution of the minewaters is traced in stages. *Stage 1* portrays the increasing salinity, δD values, and $\delta^{18}O$ values of sedimentary formation waters as they evolve from meteoric waters initially entering the ground at several different latitudes. It is at this stage that the waters inherit their latitude-dependent signatures. Line A in figure 11 represents, schematically, a similar degree of isotopic evolution of the basinal waters in the three hypothetical areas. If these waters then penetrated the basement rocks, they would form alteration products whose compositions are represented along line B. In drawing this line, we have arbitrarily assumed basement reaction temperatures of 250°C and that the ^{18}O fractionation between the alteration products and the brine is 5 per mil; clearly, other assumptions could be made but would not change the trends involved. During this early stage, it is assumed that the basement rocks become strongly grouted, if not sealed off entirely, by the alteration products themselves. In *Stage 2*, the Paleozoic cover has been removed, and the brines trapped in the basement rocks undergo their retrograde exchange with the alteration products, becoming depleted in ^{18}O and possibly enriched to a small degree in deuterium under conditions of low temperature and low W/R ratios. In figure 11, a temperature of 50°C was assumed in calculating the magnitude of the retrograde isotopic shifts. A point to be stressed is that, while the magnitude of these shifts would be similar in the three localities, the final isotopic compositions of the reequilibrated brines would certainly be different, reflecting the different δD and $\delta^{18}O$ values of the alteration products in the three regions. Those differences would, in turn, relate back to the different isotopic compositions of the local meteoric waters in each region. The final *Stage 3* in figure 11 represents mixing and dilution of these highly evolved waters with local meteoric waters at some subsequent stage(s) in the history. This is the mixing trend that is so well displayed, chemically, by the "main sequence" of the Keweenaw

minewaters (fig. 2) and, isotopically, by other known Precambrian-hosted minewaters (Frape and Fritz, 1982). Clearly, much time could lapse in Stage 3 with attendant changes in local meteoric water isotopic compositions, and so isotopic paths different from those shown in figure 11 might be followed by the waters at this stage. The Stage 3 paths chosen for figure 11 approximate actual mixing paths of the Canadian Shield waters as evidenced in the data of Frape and Fritz (1982).

Although presented only schematically here, the proposed basinal water model can be quantitatively tested. Isotopic analyses of the basement alteration products themselves are needed, because, if the model is correct, the δD and $\delta^{18}O$ values of the alteration minerals along fractures and grain boundaries in the crystalline rocks should vary with latitude. The most direct test of the proposed model would be to obtain radiometric ages for the basement alteration products. For example, Mensing

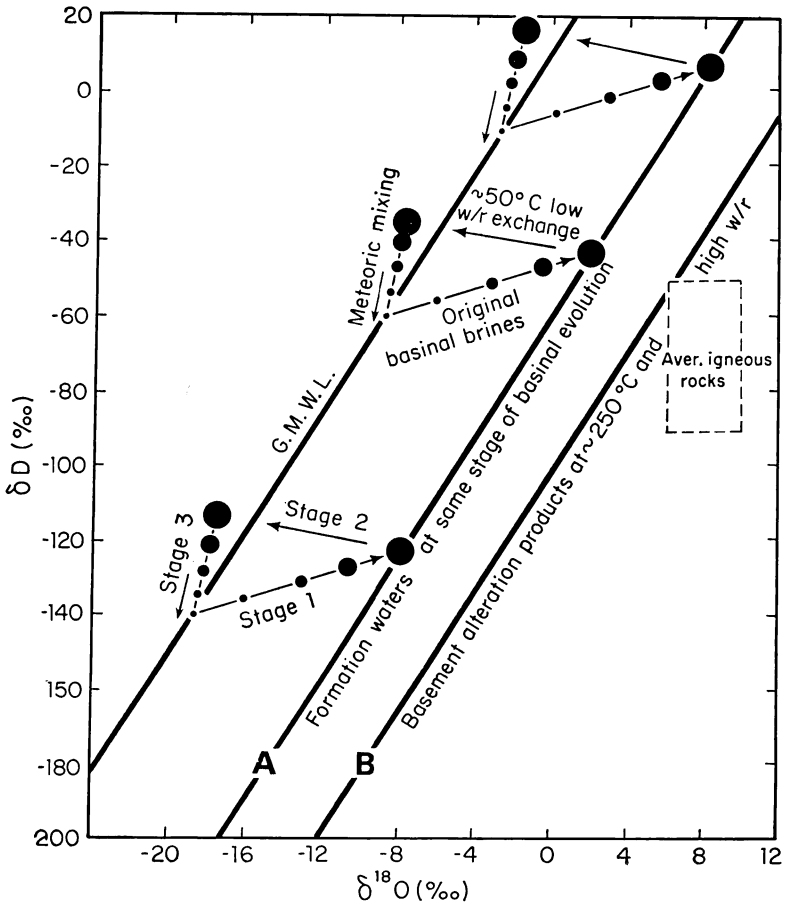

Fig. 11. Schematic illustration of isotopic evolution of Precambrian-hosted brines according to the basinal water model. See text for full discussion.

and Faure (1983) obtained a Rb-Sr date of 599 ± 69 Ma for late adularia in crystalline basement rocks in Ohio and related this to reactions of basement Precambrian weathering products with brines derived from the overlying Mount Simon Formation of Cambrian age. Further dating of this kind is critically needed.

GEOLOGICAL FACTORS

The basinal water model is difficult to prove or disprove on geological grounds, in part because the sedimentological, uplift, and erosional histories of the Canadian Shield are not well known. It is perhaps significant that the most saline minewaters yet reported all occur close to the eroded apron of Paleozoic and younger sediments lapping onto the Shield today (fig. 1). In the Keweenaw Peninsula, outliers of Silurian through Devonian sediments are preserved close to the native copper district (Case and Robinson, 1915), and coal maturation studies in the northern part of the Michigan Basin (Cercone, 1984) suggest that the Paleozoic cover in this region was about 1 to 2 km thick in Late Jurassic time. Similarly, in northern Illinois, fission track studies of crystalline basement rocks indicate removal of large thicknesses of sediments in Paleozoic time (C. Naeser, personal commun., 1984). The ages and thicknesses of former sedimentary cover are difficult to estimate in interior parts of the Canadian Shield, where Frape and Fritz (1981, 1982) and others have recorded similar, albeit less saline, Precambrian-hosted groundwaters. For the basinal model to work, clearly some sedimentary cover had to have existed over areas where the saline waters now occur, but the thickness of that original cover may not have been a critical factor. Numerous hydrological studies have shown that hot, relatively dense brines sourced at depth in Phanerozoic basins can be driven hundreds of kilometers to thin basin edges by topographically-controlled, gravitational potential alone (Garven, 1985; Garven and Freeze, 1984a and b; Toth, 1978, 1980; Toth and Millar, 1983). Thus, the ultimate basinal source of saline basement brines may have been geographically far removed from the area in which those brines occur today.

The most difficult, yet critical, problem of all is one of assigning an age to the Precambrian-hosted brines. Virtually all researchers of these brines have been careful to distinguish between the age of the water and the age of the dissolved salts, as the two need not be the same. By the basinal model we support, both the water and the dissolved salts are thought to have infiltrated basement rocks together, though both were subsequently modified by silicate-water exchange. The chief evidence for a similar infiltration age for the scattered Canadian Shield waters is the apparent latitudinal dependence of their isotopic compositions. It is certainly possible that infiltration/re-equilibration processes of the kind described could have operated continuously or repetitively over enormous spans of geologic time, but, were that the case, it seems overly fortuitous that they would have produced the present-day set of brines with such a systematic latitudinal variation.

Theoretically, the latitudinal signature of these waters might be used to assign a specific age, but the problem here is that, while paleo-latitude may be one important factor, we do not know enough about the history of other variables affecting meteoric water compositions (global climate, topographic elevations, ocean distributions) to assign an age on the basis of latitudinal water signatures alone. For example, there is mounting evidence in Montana that the isotopic compositions of Precambrian meteoric waters involved in diagenesis of the 1 Ga-old sediments of the Belt Basin were more typical of present-day latitudes than of equatorial latitudes in which the deposition and diagenesis of these sediments are known to have occurred (Rye and others, 1984). Also, in Michigan, a purely latitudinal interpretation of isotopic compositions of the meteoric waters present in the Keweenaw Peninsula in late Precambrian time (Livnat, ms) would place this part of Michigan in a sub-polar region, not in the equatorial location indicated by paleomagnetic evidence (Van der Voo and French, 1974).

Some crude constraints can be placed on the age of the minewaters of the Keweenaw Peninsula. These waters are isotopically much heavier than Pleistocene waters locally preserved in sediments of the Michigan Basin (Graf, Friedman, and Meents, 1965; Clayton and others, 1966; see fig. 3), and we can be reasonably confident that these waters are at least pre-Pleistocene in age. At the other extreme, it is unlikely that these waters date all the way back to Precambrian time. As previously noted, and as was shown in figure 3, their combined δD and $\delta^{18}O$ values are distinctly different from those of the Precambrian metamorphic fluids that produced the native copper mineralization (Livnat, ms) and from meteoric waters present in this region in late Precambrian time (Livnat, ms; Kelly and others, 1985, in preparation. Moreover, it is difficult to imagine any reasonable mechanism, whereby the minewaters could have evolved isotopically from these known Precambrian waters. Together, these constraints indicate a Phanerozoic, pre-Pleistocene age for the waters, but, beyond these broad limits, dating becomes highly speculative. If the basinal water model is correct and the minewaters were initially derived from Paleozoic cover, then for the Keweenaw Peninsula a minimum Late Jurassic ($\sim$ 150 Ma) age is indicated, because, soon thereafter, the Paleozoic cover had been removed from this region. The extent to which these age constraints extend to other brine occurrences of the Canadian Shield depends on the assumption that the latitudinal dependence of the isotopic compositions of all these Precambrian-hosted waters is reliable evidence of the same or a similar age.

SUMMARY AND IMPLICATIONS

The highly saline waters present in deep levels of the copper mines of Michigan's Keweenaw Peninsula are essentially the "type waters" for brines now known to be extremely common at depth in crystalline rocks of the Canadian and other, if not all, Precambrian shields. This paper has summarized the currently known properties of these Keweenaw waters

and has attempted to explain them in the broader context of the shield waters they represent.

Among numerous origins that have been suggested for such waters, we have advocated a basinal water model in which the waters initially evolve as formation waters in Paleozoic sediments. Details of the model will not be repeated here, but its critical elements are: (1) that the infiltrated basinal brines alter basement silicates under conditions of elevated temperatures and high W/R ratios such that they impart their own latitude-dependent, meteoric signatures to the alteration products; (2) that the alteration products partially or wholly seal off samples of these infiltrated basinal brines, allowing them to "back-react," both chemically and isotopically under new conditions of low temperature and low W/R ratios once the sedimentary cover is removed; and (3) that these evolved waters have been subsequently contaminated to varying degrees and at uncertain times by fresh meteoric waters.

The basinal water model is supported by the facts: (1) that it provides a geological denominator common to the otherwise geologically diverse areas in which the deep brines occur; (2) that basinal waters would provide an ample and reasonable source of chlorine which dominates the deep waters; (3) that the Precambrian- and Paleozoic-hosted brines have many similarities in their bulk salt compositions, Br–Ca systematics, and similar δD values within latitudinally similar regions; and (4) that both water types show a latitudinally dependent shift in their isotopic compositions. There are also conspicuous differences between these two water types, but they are the very differences to be expected if basinal waters were to re-equilibrate over long time periods with basement silicate rocks under conditions of low temperature and low W/R ratios. Such re-equilibrations include major ^{18}O depletions and the readjustment of dissolved Na–K–Ca–Mg proportions to, or nearly to, low temperature silicate buffered values. McNutt, Frape, and Fritz (1984) present strong evidence of similar equilibration of strontium isotopic compositions of the deep minewaters with their enclosing rocks.

The basinal water model is unproven, but it can be tested in specific ways. If it is correct, then the isotopic compositions of silicate alteration products associated with the Precambrian-hosted brines should, like the waters themselves, show a latitudinal dependence. An even more direct test would be provided by radiogenic dating of the silicate alteration products associated with the brine occurrences in a number of the Canadian Shield localities.

At present, ages of the Precambrian-hosted brines are poorly constrained. In the Keweenaw Peninsula, the waters and their salts are almost certainly pre-Pleistocene in age and are very probably younger than Precambrian. If, as we propose, they initiated as Paleozoic formation waters, they must have infiltrated by Late Jurassic time while some Paleozoic cover still existed in this region. The isotopic systematics suggest a similar age for all the Precambrian-hosted saline waters, but this linkage rests on the assumption that the latitudinal correlation of isotopic compositions of all these waters speaks to a similar age.

In this study, fluid inclusions in the minerals of the Keweenaw copper deposits failed to provide unambiguous clues as to the origin of the present-day Keweenaw minewaters, because the inclusion record has been contaminated by late fluids of uncertain, but probable Precambrian, age. However, it is suggested that similar fluid studies might prove more diagnostic in other regions of saline minewater occurrence where the inclusion record might be more clear-cut.

Much of the recent interest in the Precambrian-hosted waters has focussed on their possible implications with respect to subsurface storage of high level nuclear wastes. We lack expertise in this area but do believe that these waters have several implications of a seemingly contradictory nature. If the basinal water model is correct, then these present-day minewaters mark the *minimum* extent of basement penetration by basinal fluids, an extent that is remarkably deep and geographically awesome. Vovk (1985), for example, describes brine occurrences at depths as high as 11 km in boreholes penetrating the crystalline basement of the East-European platform. In contemporary hydrological modeling of sedimentary basins, crystalline basement is typically treated as an impermeable floor. This may be realistic in terms of relative permeabilities and fluid flow velocities, but the implication of the present basinal water model is that, at least in the initial stage of high W/R ratios, there was fairly efficient circulation and replenishment of basinal waters to depths in excess of at least 1 km in the fracture systems of basement rocks. Given such basement circulation, it may seem contradictory to think that waters could remain truly isolated in such an environment for any significant period of geologic time. Nevertheless, the most saline minewaters appear to present a case of natural fluid storage in which pockets of brine have been hydrologically isolated for at least 1 Ma and probably *much* longer. In our model, this isolation is due to self-sealing of the brines by their own reaction products with basement silicates. In a sense, these brine pockets might be regarded as megascopic "fluid inclusions" in which the fluid phase is a basinal brine and the host a grouted silicate rock. Like other fluid inclusions, these large ones have back-reacted, chemically and isotopically with the enclosing host upon cooling.

The implications of the saline minewaters are clearer with respect to economic mineral deposits. Whatever their age and origin, the mere presence of such chloride-rich brines in contact with ore deposits can cause mineralogical alterations and metal re-distributions. Crisman (1982), for example, has described alteration of the Keweenaw native copper ores by the saline Keweenaw minewaters. Of greater economic consequence, Guya and Kanwar (1985) have shown that secondary gold concentrations in the Copper Rand mine (Chibougamau district, Quebec) are spatially associated with pockets of the highly saline minewaters.

Finally, the basinal water model has important implications with respect to genesis of sediment-hosted Mississippi Valley-type (MVT) ore deposits. In the past, several researchers have suggested that the basinal fluids responsible for MVT deposits may have extracted some of their dissolved components during deep circulation through basement crystal-

line rocks (White, 1968, 1974; Heyl, Landis, and Zartman, 1974; Hanor, 1979; Jessey, 1983). This is suggested, if not required, by the anomalously radiogenic leads that characterize many of the North American MVT deposits (Heyl, Landis, and Zartman, 1974; Doe, Stuckless, and Delevaux, 1983), and it is further supported by the fact that, in some areas, MVT veins pass directly from the Paleozoic host rocks into underlying Precambrian basement (Guillet, 1963). The principal thrust of this paper has been to marshall the evidence that basement rocks are an integral part of basinal hydrologic regimes, and, in this respect, it is fully supportive of these earlier views on MVT mineralization.

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