

HISTORY OF MARINE EVAPORITES: CONSTRAINTS
FROM RADIOGENIC ISOTOPES

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Ancient marine evaporite deposits represent important records of past marginal marine environments and climatic conditions, and therefore bear witness to chemical history of the past oceans. Borchert and Muir (1964) and Braitsch (1971) gave a list of marine evaporite minerals and summarized the tectonic and climatic conditions favorable for the formation of such deposits. Holland (1984) elaborated on the variations of the major chemical composition of sea water during the Phanerozoic Era and concluded from mineralogic and chemical data of marine evaporite deposits that the major composition of sea water remained nearly constant during the last 600 million years. This constancy contrasts with prominent shifts in the isotopic compositions of S and O in dissolved sulfate and in the isotopic compositions of marine Sr, Nd and C. The trend and significance of the isotopic excursions of these elements have been

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described in companion contributions in this book and by Holser (1966), Holser et al. (1979), Claypool et al. (1980), Holland (1984), Shaw and Wasserburg (1985), Faure (1986), and Stille and Fischer (1990).

The present article gives a review of available information on Rb-Sr, K-Ca and K-Ar isotopic investigations of marine evaporite deposits to emphasize that radiogenic isotopes provide increased understanding of both the depositional and the post-depositional history of these marine sediments. Radiogenic isotope data may also help to determine the state of isolation of evaporite deposits from recent groundwater activities, as such information is critical to the assessment of the suitability of these deposits as repository of high-level radioactive wastes. Furthermore, analysis of radiogenic isotopes can lead to improved understanding of the relation between physical deformation and chemical modification of evaporite deposits and consequently can enhance knowledge of the development of salinity in continental subsurface waters. Finally, isotopic data can, in some instances, be useful in studies of stratigraphic correlations and tectonometamorphic evolutions of evaporite deposits.

PRIMARY STRONTIUM ISOTOPIC SIGNATURES OF EVAPORITES

The $^{87}\text{Sr}/^{86}\text{Sr}$ of modern sea waters has been found to be widely uniform at about 0.70901 (Burke et al., 1982), but the past ocean waters experienced excursions in the Sr isotopic composition through time in response to irregular changes in the balance between contribution of Sr with high $^{87}\text{Sr}/^{86}\text{Sr}$ from continents and input of Sr with low $^{87}\text{Sr}/^{86}\text{Sr}$ from submarine activities. Since the work of Peterman et al. (1970) on paleontologically well-dated carbonate fossils, many studies, especially that of Burke et al. (1982), have contributed to the knowledge of the Sr isotopic excursion during the Phanerozoic (see figure in Holser's companion contribution). This secular variation of the marine $^{87}\text{Sr}/^{86}\text{Sr}$ ratio during the

Phanerozoic can serve as a basis for the study of chemical evolution of ancient marine evaporite deposits.

Models for deposition of ancient marine evaporite deposits most frequently invoke the popular bar theory of Ochsenius (1877), or some modified version of it, which postulate a continuous supply of open ocean water across a barrier into an evaporating basin adjacent to the coast. As an alternative to the barred-basin model, Hsü (1972) advocated that ancient giant saline deposits could have formed from dessication of small ocean basins. Following the popular model of deposition in a barred basin, marine evaporite minerals should have the same Sr isotopic composition as open ocean water at the time of deposition, and any measurable deviation from this specific marine Sr isotopic value for an evaporite deposit should be related to post-depositional chemical modification. However, this generalization of the same Sr isotopic value for both water of the open ocean and water of an evaporating basin along a continental margin should be viewed with some caution. Indeed, if saline deposits formed from dessication of small ocean basins, as suggested by Hsü (1972), their primary Sr isotopic signatures could be different from that of contemporaneous open ocean water due to increased influence of input of continental Sr in the depositional basin. Moreover, the rate of precipitation can be faster than the rate of mixing of dissolved Sr in an evaporating basin dominated by restricted water circulation, in which case the evaporitic minerals can be spatially and temporally varied in their Sr isotopic compositions due to varied inputs of continental Sr in the basin.

STRONTIUM ISOTOPIC SIGNATURES OF ANCIENT BEDDED EVAPORITES

For lack of data from any representative modern bedded evaporite deposits, no conclusive argument can be made whether or not Sr isotopic difference could exist between the waters of evaporating basins and the open ocean. Nevertheless, the results of two studies suggest that primary Sr isotopic signatures of evaporites

may not be the same as that of contemporaneous open ocean water. Clauer (1976) found that two sulfate deposits at different depths in the Messinian (Late Miocene) evaporite sequence of the Mediterranean Sea to be isotopically similar at an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70814, in clear contrast to 0.70890 for the contemporaneous open ocean water. Clauer proposed that the Sr isotopic deviation of the evaporite deposits could have been induced by the introduction of continental waters into the evaporating basin, which also appeared to be reflected in the O isotope composition of the sulfate deposits. Recently, we measured the Sr isotopic composition of three other Messinian sulfate deposits from different depths of the same Messinian sequence. The measurements were precise enough, with values ranging from 0.708730 ± 0.000008 to 0.708781 ± 0.000009 , to suggest that the Sr isotopic compositions of the evaporite sulfates are slightly varied and that, as proposed by Clauer (1976), the Sr isotopic composition of the Messinian evaporitic deposits in the Mediterranean Sea differed from that of the contemporaneous open ocean water. The difference most likely relates to the paleohydrology of the evaporating basin and not to any post-depositional modification. Existence of a Sr isotopic difference between water of an evaporating basin and open sea can be defended on evidences presented by Aaberg and Wickman (1987) on Sr isotopic compositions of waters of the Bothnian Bay which has a restricted circulation relative to the open Baltic Sea. The authors found that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the water in the bay were between 0.70935 and 0.70951. The ^{87}Sr -enrichment of the Bothnian water relative to that of the open ocean is induced by the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.71772 and 0.73056 for the tributaries around the bay.

Evaporite deposits are known to be highly susceptible to post-depositional physical and chemical modifications. Hence, minerals in ancient evaporite deposits, especially in diapiric evaporite deposits, are suspect of varied isotopic modifications. The potential for modification of the depositional Sr isotopic signatures is also high for those mineral deposits with low Sr contents, so that halite or other highly soluble salt deposits known for their low Sr contents can be subject to greater degree of post-depositional Sr isotopic modifications than gypsum or anhydrite deposits which are known to be very high in Sr contents. Several recent

studies on Sr isotopic compositions of sulfate and associated chloride, and mixed salts in ancient diapiric and bedded evaporite deposits, have been made to explore the use of Sr isotopes as tracers to constrain the evolutionary history of ancient evaporite deposits.

Chaudhuri et al. (1986) reported that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of marine-bedded anhydrite and halite samples from Lower Permian evaporite deposits in central Kansas, to be varied between 0.70815 and 0.70885, and between 0.70848 and 0.70897, respectively. The Sr isotopic ratios for the anhydrite samples are higher than that of contemporaneous sea water, whose values ranged between 0.70740 and 0.70810, as suggested by the refined sea-water curve of Burke et al. (1982). The Sr contents of the anhydrite samples ranged from 1,638 to 3,842 $\mu\text{g/g}$, which is well within the values given by Ichikuni and Musha (1978) for primary marine sulfate deposits. Chaudhuri et al. claimed that the Sr isotopic signatures of the anhydrite samples from Kansas are primary and that their variations reflect the variations in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of waters of the evaporating basin, as a result of varied influence of the input of continental Sr to the basin.

The Br contents of the analyzed halite samples ranged from 46 to 100 $\mu\text{g/g}$. Although a linear relationship between the Br contents and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios was not too convincing, Chaudhuri et al. noted that the salt with highest Br content had the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and that those with low Br contents generally had low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. At least some of the halites, whose Br contents were less than that of primary halite, which is known to have a Br content of about 65 $\mu\text{g/g}$, appear to have been recrystallized. But, as evident from data, the effect of such recrystallization was to lower the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the salts. Chaudhuri et al., therefore, claimed that, unless the salts were recrystallized also at other earlier time or times, the apparently high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the salts relative to contemporaneous sea water reflect the waters in the evaporating basin. As the data suggest, the brines from which halite precipitated were slightly enriched in ^{87}Sr as compared to brines from which the sulfate minerals precipitated. They attributed this difference to increased influence of input of continental

Sr to the basin with Sr-poor brines when the precipitation of halite occurred as compared with Sr-rich brines when the precipitation of sulfate minerals occurred.

Brookins (1988) recognized Sr isotopic variations of waters of an evaporating basin from studies of marine bedded anhydrite and gypsum deposits in the Castille, Salado, and Rustler Formations, occurring in stratigraphically ascending order of the Late Permian Ochoan Group in the Delaware Basin of New Mexico (U.S.A.). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of sulfate deposits in the Rustler Formation ranged from 0.70692 to 0.70707, whereas those in the Salado and Castille Formations were nearly uniform at about 0.70688. On the other hand, secondary selenite veins occurring in the overlying siltstone and sandstone of the Dewey Lake Red Beds of the Ochoan Group were high in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with values between 0.70722 and 0.70861. The Sr isotopic values of the sulfates in the Rustler, Salado and Castille Formations were found to be well within the Sr isotopic values of contemporaneous sea water, which have rapidly increased from about 0.7068 at the beginning of the Late Permian time to about 0.7073 during the Permo-Triassic time (see figure 2 in Hoser's companion contribution). Like the temporal changes in the Sr isotopic composition of the sea waters, the bedded evaporite deposits of the Ochoan Group also increased in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from low values during the Salado-Castille time to high values during the Rustler time. The internal variations in the Sr isotopic values (0.70692-0.70707) of the bedded anhydrite and gypsum deposits of the Rustler Formation is evident. Although he was unable to find a satisfactory explanation for the apparent variations in the Sr isotopic compositions, Brookins (1988) maintained that these variations were unlikely to have occurred from reaction with Sr released from a recrystallization process of clay minerals in clastic interbeds, as the amount of clays present is insufficient to reset the isotopic composition of anhydrites which contain a few thousands $\mu\text{g/g}$ of Sr. We tend to believe that such small variations can arise from variations in the isotopic composition of waters in an evaporating basin. The aspect of how primary Sr isotopic records could have vary during evaporite deposition is discussed later.

The study of Posey and Fisher (1989) on evaporite deposits of

Lower Permian Wolfcampian and Leonardian series in the Palo Duro Basin of Texas is an additional illustration of an apparent retention of syn-depositional Sr isotopic signatures by ancient bedded marine anhydrite deposits. The authors noted that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of both bedded nodular mosaic anhydrites (0.70753-0.70824) and replacive nodular anhydrites (0.70796-0.70841) corresponded to that of Early Permian sea water (0.70740-0.70815), in contrast to those of vein-filling anhydrites (0.70828-0.70895) which obviously contained post-depositional Sr. The Sr isotopic compositions of the bedded anhydrite in the Palo Duro Basin of Texas, like similar anhydrite and gypsum deposits of other ages elsewhere (Clauer, 1976; Chaudhuri et al., 1986; Brookins, 1988), appeared to have varied randomly through time. Again, the variations in the Sr isotopic compositions of the bedded sulfate deposits in the Palo Duro Basin can be due to fluctuation in the Sr isotopic composition of the waters in the evaporating basin and not to any global excursion in the isotopic composition of sea water.

STRONTIUM ISOTOPIC SIGNATURES OF DIAPIRIC EVAPORITES

Diapiric evaporite deposits often record a long history of physical and chemical modifications involving complex episodes of water-rock interactions. An effect of these modifications is the formation of cap rocks over some of the salt domes. Perhaps the most thoroughly investigated diapiric evaporite deposits are the salt domes and associated cap rocks in the Gulf Coast of the U.S.A. Many of these salt diapirs contain cap rocks with a sequence of salt-dissolution related anhydrite accumulation directly overlying the halite diapir and of hydrocarbon-reaction related calcite, gypsum and sulfur above the anhydrite deposits. The salt diapirs in the Gulf Coast appear to have different ages, but the domes are believed to have originated from the extensive late Middle Jurassic Louann Formation (Salvador, 1987). Recent studies of Posey et al. (1987) and Land et al. (1988) have elucidated the Sr isotopic history of salt domes and associated cap rocks in the Gulf Coast area.

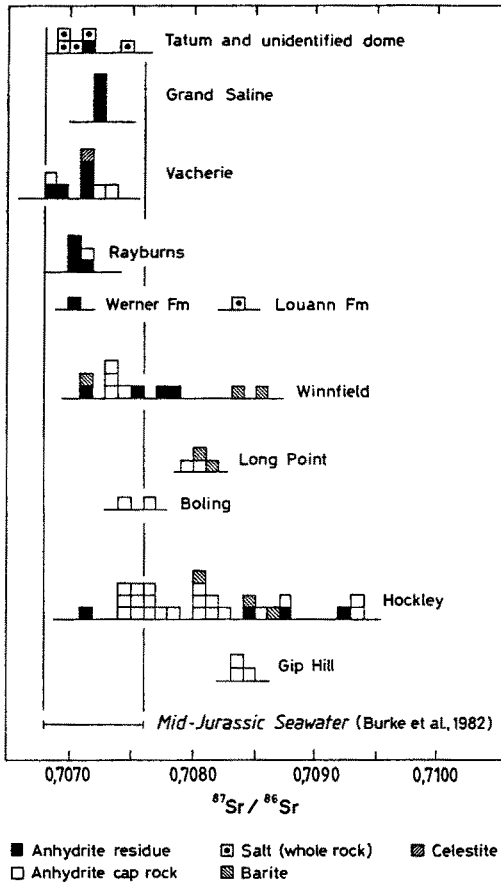


Figure 1: Sr isotopic compositions of salt domes and cap rocks from the Gulf-Coast region (Posey et al., 1987)

Posey et al. (1987) presented a summary of Sr isotopic ratios of a number of anhydrite cap rocks over salt domes from different locations in the Gulf-Coast region (Fig. 1). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of several cap-rock anhydrites were found to be the same as that of the Middle Jurassic sea water (0.7068-0.7076) as defined by Burke et al. (1982), suggesting that the Sr in these cap-rock anhydrites derived from dissolution of Louann salt minerals. But the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of many other cap-rock anhydrites exceeded the Middle Jurassic marine Sr isotopic values. These high values could have resulted from invasion of ^{87}Sr -enriched formation waters into the salt domes, probably during diapirism. Posey et al. believe that either feldspar or clay within the clastic section could have been the source of the radiogenic ^{87}Sr in the cap-rocks. Regardless of the

Sr isotopic values, the Sr contents (550-1050 $\mu\text{g/g}$) of the cap-rock anhydrites are low in comparison to the Sr contents of many bedded evaporite deposits, which are frequently in the range of a few thousands of $\mu\text{g/g}$.

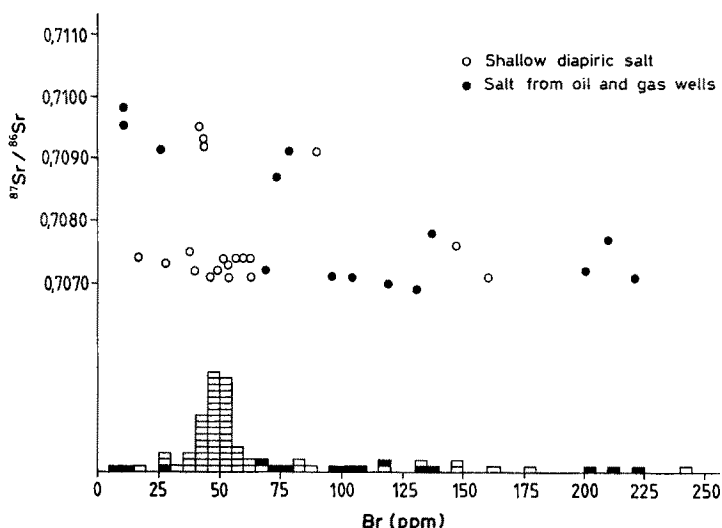


Figure 2: Sr isotopic compositions and Br contents of diapiric salts from the Gulf Coast area (Land et al., 1988)

In their study of Gulf Coast salt deposits, Land et al. (1988) observed that, although the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of some anhydrites and halites were nearly the same as that of the Middle Jurassic sea water, the isotopic values of these deposits were distinctly varied and that the variations occurred within a very short time as the samples analyzed came from a core less than 200 m thick. Considering that wide isotopic shifts in short times are unlikely to be related to any global sea water isotopic effect, Land et al. concluded that the isotopic variations must be due to syn- or post-depositional introduction of continental Sr. They also noted that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of many samples of diapiric halite were commonly between 0.7075 and 0.7095. The ^{87}Sr -enriched halites were found to be either depleted or similar in Br contents relative to primary marine salts, the latter presumably having more than 60 $\mu\text{g/g}$ of Br (Fig. 2). The ^{87}Sr -enriched salts with low Br contents were clearly the products of recrystallization of primary halites in presence of radiogenic ^{87}Sr -bearing fluids. The authors suggested that those salts with only slightly elevated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios relative to sea

water, but with Br contents similar to primary marine salts, either deposited from or recrystallized in ^{87}Sr -enriched fluids. The deeply buried ^{87}Sr -enriched salt minerals with very high Br contents (200 $\mu\text{g/g}$ or higher) were related to interactions with dense Br-rich brines generated at shallow depths as a result of salt recrystallization during diapirism. The study of Land et al. emphasized that many deformed or deeply buried salts probably evolved through complex rock-water interactions which can result in high Br contents for deep ground waters.

SOURCES OF CONTINENTAL STRONTIUM IN EVAPORATING BASINS

If Sr isotopic excursions of evaporating waters occur during the time span of the deposition of a few tens or hundreds of meters of evaporite deposits, as suggested by data from many bedded marine evaporite deposits described above, the isotopic variations are unlikely to be related to any global sea water Sr isotopic changes. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of some bedded evaporite deposits were found to be different from that of the contemporaneous sea water. These isotopic perturbances can represent primary isotopic records of the evaporite deposits. To have such varied isotopic signatures, the waters in an evaporating basin would have to receive some continental Sr during the precipitation of the minerals. What is not clearly understood is the mode of transport of sufficient amounts of continental Sr to a marine water dominated evaporating basin causing the Sr isotopic compositions of the waters and precipitating minerals to be different from that of the contemporary sea water. The magnitude of the difference in the Sr isotopic composition between the water in the evaporating basin and the contemporaneous sea water would depend on the Sr isotopic composition and the relative contribution of Sr from the marine and continental sources. In a system with mixing of two-components, the resultant isotopic ratio R is expressed as:

$$R = (f_A \cdot i_A) + (f_B \cdot i_B)$$

where f represents fraction of Sr, i the Sr isotopic ratio, and subscripts A and B the two components. Considering this equation, the waters of an evaporating basin can contain $^{87}\text{Sr}/^{86}\text{Sr}$ ratios significantly different from that of the contemporaneous sea water, provided the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the continental Sr are either much higher or much lower than that of sea water when the net contribution of Sr from the continental source is low, or only slightly above or below that of sea water when the relative contribution of continental Sr is high. Different sources of continental Sr to an evaporating basin need to be considered and their potentials of modifying the Sr isotopic compositions of the basin waters relative to that of the contemporaneous ocean may be assessed using the above isotopic mass balance equation.

River inflow represents one potential source of continental Sr entering an evaporating marginal marine basin, but the conditions necessary for evaporite deposition limit the river inflow to a small factor. Run-offs can have varied Sr contents and Sr isotopic compositions depending upon the age and the lithology of the rocks surrounding an evaporating basin (see companion paper by Chaudhuri and Clauer, this volume). In most instances, run-offs have low Sr contents and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios; the average Sr isotopic value of run-off being slightly higher than that of sea water. The generally small difference in the Sr isotopic values between sea and continental water and the input of only limited amounts of run-off, are too small a factor to cause the evaporating waters to be measurably different in Sr isotopic composition from contemporaneous sea water.

Run-out or subsurface flow of waters is another potential source of continental Sr that may be added to the waters of an evaporating basin. Many moderately deep subsurface waters are commonly enriched in ^{87}Sr relative to sea water and have Sr contents which can be as high as 2,800 mg/l (see companion paper by Chaudhuri and Clauer, this volume). An isotopic mass balance calculation shows that 0.5% or less of subsurface water having a Sr content of about 2,000 mg/l with an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of about 0.7095 mixed with 99.5% of contemporaneous sea water in an evaporating basin can explain the Sr isotopic variations of the bedded

Permian evaporite deposits of Kansas and New Mexico. In fact, the importance of the addition of continental subsurface water to an evaporating basin as a cause for Sr isotopic variations of the evaporite deposits is difficult to assess because of the uncertainty in knowledge of the paleotopographic and paleohydrologic conditions of ancient evaporites.

Terrigenous clay-size and fine silt-size particles depositing into an evaporation basin could serve as an important source of continental Sr in the waters of the basin. A large amount of these particles might be transported by the wind, and the overall arid climate around evaporating basins can induce the conditions for high amounts of salts to be adsorbed on the surface of these fine particles which are, therefore, able to carry significant amounts of Sr simply adsorbed onto the surface of the minerals. We consider that the deposition of wind-transported, salt-encrusted fine particles in an evaporating basin might represent the major cause for the Sr isotopic excursions of many bedded evaporite deposits.

CHRONOLOGY OF EVAPORITE DEPOSITS

Geochronologic investigations of evaporite deposits are few for several reasons: (1) the abundance of evaporite deposits is small in comparison to that of other common sedimentary rocks and hence only in a few instances the stratigraphic positions of evaporite deposits are in question, (2) most common evaporite minerals are not amenable to dating by any conventional isotopic method due to their very unfavorable parent to daughter isotopic ratios and hence the dating of a deposit depends on the presence of some less common K-bearing salts, and (3) the origin of salt minerals amenable to isotopic dating is often not clearly understood and some of these minerals may be even always secondary, in which case the isotopic dates bear no relation to the depositional age of the evaporite. However, any potential failure of the isotopic data to yield a depositional age should not be construed as the isotopic data being of little value. On the contrary, the data can shed

light on the post-depositional chemical history of the rocks and can give increased understanding of the origin of salinity of continental subsurface waters.

Because of its high K content, sylvite (KCl) became a subject of isotopic analyses as early as 1958, when Polevaya et al. (1958) reported K-Ar and K-Ca ages of one recrystallized and one primary Permian sylvite samples, and of one crystallized Cambrian sylvite. The two recrystallized sylvites gave K-Ar dates of about 165 and 162 Ma, but the primary lower Permian sylvite yielded a higher K-Ar date of 236 Ma, still lower than its stratigraphic age. The K/Ca dates were higher than the K/Ar dates for the recrystallized sylvite samples, but the dates still appeared anomalously low with respect to the stratigraphic ages.

Since the work of Polevaya et al. (1958), many others also found that K-Ar and Rb-Sr dates on sylvite, carnallite, and other K-bearing salt minerals are anomalously low as compared to the stratigraphic ages (Pilot and Blank, 1967; Pilot and Rösler, 1967; Dalrymple and Lanphere, 1969; Oesterle and Lippolt, 1975, 1976; Lippolt and Raczek, 1979; Brookins et al., 1980; Register and Brookins, 1980). Different explanations have been offered for the anomalously low dates for sylvite. Dalrymple and Lanphere (1969) and Huff and Wampler (1990) favored a diffusion-related loss of ^{40}Ar , whereas Macintyre (1978) recommended dissolution-recrystallization related loss of ^{40}Ar . In many instances, sylvites are secondary in origin, forming from transformation of carnallite in presence of fresh water (Holser, 1979b), and their isotopic dates may then represent the time of recrystallization and by extension the time of introduction of fresh water into the evaporite deposits.

Pilot and Blank (1967) and Pilot and Rösler (1967) reported results of K-Ar analyses on 20 langbeinite, 5 polyhalite, 12 carnallite, and 10 sylvite samples from Permian Zechstein. The dates ranged from about 280 to 50 Ma for the langbeinite, about 230 to 190 Ma for the polyhalite, about 160 to 10 Ma for the sylvite, and about 120 to 10 Ma for carnallite. Nearly two-thirds of the samples of langbeinite yielded K-Ar dates which corresponded to the

deposition of the Zechstein, but all other minerals gave varying degrees of anomalously low ages. These low ages could have been, at least in part, related to Tertiary basaltic intrusion in the vicinity of the deposits. The observations of Pilot and his colleagues that evaporite minerals yield randomly anomalous ages have been confirmed by many subsequent studies.

Wardlaw (1968) analyzed K-Ar dates on 19 sylvite samples from potash zones in the Middle Devonian Prairie Evaporite Formation in Saskatchewan, Canada. The K-Ar dates of the minerals ranged from about 344 to about 56 Ma. As the author noted, this spectrum of young dates, in contrast to the depositional age of about 380 Ma for the evaporite rocks, is related to complex diagenetic history of the evaporite minerals, which at least included reaction of sylvite with Mg-Cl brine to produce carnallite, formation of sylvite from carnallite by leaching of Mg chloride, and recrystallization of early-formed sylvite.

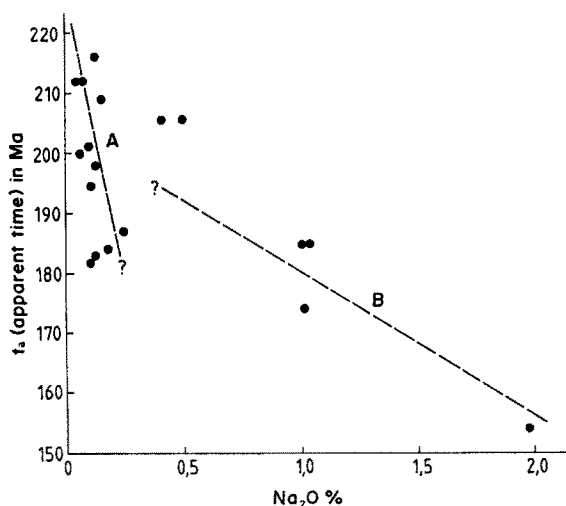


Figure 3: K-Ar apparent ages vs. Na contents of polyhalite samples from Late Permian evaporitic deposits in southeastern New Mexico (Brookins et al., 1980)

To understand the evolution of hydrous salts in relation to recent groundwater activities, Brookins et al. (1980) studied pure polyhalite, $K_2MgCa_2(SO_4)_4 \cdot 2H_2O$, from the Late Permian evaporitic deposits in southeastern New Mexico. The K-Ar dates of these pure

polyhalite samples varied between 216 and 198 Ma, which are still less than the depositional age of the minerals. Brookins (1982) observed a correlation between K-Ar ages and Na contents of the polyhalites (Fig. 3). This Na content was thought to record the occurrence of halite or mix crystals of (Na,K)Cl salt in the polyhalite samples. The process responsible for the lowering of the age is still not clear, but when the correlation is extended to zero content of Na, the K-Ar date of the polyhalite becomes very similar to the stratigraphic age of the evaporite deposits.

Huff and Wampler (1990) measured the K-Ar ages of several samples of carnallite, $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$, from Pennsylvanian Paradox Formation in Utah, U.S.A. The K-Ar dates ranged from about 27 to 9 Ma. The authors claimed that the older ages correspond to the igneous intrusions in the Colorado Plateau between 30 and 20 Ma ago, and the younger dates relate to the continuous loss of radiogenic ^{40}Ar as these carnallites remain non-encapsulated by other evaporite minerals.

Evaporite minerals yielding K-Ar isotopic ages in agreement with the depositional age are probably few. Langbeinite, $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$, has been occasionally found to yield K-Ar ages which correspond to the time of deposition. Schilling (1973) reported a K-Ar age of 240 ± 10 Ma for a pure langbeinite from Late Permian deposits in southeastern New Mexico, which is in agreement with the stratigraphic age, but two associated sylvites gave values of about 74 and 18 Ma. Oesterle and Lippolt (1975, 1976) found concordant K-Ar and Rb-Sr dates for each of three different langbeinite samples. They reported dates of 230, 150 and 100 Ma, none of which corresponds to sedimentation times. Considering that the langbeinite minerals have high retentivity of both radiogenic ^{40}Ar and ^{87}Sr , the authors felt that the isotopic dates of langbeinite might be indicative of recrystallization processes related to different tectono-metamorphic activities in Western Europe.

Most of the common evaporite minerals have limited amount of radiogenic ^{87}Sr due to high amounts of Sr relative to Rb and are therefore unsuitable for dating by the Rb-Sr method. But sylvite or mix crystals of (Na,K) chloride salts and (K-Mg) sulfate salts,

such as carnallite, langbeinite and rinneite, can have sufficient radiogenic ^{87}Sr relative to normal Sr due to very high Rb/Sr ratios. However, the low Sr content of $1\ \mu\text{g/g}$ or less and the complex evolution processes of these minerals often lead to ambiguous interpretations of the dates. Lippolt and Raczek (1979a) determined the Rb-Sr isotopic dates on two carnallitic salt rock samples, only a few meters apart from each other, of Permian evaporite deposits in northern Germany. The model Rb-Sr ages of these two samples were found to be different and anomalously low at 96 and 82 Ma. In another study, Lippolt and Raczek (1979b) observed Rb-Sr model ages ranging from about 84 to 20 Ma on four samples of rinneite which is known to occur as metasomatic product in Permian salt deposits in Germany. A sample of carnallite associated with the youngest rinneite (20 Ma) gave a much younger age of about 8.5 Ma. The meanings of these differing ages for evaporite minerals in the proximity of each other are not clear.

Register and Brookins (1980) reported a Rb-Sr isochron date of about 214 Ma from some scattered data on evaporite minerals of the late Permian Salado Formation in southeastern New Mexico. Model ages were calculated based on the assumption of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio being the same as that of the contemporaneous sea water. These model ages ranged from 270 to nearly 0 Ma, and clearly the Rb-Sr isochron age of 214 Ma has an ambiguous meaning, suggesting that the chemical evolution of minerals in the evaporite deposit was very complex. Some mineralization event must have occurred in the last few million years in the late Permian evaporite deposit of eastern New Mexico, as evident from data on a halite sample whose Rb/Sr ratio was about 1 and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was 0.7076. This Sr isotopic ratio is close to that of the anhydrite deposits, suggesting that the Sr in the halite could have derived primarily from evaporite deposit.

To understand diagenetic recrystallization and mineralization in an evaporite deposit, Baadsgaard (1987) examined the K-Ar, Rb-Sr, and K-Ca isotopic systematics of a large number of sylvite, carnallite, and halite minerals and also of whole-rock samples from potash zones in the Middle Devonian Prairie Evaporite Formation in western Canada. The ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were between 0.7085

and 0.7406 for the halite samples, between 0.7157 and 2.2256 for the sylvite samples, and between 0.7093 and 2.7529 for the carnallite samples. The Rb-Sr model ages of nearly all sylvites, with the exception of a few, were between 20 to 60 Ma (Fig. 4). By comparison, the Rb-Sr model ages of carnallites, were low between 20 and 2 Ma.

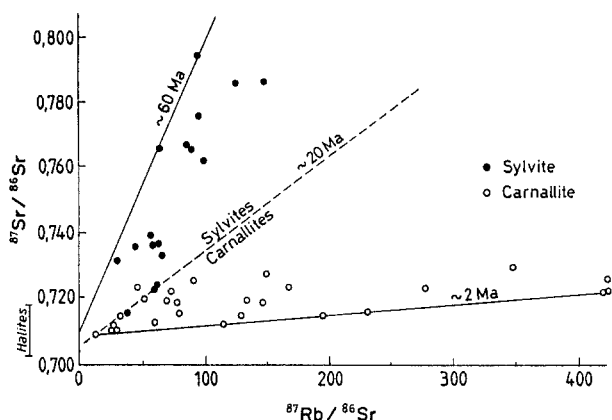


Figure 4: Rb-Sr isotopic compositions and the range of model ages for sylvites and carnallites of the Middle Devonian Prairie Evaporite in western Canada (Baadsgaard, 1987)

The $^{40}\text{Ca}/^{44}\text{Ca}$ ratios of halites were distinctly varied between 47.17 and 47.62, as compared to the value of 47.18 for the modern sea water. This suggests that the halites either locally recrystallized or precipitated in the presence of varied amounts of ^{40}Ca -bearing fluids. Because of the very low K/Ca ratios of the halites, their K-Ca model ages could not be calculated. But due to their favorable K/Ca ratios, sylvites and carnallites could be analyzed for the K-Ca isotopic dates. Like the Rb-Sr isotopic data, the K-Ca isotopic data were non-coherent failing to yield any distinct isochron (Fig. 5). As shown in the diagram, the calculated K-Ca model ages for the sylvites are lower than those for carnallites. The relative difference in the K-Ca model ages between the two minerals is opposite to that in the Rb-Sr model ages between the same two minerals. Baadsgaard noted that the disagreement between the two sets of results can be related to the different chemical behaviors of K, Rb, Ca, and Sr during the sylvite-carnallite diagenetic transformation or recrystallization. Baadsgaard also noted that whereas the Rb-Sr and the K-Ca dates of sylvites were

less than 100 Ma, the K-Ar dates of sylvites were mostly between 344 and 207 Ma. He concluded that the older K-Ar ages in comparison to the other isotopic ages might be the reflection of local incorporation of varied amounts of radiogenic ^{40}Ar by the diagenetically formed sylvites.

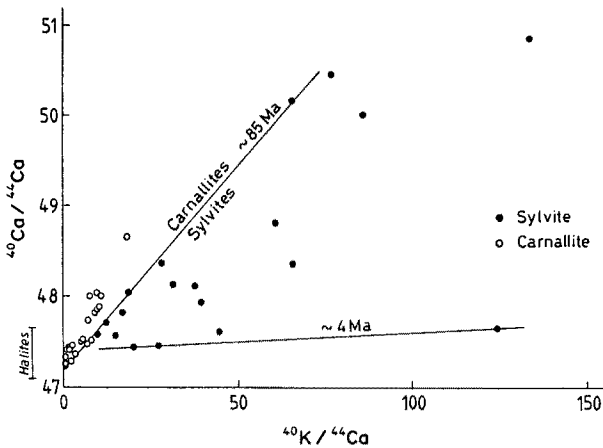


Figure 5: K-Ca isotopic data of sylvites and carnallites of the Middle Devonian Prairie Evaporite in western Canada (Baadsgaard, 1987)

The global marine Sr isotopic secular variation curve has also been used to determine the age of evaporite deposits from their Sr isotopic compositions (Posey and Fisher, 1989). But such a chronostratigraphic approach must be carefully considered. The Sr isotopic age-curve for the pre-Tertiary period is based on a limited number of scattered isotopic data at each geologic time. The accuracy for the isotope curve based age can therefore be severely limited even when the global marine Sr isotopic composition apparently shifted very rapidly. The utility of the isotope-age curve for chronostratigraphy of evaporite deposits is further limited by the Sr isotopic data of the deposit itself. We have already pointed out that even the primary $^{87}\text{Sr}/^{86}\text{Sr}$ records of bedded evaporite deposits may not bear the marine isotopic signature of the contemporary ocean waters.

SUMMARY

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of minerals in marine, bedded evaporite deposits are often higher than that of contemporaneous sea water. The deviations are often explained in terms of secondary origin or recrystallization of these minerals in presence of radiogenic ^{87}Sr -bearing fluids, but such small isotopic variations recorded in ancient bedded evaporite deposits could also be due to the introduction of continental Sr into the evaporating basins during the time of deposition. A logical source for this continental Sr could be the release of continental salts from salt-encrusted fine clay- and silt-sized silicate particles, transported into the basins by wind.

The conventional isotopic dates of most evaporite minerals are often lower than their stratigraphic ages. If the loss of radiogenic isotopes occurs by a process of continuous diffusion, the anomalously low dates are geologically meaningless. On the other hand, if the loss relates to episodic events, then the data are useful to understand the halokinesis of an evaporite deposit. More studies are needed to define the criteria for recognition of the process by which isotopic disturbances might have occurred for any particular evaporite deposit. Undoubtedly, many evaporite minerals are secondary in origin and are related to several cycles of chemical disturbance. Groundwaters play an important role in the deformation of evaporite deposits, but connate fluids and crystallization waters become also important in bedded deposits to produce recrystallized or authigenic minerals. Knauth and Beeunas (1986) maintained from analyses of D and ^{18}O in fluid inclusions in salts that the fluids originate as highly evaporated sea water or synsedimentary brines mixed with meteoric water.

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