

**SIGNATURES OF RADIOGENIC ISOTOPES IN DEEP  
SUBSURFACE WATERS IN CONTINENTS**

**Sam CHAUDHURI<sup>(\*)</sup>**

Department of Geology, Kansas State University  
Manhattan, Kansas 66506 (U.S.A.)

and

**Norbert CLAUER**

Centre de Géochimie de la Surface  
1, rue Blessig, 67084 Strasbourg (France)

Deep continental waters may be broadly divided into those occurring in sedimentary basins and those found in crystalline rocks of metamorphic and igneous origin. Whereas they have a similar range of salinities, these two water types are chemically dissimilar and have very different flow characteristics. The high salinities common to both waters have been known for more than hundred years due mainly to exploration activities in search of hydrocarbon deposits and to extraction activities of ore deposits from mines in crystalline rocks. In recent years, interest in evaluating the potential of crystalline rocks for storage of wastes in the subsurface and for geothermal energy has enhanced our understanding of the origin of saline waters in these rocks.

The use of radiogenic isotopes is relatively recent in studies

---

<sup>(\*)</sup> Presently at the Centre de Géochimie de la Surface Strasbourg (France)

of waters deep in the continent and only began in the late 1970s with investigations of Sr isotopic compositions of oil-field waters (Chaudhuri, 1978; Sunwall and Pushkar, 1979). Works in the last decade have shown that Sr isotopes can be very useful to study the origin of solutes in these waters and the flow dynamics of subsurface waters in sedimentary basins. By comparison, studies of radiogenic isotopes in waters in crystalline rocks are few, beginning with the work of McNutt et al. (1984). These studies, while providing some important clues to the understanding of origin of the solutes, have offered some fresh perspectives to the intriguing question of any genetic link between the waters in sedimentary basins and those in crystalline rocks in the continent. Although reports on Sr isotopic compositions of deep subsurface waters in the continent are still few, literature on their Nd and Pb isotopic compositions is non-existent. This discussion will therefore focus on the significance of Sr isotopic data.

Deep subsurface waters have been variously termed as brines, formation waters, oil-field waters, or connate waters. The description for each of these terms has been well covered in the publications of White (1965) and Collins (1975). The salinities of deep subsurface waters are varied from a value nearly the salinity of average sea water to as much as ten times that of sea water. Although the term brine has been used loosely by many to include all formation waters, Davis (1964) preferred to apply the term brine to only those waters whose salinities are at least 100,000 mg/l. In this paper we use the term brine or highly saline water interchangeably to include all formation waters whose salinities are higher than that of the average sea water. We also use the terms formation water and oil-field water interchangeably to include those waters which have been produced recently from wells not experiencing any artificial recharge.

#### DEEP SUBSURFACE WATERS IN SEDIMENTARY STRATA

Oil-field waters are mainly of Na-Cl to Na-Ca-Cl type. Some

perspectives on the ranges of concentrations of the different dissolved constituents in formation waters of sedimentary basins can be obtained from a large collection of data published in articles by White (1965) and Collins (1975).

In early debates the high salinity of waters in deep basins was generally attributed to a connate marine origin. But this idea was radically changed when Clayton et al. (1966) demonstrated from stable isotope compositions that local meteoric water is a major component in many deep basinal waters. Subsequent studies on stable isotope compositions of many formation waters have generally corroborated Clayton et al.'s conclusions. Hitchon and Friedman (1969) showed that the other component of deep basin waters could be either evaporated sea water or diagenetic water. However, as documented by Kharaka et al. (1979) in northern Gulf of Mexico basin, meteoric water can be absent in formation waters such as in geopressured zones. Kharaka and Carothers (1986) provided examples of a wide variety of relationships between D and  $^{18}\text{O}$  contents of formation waters and offered genetic implications of these relationships. An elaborate account of stable isotope compositions of formation waters is given in the companion publication of Kharaka and Thordsen (this volume).

Whilst salinities of deep subsurface waters may be compared to that of an average sea water or an evaporated sea water, the two types of water are in many ways different from each other. Collins (1975) provided a convenient way of comparing the chemical compositions of oil-field waters with that of sea water. The concentration of an element in formation water is compared to the expected concentration of the same element in sea water with its chloride content being the same as that in the formation water. In general, deep continental waters are highly enriched in Ca, Sr, and Li contents, slightly to moderately enriched in Br contents, and moderately to highly depleted in Mg, K, and  $\text{SO}_4$  contents relative to sea water. The Na concentrations of deep continental waters are either the same as or slightly different than that of sea water. Relative abundances of some elements between deep continental waters and sea water are illustrated in figure 1.

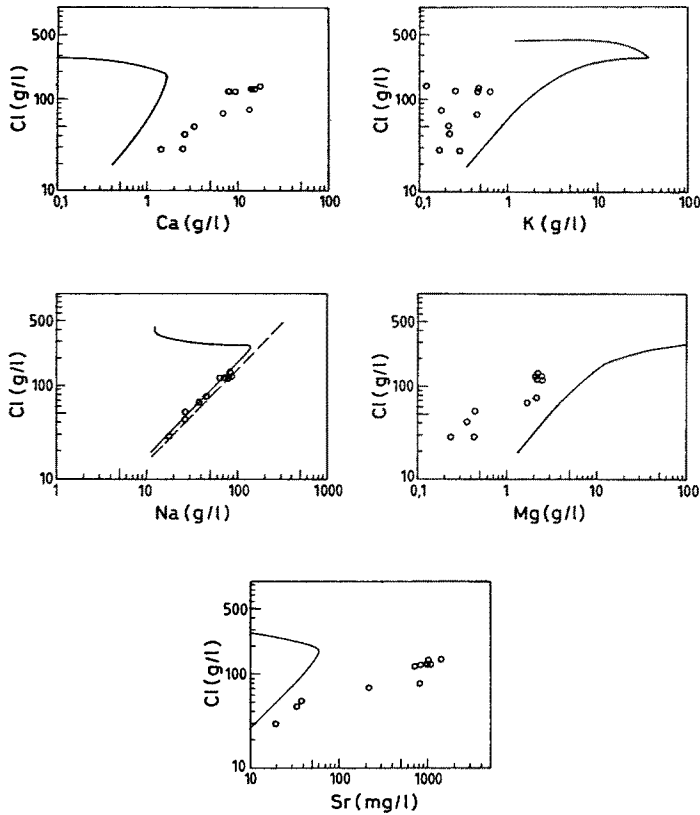


Figure 1: Relative abundances of different elements in deep subsurface waters relative to sea water. In each diagram, the curve represents the evolutionary pathway of the elements in evaporating sea water

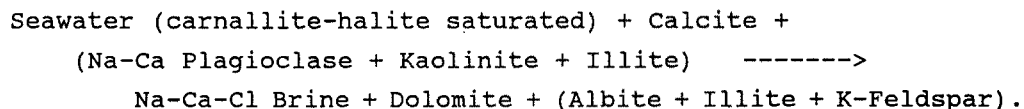
### Origin of Salinity of Waters in Sedimentary Basins

Notwithstanding the long interest in studies on oil-field waters, interpretation of their salinity or of the origin of their solutes remains controversial. Russell (1933) listed four potentially important mechanisms which can account for the origin of dissolved solids in waters deep in sedimentary basins: (a) infiltration of brines from evaporation of sea water at the surface, (b) exchange and adsorption of anions and cations by clays, (c) dehydration and hydration of minerals, and (d) reverse osmosis. In the current debate, some of Russell's suggestion have been modified or rejected in light of continued emergence of new information about the chemical and isotopic compositions of the waters.

Saline subsurface waters in sedimentary basins have generally been explained in terms of either some sea waters or continental meteoric waters whose chemical compositions have evolved in the subsurface by combined effects of physical and chemical processes including dissolution-precipitation and recrystallization of minerals, oxidation-reduction, ion exchange, and mixing with other waters. The models which have been advanced in recent years to account for the origin of solutes in formation waters in sedimentary basins are: (a) release of interstitial sea water from evaporitic deposits in subsiding basins and subsequent reactions with carbonate and silicate minerals in the overlying sedimentary strata (Carpenter, 1978; Egeberg and Aagaard, 1989), (b) dissolution of salts and subsequent albitization of feldspar, especially plagioclase, and illitization of smectite (Land and Prezbindowski, 1981; Land, 1987), (c) shale-membrane filtration (McKelvey and Milne, 1962; Hanshaw and Coplen, 1973; Kharaka and Berry, 1973), (d) mineral dehydration reactions (Graf and Anderson, 1981), and (e) infiltration of sea water in equilibrium with ice and subsequent reactions with carbonate and clay minerals (Herut et al., 1990).

The influence of membrane filtration by clays and shales, also known as ultrafiltration or reverse osmosis, on the chemical and stable isotope compositions of waters has been documented by experimental studies (McKelvey and Milne, 1962; von Engelhardt and Gaida, 1963; Coplen and Hanshaw, 1973; Hanshaw and Coplen, 1973; Kharaka and Berry, 1973; Fritz and Edy, 1985). These experiments support the importance of this process, but field evidence questions its efficiency. Indeed, many field data have shown that the Ca/Na ratio of subsurface waters often increases with depth, which is contrary to the experimental observations of Kharaka and Berry (1973) who related the discrepancy to the effects of unnaturally high pressure gradients needed to perform the experiments. Ultrafiltration has been viewed skeptically because subsurface brines occur in many areas where sedimentary sequences lack clay-rich beds necessary to generate increased salinity in waters. The difficulty of explaining linear increases in salinity with depth is another reason for questioning the influence of ultrafiltration in the chemical evolution of deep subsurface waters (Dickey, 1969).

Current prevalent ideas on the origin of salinity of formation waters are along the lines of mineral-water interactions. The work of Rittenhouse (1967) on variations in Br contents of oil-field waters provided the basis for developments of some of the more recent chemical models emphasizing the roles of mineral-water interactions in the evolution of high salinity in formation waters. Evaluating Br/Cl of brines in Upper Jurassic sedimentary strata in central Mississippi, Carpenter (1978) contended that many subsurface brines could have evolved from evaporated sea water, possibly carnallite-saturated water, entrapped as interstitial fluids in evaporite deposits in a subsiding basin and subsequently expelled to overlying sedimentary strata where the fluids inherited Na-Ca-Cl characteristics through different diagenetic mineral-water reactions, dolomitization accounting for depletion of Mg and some enrichments of Ca and Sr in the waters. Carpenter also suggested that the study of spatial variations in authigenic minerals and chemical compositions of brines in sedimentary basins could help to establish migration and evolutionary paths of marine brines. Carpenter's model depicts the following reaction for the chemical evolution of brines:



Land and Prezbindowski (1981) presented a different view for the evolution of subsurface brines in carbonate rocks of the Lower Cretaceous Edwards Group in south-central Texas. They questioned Carpenter's model because of lack of evidence of dolomitization in the subsurface in south-central Texas and of the requirement of very high temperature unlikely for the brines to be in thermodynamically equilibrium during calcite-dolomite reaction. They also remarked that Carpenter's model requires an unlikely high amount of carnallite to explain the origin of the brines. Land and Prezbindowski, therefore, suggested that dissolution-recrystallization of halite followed by albitization of plagioclase could be a logical mode of evolution of the brines in south-central Texas. The reaction in Land and Prezbindowski's model may be expressed as:

Halite + Na-Ca Plagioclase + Water ----->

Na-Ca-Cl Brine + Albite.

More recently, Land (1987) propounded another model to explain the origin of many Ca-Cl type brines characterized by molar Na/Cl ratio much less than 0.86, a value which is typical for average sea water. According to this model, meteoric water in its involvement with dissolution-recrystallization of salts in the subsurface becomes nearly saturated with respect to halite and subsequently the water evolves through reactions with several different major silicate minerals, which include albitization of detrital feldspar, especially plagioclase, and formation of illite from smectite. The albitization leads to removal of Na from the water and addition of Ca, Sr, K, Ba, etc. to the water and the illitization results in loss of K by the water. The reaction according to this model is expressed as:

Halite + Plagioclase + K-Feldspar + Smectite + Meteoric Water

-----> Na-Ca-Cl Brine + Albite + Illite.

Graf and Anderson (1981) advocated that mineral dehydration reactions are important for the origin of salinity of formation waters in sedimentary basins. They suggested that conversion of gypsum to anhydrite, halloysite to kaolinite, smectite to illite, and analcime to albite could be potentially important reactions which influence the chemical compositions of subsurface waters. Dehydration of both gypsum and halloysite is dependent on the pore-fluid salinity and the reactions can affect the concentrations of some trace elements in the waters. As conversion of analcime to albite and smectite to illite involves other sedimentary minerals, the reactions can lead to significant changes in both major and trace element contents of the waters. Zeolite and halloysite occur in restricted geologic environments, and hence the dehydration reactions involving these minerals appear to have limited roles in influencing the chemical compositions of subsurface waters in sedimentary basins. More recently, Herut et al. (1990) advanced the idea that salinity of formation waters may be linked to mineral-water reactions by residual sea waters after ice formation. The reaction suggested is expressed as:

Sea Water (in equilibrium with ice) + Calcite + (Smectite)  
 -----> Na-Ca-Cl Brine + Mirabilite + Dolomite + (Chlorite).

### Strontium Isotopes and Origin of Salinity in Basinal Waters

Chaudhuri (1978) was the first to suggest that Sr isotopic data could be potentially very useful in the investigation of chemical evolutionary history of subsurface brines. Analyzing Sr isotopic compositions of oil-field waters from Kansas and Colorado, he found that these waters to be significantly enriched in  $^{87}\text{Sr}$  relative to their host carbonate rocks, indicating that the waters inherited their isotopic signatures outside the present aquifers and that the Sr isotopic compositions may provide important clues to origin and migration of the fluids and hydraulic relations among different aquifers. Subsequent Sr isotopic studies of other subsurface waters from elsewhere have generally confirmed these observations (Sunwall and Pushkar, 1979; Starinsky et al., 1983; Stueber et al., 1984, 1987; Burtner, 1987; Chaudhuri et al., 1987; McNutt et al., 1987; Lowry et al., 1988; Banner et al., 1989; Egeberg and Aagaard, 1989; Chaudhuri et al., in press).

Table 1 provides a list of Sr isotopic values for formation waters from a wide variety of locations. The Rb/Sr ratios of the waters are very low, generally less than 0.05, due to very low Rb contents of commonly less than 1 mg/l and very high Sr contents of several tens to few hundreds of mg/l. Hence the growth of radiogenic  $^{87}\text{Sr}$  from the decay of  $^{87}\text{Rb}$  in these waters is negligibly small. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of a large number of oil-field brines and other deep saline waters are between 0.707 and 0.710 (Fig. 2). Illustrations of formation waters with this range of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are from the Smackover Formation in southern Arkansas (Stueber et al., 1984) and from Paleozoic strata in the Illinois, the Michigan and the Appalachian basins (Stueber et al., 1987; McNutt et al., 1987). The number of formation waters with  $^{87}\text{Sr}/^{86}\text{Sr}$  higher than 0.710 is relatively small (Chaudhuri, 1978; Burtner, 1987; Chaudhuri et al., 1987; Lowry et al., 1988; Banner et al., 1989; Egeberg and Aagaard, 1989; Chaudhuri et al., in press). The Sr contents of these waters are often limited to only few tens of mg/l or less .



Table 1: Range of Sr contents and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in subsurface waters

Samples	Data (1)	Sr (2)	$^{87}\text{Sr}/^{86}\text{Sr}$	
<u>Israel</u>				
Ss+Ds (U.Mioc.)	2	57-350	0.7087-0.7090	(1)
Ss+Ds (L.Cret.)	14	28-211	0.7075-0.7081	(1)
<u>Kansas</u>				
Ds (Hunton-Sil.)	4	6.9- 7.1	0.7113-0.7118	(2)
Ss (Cherokee-Penn.)	4	45- 115	0.7128-0.7248	(2)
Ls (Warsaw-U.Miss.)	13	40- 46	0.72195-0.72306	(5)
<u>Kansas and Colorado</u>				
Ds (Osage-Miss.)	3	21- 660	0.7129-0.7341	(2)
Ds Spergen-Miss.)	2	22- 42	0.7264-0.7341	(2)
<u>Arkansas</u>				
Ls (Smackover-U.Jur.)	32	169-2960	0.7080-0.7101	(3)
Sh+Ls (Hossten-L.Cret.)	6	239-1540	0.7090-0.7112	(3)
<u>Ontario and Michigan</u>				
Ls (Black River-M.Ord.)	7	418-1319	0.70957-0.71032	(4)
Ls (Trenton-M.Ord.)	28	400- 765	0.70901-0.71041	(4)
Ds (Guelph-M.Sil.)	12	436-1220	0.70849-0.70946	(4)
St (A2 Unit-U.Sil.)	2	1620	0.70853-0.70866	(4)
Ls (Dundee-M.Dev.)	4	12-1120	0.70816-0.70949	(4)
Ss (Berea-L.Miss.)	6	1210-1750	0.70807-0.70915	(4)
<u>Illinois</u>				
Ls (Galena-U.Ord.)	7	34- 873	0.70848-0.71043	(6)
Ds (Kankakee-L.Sil.)	9	6.6- 252	0.70952-0.71084	(6)
Ls (Niagara-U.Sil.)	28	1.7- 908	0.70913-0.71076	(6)
Ds (Geneva-M.Dev.)	2	177- 180	0.70978	(6)
Ls (Lingle-M.Dev.)	3	256- 390	0.70955-0.70996	(6)
Ss (Carper-L.Miss.)	3	133- 745	0.70871-0.70933	(6)
Ls (Ste Genev.-Miss.)	5	131- 641	0.70812-0.70895	(6)
Ss (Aux Vases-Miss.)	3	171- 418	0.70886-0.70967	(6)
Ss (Cypres-Miss.)	2	138- 377	0.70928-0.71041	(6)
Ss (Spoon-Penn.)	2	103- 109	0.71051-0.71052	(6)
<u>Utah and Colorado</u>				
Ss (Weber-Perm.Penn.)	9	4.7- 201	0.7104-0.7195	(7)
<u>Wyoming</u>				
Ss (Tensleep-Perm.Penn.)	5	7.6- 9.5	0.7131-0.7179	(7)
<u>Missouri</u>				
Ls+Ds (Burlingt.-Miss.)	3	8.1-11.6	0.71578-0.71607	(8)

Ls=limestone; Ds=dolostone; Ss=sandstone; Sh=shale; St=salt;  
 (1) number of measurements for each unit; (2) amounts in  $\mu\text{g/g}$ ;  
 Ref. 1=Starinsky et al., 1983; 2=Chaudhuri, 1978; 3=Stueber et  
 al., 1984; 4=McNutt et al., 1987; 5=Chaudhuri et al., 1987;  
 6=Stueber et al. 1987; 7=Burtner, 1987; 8=Banner et al., 1988.

As compared to sea water, many brines are often considerably enriched in Sr. The concentrations of Sr in oil-field brines are highly varied from about 0.1 to more than 2,900 mg/l (Table 1), whereas that of average sea water is about 8 mg/l and that of evaporated sea water could be as much as 20 mg/l. Thus, high Sr contents for many brines suggest that they had to evolve through some processes of Sr enrichment, such as dolomitization, recrystallization of calcite, conversion of calcite to aragonite, conversion of anhydrite to gypsum, albitization of plagioclase, dissolution of celestite, ultrafiltration, and/or ion exchange with clay minerals. Dissolution of gypsum or calcite can also increase the Sr content of the waters, but the amount of Sr which may be released from this process would be generally too small to account for

the very high Sr contents of most brines. Depending on the process of Sr enrichment, the marine Sr isotopic signature of the original interstitial water may or may not be obliterated. Dolomitization, recrystallization of marine carbonate minerals, rehydration of anhydrite, and dissolution of celestite are not likely to change significantly the marine isotopic signatures of the waters, because Sr in rocks and minerals involved in these diagenetic processes is also of marine origin. The effect of albitization of plagioclase on the Sr isotopic composition of marine water cannot be accurately predicted, because the Sr isotopic compositions of plagioclase minerals are commonly widely varied, ranging from values which are less than to somewhat more than that of sea water. It can, however, be assumed that plagioclase minerals, unless they are very old, are not very high in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios due to their very low Rb/Sr ratios, in which case the albitization process may not greatly increase the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the waters. Thus, from the viewpoint of Sr isotopic composition, Sr enrichment processes of subsurface waters cannot be distinguished when the isotopic values of the waters are within the range of values for marine Sr. The data presented in figure 2 indicate that nearly 50% of the samples have Sr isotopic values which are within the Phanerozoic marine Sr isotopic values between 0.7068 and 0.7092. In these instances, as discussed above, while the Sr isotopic data strongly suggest a source for marine Sr in the waters, they do not provide any definitive clue as to the

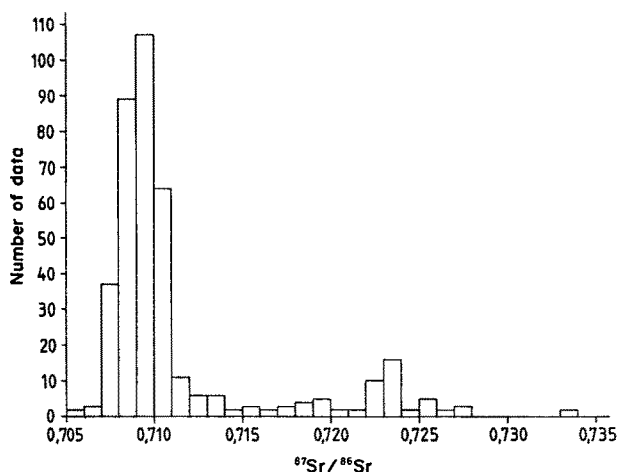


Figure 2: Histogram of Sr isotopic data of formation waters

process that might have caused the enrichment of Sr in these waters.

As noted earlier, many deep subsurface waters have Sr isotopic values which are well above the range of isotopic values for marine Sr. Evidently these waters acquired during their chemical evolution some radiogenic Sr from one or several sources. Different explanations have been offered for these  $^{87}\text{Sr}$  enrichments. Ion exchange with clay minerals such as illite (Stueber et al., 1984, 1987; McNutt et al., 1987) and leaching and dissolution of  $^{87}\text{Sr}$ -enriched alkali feldspar or even albitization of plagioclase (Burtner, 1987; Chaudhuri et al., 1987) are the common explanations for isotopic signatures above the value of marine Sr. We should add that evaporite deposits could also serve as a source of radiogenic  $^{87}\text{Sr}$  in some instances, as Register and Brookins (1980) reported  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios as high as 1.641 for potassium-rich salts, suggesting that dissolution of these salts can contribute to the high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for brines.

While illite and illite-smectite mixed-layer minerals do contribute some Sr high in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios relative to the values for marine Sr, we view the role of ion exchange by clay minerals to be minor in elevating the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, at least those of deep subsurface waters whose values are higher than 0.715. The reaction between clay minerals and formation waters can be described as either an ion-exchange phenomenon, or a recrystallization or transformation process of clay minerals. Leaching experiments on illite and illite-smectite mixed-layer minerals have shown that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the exchangeable Sr, which includes both the surface-adsorbed and interlayered Sr, are seldom higher than 0.714 and often less than 0.712 (Clauer, 1976; Chaudhuri and Brookins, 1978; Clauer et al., 1984; Clauer et al., 1989). These studies also indicate that the amount of exchangeable Sr in illite-rich clay minerals is only about a few micrograms per gram of the materials, while in smectite it is about ten times that in illite. We also measured the total amounts of exchangeable Sr in an illite and a smectite. In leaching 1g of each sample in 25 ml of 0.2 molar HCl at room temperature, the total amount of exchangeable Sr for the illite sample was found to be about 0.1  $\mu\text{g/g}$  of material per ml

solution, and that for the smectite sample was about 6 times higher. The data on the illite were used to evaluate the possible influence of ion-exchange reactions on the Sr isotopic compositions of brines from Smackover Formation in Arkansas for which Stueber et al. (1984) reported  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ranging from 0.7100 to 0.7110 and Sr contents between 580 and 2,930 mg/l. If we assume that Sr in these brines derived from two sources, one of which came from a marine source with an  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of about 0.709 and the other from exchangeable Sr of clay minerals having an  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of about 0.712, the mass balance calculation shows that about 200 to 980  $\mu\text{g}$  of Sr in each ml of brine had to be derived from clay minerals through ion-exchange process. This would necessitate that each ml of water had to react with 2,000 to 10,000 g of clay minerals. Such a low water/illite ratio renders the ion-exchange with illite as an unlikely cause for the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the brines to be significantly higher than the sea-water value. A similar mass balance calculation with smectite, which has a lower overall  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio than illite, would also require an unreasonably low water/smectite ratio to elevate significantly the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the water above the sea-water value. Ion-exchange with clay minerals is even more unlikely for the waters with Sr isotopic values much above 0.715, such as those found for the oil-field waters in Paleozoic sedimentary rocks in western Kansas and eastern Colorado (Chaudhuri, 1978; Chaudhuri et al., 1987; Chaudhuri et al., in press).

Transformation of smectite to illite is a common process of clay mineral alteration during burial diagenesis. Noting that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of brines in the Illinois basin with values around 0.710 are higher than the isotopic values of marine Sr, Stueber et al. (1987) related the high values for the brines to movements of evaporite-related K-rich brines through shale beds causing transformation of smectite to illite, as Carpenter (1978) previously suggested, with attendant elevation of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the waters. Many believe that the K necessary for the transformation of smectite to illite in deep diagenetic environment comes from destruction of alkali-feldspar or detrital mica (e.g. Hower et al., 1976). This destruction of alkali-bearing silicate minerals, often highly enriched in  $^{87}\text{Sr}$ , would elevate the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the

pore waters. Hence, the destruction of alkali-bearing silicate minerals such as feldspar and mica, and not the transformation of smectite to illite, is the most dominant cause for the elevated  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of brines in the Illinois basin. This argument does not rule out the importance of transformation of smectite to illite in causing elevation of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of pore waters, but the effect by the clay transformation is in most cases overshadowed by the destruction of alkali-bearing silicate minerals. Independent criteria are needed to evaluate the importance of the role of illitization of smectite.

In summary, we believe that reaction with feldspar more than that with clay minerals causes the elevation of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of many deep subsurface waters. The role of clay minerals can become important in the filtration processes, but experimental studies are needed to assess the importance of ultrafiltration in the evolution of Sr isotopic compositions of formation waters.

#### Strontium Isotopic Relations between Waters and Host Rocks

The Sr isotopic relationship between deep subsurface waters and their present-day host rocks is an important consideration in the reconstruction of the chemical evolution of the waters and in the determination of the role of formation waters in the diagenetic modifications of the host rocks. Many studies on deep subsurface waters have shown that these waters are not in Sr isotopic equilibrium with carbonate minerals of their host rocks. For example, highly saline oil-field waters having  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of about 0.722 were found in Paleozoic carbonate rocks of west-central Kansas with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of about 0.709 (Chaudhuri et al., 1987). Similarly, in southwestern Kansas, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of oil-field waters have been found to be different from  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of ankerite cements in Pennsylvanian sandstone reservoir rocks (Chaudhuri et al., 1985). McNutt et al. (1987) investigated several reservoir rocks and late-stage diagenetic mineral phases associated with brines in the Michigan and the Appalachian basins. Except in one case where diagenetic calcite appeared to have nearly the same Sr isotopic composition as the brine, secondary mineral deposits and their host

rocks were found to be isotopically different from the present-day brines. Stueber et al. (1984), in their studies of brines in the Smackover Formation of Arkansas, also found Sr isotopic dissimilarities between brines and host rocks. Recognizing that oil-field brines are often deficient in Mg, many have been inclined to believe that existing formation waters were responsible for large scale dolomitization of limestones in the sedimentary basins. But the numerous examples of the lack of isotopic equilibrium between deep subsurface waters and the associated reservoir rocks suggest that much of recrystallization-precipitation history of reservoir rocks pre-dates the migration and entrapment of the existing waters. This observation of the lack of isotopic equilibrium between waters and host rocks also strengthens the argument that much of mineralogic stabilization of carbonate rocks in sedimentary basins occurs during early diagenesis as suggested by Clauer et al. (1989).

Aquifer in deep subsurface often contains records of different episodes of influxes of chemically different waters that entered the aquifer. Secondary vug-filling minerals in the same reservoir rock can differ from each other in their Sr isotopic compositions (Cassan et al., 1983; Chaudhuri et al., 1987; McNutt et al., 1987; Stueber et al., 1987). The chemical relationship between the present formation waters and the previous ones, the clue of which resides in the secondary minerals, has not been seriously examined. Studies of fluid inclusions in secondary minerals of reservoir rocks are needed along with the studies of the formation waters to describe time-dependent changes in the chemistry of waters which have infiltrated the aquifer. The work of Rickenbach (1988) has shown considerable promise in the value of combining fluid-inclusion data with the geochemical data on formation waters to understand the hydrochemical evolution of a reservoir. He described two generations of fluid inclusions in quartz overgrowths in sandstones of the Mahakam delta in Indonesia and noted that both the temperature and the salinity of the late included fluids are apparently the same as that of the saline waters presently occurring in the rocks, the temperature and salinity of the early fluid being higher.

### Variations in Strontium Isotopic Composition of Formation Waters

Knowledge of Sr isotopic variations of formation waters in different stratigraphic units of a sedimentary basin can give insight to the configurations of fluid paths. Such knowledge can be used to understand movement of ore fluids, migration and accumulation of hydrocarbons, and hydraulic relations among different stratigraphic units in a basin.

A wide variety of Sr isotopic relationships exists among formation waters in different stratigraphic units of a sedimentary basin. Stueber et al. (1987) examined the Sr isotopic compositions of formation waters from stratigraphic units ranging in age from Ordovician to Pennsylvanian in the Illinois basin (U.S.A.). They noted that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the waters from nearly all major stratigraphic units, with the exception of waters from a Silurian unit, ranged from 0.7087 to 0.7108 and that the Sr contents of these waters differed by as much as 906 mg/l. The isotopic values for waters from the Silurian unit were between 0.7091 and 0.7108, but their Sr contents were widely varied between about 2 and 908 mg/l. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of formation waters in the Silurian unit,

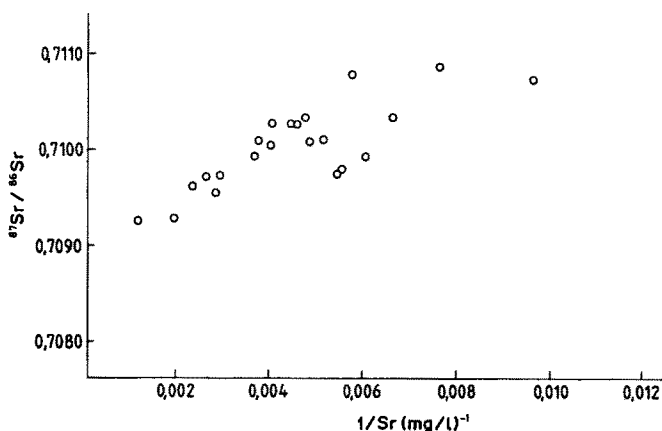


Figure 3a: Sr isotopic values vs. 1/Sr for Silurian and Devonian formation waters in the Illinois Basin (After Stueber et al., 1987)

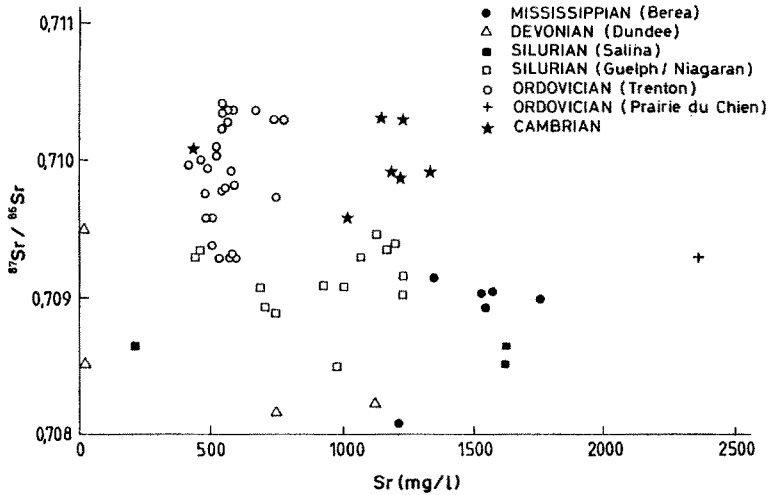


Figure 3b:  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios vs. Sr contents for Paleozoic units other than the Silurian and Devonian strata (After Stueber et al., 1987)

and also of some formation waters in Devonian strata, were found to bear an approximately linear relationship to the  $1/\text{Sr}$  ratios of the waters (Fig. 3a). Stueber et al. concluded that the waters from these Silurian and Devonian units were forming a single hydrologic system which evolved through mixing of two isotopically different formation waters. They also suggested that the limited variations in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the waters in the Silurian strata reflect a period of regional ground-water flow. In contrast to the data from Silurian-Devonian units, the relationship between the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and the Sr contents of the waters from other Paleozoic units is highly scattered (Fig. 3b). The high degree of scatter suggests that the evolution of Sr in formation waters within an entire basin is more complex than a simple mixing of two components. The study of Clayton et al. (1966) previously indicated that the stable isotopic compositions of water molecules in formation waters from an entire basin might be explained in terms of mixing of two components, one component of which having the  $^{18}\text{O}$  and D contents about the same as the local meteoric water. McNutt et al. (1987) also observed such differences between the Sr isotopic data and the stable isotope data for brines in the Michigan and the Appalachian basins. Varied mixing of two components can explain the stable



isotope data of these brines, but not the Sr isotopic data. A possibility for the failure of the Sr isotopic data to reveal the two component mixing is that in addition to two-component mixing, varied rock-water interactions occurred during migration and residence of the waters in the reservoir rock. But no study yet has clearly identified different sources of Sr for brines in sedimentary basins.

Analyzing the Sr isotopic compositions of formation waters in rocks from Cambrian to Mississippian ages in the Michigan and the Appalachian basins in southwest Ontario, Canada and the U.S.A., McNutt et al. (1987) also noted that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of dissolved Sr were limited to a narrow range between 0.7081 and 0.7104 with a wide range of Sr concentrations between 12 and 2,350 mg/l, like the waters in the Illinois basin analyzed by Stueber et al. (1987). Despite limited variations in the Sr isotopic compositions, the data proved useful to differentiate brines produced from different major stratigraphic units (Fig. 4). For example, brines from Cambrian and Ordovician units with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between 0.7090 and 0.7104 and Sr contents between 418 and 2,350 mg/l were found to be somewhat enriched in  $^{87}\text{Sr}$  compared to brines produced from Mississippian and Silurian units with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between 0.7081 and 0.7095 and Sr contents between 214 and 2,060 mg/l. None

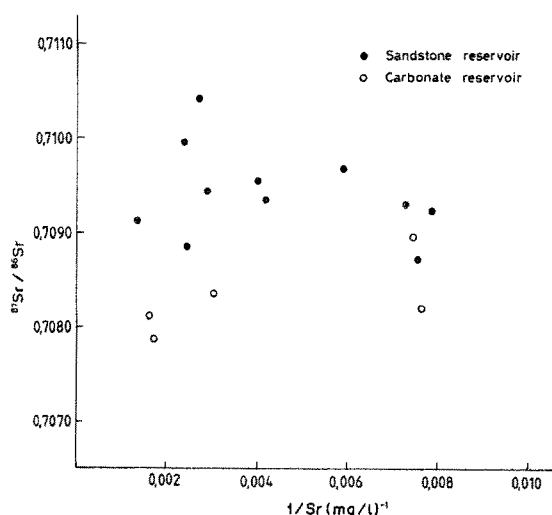


Figure 4: Sr isotopic data of oil-field waters from the Michigan and the Appalachian basins (McNutt et al., 1987)

of the Sr isotopic data for the waters of any of the major stratigraphic units can be described in terms of mixing of two components with distinct Sr isotopic compositions. Nevertheless, McNutt et al. noted that in the Ordovician unit, where the formation waters had a very narrow  $^{87}\text{Sr}/^{86}\text{Sr}$  range (0.7092-0.7105), brines from the edge of the basin in Ontario had nearly the same Sr isotopic values as those from the deep parts of the basin in Michigan. They alluded the isotopic uniformity to migration of brines over hundreds of kilometers, supporting a popular concept of long distance migration for fluids in sedimentary basins.

Unlike formation waters in the Illinois, the Michigan, and the Appalachian basins, those from Paleozoic beds in the northern shelf of the Anadarko basin in Kansas and Colorado are widely varied in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between 0.708 and 0.724. For example, waters from carbonate rocks of Upper Pennsylvanian Lansing-Kansas City Groups were found to have  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between 0.7088 and 0.7102 and Sr contents ranging from 21 to 1,400 mg/l (Stell et al., 1988), but formation waters in carbonate and siliciclastic rocks of Middle to Lower Pennsylvanian, Mississippian, and Cambro-Ordovician were found to have  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios as high as 0.724 with Sr contents often less than 80 mg/l.

The lateral variations in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of formation waters from a single stratigraphic unit could be as much as the vertical variations in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of waters across several stratigraphic intervals. For example, formation waters in Lower Pennsylvanian Morrow sandstones in western Kansas and eastern Colorado have  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between 0.718 and 0.722 and Sr contents ranging from over 50 mg/l to less than 150 mg/l, but those in Morrow sandstones in southwestern and southern Kansas had  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between 0.709 and 0.711 with Sr contents as high as 900 mg/l (Fig. 5). The precise cause for these isotopic variations has yet to be determined, although the isotopic data appeared to correspond broadly with the depositional environments of the sandstones. The high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were found for waters occurring in fluvial facies in western Kansas and eastern Colorado, whereas the low isotopic values were observed for waters associated with equivalent rocks of marine facies in southern and southwestern Kansas.

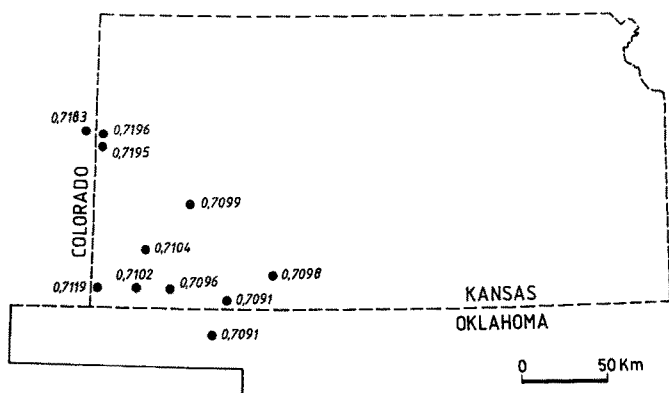


Figure 5: Sr isotopic data of Morrowan formation waters in the Hugoton Basin (Chaudhuri et al., in press)

The Sr isotopic compositions of formation waters have also been found to be varied within a single oil field. Stueber et al. (1984) reported a small range of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from 0.70802 to 0.70867 with Sr contents ranging from 169 to about 2,800 mg/l for waters of the Smackover carbonates in Walker Creek field in south Arkansas. Chaudhuri et al. (1987) reported a somewhat larger spread in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from 0.72195 to 0.72300 but with a limited variation in the Sr contents between 40 and 46 mg/l for waters in Mississippian carbonate rocks of Bindley field in west-central Kansas. Isotopic variations of similar magnitude were found in other individual oil-fields in the Illinois, the Michigan, and the Appalachian basins (Stueber et al., 1987; McNutt et al., 1987). Chaudhuri et al. (1987) suggested that the variations in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios among the waters of Bindley field in Kansas reflect isolated pools and that the small isotopic variations obtained are related to limited local dissolutions of the host carbonate rocks. Stueber et al. (1987) and McNutt et al. (1987) similarly explained the intra-field variations in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of formation waters from the Illinois and the Michigan basins.

#### FORMATION WATERS IN CRYSTALLINE ROCKS

A number of studies in recent years have addressed the origin

of saline waters in crystalline rocks (Frape and Fritz, 1981, 1982; Fritz and Frape, 1982; Frape et al., 1984; McNutt et al., 1984; Edmunds et al., 1984; Kelly et al., 1986; Edmunds et al., 1987; McNutt, 1987; McNutt et al., 1987; Fritz and Frape, 1987; Fritz et al., 1987; Nordstrom and Olsson, 1987; Pearson, 1987; Smalley, et al., 1988; Nurmi et al., 1988; Clauer et al., 1989; Moser et al., 1989; Nordstrom et al., 1989a, 1989b, 1989c; McNutt et al., 1990). While reconfirming the results of early studies concerning the broad chemical characteristics of these waters, the recent studies have revealed many different complexities in the source of these waters and also in the evolution of their solutes. But the results have yet to develop a consensus of opinion on the origin of saline waters in crystalline rocks.

#### Chemical Characteristics of Deep Ground Waters in Crystalline Rocks

Total dissolved solids in waters of crystalline rocks are widely varied ranging from about 50 mg/l at shallow depths of few tens of meters to more than 320,000 mg/l at depths of several hundred meters. Whereas the shallow waters with low salinity are typically of Ca-HCO<sub>3</sub> type, the highly saline deep waters are frequently of Ca-Na-Cl type and less commonly of Na-Ca-Cl type. Fritz and Frape (1982) provided an overview of the composition of dissolved constituents in saline waters in crystalline rocks of the Canadian Shield, and a recent summary of the composition is given by Fritz and Frape (1987). Table 2 is a compilation of major chemical data, following the works of Fritz and Frape (1982), Kelly et al. (1986), Nordstrom et al. (1989b), and McNutt et al. (1990), for saline waters from different localities in Precambrian shields in Canada and the U.S.A. and from a granitic pluton at Stripa in Sweden. The content of total dissolved solids in deep ground waters in Stripa granite is only a small fraction as compared to the total dissolved solids of deep ground waters in the Precambrian shields in Canada and the U. S. A. The Stripa waters are of Na-Ca-Cl type, whereas the waters in the Precambrian shields in Canada and the U.S.A. are primarily of Ca-Na-Cl type. Fritz and Frape (1982) considered that Ca-Na-Cl waters evolve from Na-Ca-Cl waters. While deep ground waters in crystalline rocks range from Na-Ca-Cl type

to Ca-Na-Cl type, the common chemical traits between these two types of waters are the very low abundances of K relative to Na and the low contents of Mg relative to Ca. The Na/Cl molar ratios in highly saline waters in crystalline rocks are often less than 0.6.

**Table 2:** Range of total dissolved solids and contents of some constituents in saline waters from crystalline rocks

Components	Contents in mg/kg
TDS	20,340 - 324,500
Ca	3,740 - 65,000
Na	2,200 - 45,000
Mg	12 - 5,100
K	32 - 495
Sr	65 - 1,640
Cl	11,520 - 207,000
Br	111 - 1,760
SO <sub>4</sub>	1 - 405
HCO <sub>3</sub>	2 - 141

compiled from Frape and Fritz (1987)

The origin of the dissolved constituents in saline waters in crystalline rocks is complex and a contentious issue. Nordstrom et al (1989) have recently summarized different processes which have been suggested for the source of salinity and the origin of these waters. Taking into consideration of whether or not the major dissolved constituents derived from outside or inside the rock mass, Nordstrom et al. categorized the sources of solutes in the deep saline waters into three groups: allochthonous, autochthonous, or both. Advocates of allochthonous source for the solutes advance several different processes which include involvement of basinal brine or sea water whose composition could have been modified by evaporation or dissolution of marine evaporites (Lindewald, 1981; Lahermo and Lampen, 1987; Michelot et al., 1984; Spencer, 1987), or by long-term low temperature water-rock interactions (Kelly et al., 1986; Guha and Kanwar, 1987). Proponents of autochthonous source emphasize the importance of indigenous water-rock interactions which involve reactions with silicate minerals (Edmunds et al., 1984, 1985, 1987; Kamineni, 1987; Pearson, 1987; Fritz et al., 1987; Clauer et al; 1989), radiolysis of water (Vovk, 1981, 1987), and leakage of highly saline fluid inclusions (Grigsby et al., 1983; Nordstrom et al., 1985; Nordstrom and Olsson, 1987; Peters, 1986; Gascoyne et al., 1987). Both autochthonous and allochthonous sources for the solutes were proposed by Fritz and Frape (1982),

Frape et al. (1984), and Fritz and Frape (1987).

### Strontium Isotopes and Origin of the Dissolved Components

Fritz and Frape (1982) and others noted that the stable isotope compositions of deep subsurface waters in crystalline rocks are systematically varied both within a single area and from one area to another. In studies of subsurface waters from several different districts in the Canadian Shield, Fritz and Frape (1987) recognized that in many instances the  $\delta D$  and  $\delta^{18}O$  values of the waters lie above the global meteoric water line and define a linear trend with a slope greater than that of the meteoric water line. The isotopic compositions of the waters from each district may be described by mixing of local meteoric water with a highly saline water source (Fig. 6). Despite wide spatial variations in the occurrences of subsurface waters, the highly saline fluid component of ground water in each of the areas studied appears to have very similar stable isotope compositions. The stable isotope composition of this highly saline component may be roughly described by a  $\delta^{18}O$  value above -11 per mil and a  $\delta D$  value above -30 per mil. Although

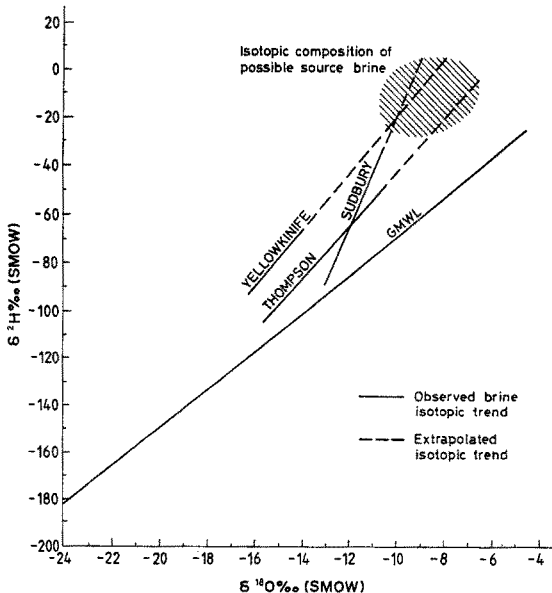


Figure 6: The stable isotope compositions of waters in crystalline rocks (Frape and Fritz, 1987)

the chemical composition of the highly saline component may be approximately described by extrapolations from relationships between the  $\delta^{18}\text{O}$  values and different chemical parameters, the origin of the saline component, that is the source of the water and the evolution of the chemical components in the water, remains largely unknown.

To assess how Sr and Ca of highly saline waters in crystalline rocks have evolved from water-rock interactions, McNutt et al. (1984) made some Sr isotopic studies on both waters and associated minerals and rocks. This early study showed strong similarity in the range of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between the water samples and their associated Precambrian crystalline rocks in the Sudbury district of Canada. The results indicated that the Sr in the water is the result of extensive water-rock interactions within the locality. The authors also observed two isolated pockets of water in the North Range having  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.711 and 0.716, which they attributed to different modal compositions of the noritic host rocks consisting primarily in plagioclase and pyroxene minerals with different Sr isotopic compositions. McNutt et al. suggested that isotopic exchange at all sites probably continued till the present time. In contrast to the waters in the North Range area, those in the South Range were found to be highly enriched in  $^{87}\text{Sr}$  with Sr isotopic values between 0.725 and 0.740. The high content of  $^{87}\text{Sr}$ -enriched minerals, such as biotite, and to some extent hornblende, in quartz diorite rocks in the South Range, has been considered to be the cause for the high Sr isotopic values of the waters. In the Sudbury district of Canada, McNutt et al. (1984) noted that fracture-filling gypsum and brines had the same Sr isotopic values. In a later study of highly saline waters in the Canadian Shield, McNutt et al. (1987) noted that many secondary carbonate and sulfate minerals in the crystalline rocks, such as calcite and gypsum, had nearly the same Sr isotopic values as those of the associated brines. The isotopic similarity suggests that either the minerals precipitated from the brines or complete isotopic exchange occurred through interactions between the minerals and the brines.

McNutt et al. (1987) observed Sr isotopic similarity between

brines and fracture filling materials, but isotopic dissimilarity between brines and host rocks. This isotopic relationship among host rocks, fracture filling-materials, and brines raised a prospect that ages of the highly saline waters may be determined, assuming that: (1) the water remained in a closed system and did not react with the wall-rock since the formation of the secondary mineral, (2) the reaction was a whole-rock reaction so that the secondary mineral, the brine and the whole rock had the same Sr isotopic composition, and (3) the water at the time of the reaction carried no isotopically different extraneous Sr (McNutt et al., 1990). Because many of the secondary minerals had very low Rb/Sr ratios, their initial isotopic compositions may be taken as the Sr isotopic composition of the rock at their time of formation. And hence from knowledge of the present-day  $^{87}\text{Sr}/^{86}\text{Sr}$  and Rb/Sr ratios of the rock, an age may be obtained which will correspond to the time of the rock-water interaction and the age of the water. But such an approach to date ground waters must be viewed with extreme caution, because the requirements for the dating are too specific to be met by most natural systems.

The works of Fritz et al. (1987) and Clauer et al. (1989) on ground waters and secondary minerals of the Stripa granite in central Sweden have shown that the evolution of secondary minerals might be complex. Fritz et al. observed that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of deep ground waters with values between 0.7475 and 0.7536 are very close to that of fracture coating minerals, which consist mainly of chlorite. They concluded that the chemistry of the waters resulted from long term interactions with the fracture coating minerals and not with the major minerals of the host rock. In a more recent study on fracture minerals of the same granite, Clauer et al. recognized at least three generations of calcite, each having a distinct range of Sr isotopic values and distinctive O and C isotope compositions. The group of calcite with the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between 0.7264 and 0.7406 appeared to be the youngest among the different generations. The O and C isotopic data on this group of calcite suggest that the vein calcites formed during low temperature reactions involving methane oxidation or sulfate reduction. Another group of calcite, which was mainly associated with chlorite, had  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between 0.7406 and



0.7536, which were nearly the same as that of ground waters in the same general locality. The third group of calcite, associated with epidote and chlorite, had very high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between 0.7814 and 1.0696. This group of calcite is believed to have formed at temperatures above 200°C during some metamorphic events between 1.4 and 0.8 billion years ago.

In a recent study of deep ground waters, generally brackish to saline and of Ca-Na-Cl type, from Late Archean felsic plutonic rocks located in NW Ontario in the Superior Province of the Canadian Shield, Franklyn et al. (1991) observed that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the waters were controlled primarily by rapid plagioclase-water interaction relative to other rock forming minerals (K-feldspar and biotite) and water interactions. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the waters ranged from 0.7057 to 0.7070, which are similar to the values for unaltered plagioclase minerals. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of calcite and gypsum, occurring as fracture filling minerals in the host rocks, were also similar to that of the present deep ground waters.

The studies of Clauer et al. (1989), McNutt et al. (1990), and Franklyn et al. (1991) have clearly shown that very often the Sr of the brines is not in isotopic equilibrium with that of the present-day host rocks. Many explanations may be given for these isotopic differences, but the identification of the cause or causes in any situation remains a formidable task.

#### CONCLUSION

Studies on Sr isotopic compositions of formation waters in sedimentary rocks can provide critical constraints on a model which may be developed to explain the evolution of chemical compositions of these waters. The dissolved Sr in formation waters are often enriched in  $^{87}\text{Sr}$  relative to marine Sr. Most of the enrichment in  $^{87}\text{Sr}$  of deep subsurface waters in sedimentary basins cannot be attributed to ion-exchange reaction between clay minerals and water

or reaction between plagioclase and water. Illitization of smectite and dissolutions of  $^{87}\text{Sr}$ -enriched evaporite minerals, alkali feldspar, and also of detrital mica in the deep subsurface are potential sources for radiogenic  $^{87}\text{Sr}$  in formation waters in sedimentary basins.

Investigation of isotopic compositions of dissolved Sr in formation waters is important because such data can greatly expand our knowledge on the hydrology in sedimentary basins. The results of studies made thus far suggest that while pervasive hydraulic intercommunications may exist among some adjacent major stratigraphic units in a sedimentary basin, hydraulic isolations is common among major stratigraphic units on a basin scale. If cross-formational flows in sedimentary basins are of limited nature, as suggested by the Sr isotopic data, then hydrologic models based on major cross-formational flow to drive the process of membrane filtration (e.g. Bredehoeft et al., 1963), appear inadequate for the process of ultrafiltration needed to account for the high salinity of the waters.

In some instances, the array of Sr isotopic data of formation waters can be described in terms of mixing of two distinct components of Sr. A linear relationship between  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and the reciprocal of Sr contents of the waters is indicative of mixing of Sr from two sources. The apparent linearity suggests either that the dissolved Sr in the waters results from mixing of two isotopically and chemically distinct waters, or that waters with narrow ranges of Sr isotopic compositions and Sr contents derived varying amounts of Sr from one or several types of minerals with narrow limits in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and Sr contents. However, non-linear relationships, rather than linear relationships between  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $1/\text{Sr}$  ratios, are the most common phenomena for formation waters in sedimentary basins. Any rational solution to the presence of both phenomena of linearity and non-linearity in the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $1/\text{Sr}$  relations in the same sedimentary basin would require integration of inputs of both chemical and physical information of the hydrostratigraphic units.

More studies are needed to derive full benefits of the isoto-

pic data of formation waters relating to basinal hydrology and diagenetic history of sedimentary rocks. Geochemical and isotopic studies on basinal rocks should be conducted simultaneously with those on formation waters. Because of many complexities involved in water-rock interactions, the results from radiogenic isotopes should be integrated with those from the analyses on stable isotope compositions and major and trace elemental compositions of waters to determine paths of chemical evolution of formation waters and hydraulic relationships of different waters in a sedimentary basin.

The deep formation waters in crystalline rocks from the Canadian Shield have total dissolved solids of more than 200,000 mg/l and they are of Ca-Na-Cl type with molar Na/Cl often much less than 0.6. Similar high salinity and Ca-Na-Cl type waters have been found in very deep drillholes in Kola Peninsula. The deep groundwaters of the Stripa granite in central Sweden, on the other hand, generally have TDS of less than 1,300 mg/l and they are of Na-Ca-Cl type with molar Na/Cl of about 0.70. By contrast, formation waters in sedimentary basins often range from nearly Na-Cl type with molar Na/Cl of about 1 to Na-Ca-Cl type with molar Na/Cl around 0.6 and seldom less than 0.5. The comparison between the formation waters in the Stripa granite and those in the Canadian Shield suggests that the progressive development of brines in crystalline rocks takes place along the line from Na-Ca-Cl type to Ca-Na-Cl type. Speculation may be made that very deep brines in crystalline rocks may evolve toward a Ca-Cl end member by appropriate dissolution-precipitation reactions in the subsurface. The overlap in the chemical evolutionary paths between the brines in sedimentary basins and those in crystalline rocks has led to two lines of speculation about the hydrodynamic linkage between the two distinct reservoirs deep in the subsurface (McNutt et al., 1987). One interpretation is that brines formed in crystalline rocks migrate to sedimentary basins where Na-enriched rocks are common to influence the composition of the brines toward a Na-Cl end member, the other interpretation is that the brines formed in sedimentary basins move deep into crystalline rocks where water-rock reactions lead to an evolution of the brines toward a Ca-Cl end member. The debate may be somewhat resolved if the brines in crystalline rocks are proved to be primarily of autochthonous

origin, as the evidence is overwhelming that brines in sedimentary basins often appear to have migration histories of several tens or few hundred kilometers suggesting an allochthonous origin with respect to the reservoir rocks.

#### ACKNOWLEDGEMENTS

We thank P. Stille (Centre de Géochimie de la Surface, Strasbourg, France) and R.H. McNutt (Mac Master University, Hamilton, Canada) for constructive discussions and review of the manuscript, and Mr. C. Hammel for drafting the figures.

#### REFERENCES

- Banner J.L., Wasserburg G.J., Dobson P.F., Carpenter A.B. and Moore C.H. (1989) Isotopic and trace element constraints on the origin and evolution of saline groundwaters from central Missouri. *Geochim. Cosmochim. Acta*, 53, 383-398.
- Bredehoeft J.D., Blyth C.R., White W.A. and Maxey G.B. (1963) Possible mechanism for concentration of brines in subsurface formations. *Am. Ass. Petrol. Geol. Bull.*, 47, 257-263.
- Burtner R.L. (1987) Origin and evolution of Weber and Tensleep formation waters in the green River and Uinta-Piceance basins, northern Rocky Mountain area. *Chem. Geol.*, 65, 255-282.
- Carpenter A. B. (1978) Origin and chemical evolution of brines in sedimentary basins. *Oklahoma Geol. Surv. Circ.*, 79, 60-77.
- Cassan J.P., Clauer N., Fritz B. and Tardy Y. (1983) Water circulations and mass transfers during the diagenesis of oil-bearing reservoirs. In: *Extended abstracts, Seki I. (ed.), 4th Int. Symp. Water-Rock Interaction, Misasa, Japan*, 75-78.
- Chaudhuri S. (1978) Strontium isotopic composition of several oilfield brines from Kansas and Colorado. *Geochim. Cosmochim. Acta*, 42, 329-332.
- Chaudhuri S. and Brookins D. G. (1978) The Rb-Sr systematics in acid-leached clay minerals. *Chem. Geol.*, 24, 327-338.
- Chaudhuri S., Clauer N. and O'Neil J.R. (1985) Hydrochemical evolution of some oil-field waters from central Kansas, U.S.A.. *Terra cognita*, 3, 177-178.
- Chaudhuri S., Broedel V. and Clauer N. (1987) Strontium isotopic evolution of oil-field waters from carbonate reservoir rocks in Bindley field, central Kansas, U.S.A. *Geochim. Cosmochim. Acta*, 51, 45-54.
- Chaudhuri S., Robinson R., Clauer. N. and Jones L. M. (in press) Evolution of formation waters in early Pennsylvanian Morrowan sandstones in the Hugoton embayment of the Anadarko basin in southern midcontinent of the U.S.A. *Oklahoma Geol. Surv. Circ.* (in press).
- Clauer N. (1976) *Géochimie isotopique du strontium des milieux sédimentaires. Application à la géochronologie de la couver-*

- ture du craton ouest-Africain. Sci. Géol. Mém. Strasbourg, 45, 256p.
- Clauer N., Gibling P. and Lucas J. (1984) Sr and Ar isotope studies of detrital smectites from the Atlantic Ocean (DSDP, Legs 43, 48 and 50). *Isot. Geosc.*, 2, 141-151.
- Clauer N., Frape S.K. and Fritz B. (1989) Calcite veins of the Stripa granite (Sweden) as records of the origin of the groundwaters and their interactions with the granitic body. *Geochim. Cosmochim. Acta*, 53, 1777-1781.
- Clayton R.N., Friedman I., Graf D.L., Mayeda T.K., Meents W.F. and Shimp F. (1966) The origin of saline formation waters, I: Isotopic composition. *Jour. Geophys. Res.*, 71, 3869-3882.
- Collins A. G. (1975) *Geochemistry of oilfield waters*. Elsevier, New York, 496p.
- Coplen T.B. and Hanshaw B.B. (1973) Ultrafiltration by a compacted clay membrane, I. Oxygen and hydrogen fractionation. *Geochim. Cosmochim. Acta*, 37, 2295-2310.
- Davis S.N. (1964) The chemistry of saline waters - Discussion. *Groundwaters*, 2, 51.
- Dickey P.A. (1969) Increasing concentration of subsurface brines with depth. *Chem. Geol.*, 4, 361-370.
- Edmunds W.M., Andrews J.N., Burgess W.G., Kay R.L.F. and Lee D.J. (1984) The evolution of saline and thermal groundwaters in the Carnmenellis granite. *Min. Mag.*, 48, 407-424.
- Edmunds W.M., Kay R.L.F. and MacCartney R.A. (1985) Origin of saline groundwaters in the Carnmenellis granite: Natural processes and reaction during Hot Dry Rock reservoir circulation. *Chem. Geol.*, 49, 287-302.
- Edmunds W.M., Kay R.L.F., Miles D.L. and Cook J.M. (1987) The origin of saline groundwaters in the Carnmenellis granite, Cornwall (U.K.): Further evidence from minor and trace elements. In: *Saline water and gases in crystalline rocks*, Fritz P. and Frape S.K. (eds.), *Geol. Ass. Canada, Spec. Paper*, 33, 127-144.
- Egeberg P. K. and Aagaard P. (1989) Origin and evolution of formation waters from oil fields on the Norwegian shelf. *Applied Geochem.*, 4, 131-142.
- Engelhardt W. von and Gaido K.H. (1963) Concentration changes of pore solutions during the compaction of clay sediments. *Jour. Sediment. Petrol.*, 33, 919-930.
- Franklyn M.T., McNutt R.H., Kaminen D.C., Gascoyne M. and Frape S.K. (1991) Groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  values in the Eye-Dashwa Lakes pluton, Canada: Evidence for plagioclase-water reaction. *Chem. Geol. (Isot. Geosc. Sect.)*, 86, 111-122.
- Frape S.K. and Fritz P. (1981) A preliminary report on the occurrence and geochemistry of saline groundwaters on the Canadian Shield. *Atom. Energ. Canada Ltd, Technical Record*, 136, 71 pp.
- Frape S.K. and Fritz P. (1982) The chemistry and isotopic composition of saline groundwaters from the Sudbury Basin, Ontario. *Can. Jour. Earth Sci.*, 19, 645-661.
- Frape S.K., Fritz P. and McNutt R.H. (1984) The role of water-rock interaction in the chemical evolution of groundwaters from the Canadian Shield. *Geochim. Cosmochim. Acta*, 48, 1617-1627.
- Fritz B., Clauer N. and Kam M. (1987) Strontium isotopic data and geochemical calculations as indicators for the origin of saline waters in crystalline rocks. In: *Saline water and gases in crystalline rocks*, Fritz P. and Frape S.K. (eds.), *Geol.*

- Ass. Canada, Spec. Paper, 33, 121-126.
- Fritz P. and Frape S.K. (1982) Saline groundwaters in the Canadian Shield - a first overview. *Chem. Geol.*, 36, 179-190.
- Fritz P. and Frape S.K. (eds.) (1987) Saline water and gases in crystalline rocks, *Geol. Ass. Canada, Spec. Paper*, 33, 253 pp.
- Fritz S.J. and Edy C.G. (1985) Hyperfiltration-induced precipitation of calcite. *Geochim. Cosmochim. Acta*, 49, 761-768.
- Gascoyne M., Davison C.C., Ross J.D. and Pearson R. (1987) Saline groundwaters and brines in the Canadian Shield. In: *Saline water and gases in crystalline rocks*, Fritz P. and Frape S.K. (eds.), *Geol. Ass. Canada, Spec. Paper*, 33, 53-68.
- Graf D. L. and Anderson D. E. (1981) Geochemical inputs for hydrologic models of deep-lying sedimentary units. *Jour. Hydrol.*, 54, 297-314.
- Grigsby C.O., Tester J.W., Trujillo P.E., Counce D.A., Abbott J., Holley C.E. and Blatz L.A. (1983) Rock-water interactions in hot dry rock geothermal systems: field investigations of in situ geochemical behavior. *Jour. Volcan. Geoth. Res.*, 15, 101-136.
- Guha J. and Kanwar R. (1987) Vug brines-fluid inclusions: a key to the understanding of secondary gold enrichment processes and the evolution of deep brines in the Canadian Shield. In: *Saline water and gases in crystalline rocks*, Fritz P. and Frape S.K. (eds.), *Geol. Ass. Canada, Spec. Paper*, 33, 95-102.
- Hanshaw B.B. and Coplen T.B. (1973) Ultrafiltration by a compacted clay membrane, II. Sodium ion exclusion at various ionic strengths. *Geochim. Cosmochim. Acta*, 37, 2311-2327.
- Herut B., Starinsky, A., Katz, A. and Bein, A. (1990) The role of sea water freezing in the formation of subsurface brines. *Geochim. Cosmochim. Acta*, 54, 13-21.
- Hitchon B. and Friedman I. (1969) Geochemistry and origin of formation waters in the western Canada sedimentary basin, I. Stable isotopes of hydrogen and oxygen. *Geochim. Cosmochim. Acta*, 33, 1321-1349.
- Hower J., Eslinger E.V., Hower J. and Perry E.A. (1976) Mechanism of burial metamorphism, I. Mineralogical and chemical evidence. *Geol. Soc. Am. Bull.*, 87, 725-737.
- Kamineni D.C. (1987) Halogen-bearing minerals in plutonic rocks: a possible source of chlorine in saline groundwater in the Canadian Shield. In: *Saline water and gases in crystalline rocks*, Fritz P. and Frape S.K. (eds.), *Geol. Ass. Canada, Spec. Paper*, 33, 69-80.
- Kelly W.C., Rye R.O. and Livnat A. (1986) Saline mine waters of the Keweenaw Peninsula, northern Michigan: Their nature, origin and relation to similar deep waters in Precambrian crystalline rocks of the Canadian Shield. *Am. Jour. Sci.*, 286, 281-308.
- Kharaka Y.K. and Berry F.A.F. (1973) Simultaneous flow of water and solute through geological membranes: I. Experimental investigations. *Geochim. Cosmochim. Acta*, 37, 2577-2604.
- Kharaka Y.K., Lico M.S., Wright V.A. and Carothers W.W. (1979) Geochemistry of formation waters from Pleasant Bayou No. 2 well and adjacent areas in Coastal Texas. *Proc. 4th Conf. Geopressured-Geothermal Resources*, Austin, Texas, 168-193.
- Kharaka Y.K. and Carothers W.W. (1986) Oxygen and hydrogen isotope geochemistry of deep basin brines. In: *Handbook of Environmental Isotope Geochemistry*, Fritz P. and Fontes J.C. (eds.),

- 2, 8, 305-360.
- Lahermo P.W. and Lampen P.H. (1987) Brackish and saline groundwaters in Finland. In: Saline water and gases in crystalline rocks, Fritz P. and Frape S.K. (eds.), Geol. Ass. Canada, Spec. Paper, 33, 103-110.
- Land L. S. (1987) The major ion chemistry of saline brines in sedimentary basins. In: Physics and Chemistry of Porous Media II, Banavar J.R., Koplik J. and Winkler K.W. (eds.), Am. Inst. of Phys. Conf. Proc., 154, 160-179.
- Land L. S. and Prezbindowski D. R. (1981) The origin and evolution of saline formation water, Lower Cretaceous carbonates, south-central Texas, U.S.A. Jour. Hydrol., 54, 51-74.
- Lindewald H. (1981) Saline groundwater in Sweden. In: Intruded and relict groundwater of marine origin, 7th Salt-Water Intrusion Meeting, 24-32.
- Lowry R.M., Faure G., Mullet D.I. and Jones L.M. (1988) Interpretation of chemical and isotopic compositions of brines based on mixing and dilution, "Clinton" sandstones, eastern Ohio, U.S.A. Applied Geochem., 3, 177-184.
- McKelvey J.G. and Milne I.H. (1962) The flow of salt through compacted clay. Clays and Clay Min., 9, 248-259.
- McNutt R.H. (1987)  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios as indicators of water/rock interactions: Application to brines found in Precambrian age rocks from Canada. In: Saline water and gases in crystalline rocks, Fritz P. and Frape S.K. (eds.), Geol. Ass. Canada, Spec. Paper, 33, 81-88.
- McNutt R.H., Frape S.K. and Fritz P. (1984) Strontium isotopic composition of some Precambrian Shield brines. Isot. Geosc., 2, 205-215.
- McNutt R. H., Frape, S. K. and Dollar P. (1987) A strontium, oxygen and hydrogen isotopic composition of brines, Michigan and Appalachian basins, Ontario and Michigan. Applied Geochem., 2, 495-505.
- McNutt R.H., Frape S.K., Fritz P., Jones M.G. and MacDonald I.M. (1990) The  $^{87}\text{Sr}/^{86}\text{Sr}$  values of Canadian Shield brines and fracture minerals with applications to groundwater mixing, fracture history, and geochronology. Geochim. Cosmochim. Acta, 54, 205-215.
- Michelot J.L., Bentley H.W., Brissaud I., Elmore D. and Fontes J.C. (1984) Progress in environmental isotope studies ( $^{36}\text{Cl}$ ,  $^{34}\text{S}$ ,  $^{18}\text{O}$ ) at the Stripa site. Isotope Hydrology, 1983, I.A.E.A., Vienna, 207-229.
- Moser H., Wolf M., Fritz P., Fontes J.C., Florkowski T. and Payne B.R. (1989) Deuterium, oxygen-18, and tritium in Stripa groundwater. Geochim. Cosmochim. Acta, 53, 1757-1763.
- Nordstrom D.K., Andrews J.N., Carlsson L., Fontes J.C., Fritz P., Moser H. and Olsson T. (1985) Hydrogeological and hydrogeochemical investigations in boreholes: Final report of the phase I geochemical investigations of the Stripa groundwaters. S.K.B. Stripa Project Report, Stockholm, 85-06, 250 p.
- Nordstrom D.K. and Olsson T. (1987) Fluid inclusions as a source of dissolved salts in deep granitic groundwaters. In: Saline water and gases in crystalline rocks. Fritz P. and Frape S.K. (edit.), Geol. Ass. Canada, Spec. Paper, 33, 111-120.
- Nordstrom D.K., Olsson T., Carlsson L. and Fritz P. (1989a) Introduction to the hydrogeochemical investigations within the International Stripa Project. Geochim. Cosmochim. Acta, 53, 1717-1726.

- Nordstrom D.K., Lindblom S., Donahoe R.J. and Barton C.C. (1989b) Fluid inclusions in the Stripa granite and their possible influence on the groundwater chemistry. *Geochim. Cosmochim. Acta*, 53, 1741-1755.
- Nordstrom D.K., Ball J.W., Donahoe R.J. and Whittemore D. (1989c) Groundwater geochemistry and water-rock interactions at Stripa. *Geochim. Cosmochim. Acta*, 53, 1727-1740.
- Nurmi P.A., Ilmo T.K. and Lahermo W. (1988) Geochemistry and origin of saline groundwaters in the Fennoscandian Shield. *Applied Geochem.*, 3, 185-203.
- Pearson F.J., Jr. (1987) Models of mineral controls on the composition of saline groundwaters of the Canadian Shield. In: Saline water and gases in crystalline rocks, Fritz P. and Frapre S.K. (eds.), *Geol. Ass. Canada, Spec. Paper*, 33, 39-52.
- Peters T. (1986) Structurally incorporated and water extractable chlorine in the Boettstein granite (N. Switzerland). *Contrib. Miner. Petrol.*, 94, 272-273.
- Register J.K. and Brookins D.G. (1980) Rb-Sr isochron age of evaporite minerals from the Salado Formation (Late Permian), Southeastern New Mexico. *Isochron/West*, 29, 39-42.
- Rinckenbach T. (1988) Diagenèse minérale des sédiments pétrolifères du delta fossile de la Mahakam (Indonésie). Evolution minéralogique et isotopique des composants argileux et histoire thermique. Thèse Univ. Strasbourg.
- Rittenhouse G. (1967) Bromine in oil field waters and its use in determining possibilities of origin of these waters. *Am. Ass. Petrol. Geol. Bull.*, 51, 2430-2440.
- Russell W. L. (1933) Subsurface concentration of chloride brines. *Am. Ass. Petrol. Geol. Bull.*, 17, 1213-1228.
- Saigal G. C., Morad S., Bjorlykke K, Egeberg P. K. and Aagaard P. (1988) Diagenetic albitization of detrital K-feldspars in Jurassic, Lower Cretaceous and Tertiary clastic reservoir rocks from offshore Norway. I. Textures and origin. *Jour. Sedimen. Petrol.*, 58, 1003-1013.
- Smalley P.C., Blomqvist R. and Raheim A. (1988) Sr isotopic evidence for discrete saline components in stratified ground waters from crystalline bedrock, Outokumpu, Finland. *Geology*, 16, 354-357.
- Spencer R.J. (1987) Origin of Ca-Cl brines in Devonian formations, western Canada sedimentary basin. *Applied Geochem.*, 2, 373-384.
- Starinsky A., Bielski M., Lazar B., Steinitz G. and Raab M. (1983) Strontium isotope evidence on the history of oilfield brines, Mediterranean coastal plain, Israel. *Geochim. Cosmochim. Acta*, 47, 687-695.
- Stell M. J. (1988) Isotopic and chemical compositions of oil-field waters in Upper Pennsylvanian Lansing-Kansas City rocks in western Kansas. M.S. Thesis, Kansas State University.
- Stell M.J., Chaudhuri S., Jones L.M. and Clauer N. (1987) Origin and evolution of oil-field brines in Upper Pennsylvanian Lansing-Kansas City Groups in western Kansas. *Trans. Am. Geophys. Union*, 68, 1275.
- Stueber A. M., Pushkar P. and Hetherington E. A. (1984) A strontium isotopic study of Smackover brines and associated solids, southern Arkansas. *Geochim. Cosmochim. Acta*, 48, 1637-1649.
- Stueber A. M., Pushkar P. and Hetherington E. A. (1987) A strontium isotopic study of formation waters from the Illinois basin.



- Applied Geochem., 2, 477-494.
- Sunwall M. T. and Pushkar P. (1979) The isotopic composition of strontium in brines from petroleum fields of southeastern Ohio. *Chem. Geol.*, 24, 189-197.
- Vovk I.F. (1981) Radiolytic model of formation of brine compositions in the crystalline basement of shields. *Geokhimiya*, 4, 467-480.
- Vovk I.F. (1987) Radiolytic salt enrichment and brines in the crystalline basement of the East European Plateform. In: *Saline water and gases in crystalline rocks*, Fritz P. and Frape S.K. (eds.), *Geol. Ass. Canada, Spec. Paper*, 33, 197-210.
- White D. E. (1965) Saline waters of sedimentary rocks. In: *Fluids in Subsurface Environments*. Young Y. and Galley G.E. (eds.), *Am. Ass. Petrol. Geol. Mem.*, 4, 342-366.