ENVIRONMENTAL ISOTOPES AND GROUND WATER AT TEST SITES FOR WASTE REPOSITORIES

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ABSTRACT. — This presentation attempts to show that environmental isotopes should play a major role in hydrogeological investigations. The examples quoted are from case studies dealing with the development of waste repositories and many of the techniques described can be applied in other investigations with equal or better success.

Specifically, the presentation discussed the following approaches:

a) Deuterium (^{2}H) and ^{18}O analyses on water samples were used to characterize/distinguish different ground waters and to help define their origin and subsurface history.

b) Tritium (^{3}H) and radiocarbon (^{14}C) determinations are the most conventional tools to age date the ground waters and were especially useful to distinguish modern recharge from older ground water.

c) ^{13}C and ^{18}O abundances in fracture calcites provide an insight into the origin of the carbon and permit comments on past ground water regimes in these fracture systems.

d) ^{13}C in the aqueous carbonate species reflects the recharge environments of ground water or geochemical processes which may take place in the subsurface.

e) ^{18}O and ^{34}S in aqueous sulphate were determined to identify the origin of this ion. ^{18}O in sulphate has a special importance since oxygen isotope exchange between water and sulphate is very slow and can be used as an indirect age indicator.

An attempt was also made to show that « absolute age dating » of a ground water is not on easy task. The problem stems not only from the fact that it is difficult to define a water-mass with an unique age since flow through porous or fractured media will cause dispersion and mixing, but this inability to attach absolute ages to a water sample is also a consequence of the mode of occurrence of radioisotopes. All but tritium are present either as dissolved gases or in aqueous compounds and their abundance is, therefore, influenced by geochemical and biological processes.

However, indirect « guesstimates » are often possible especially if different techniques are combined. Thus, an integrated approach of isotopic, geochemical and hydrogeological tools is recommended and will yeld information none of these tools alone can yield.

The isotopic compositions of ground water and its dissolved constituents are dependent on recharge environments and geochemical/ biological processes within the unsaturated zone and aquifers. Numerous publications have treated this subject and comprehensive summaries on isotopic abundances can be found in FONTES (1980) and GAT and GONFIANTINI (1981). This presentation discusses applications of these techniques to problems related to the construction of repositories in geological media for the longterm containment of toxic and/or radioactive materials. In such studies the suitability of environmental isotopes as practical tools is being extensiveley tested. Results show that some are exceedingly well suited to obtain information about the origin, age and geochemical history of ground waters. For this reasons they are an integral part of hydrogeological and geochemical investigations at many test sites and potential repository environments.

Much of the work reported here has been done at a test site in Stripa (Sweden) where Swedish organizations in collaboration with foreign institutions test the behaviour of granitic rocks, in Germany and the USA where salt is considered as a disposal medium, and in Canada where crystalline rocks in general are under investigation. It is, unfortunately, not possible to discuss in this presentation all aspects of these programmes. Therefore, following an introduction to the various isotopes considered in repository studies the discussion will be limited to isotopes which fit into the general theme of this meeting. These are the stable isotopes of oxygen and hydrogen and to a lesser degree carbon and sulphur isotopes. The preceeding presentation by R. GONFIANTINI provides a

basic introduction to the topic and the following note by J.C. FONTES will explore additional aspects of isotope hydrology.

Environmental isotopes in repository studies

Several hundred stable and radioactive isotopes occur with the elements of the terrestrial environment and many of these are potential tools in hydrogeological and geochemical research because analysis of their distribution would aid in the understanding of the origin of movement of ground water
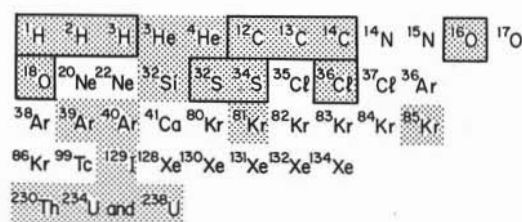

Fig. 1. — Environmental isotopes of interest in hydrogeological investigations. Those used in routine applications are circled.

as well as the genesis and geochemical history of dissolved compounds. However, very few can be used as routine tools, with limitations imposed primarily by analytical restrictions. As the analytical techniques improve many more might become available. However, in each case extensive testing and survey work has to be done before practical, routine applications are possible.

Figure 1 summarizes the isotopes which have been or will be considered in repository studies. Circled are those which today find routine applications.

Amongst the most important elements in the terrestrial environments and specifically the hydrosphere, is hydrogen. It has three isotopes: ^1H, the « normal » hydrogen which has an abundance of 99.98 %, deuterium ^2H, the principal component of heavy water $^1H^2HO$, and tritium ^3H a radioactive isotope with a halflife of 12.43 years and an abundance of $\sim 10^{-14}$ to less than 10^{-16} %. As pointed out by R. GONFIANTINI, all three isotopes are found in the water molecules and are, therefore, almost ideal tracers: deuterium to describe the origin and history of

a watere-mass and tritium to determine its age.

Equally important for hydrogeological investigations are oxygen isotopes amongst which only two play a practical role: ^{18}O and ^{16}O. Like hydrogen, both oxygen isotopes are present in water molecules and are thus direct tracers for a given water-mass. However, oxygen is even more abundant in rock forming minerals, and therefore rock-water interactions are often reflected in the isotopic composition of the participating water. Oxygen isotopes are thus ideal tracers to describe the « geochemical » history of a water-mass and, if used in conjunction with hydrogen isotope analyses, detailed information can be obtained about ground water recharge environments, the subsurface history of ground water, and the geochemical evolution of the dissolved load in a water (see below).

The chemistry of a water is related to its subsurface history and gives indications about flow paths and residence times. Isotope analyses carbon isotopes have probably been used more than any other. Carbon has three important isotopes: the common ^{12}C with a terrestrial abundance of 98.89 %, the stable isotope ^{13}C which comparises about 1.1 % of all carbon and the radioactive ^{14}C which makes up less than about 10^{-10} % of the terrestrial carbon pool, and has a half-life of 5730 years. Stable isotope analyses on aqueous carbon and carbonate minerals are an integral part of many hydrogeological studies, because such analyses contribute greatly to the understanding of the very important carbon geochemistry. ^{14}C is used to date terrestrial, carbon bearing materials but can also be used for information of the age of the inorganic aqueous carbon in a ground water and thus, indirectly, the «age» of a given ground water.

Nitrogen isotopes have been used in relatively few hydrogeological investigations, and the tool is based on variation of the ^{15}N contents (about 0.37 % of the terrestrial nitrogen pool) in nitrogen compounds in which ^{14}N in the dominant isotope (~ 99.34 %). However, the isotopic composition of nitrogen bearing substances is very strongly affected by biological processes and, therefore, the interpretation of isotope

data is difficult. For this reason, it is of limited importance in nuclear waste disposal studies except where the origin of nitrogen gas has to be discussed.

Sulphur isotopes in hydrogeological systems are affected by biological activities. For example, bacterial reduction of aqueous sulphate causes very large isotope effects between the residual sulfate and the sulfides. These differences could mask any primary differences or isotopic characteristics of the dissolved sulphate. Despite this, ^{34}S determinations should be done in all repository studies because it is possible to obtain from such analyses a large amount of information about geochemical/biological processes in aquifers, or the origin of dissolved sulfate. In hydrogeological investigations ^{34}S is the most important heavy sulphur isotope and makes up 4.21 % of all natural sulphur which is composed to 95.02 % of the ligher ^{32}S.

Sulfur isotope analyses should be combined with determinations of ^{18}O contents in the dissolved sulphate. Since the sulphate molecule is relatively stable and exchanges only slowly its oxygen isotopes with those of the water, it can either provide information about the origin of the sulfate or the degree of a time dependent equilibrium between aqueous sulfate and water.

The element following sulphur on the periodic table is chlorine which has a large number of isotopes. Of special interest, however, is ^{36}Cl a cosmogenic, radioactive isotope which has a halflife of slightly more than 300,000 years. It might prove very useful for the identification of very old ground waters although subsurface production through the action of neutrons from the uranium decay series on ^{35}Cl may be very significant (DAVIS and BENTLEY, 1981). The most abundant chlorine isotope is ^{35}Cl and less than 10^{-13} % of all chlorine in the terrestrial environment is ^{36}Cl.

Potassium is a common element in all crystalline rocks and many sedimentary minerals. It contains the isotope ^{40}K which decays into ^{40}Ar, a stable argon isotope, and ^{40}Ca. If the potassium decay occurs ina closed system then ^{40}Ar will accumulate. This accumulation can be assessed by measuring the isotopic ration of $^{40}Ar/^{36}Ar$, the lighter being the most common argon isotope. Such enrichments will be important only in very

old systems because ^{40}K has a halflife of close to 10^9 years. For the « age dating » of younger waters the cosmogenic and radioactive isotope ^{39}Ar might be used since it has a halflife of only 269 years. Unfortunately, subsurface production is again a problem and invalidates the tool in granitic rocks (LOOSLI and OESCHGER, 1979).

A very longlived and thus interesting isotope is ^{81}Kr. This noble gas isotope has a cosmogenic origin and, with a halflife of about 210,000 years has a potential of being able to characterize very old ground water systems. No routine applications have yet been performed but refined analytical techniques are presently being tested by Swiss and U.S. researchers (H. LOOSLI, pers. comm.).

The uranium decay series offers a wide variety of potential « age dating » tools. In addition, some isotopes in this series may also reflect, through their abundance in various minerals and aqueous components, the geochemical evolution of the dissolved uranium in a ground water. The decay series of interest commences with the longlived ^{238}U ($t_{1/2} = 4.47 \times 10^9$ years) which decays via ^{234}U ($t_{1/2} = 2.45 \times 10^5$ years) and many other intermediate daughters to ^{206}Pb. Applications in repository studies have recently been discussed by ANDREWS et al. (1982).

Oxygen-18 and deuterium in repository studies

General remarks

Scientific approval and construction of a nuclear waste repository will have to be preceded by extensive test site studies. These are necessary because disturbances through drilling and other activities will have to be kept to a minimum and, therefore, the number of sampling points for hydrogeological and geochemical studies will be limited. Thus, the data base needed for the interpretation of repository site data will have to be accumulated at test sites. This is especially so for geochemical data required to describe the geochemistry and evolution of ground waters encountered at depth. An important link between the two levels of investigations are ^{18}O and ^2H analyses on the waters because chemistry does not characterize a water-mass

but only its dissolved load, whereas this is achieved by isotope analyses. Where increasing salinity with depth, for example, could be considered to reflect geochemical evolution within a flow system, isotope analyses can verify this concept.

It is thus essential to undertake at test and repository sites a broad based stable isotope programme. Ideally it would commence with the establishment of a meteorological site which can be used for precipitation sampling. In order to obtain data for a local meteoric waterline, data on shallow ground waters will confirms the line and define the modern input into deeper hydrological systems. Spring data may reflect either shallow or deep systems. A monitoring programme with at least monthly sampling is recommended for a selected number of shallow wells and all springs; it will provide a first idea on the magnitude of local, active flow systems. As the drilling and exploration programmes proceed, effort should be made to collect as many subsurface samples as possible for ^{18}O and ^{2}H analyses.

If the stable isotope analytical programme is executed soon after sample collection, then the results can have an important bearing on downhole hydrological testing programmes, because they can define different watermasses and thus specify testing intervals of special importance.

The basis of all stable isotope studies is the observation that differences in isotope contents exist between different terrestrial materials. It has been shown by R. GONFIANTINI that in many instances these are a consequence of energy differences between isotopic compounds and thus differential thermodynamic behaviour. These thermodynamic isotope effects are temperature dependent and usually decrease with increasing temperature. Thus, at 30° C the isotopic difference between vapour and water is approximately 8.7 ‰ but increases to about 11.5 % at 0°. In the preceeding presentation R. GONFIANTINI also demonstrated that most precipitations in moderate and cold climates (but not tropical islands, fall on a meteoric waterline which on a global basis (YURTSEVER and GAT, 1981) is described by

$$\delta^{2}H = (8.167 \pm 0.079) \, \delta^{18}O + \\ + (10.55 \pm 0.64).$$
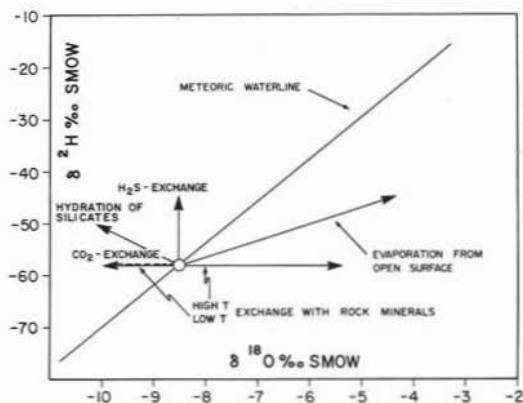

Fig. 2. — Schematic presentation of secondary processes which can alter the isotopic composition of precipitations and ground waters.

This relationship is shown in figure 2 and one must only note, that locally minor variations in slope and intercept may occur. Important, however, is that normal ground waters also fall onto this line and their isotopic compositions reflect the average ^{18}O and ^{2}H contents in the precipitations at the recharge area. An example for this is given in figure 3 which shows monthly average precipitation data collected since 1975 at a meteorological station in Atikokan (Ontario, Canada) and results obtained on shallow ground waters at a test site at Pinawa, Manitoba, which is under the same meteorological regimes.

Since the average ^{18}O and ^{2}H contents in a recharge area depend on the climatic conditions, it is possible to distinguish ground water which recharged under different environmental conditions. J.C. FONTES will explore this aspect in his presentation and a further example is quoted below.

Many processes in the hydrological cycle do not occur under isotopic equilibrium conditions since kinetic effects will determine isotopic differences between the various phases. In the hydrological cycle this is especially important for isotopic changes associated with evaporation from open water surfaces. The isotope effects which occur have been discussed by R. GONFIANTINI and are shown in figure 2. It is then important to notice that ^{18}O and ^{2}H data on water samples identify water which has undergone surface evaporation.
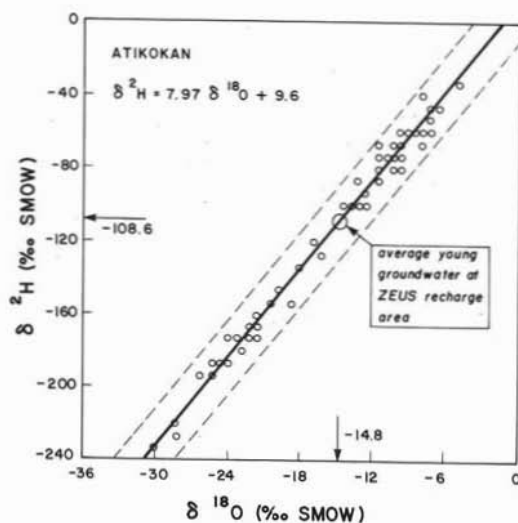
Fig. 3. — The oxygen and hydrogen isotopic composition of average monthly precipitations at Atikokan, Ontario, and average, shallow ground waters at a test site in Manitoba.

Rock-water interactions in closed systems and at elevated temperature or, possibly, during millions of years in low temperature environments, can cause significant alterations of primary isotopic compositions. Since most rock-forming minerals contain only a limited amounts of hydrogen, such exchange reactions affect primarily the oxygen isotopic composition of the water. Rock forming minerals are enriched in ^{18}O compared to normal precipitations and ^{18}O enrichments thus take place during high temperature exchange, whereas low temperature exchange can cause depletions. Figure 2 shows schematically the « oxygen-18 » shifts which results from such interactions.

In sedimentary basins where hydrogen-bearing compunds are relatively abundant (H_2S, CH_4, etc.) this ^{18}O exchange can be paralleled by minor hydrogen isotope exchange. Deuterium exchange always causes isotope enrichments in the aqueous phase as as indicated in figure 2. Also shown are other, minor processes which locally may have some influence. However, their recognition requires very detailed knowledge of the geochemical history of a water mass. Fortunately, in most cases back extrapolation to intercept with the meteoric waterline permits the determination of original, recharge com-

positions. The presentation by G. PANICHI discusses this in more detail.

^{18}O and ^2H at test sites

At the Stripa test site in Sweden numerous boreholes in the granitic pluton and the surrounding rocks yielded water and because several boreholes were drilled from mine levels (330 and 410 m below ground surface). The interception of water-bearing fractures resulted in artesian flows. It was thus possible to sample ground waters from shallow depth to depths exceeding 800 m.

The results were surprising since it was found that the deep ground waters had not only elevated salinities but also lower ^{18}O and ^2H concentrations (FRITZ et al., 1980). The ^{18}O data are summarized in figure 4 and the much lower $\delta^{18}O$ values in the deep waters are clearly visible. Since these deep waters are free of tritium, we concluded that they did not have a local, modern origin, although comparison of deuterium and ^{18}O concentrations show that they have a meteoric origin, i.e. they fall on the meteoric waterline.

The most important observation made on the basis of ^2H and ^{18}O analyses is that the deep waters, could not have formed under the climatic conditions which exist today in the Stripa area. They infiltrated during a much cooler climate and must either have travelled in the subsurface from colder inland mountain areas or formed locally
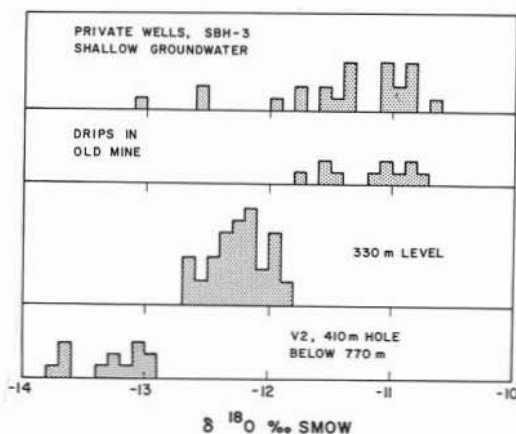

Fig. 4. — The oxygen isotopic composition of ground waters at the Stripa test site in Sweden (FRITZ et al., 1983).
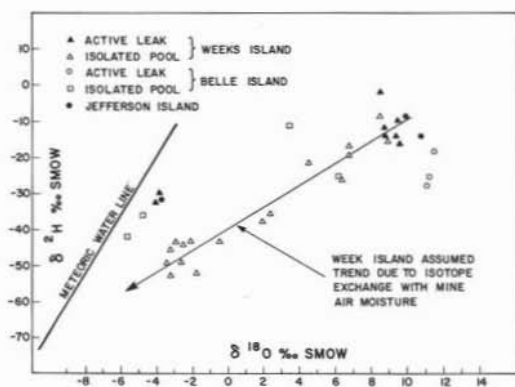
Fig. 5. — The isotopic composition of mine waters in salt domes in Louisiana (USA). Note the displacement from the meteoric waterlines of the active leaks. Ground waters which are exposed to mine air appear to re-equilibrate with mine air moisture.

Fig. 6. — Isotopic trends in the salt waters and brines occuring on the Canadian Shield. The extrapolation towards brine compositions (arrows) is possible because mixing with dilute surface waters does occur in the mines.

under cooler climatic conditions. The geochemical evolution of these waters and increasing salinities — possibly caused by the presence of minor amounts of seawater — had no measurable effect on isotopic compositions.

The situation is quite different for brines collected by KNAUTH et al. (1980) in a salt dome of Louisiana. Figure 5 summarizes his results and clearly shows the displacement of isotope data from the meteoric waterline. As pointed out above such displacement is typical in waters whose ^{18}O contents were affected by isotope exchange with rocks at elevated temperatures. The degree of this ^{18}O shift, i.e. the ^{18}O concentrations obtained by the water, are a function of temperature. They may reflect an equilibrium distribution between rock and water, and because the ^{18}O contents of the carbonate host rock into which the salt dome intruded are known, it is possible to calculate the temperature at which the exchange occurred (FRIEDMAN and O'NEIL, 1977). KNAUTH (op. cit.) suggests that in this case exchange occured at 3-4 km depth which in turn would suggest that these brines were included into the salt during diapirism which occurred 13-14 Million years ago. Thus, the fluids would be « old » waters whose presence would be a reflection of the impermeability of this salt mass and potential suitability for waste disposal.

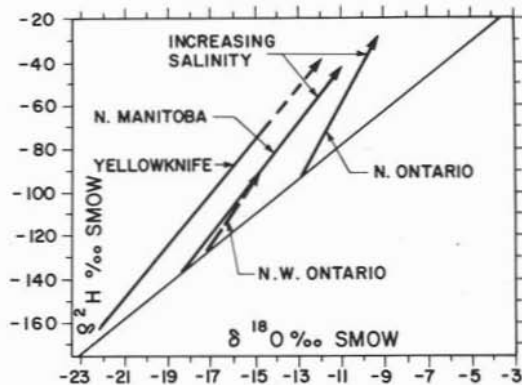This observation is very important since salt, despite its plasticity, can be disturbed

through mining so that passage ways for young ground waters are opened. This occurred in a number of salt domes in Poland, where ZUBER et al. (1979) show on the basis of tritium and radiocarbon analyses that young ground waters had penetrated to deep mining levels.

A third situation is found in the Canadian Shield where very saline ground waters occur at depths exceeding 500 m (FRITZ and FRAPE, 1982). They are Ca-Na-Cl waters with salinities exceeding 250 g/L and an isotopic composition which places them above the meteoric waterline. Their extrapolated $\delta^{18}O \sim -10 \pm 2\%_o$ and their $\delta^2H = 0 \pm 20\%_o$ (figure 6). They discharge in boreholes which intersect water-bearing fractures and shear zones and presumably were under closed system conditions enclosed in the rock mass for very long times.

Both, their chemistry and isotope contents are not easily explained and one of the key questions is whether the high chloride content is a primary feature which predates enclosure or whether it is the result of intense rock-water interactions during which fluid inclusions were leached. This latter hypothesis has been invoked for the Stripa samples (NORDSTROM, 1982) and cannot a priori be excluded for the Canadian Shield brines. However, as discussed below, in Stripa the leaching hypothesis is less convincing than the assumption that fossil seawater is present. If one assumes as a working hypo-

thesis, that the brines in the Canadian Shield had a marine origin then one either has to assume that they infiltrated after strong evaporation or that water was « consumed » under closed system conditions.

Water loss may be possible if hydration of primary silicates and formation of clay minerals takes place. If a significant portion of the water in these fracture systems were « lost » in clay minerals then the residual water would also plot above (to the left) of the meteoric waterline, because thec lay minerals « take » preferentially ^{18}O-enriched and ^2H-depleted water (figure 2). Another explanation for the low ^{18}O contents in these brines would be to assume that equilibration with the host rock occured at low temperatures and over long time spans. This cannot be excluded since the extrapolated $\delta^{18}O$ values correspond to low temperature equilibrium values between primary silicates and water.

Available data do not yet permit conclusive answers but it is important to notice that high temperature exchange had no influence on the present day composition of the brines. It was, therefore, concluded that they must be very old fluids, and that at depth exceeding 1000 m little or no fluid movements occur under present-day hydraulic gradients. The longterm containment of waste would be possible although disturbances by mining/excavation activities could change this. Isotopic data from the Canadian Shield show that in mining environments surface waters can move fast to relatively great depth (FRITZ and FRAPE, 1982).

This brief discussion on data from the different test sites serves as a good example for the value of ^{18}O and ^2H investigation since in all cases it was not only possible to show that waters at depth did not have a recent, local meteoric origin but represent old fluids. In combination with chemical analyses, it is possible to make statements about the origin and possible age of these waters.

Carbon isotopes in repository studies

Isotope analyses — ^{18}O and ^{13}C — on components of the carbonate system contribute directly to the understanding of the carbonate geochemistry and geochemical
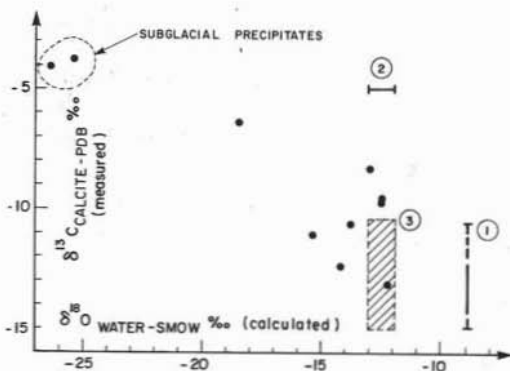

Fig. 7. — Oxygen and carbon isotopic compositions of fracture minerals and aqueous carbonate in the Stripa granite. Ranges 1 and 2 indicate present day isotope contents which determine the range of isotope contents (shaded area 3) to be expected in modern calcite deposits.

evolution of a ground water. Such knowledge is essential if ^{14}C analyses are to be interpreted (or if uranium « dating » of ground waters is attempted). Furthermore, if biologic processes occur at depth, they can often be recognized through ^{13}C analyses on the aqueous carbonate species.

Carbonate minerals precipitated from circulating ground waters are ubiquitous and occur in all types of rocks. So it is reasonable to assume that they will be encountered at test or repository sites. Their presence is a reflection of the geochemistry of the ground waters (past and present) which are/were active in the « aquifers » under investigation. Their isotopic composition indirectly describes geochemical environments. The oxygen-18 contents of carbonate minerals (e.g. calcite) reflects the isotopic composition of the water from which it was precipitated, whereas ^{13}C contents depend on the ^{13}C of the aqueous carbon (DIC). In both cases, however, the isotope uptake in the solid phase is accompanied by temperature dependent fractionation effects (see presentation by J.C. FONTES). The scientific literature reports only a limited amount of information on the isotopic composition of fracture minerals and, as example, figure 7 summarizes data obtained on fracture calcites from the Stripa granite. The oxygen isotope data document that these fracture calcites were deposited from fresh water systems with negative $\delta^{18}O$ values. The lowest values

strongly suggest that in the past glacial meltwaters with a $\delta^{18}O \sim -26\%_o$ descended to a depth of at least 200 m. Other calcite could have precipitated from the waters which today circulate through the fractures systems.

The glacial meltwater calcite show their origin also through their $\delta^{13}C$ values which approache $0\%_o$. This is expected for a system in which biogenic CO_2 is absent and atmospheric carbon dioxide or mineral carbon dominates (FRITZ et al., 1980) Biogenic CO_2 is mostly recognized by its low ^{13}C concentrations and the measured $\delta^{13}C$ value of aqueous carbonate in the Stripa ground waters (range 1 in figure 7) reflect the presence of such carbon.

The presence of biogenic soil(?)-carbon would limit recharge to pre- or post-glacial times. The ^{14}C activities of these waters are very low and correspond to values expected for carbon which is older than 25,000 years. It is virtually impossible to transform these measured radiocarbon activities into water ages (FONTES and GARNIER, 1979) but it is noteworthy that ^{14}C analyses done in Finland on saline ground waters in crystalline rocks gave high activities reflecting water ages below 5,000 years (DONNER and JUNGER, 1975). In this case the chemical data agree with the interpretation that young ground waters had mixed with fossil seawater. At Stripa, an explanation for the low activities could be that ^{14}C was lost very quickly through geochemical reactions or diffusive loss into the rock matrix (NERETNIEKS, 1981) or that seawater mixed with old ground water which already had very low ^{14}C concentrations. The latter appears to be a strong possibility since invading seawaters will not only displace pre-existing ground water but mix with it.

The problem of ground water dating with radio-isotopes is not a topic to be discussed here, but it must mentioned that at present no absolute age dating techniques exist — with the possible exception of the shortlived tritium. This is not a consequence of poor analytical techniques but simply reflects the fact that geological and geochemical systems can seldom be described with the simple assumptions implicit in most thermodynamic models.
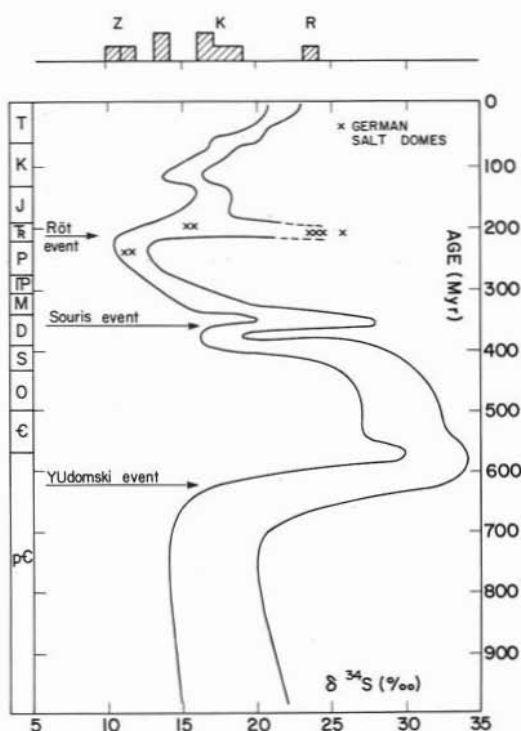

Fig. 8. — Sulphur-34 contents of marine evaporites and the aqueous sulphate in ground waters at the Asse salt-mine in Germany.

The water-sulphate system

A major constituents of many ground waters is sulphate which originates in the dissolution of sulphate minerals, primarily calcium sulphates, or the oxidation/dissolution of minerals with reduced sulphur. Thus the ^{34}S contents of this sulphate reflect the origin of the sulphur — provided no major redox-reactions occur within the aquifer. The ^{18}O contents are either determined by the dissolving sulphate, by the environments in which the reduced sulphur became oxidized, or by isotope exchange between sulphate and water. The latter aspect is very important because under favourable circumstances it can provide a tool for age estimates of the sulphate-water system and thus the ground water.

Oceans and evaporitic rock sequences are the largest reservoirs of sulphate whose isotopic composition is largely determined by a balance between input and output (CLAY-

POOL et al., 1980). The $\delta^{34}S$ of modern marine sulphate is close to $+20\%$ CDT and shows remarkably little variation. Large global changes did occur, however, and are reflected in the $\delta^{34}S$ values of evaporitic sequences. Figure 8 summarizes these changes which cover a range of about 20%. Since the dissolution of these sulphates by percolating ground waters is not accompanied by any measurable isotope effects the $\delta^{34}S$ values of the aqueous sulphate will give indication about the flow path of a ground water. This assumes that sulphur reducing bacteria are not active in the subsurface.

Also shown in figure 8 are data obtained on sulphate analyses from ground waters in the vicinity of the Asse salt dome in Germany. They distinguish ground waters which had reached the salts of the Zechstein Formations from those which obtained their chemical load in Middle and Upper Triassic rocks. Gypsum in the Zechstein has $\delta^{34}S$ values close to $+11\%$, whereas the latter may be as high as $+24\%$. These differences are reflected in the aqueous sulphate (FRANK, 1974).

An intersting aspect in these studies concerns the ^{18}O contents in aqueous sulphate: it can reflect the solid sulphate source in the case of gypsum dissolution, the isotopic composition of water and oxygen which participate in the oxidation of reduced sulfur to sulphate or an isotope exchange between water and sulphate. The rate or ^{18}O exchange between aqueous sulphate and water is strongly dependent on pH and can be very variable. LLOYD (1968) attempted to evaluate this relationship and from his data PEARSON and RIGHTMIRE (1980) derived the folloing tentative relationship for the half time of exchange:

$$log\ t\ 1/2\ (hours) = 2.15 \times 10^3 \times T^{-2} + 0.44\ pH - 3.09.$$

The relationship shows that in an acid environment the exchange occurs rather rapidly but at normal ground water pH many thousands of years are required before equilibrium is established. Thus, if a ground water is rather young it is unlikely that equilibria values are found.

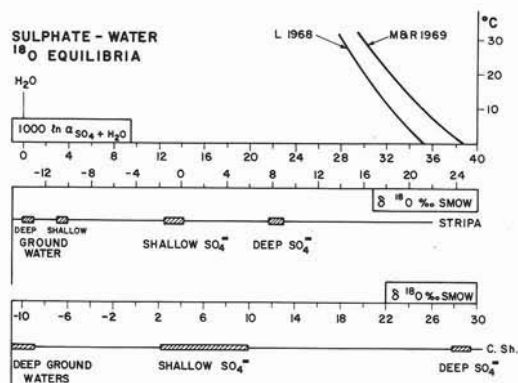This is the case in Stripa, as shown in figure 9. The equilibrium difference in ^{18}O

Fig. 9. — Oxygen-18 in the sulphate-water system. The top of the figure shows the expected ^{18}O fractionation between aqueous sulphate and water (MIZUTANI and RAFTER, 1969; LLOYD, 1968). The central part shows the data obtained on the Stripa samples and below are the results obtained on aqueous sulphate from Canadian Shield waters. Isotopic equilibrium has apparently been established in the latter.

would be close to 30% (see top of figure 9) and under equilibrium conditions the expected value would be $+17\%$, a value quite different from the measured one. As mentioned this isotope exchange is strongly pH dependent, and the estimated halftime of reaction is close to 150,000 years in the deep Stripa ground waters which have pH values close to 10 but only 5,000 years if the pH were about 7. Thus, age estimates are difficult to make. The initial $\delta^{18}O$ value of the sulphate is unknown as is the degree of mixing of multiple sources. Furthermore, the pH of the deep water might not have been near 10 throughout its total residence time and thus ^{18}O exchange between sulphate and water would have been much faster than under today's condition. However, should the sulphate have a marine origin and should the pH have been high during most of the subsurface history of these waters, then the lack of isotopic equilibrium would indicate an age of at most a few thousand years. If these conditions are not met, then a preglacial marine origin cannot be excluded.

The situation is quite different for the waters in the Canadian Shield because there there equilibrium conditions appear to exist. Moreover, one notes again that the equilibrium values correspond to a low temperature environment such as also suggested by

the ^{18}O in the water. Chemical and isotope data provide thus a strong argument to suggest that these waters have been a long time in the subsurface, and if indeed low temperature equilibria between water and hardrock were established they would have to be millions of years old.

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