

STABLE ISOTOPE GEOCHEMISTRY OF SULFATE
AND CHLORIDE ROCKS

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Sulfate and chloride deposits are a prominent constituent of evaporite rocks, formed by the evaporative concentration of marine or non-marine waters. The geology and geochemistry of evaporite rocks has been well reviewed by Holser (1979a, b), Kendall (1984), Schreiber (1988) and Warren (1989), and will be summarized only briefly here.

The amount of concentration required to precipitate evaporite minerals ranges from about three times the concentration of normal modern sea water, when gypsum or anhydrite crystallize, to virtual dessication (60 to 80 times sea water) when the most soluble chlorides finally precipitate (Table 1). Rivers or other non-marine waters, starting from solutions that are much more dilute, require more intense evaporative regimes to reach corresponding saturations of sulfate and chloride minerals. It is clear that in either case the essential requirement for the formation of sulfate and chloride minerals is a high rate of net evaporation (evaporation minus rainfall) combined with a relatively restricted inflow of water. Evaporation, which depends on low atmospheric humidity aided by brisk wind speeds, is predominant in continental climates of middle to low latitudes. In such areas the restricted input necessary for evaporite deposition may be found in a variety of physical situations: (a) coastal intertidal and supratidal zones called sabkhas,

(b) small lagoons on coasts and atolls, (c) large deep-water marine basins, (d) sub-sea level basins with limited marine inflow, and (e) non-marine interior basins. One tectonic setting that has been particularly conducive to evaporite deposition is continental rifts. Beginning with dry interior rift valleys, sedimentation proceeds through marine evaporites controlled by restricted input of sea water, to deposition of normal marine deposits as inflow exceeds evaporation. Some "saline giants" accumulated in this manner in rifts of the North Atlantic and Gulf of Mexico during the Triassic-Jurassic, in the South Atlantic during the Cretaceous, and in the Red Sea in the Late Miocene. The tectonic control of extensive evaporite deposition on the craton, such as in the mid-Paleozoic on the North American craton and in the Permian on the European craton, is not so clear but may be incipient rifting or stretching. In contrast to these enormous deposits rich in salt rocks, more limited evaporites of predominantly Ca-sulfate mineralogy formed as sabkhas on shallow shelves such as those along present-day coasts of the Mediterranean, Red Sea and Persian Gulf.

These tectonic controls on restricted marine input are critical, shifty and transitory, short-lived geological accidents. Conditions may have been just right for an evaporitic episode for only a geological "instant" - at most a fraction of a million years. Though the interval of evaporite deposition was short, the rate of accumulation was extraordinarily rapid. Consider that once saturation had been reached, in a basin of whatever depth, a nominal rate of net evaporation, say two meters of water per year, would result in Ca-sulfate deposition at 1.2 mm/yr or salt at 25 mm/yr, compared with a typical rate of carbonate sedimentation of about 0.1 mm/yr. Consequently preformed evaporite basins tend to fill quickly to their level of input even during an episode of relatively short duration.

A facies classification of evaporite rocks is analogous to the facies classification of metamorphic rocks: it is based on the appearance of the indicated mineralogy, although this is due to the degree of evaporation rather than a maximum temperature or pressure. Table 1 outlines some of the characteristics of marine evaporite facies. A departure from this mineralogy or from its sequence

indicates a differing chemistry of input waters, evidence of a non-marine component (Hardie, 1984), although non-marine evaporites are not commonly preserved in pre-Tertiary sediments (Holser, 1979c). Just as in metamorphic rocks, primary facies mineralogy may be accompanied by prograde or retrograde replacement of pre-existing minerals. Thus halite may crystallize directly, or replace earlier gypsum, and vice-versa; polyhalite may replace anhydrite which may in turn have replaced gypsum; primary calcitic limestone lamellae may be dolomitized. Along with the changes in mineralogy, the overlying or included brine also varies in density (Table 1) as well as chemistry. Because of its high density the brine will tend to become stratified, and because of stratification and low solubility of O, the deeper layers will tend to anoxic and their deposits laminated and rich in organic C and sulfides (Evans and Kirkland, 1988).

Table 1: Summary of Evaporite Facies (After Holser, 1979a)

Facies	Mineralogy	Measures of evaporation stage				
		Salinity wt %	Density g/ml	Percent H ₂ O evap.	Conc. Xs.w.	Activity H ₂ O
Potash- magnesia facies	: Bittern Bischoffite,					
	: subf. Tachyhydrite					
	: Potash Carnallite,			99.2	120	
	: subf. Sylvite, Kainite,					
	: Kieserite, Halite,					
	: Anhydrite or Polyhalite					
	: MgSO ₄ ^a Epsomite, Bloedite,	380	1.31	98.7	78	
	: subf. Halite, Polyhalite or Anhydrite					
Halite facies	Halite, Anhydrite or Gypsum	375	1.29	98.4	68	0.67
CaSO ₄ facies	Gypsum or Anhydrite Dolomite	300	1.20	91.0	12.2	0.76
Dolomite facies	Dolomite, Calcite	150	1.10	72.0	3.6	0.93
		35	1.02	0	1.0	1.00
Marine facies	Calcite, Aragonite					

^a usually altered to potash subfacies

In deep basins relatively isolated from the sea, brines will move quickly through the Ca-sulfate facies, the thickness of which will amount to only 0.6% of the basin depth before halite must start to crystallize, unless residual brines are also refluxed back to the sea (Holser, 1979a, p. 264). Burial under the succeeding weight of sediments leads to important changes in evaporite rocks. Primary deposition in the Ca-sulfate facies is commonly as gypsum, although at higher salinities and higher temperatures primary anhydrite may either precipitate directly or replace primary

gypsum. However, as the temperature rises along the geothermal gradient during burial, any gypsum tends to dehydrate to anhydrite plus water; on being exhumed by erosion and exposed to cool fresh ground water the anhydrite cycles back to gypsum. Higher temperatures under burial also lead to plastic flow in salt rock, which under buoyant or tectonic forces moves upward to form salt pillows and eventually intrudes the overlying sedimentary section as salt domes or even extrusions (Lerche and O'Brien, 1987). The plastically deforming salt rock carries along admixed anhydrite and other accessory minerals. At shallow depths the top of the salt dome is attacked by ground water, which easily dissolves the halite and leaves a "cap rock" of residual anhydrite or its gypsum alteration. This gypsum is further altered by S-reducing bacteria to form H_2S , pyrite and other sulfides, native S, and calcite (as a byproduct of the bacterial activity).

STABLE ISOTOPES IN SULFATE AND CHLORIDE DEPOSITS

The deposition and subsequent erosion of evaporite rocks is a primary feature of the sedimentary cycle of chloride (Holser et al., 1980), S and (to a lesser extent) C (Holser et al., 1988). Isotopic studies have been helpful in untangling the complex cyclical history, particularly of sulfate rocks, and in attacking other questions of interest to geologists. Some of the questions for which isotopes are of potential value are:

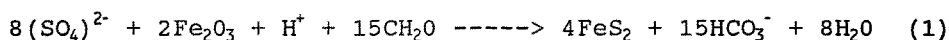
- (1) What was the time (age date) of primary deposition?
- (2) Was the deposition from a marine, or from a non-marine source?
- (3) Is the present mineralogy primary, or is it a diagenetic or later replacement of the original deposit?

The main features of stable isotopes in evaporite rocks have been reviewed by Holser (1979b), Arthur et al. (1983) and Pierre (1988, 1989). The most informative stable isotope system is that for S; the discussion will include the related events in the C isotope system. The $^{87}Sr/^{86}Sr$ ratio can be used as a tracer in the sedimentary cycle, directly on Recent sediments or on any Rb-poor

mineral phase in any old geologic material. The discussion concludes with consideration of the isotope systems of H and O in water.

THE MARINE ISOTOPE SYSTEMS AND AGE CURVES

The exogenic geochemical cycles (sedimentary rocks, world ocean and atmosphere) of S and C are critically reviewed by Holser et al. (1988), and the corresponding cycle of Sr is discussed by Palmer and Elderfield (1985) and Wadleigh et al. (1985). The ocean is substantially mixed for each of these elements, so an isotope ratio for sea water reflects the balance of isotope transfers from rivers and ridges and out to the sediments. As indicated in figure 1, biological fractionations dominate the marine geochemistry of both S and C. The S of sea-water sulfate is fractionated by about -40 per mil by S-reducing bacteria that are ubiquitous in marine muds, and the sulfide product may be fixed as pyrite:



This reaction favors light S (low $\delta^{34}\text{S}$), consequently an increase in the proportion of S reduced to sulfide raises the $\delta^{34}\text{S}$ of the

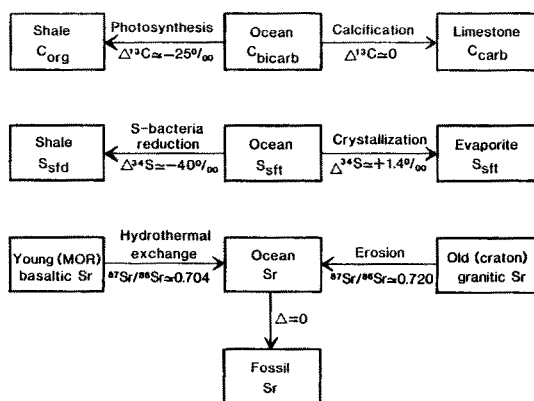


Figure 1: Schematic representation of the relations of the isotopes of C, S and Sr in the oceans (Holser et al., 1986)

sulfate remaining in the ocean; a decrease in S reduction reduces ^{34}S . The $\delta^{34}\text{S}$ can be sampled, anywhere in the world, by contemporary sulfate deposition (involving only a small fractionation), which thus maintains a record of secular shifts in sulfide-sulfate transfers. The record of such shifts during Phanerozoic time is embodied in the "sulfur isotope age curve" of figure 2a (Holser, 1984).

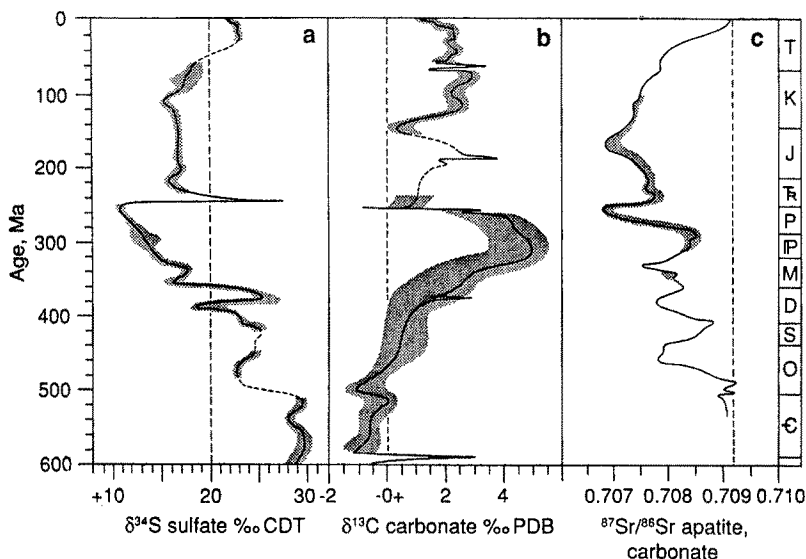


Figure 2: Age curves of (a) S isotopes in evaporite sulfate, (b) C isotopes in carbonates, and (c) Sr isotopes in carbonates and fossil apatite. Adapted from Holser (1984), taking into account new data for Carboniferous to Triassic for C (Popp et al., 1986; Baud et al., 1989) and Sr (Popp et al., 1986; Holser and Magaritz, 1987; Brookins, 1988), for Jurassic C (Jenkyns and Clayton, 1986), and for Tertiary C (Loutit et al., 1983; Vincent et al., 1985; Shackelton, 1986), S (Burdett et al., 1989) and Sr (Elderfield, 1986; McKenzie et al., 1988)

The photosynthesis of bicarbonate to organic C is accompanied by a fractionation that is similar (the organic product also prefers the light isotope) but smaller (Fig. 1). The fraction of C involved in organic synthesis is also smaller, and the consequent secular shifts in $\delta^{13}\text{C}$ of the residual bicarbonate (plus atmospheric CO_2 equilibrated with sea water) are correspondingly smaller (Fig. 2b). The marine bicarbonate is sampled (with negligible to minor fractionation) by limestones or dolostones, including those interlaminated with sulfate evaporites (e.g., Magaritz et al.,

1983).

In contrast to this record of high but variable $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$ exhibited by the residual oxidized components of sea water, sulfate and carbonate of other origins will show very different and mostly much lighter values of $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$. For example, oxidation of pyrite on an outcrop of shale will mimic without fractionation the very light S of the pyrite ($\delta^{34}\text{S}$ -30 to +5 per mil). The sulfate with low $\delta^{34}\text{S}$ may be fixed on the outcrop as gypsum, or move into the river system, perhaps ending as a lacustrine sulfate deposit. Similarly, oxidation of organic C retains a light isotope ratio ($\delta^{13}\text{C}$ -30 to -10 per mil) in the product CO_2 . For example, the bicarbonate byproduct of sulfur reduction (Eq. 1) may reduce $\delta^{13}\text{C}$ in that milieu (e.g. Pierre and Rouchy, 1988).

Strontium is a different story: it does not fractionate, so its isotope ratio in sea water represents a balance of the input fluxes of Sr from old continental granites enriched in ^{87}Sr , and Sr exchanged from young basalts like those of the mid-ocean ridges depleted in ^{87}Sr (Palmer and Elderfield, 1985; Chaudhuri and Clauer, 1986; Veizer, 1989; Fig. 1). The sea water isotope ratio of Sr may be sampled by limestones, phosphate or sulfate rocks, the latter accept a few tenths percent Sr in place of Ca (Holser, 1979b). The compiled Sr-isotope age curve (Fig. 2c) presumably records the history of varying input sources with time.

The age curves for S, C and Sr are an empirical record of changes in sea water, verified where possible by analyses from two or more basins that would be expected to sample the world ocean independently of any local anomalies. Their validity has also been tested in varying degrees by computer modelling in which the empirical age data serve as input or comparative output (Holser et al., 1988), but these calculations depend on many assumptions and do not furnish robust constraints.

The $\delta^{18}\text{O}$ values in the sulfate ion of sea water were also evaluated as a balance of inputs and outputs, equilibration with ^{18}O of the water being so slow as to be ineffectual (Holser et al., 1979; Zak et al., 1980). On this basis, an age curve for $\delta^{18}\text{O}$ of

sulfate in marine evaporites was proposed (Claypool et al., 1980). However, some studies of this system suggest that other factors such as local reduction-oxidation cycling, or diagenetic reaction with meteoric waters, may be dominant (Cortecci et al., 1981; Perry et al., 1982; Pierre, 1985; Richardson and Hansen, 1988). Until these additional complicating factors have been better evaluated, there is considerable question as to whether an age curve for $\delta^{18}\text{O}$ in marine sulfates can be defined and applied to geological problems.

APPLICATIONS OF THE AGE CURVES

An isotope age curve is simply our best estimate of the isotope ratio in (world-mixed) sea water, or in sediments directly deposited from that sea water. If a new evaporite of questionable provenance is sampled, its isotope ratio(s) may be compared with the pre-determined isotope age curve. If the stratigraphic age of the new samples is known, and the ratio fits the age curve reasonably well, the evaporite is probably of marine origin. If the age is known, and the ratio does not fit the age curve, the evaporite (and perhaps the sedimentary section as a whole), is probably non-marine. If the sulfate is not of marine origin, what is it? It could be from the erosion of an older sulfate evaporite within the drainage basin, in which case it would have retained the isotopic signature of the original marine sulfate rock. Or it could be sulfate fed to the drainage basin from the surface weathering of sulfides, in which case it should carry the light values of sulfide of igneous ($\delta^{34}\text{S} = 0$ to $+5$ permil) or sedimentary ($\delta^{34}\text{S} = -30$ to -5 per mil) origin; hydrothermal sulfides vary extremely widely (Hoefs, 1980).

Alternatively, the newly sampled evaporite might reasonably be supposed to be marine, as verified by its marine mineralogical sequence (Table 1) or by a normal bromide content of interbedded chloride deposits (Holser, 1979b). However, its age may be in question, perhaps between two or three choices, in such a case the

decision may be made by a match of sample data with the appropriate age curve: "isotope chronostratigraphy" (Williams et al., 1988). The multi-valued aspect of the age curves (Fig. 2) means that isotope age curve dating is the more helpful as the range of choices is restricted, a characteristic that it shares with paleomagnetic stratigraphy. And of course its precision is best where the curve is most precisely defined by previous work, and where the isotope ratios are changing most rapidly (Elderfield, 1986). The precision is also improved if two isotope systems may be compared, as in the S-Sr plot of figure 3.

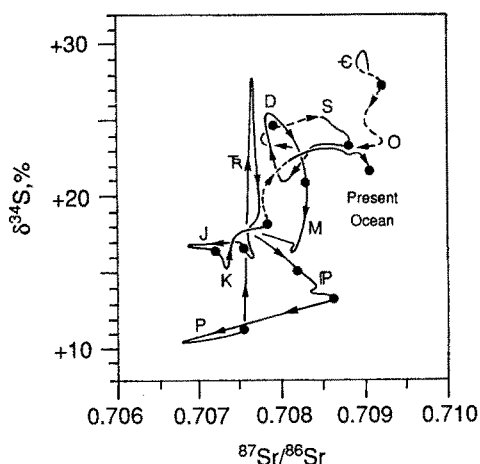


Figure 3: Cross-reference plot for marine isotope ratios of Sr vs. S (data from Fig. 2). Solid circles are boundaries of the geological periods, labelled as in Figure 2. Arrows point forward in time

Some examples may clarify the method. The Fort Dodge Gypsum covers an area of over 100 km² in Webster County, Iowa, in an inlier isolated by block faults. The gypsum overlies Pennsylvanian (Desmoinesian) shale and is covered by late Wisconsin glacial drift (Gwynne, 1957). No fossils had ever been found in the gypsum or in the rare interbedded shales, and for want of better information it had been lithologically correlated with the nearest evaporites, of Permian (Wolfcampian) age, occurring 300 km southwest in Kansas. Analyses of S isotopes in gypsum from a quarry face gave $\delta^{34}\text{S} = +16.1 \pm 0.2$ per mil. This value is quite definitely not Permian, and the deposit is probably of Mesozoic age (Middle Triassic to Early Cretaceous) (Fig. 2). In another case, deep drilling in the

Gulf of Paria, Trinidad, unexpectedly penetrated 700 m of anhydrite underlying Tertiary sediments. Sulfur isotope analyses determined the evaporite to be of pre-Late Cretaceous age (Claypool et al., 1980), and subsequently this was confirmed by micropaleontology of interbedded sediments.

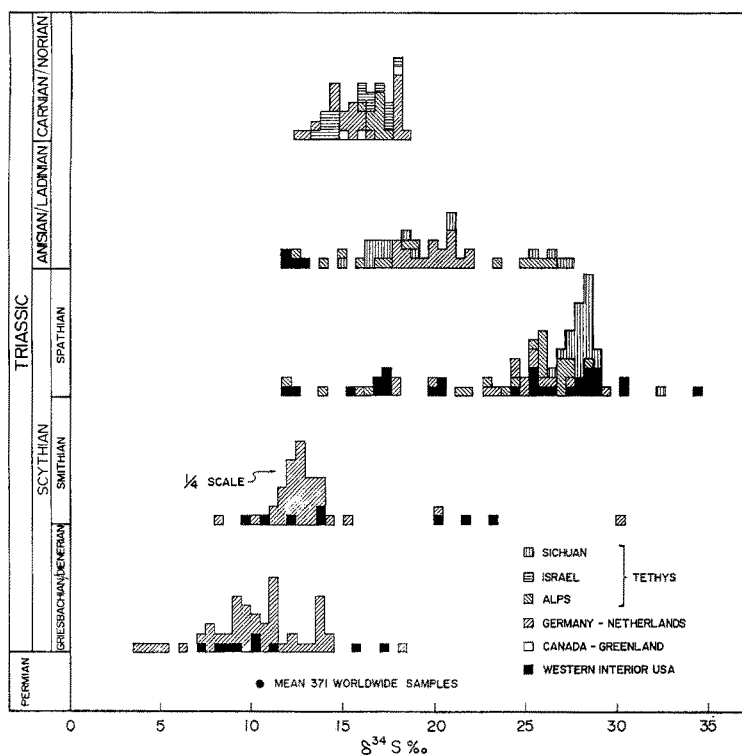


Figure 4: Detail of the sharp rise in the age curve for S in the Triassic. Each square is one analysis, except for the Smithian which is factored by 4; the time scale for the Scythian Stage (Lower Triassic) is greatly expanded. From Holser (1984)

In Europe the very widespread Zechstein evaporites of Late Permian age with $\delta^{34}\text{S}$ near +11 per mil are accompanied in some areas by evaporites of Early Triassic (Upper Buntsandstein) age with strongly contrasting $\delta^{34}\text{S}$ near +27 per mil (Fig. 4). In an overthrust zone Nielsen (1972) was able to verify by S isotopes that Zechstein gypsum actually overlies Buntsandstein (younger) evaporites. In a much more complex area of Alpine tectonics, complicated structures involving the two salts were untangled by their distinctive S isotope ratios (Pak and Schauburger, 1981; Pak, 1981;

Spotl 1988a, 1988b).

In the Tertiary (Oligocene-Miocene) Ebro Basin of northern Spain, a sequence of evaporites more than 3 km thick was known to be non-marine from the nature of the associated sediments. Within the Tertiary drainage Triassic evaporites had $\delta^{34}\text{S} = +14.7 \pm 0.7$ per mil, and the Tertiary gypsums varied from that level down to $\delta^{34}\text{S} = +9$ per mil, so it could be concluded that the source of the Tertiary evaporites was mainly from outcrops of Triassic gypsum, diluted in some cases by weathering of sulfide deposits (Birnbbaum and Coleman, 1979). There is also isotopic evidence for recycling of Triassic evaporites into late Tertiary gypsum of the Granada Basin in southern Spain (Pierre, 1988).

The sulfate ion is a very stable unit, and consequently in the absence of local biological reduction, second-cycle brines or evaporites reflect their first-cycle derivation from the ocean. Thus, anhydrites filling porosity in the San Andres Limestone in Texas, and in the Lyons Sandstone in the Denver Basin were shown to be of Permian and not of later age (Holser and Kaplan, 1966). This same stability of the sulfate ion allows S isotopes to trace the origin of sulfate contents of sabkha brines (Robinson, 1985) formation waters (Muller et al., 1966), ground waters (Bassler, 1970), springs (Michel and Nielsen, 1977) and surface waters (Nielsen and Rambow, 1969; Hitchon and Krouse, 1972), and in particular to determine the relative importance of marine evaporites in their origin.

There is much current interest in the application of Sr isotope ratios to age determination and stratigraphy, especially in the Cenozoic where the age curve is both steep (Fig. 2c) and so well defined that a precision of ± 0.5 Ma has been claimed (Elderfield, 1986; McKenzie et al., 1988). Most attention has been given to the Sr isotope record in carbonate sediments, but a few results in sulfate rocks (F. Albarède, pers. comm., 1984; Zierenberg and Shanks, 1986; Brookins, 1988; M. A. Arthur, pers. comm., 1989) suggest a great potential for application in evaporites. Some limited data indicate that the Sr isotope ratio in restricted evaporite basins is especially susceptible to the influence of

continental runoff (Clement and Holser, 1988; Muller et al., 1990).

The C-isotope age curve (Fig. 2b) has been applied to stratigraphy in the Late Permian, where paleontological correlations are inhibited by scarce and endemic fauna, especially in the evaporite basins that are characteristic of that time. Just below the base of the evaporite section in the Zechstein Basin, $\delta^{13}\text{C}$ in the inter-laminated carbonates was found to rise abruptly to high positive values, and this high level of $\delta^{13}\text{C}$ continues through the overlying evaporites to the end of the Permian (Magaritz et al., 1981). Subsequently we looked for and found an analogous sharp rise just below the Castile evaporite in the Permian Basin of West Texas (Magaritz et al., 1983) and at the contact of the Gröden and Bellerophon Formations in the Tethyan section of the Southern Alps (Holser and Magaritz, 1985). In Texas the rise could be timed by varved sedimentation to have been accomplished in less than 5 ka (Magaritz et al., 1983), giving unprecedented precision to this world-wide correlation (Holser, Magaritz and Clark, 1986). In contrast to these primary carbonates of evaporitic series, diagenetic carbonates replacing the sulfate rocks show very low and variable $\delta^{13}\text{C}$ owing to their origin as organic carbon feeding the bacterial sulfate reduction (Eq. 1; Pierre and Rouchy, 1988).

There are problems. Residual variations remain both within and between contemporaneous basins, of 1 or 2 per mil for $\delta^{34}\text{S}$, and of 0.0002 for $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 2). In some instances the residual variations of $\delta^{34}\text{S}$ have been attributed to intense sulfur reduction within the sampled basin (raising ^{34}S of sulfate locally), or to crystal fractionation in late-stage evaporites (decreasing $\delta^{34}\text{S}$) (Holser and Kaplan, 1966; Nielsen, 1972; Pierre, 1985). Residual variations in $^{87}\text{Sr}/^{86}\text{Sr}$ have been attributed to contamination by shaley radiogenic Sr or to diagenesis (Hess et al., 1986). But it is difficult to escape the conclusion that we do not yet understand these variations.

This skepticism is reinforced by a couple of dramatically anomalous results. Sulfur-isotope ratios in the lower Oligocene evaporites of the Rhinegraben vary widely from +10 to +23 per mil, but many from the potash facies are near +12 per mil (Nielsen,

1967), compared with values near +20 per mil in other marine Tertiary evaporites (Claypool et al., 1980). Nielsen (1972) suggests that during the Oligocene deep circulating brines dissolved Permian Zechstein evaporites 300 km distant, and eventually flowed into the Rhine Basin. During much of the evaporite deposition the sulfate content of the Permian brines was not sufficient to debase the incoming marine sulfate, but did have a strong influence during a sulfate-scarce late stage of evaporation. This proposal has yet to be confirmed by other evidence.

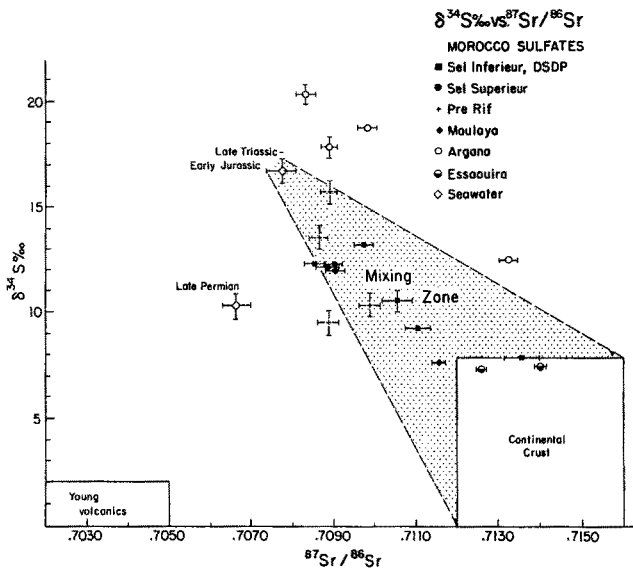


Figure 5: Isotope ratios of Sr vs. S in Moroccan evaporites. Analyses from various evaporite basins are shown relative to expected values for marine sources of Late Permian and Late Triassic-Early Jurassic ages, and for young volcanic and old continental sources. The shaded area represents possible values from mixing of Late Triassic-Early Jurassic marine waters with continental sources. From Clement and Holser (1988)

Another case proclaims the peril of conclusions with too little data. An initial geochemical study of an evaporite deep-sea core from a diapir off the coast of Morocco concluded that the evaporites were of Permian age, for a nice fit of its $\delta^{34}\text{S} = +10.1 \pm 0.9$ per mil, but in the face of much geological evidence that the salts were actually Upper Triassic to Lower Jurassic deposits (Holser et al., 1984). Fortunately geology prevailed in a later more detailed study of numerous evaporites from onshore Morocco, in which measurements of Sr isotopes were combined with those of S isotopes

(Clement and Holser, 1988). As shown in figure 5, some of the onshore evaporites had $\delta^{34}\text{S}$ down to less than +5 per mil, values not approached by marine waters of any geological age. These very low values of $\delta^{34}\text{S}$ were accompanied by levels of $^{87}\text{Sr}/^{86}\text{Sr}$ up to 0.714 - much higher than any known marine Sr (Fig. 2c). A plot of S against Sr isotopes shows a rough negative correlation (Fig. 5), which indicates a varying mixture in the evaporites of non-marine components and Upper Triassic-Lower Jurassic sea water. Apparently the offshore diapir mimicked the $\delta^{34}\text{S}$ of Permian sea water by a chance admixture of light non-marine S. Even so, it was difficult to construct a believable model that accounted for the very large volume of some of the salt deposits (and their Br content) as well as the S and Sr isotope data (Clement and Holser, 1988).

THE WATER SYSTEM

The isotope ratios of H and O co-vary in the H_2O system, and considered together they can supply interesting information about the evaporation, mixing, and crystallization of water. Figure 6 outlines some of the essential features of the water isotope system in evaporitic settings, in a plot of $\delta^2\text{D}$ ($= {}^2\text{H}$) against $\delta^{18}\text{O}$, on a scale relative to Standard Mean Ocean Water (SMOW). At the center of this system is the ocean, which is both the standard of measure (SMOW) and the principal reservoir. Present-day sea water is fairly well mixed and near SMOW in isotope ratio, although $\delta^{18}\text{O}$ may be lowered by a few per mil in coastal waters that have been freshened by, e.g., glacial melt (reviewed in Hoefs, 1980).

In the global water cycle, water evaporated from the sea is lighter in both δD and $\delta^{18}\text{O}$, and by successive evaporations both become lighter as the air masses sweep to higher elevations and higher latitudes. By rainout the resulting meteoric water lies somewhere along the line shown in figure 6, with polar latitudes in the lower left. As a consequence, liquid water remaining after evaporation increases, at first, in both δD and $\delta^{18}\text{O}$. The result complex, depending on the humidity and isotope ratios of D and O

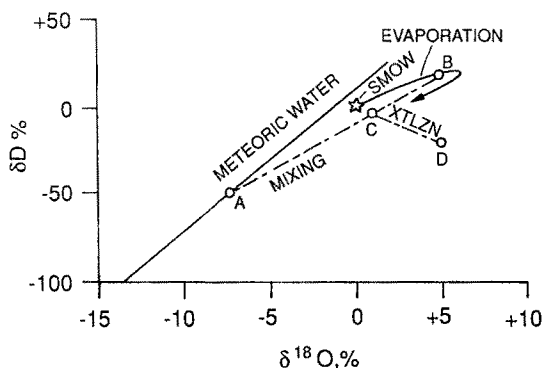


Figure 6: Schematic representation of the isotope systems for water in evaporative regimes. The evaporative loop for ocean water is as measured by Nadler and Magaritz (1980), but this is only one example of possible trajectories (Sofer and Gat, 1975). An example is given of a mixing line between an evaporated brine of composition "B" (near gypsum precipitation) and meteoric water of composition "A", in such proportions as to give a composition "C". When such a mixed water crystallizes in gypsum, δD will be lighter and $\delta^{18}O$ will be heavier at composition "D"

in the ambient air, as well as on the cationic composition of the solution, which reduces the activity of H_2O and its isotopic components (Sofer and Gat, 1975). A typical course of evaporation of sea water on the δD - $\delta^{18}O$ plot is shown in figure 6: at first it moves to more positive δD and $\delta^{18}O$, but along a slope shallower than the meteoric water line. Then it reaches equilibrium (in the $CaSO_4$ facies), first for δD and then for $\delta^{18}O$, and finally in concentrated brines (halite facies) it loops back to lower values of both δD and $\delta^{18}O$. The looped evaporation curve in figure 6 is only one observed example (Nadler and Magaritz, 1980) of a variety of possible courses of δD - $\delta^{18}O$ during evaporation under different conditions (Sofer and Gat, 1975)¹. An evaporite brine with a δD and $\delta^{18}O$ such as at point "B" in figure 6, may be lightened in both isotope ratios by the effect of meteoric water, such as at point "A", to give a resulting isotopic composition at point "C". Incorporation of water molecules into the structure of a gypsum crystal fractio-

¹ The evaporative loop illustrated by Holser (1979b, p. 329) and extensively cited in the interpretations by Knauth and Beeunas (1986) was purely diagrammatic.

nated in $\delta^{18}\text{O}$ by +4 per mil and δD by -16 per cent, to reach point "D" in the typical example displayed in figure 6. Vice versa, a plot of δD and $\delta^{18}\text{O}$ in a gypsum sample may be translated by the same vector to the upper left, to deduce the δD - $\delta^{18}\text{O}$ composition of the "mother liquid" from which it had been crystallized.

Interstitial brines at the inner edge of a modern salt pan lie generally in the region of point "C", and are interpreted as resulting from mixing of evaporative brines with continental ground waters (Pierre and Ortlieb, 1980; Pierre et al., 1984; Knauth and Beeunas, 1986). Analyses of gypsums of Tertiary age from the Mediterranean region (Rouchy and Pierre, 1979; Pierre and Fontes, 1979) and from Poland (Halas and Krouse, 1982) plot their mother liquid on the meteoric water line, or slightly below it in the mixing area. Such results may be interpreted as either: primary crystallization from brines of mixed marine-meteoric heritage (as in the above-cited modern examples), or re-gypsification in the presence of later meteoric ground waters. Some of the gypsums from Poland scatter along a mixing trend that intercepts the meteoric water line at about $\delta\text{D} = -110$ per mil, $\delta^{18}\text{O} = -15$ per mil, which is so very low that the corresponding meteoric water can only have been produced by a glacial climate. Hence the Ca sulfate that was precipitated in the Miocene was most recently gypsified during the Pleistocene (Halas and Krouse, 1982; see also Bath et al., 1987).

Alternatively the isotopic composition of old evaporite brines may be studied by analyzing fluid inclusions in salt rock. Microscopic inclusions of brine are trapped during primary crystallization of halite, especially along cubic growth planes, where they may be concentrated in a "chevron" texture. Subsequently these microscopic inclusions are reconstituted into mm-sized cubic cavities during re-crystallization of the halite, and under some conditions the brine is expelled to the intercrystalline grain boundaries (Roedder, 1984). In view of the variety of types of inclusions and other sites where water may be found in the salt rock, a clean unfractionated sample of inclusion fluid for isotopic analysis is difficult to recover and validate.

Despite these difficulties, interesting results were obtained

(J. Wright, pers. comm., 1989). Chemical compositions of fluid inclusions in halite from the Permian of Texas and New Mexico (Roedder, 1984; Knauth and Beeunas, 1986) generally lie in the same field as the brines of modern salt pans: under the hook of the evaporation curve and scattered down and to the left along possible mixing lines. Compositions of the primary chevron inclusions mostly lie closer to the evaporation curve. The isotope data have been interpreted as from primary Permian waters - a mixture of evaporated brines with contemporary meteoric waters (Knauth and Beeunas, 1986), but the variety of compositions found by analysis of fluid inclusions from the same formations cautions that the origin may be more complex and varied (Roedder, 1984; Holland et al., 1986; Roedder et al., 1987; Stein and Krumhansl, 1988). The resolution of these questions is critical for the evaluation of the integrity of salt rock as vaults for the storage of radioactive waste. Fluid inclusions are more rarely observed in anhydrite (McKibben et al., 1988), but isotope analyses are lacking.

SAMPLING PROTOCOLS

The application of isotope methods to geological problems of sulfate and chloride rocks imposes certain requirements on sampling. Sampling for comparison with the S isotope age curve is not particularly sensitive to the evaporative facies (Table 1) in which the sulfate is deposited. For routine analysis about 0.1 g of anhydrite is required, which means that a small hand specimen of anhydrite or gypsum rock suffices. A hand specimen is even sufficient for salt rock, as most such material contains at least 5 percent anhydrite. For this application sampling is generally insensitive to the form of Ca sulfate - primary gypsum or anhydrite, anhydrite replacing gypsum, or gypsum replacing anhydrite. The sampling is also relatively insensitive to the textural form of the gypsum or anhydrite: laminated, nodular, etc. In cores, anhydrite may be recognized more easily if the surface of the core is altered to a dead white adherent coat of gypsum - by exposure to water for a few hours or to a 4 M solution of K_2SO_4 for 15 or 20 minutes.

The most important precaution is to avoid areas of sulfate reduction, which are common in salt dome cap rock or in similar alteration near the outcrop of bedded sulfate rocks. The products of such reduction are sulfides and native S of low $\delta^{34}\text{S}$, leaving the remaining gypsum with high $\delta^{34}\text{S}$; contrarily, if the sulfide is back-oxidized in ground water to sulfate rather than only to native S, gypsum newly crystallized from such sulfate may be very light. Fortunately the effects of sulfate reduction are localized, so it is only necessary to move sampling to, e.g., the dome rock itself. For similar reasons it is well to avoid shaley or marly interbeds, which are likely to contain pyrite that may oxidize to sulfate on the outcrop.

The formation should be sampled at five or ten levels, and the computed mean value, discounting outlying values such as occasionally occur, should be used to calculate the age from the time-dependent isotope variation curve. For the most part, the precisions of preparation and mass spectrometry are better than the variations of up to 1 per mil or a little more that occur naturally within a formation, consequently it is usually economical to analyze more samples rather than making duplicate preparations from each sample.

Sampling for the Sr isotope age curve presents an additional problem. In order to avoid contamination by radiogenic Sr decayed from Rb in old detrital silicates (particularly clay or mica), it is recommended that samples have less than five percent insoluble residue of detritus. Alternatively the Sr isotope ratio in the sulfate phase may be derived by measuring both the isotope ratio and amount of insoluble residue in a series of samples, and extrapolating to zero insoluble residue (Lord et al., 1988). For sulfate rocks this is not as common a problem as it is with the carbonate rocks that are more usually sampled for Sr isotopes.

Sampling for analysis of fluid inclusions is concerned with salt rocks; gypsum and anhydrite have been little studied. A preliminary search through available material serves two purposes: (1) it allows the analytical procedure to concentrate on those samples richest in inclusions, and (2) it provides a qualitative judgement

as to whether the inclusions are primary (microscopic with a chevron texture), recrystallized (cubes 0.1 mm or larger randomly distributed within a halite crystal), or grain-boundary inclusions. Inclusions may be encountered by chance under the microscope in thin (or thick) sections. However, any salt rock may be prepared easily for routine examination by the following procedure. Flatten the side of a length of core or hand specimen using large flat double-cut steel files - starting with a bastard cut and smoothing with a second cut. Then wipe the surface with glycerine, mineral oil or an index oil, and look "into" the halite crystals with hand lens or binocular microscope. Observation may be improved by temporarily affixing a large cover glass.

FINAL REMARKS

At the present stage the most important application of isotope geochemistry to geological problems of sulfate and chloride rocks seems to be age determination and stratigraphic correlation with the isotope age curves of S and Sr. Future progress in this application will be aided by two new emphases: (1) the refinement of the S isotope age curve by determination of $\delta^{34}\text{S}$ in stratigraphically well-controlled carbonates (Burdette et al., 1989), and (2) the cross-correlation of isotope analyses of both S and Sr (e.g., Clement and Holser, 1988; Figs. 3, 5). Indeed, the potential for unequivocal answers to present ambiguities should be greatly enhanced by parallel studies of both isotope and chemical characteristics of fluid inclusions and their evaporite systems. Isotope studies alone will not solve the complex geological problems that confront us.

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