CHAPTER 3

Local and Global Aspects of the Sulphur Isotope Age Curve of Oceanic Sulphate

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It appears logical to assume that the total amount of oceanic sulphate and its $\delta^{34}S$ value is controlled by the flux rates of what we call the 'exogenous sulphur cycle'—namely by the inflow of weathering solutions from the continent with preferentially light sulphur on the one hand and by the deposition of S-bearing sediments with a strong S isotope fractionation involved in bacterial sulphate reduction on the other. These two competing main effects keep the $\delta^{34}S$ value of the oceanic sulphate in a steady state situation which is very sensitive to changes in the flux rates. Thus the investigation of the 'age curve' gives us a chance to get information about the variations of these fluxes.

3.1 HOW 'OCEANIC' ARE THE EXISTING EVAPORITE DATA?

Any advanced modelling of the sulphur cycle and its variations during the geological past depends on knowledge of the shape of the sulphur isotope age curve of oceanic sulphate. Several thousand samples of gypsum and anhydrite from evaporation basins of different geological ages all over the world have been measured for this purpose. Thus, from a naive standpoint, one might expect that there exists a sufficiently sound basis for advanced evaluation. In the present chapter we have to discuss how far this optimism is justified.

In this respect we have to remember that no evaporite can be deposited directly within the open ocean but only in a sabkha environment or in a (more or less) closed basin. The accumulation of thick evaporite beds needs a supply of 'fresh' seawater but the mean inflow rate must always remain lower than the maximum evaporation rate. So the isotopic composition within the basin can easily develop in a manner different from the open sea. When the basin becomes completely closed (like the Caspian) the evaporation continues under the regime of the inflowing continental waters.
The question 'open or closed' is still debatable for many fossil evaporite basins. Some authors even argue that all the extreme values expressed in the age curve do not reflect changes in the open ocean but only the local 'isotope history' of the investigated evaporite basins (see, for example, Winogradow and Schanin, 1969).

This dilemma can be ruled out only when each data point employed for the construction of the age curve is verified by evaporite samples from the basins in different continents and in connection with different oceans. Unfortunately this demand is only partly met because of the scarcity of suitable evaporite beds. So the work of the different research groups is restricted to these few well-dated evaporite sequences. No wonder the curves constructed from these data agree so nicely with each other.

Figure 3.1 refers to one of the critical points of the age curve, namely the extreme increase in $\delta^{34}S$ from the Upper Permian (+11‰) to the Röt (above +25‰) reported from northern central Europe. When both values are considered as properly 'oceanic' the increase in $\delta$ would need extremely high flux rates. Therefore we have first to check whether both values are 'oceanic'.

Figure 3.1 Palaeogeographic map of the Upper Permian with the evaporite basins sampled for sulphur isotope measurements

* Upper Lower Bunter, top of the Lower Triassic. Claypool et al. (1980), in their Figure 5, have apparently put these values into the Upper Triassic.
The values reported for the Upper Permian originate from the basins marked by black dots in Figure 3.1. All the values from the Perm basin, USSR, from northern central Europe, from the eastern Alps and Yugoslavia, and from the southern USA range around +11‰ and give the most perfect agreement of the entire age curve. The samples from Brazil have distinctly higher values.

The evaporite basin of northern central Europe was certainly fed from the Nordic Ocean and the Alpine basin from the Tethys. The evaporite basin at Bahia (east coast of Brazil) lies close to the early Atlantic but apparently too far from the ‘free’ ocean. The Amazon basin extended in an east–west direction through the South American subcontinent and was fed from the Pacific (Szatmari et al., 1979). This basin may be compared in shape and extent with the other large Permian basins and its S isotope range lies only slightly above the European and North American values. Perhaps this δ³⁴S difference reflects a slight difference in the depositional ages of the two groups.

For the Röt values the situation remains uncertain as well. Until quite recently these high values were known only from Europe, namely from an evaporitic belt ranging from southern Britain through the Netherlands, West Germany, Denmark and East Germany, to Poland, and from two localities in the Italian Alps. These high values were ascribed to extensive bacterial activity in local evaporation basins (Nielsen, 1965).

Quite recently many additional ‘typical Röt values’ have been published from Sichuan in China, quite on the other edge of the Tethys (Chen and Chu, 1988). The mean δ³⁴S value of the Sichuan evaporites from the upper Lower Triassic is 1–2‰ higher than that of the European Röt, and this range holds until the lower Middle Triassic (= Lower Muschelkalk in German nomenclature). This argues strongly for a worldwide ‘Röt event’, as proposed in Holser’s (1977) model.

Little is known about the shape of the age curve in the Upper Triassic. Claypool et al. (1980) report values around +14‰ for Keuper sulphate. The complexity of the problem is evident from Figure 3.2: the left side shows a map of northern central Europe with the border lines of the Keuper (Upper Triassic) basin. The shaded area in Denmark denotes the area where the Keuper saline basin reached the stage of potash mineral precipitation. The δ³⁴S histograms at the right side give the isotopic distribution of gypsum/anhydrite at the different geographic latitudes. The values decrease systematically from south to north and we have to decide which values are representative of the oceanic value: those in the vicinity of the potash basin or those from southern West Germany.

Figure 3.3 gives an example of how strong changes in the depositional facies may influence the S isotopic record within the same evaporite basin. In this case the lower values of the deeper core section agree with the
Figure 3.2 Regional trend in $\delta^{34}$S of Keuper evaporite sulphates from southern West Germany to Denmark (open squares = sulphates of potash facies)

Jurassic values reported from elsewhere, but if drilling had ended above the break in the curve the data would have argued for a marine value above +20‰.

A fundamental difficulty for the recovery of properly dated evaporite sulphates (especially for very old samples) comes from the high mobility of

Figure 3.3 $\delta^{34}$S profile through a Jurassic anhydrite sequence in Israel
salt. In the examples shown in Figures 3.4 to 3.8 the correct age correlation could be established only in connection with a very careful geological field investigation of the sampling sites. It is wrong to date sediments using the $\delta$ values of evaporite samples in areas with poor geological background as the isotopic composition can depend on local evolutionary history.

Figures 3.4 to 3.6 refer to a common event of ‘salt tectonics’. The two $S$ isotope profiles of Figure 3.4 contain Zechstein (Upper Permian) gypsum/anhydrite overlying Röt sulphate. The explanation of this reversed sequence is given in Figure 3.5: in connection with the tectonic evolution of the whole area the Zechstein salt has overthrusted the younger strata (upper profile) and the gypsum actually observed is the residue from leaching the overthrusted salt mass. Figure 3.6 shows an outcrop of this tectonic contact.

Figure 3.7 shows mobilized Zechstein salt sandwiched as an extended sheet into a sequence of Röt evaporites. The two $\delta^{34}S$ profiles are about two kilometres apart but the concordant Zechstein layer has been traced isotopically over several tens of kilometres. Such a layer of the ‘wrong’ age can confuse the interpretation, and certainly some of the unconformable data in previous publications must be ascribed to this effect. The reverse case—Röt included into Zechstein salt—is shown in Figure 3.8.
Figure 3.5  Overthrust structure at the western outline of the Hils syncline, about 50 km south of Hannover, West Germany. Upper profile = situation during the tectonic event and lower profile = actual situation. Zechstein Salinar = composite salt bed of the Upper Permian. su, sm = lower and middle section of Lower Triassic ('Bunter'). so = upper section of Lower Triassic ('Rot'). m = Middle Triassic (Muschelkalk). k = Upper Triassic (Keuper). jl, jb, jw = sections of Jurassic (from Hermann et al., 1967)

Figure 3.6  Tectonic contact between Rot and Zechstein at the rail cut Giesenbarg
3.2 A NEW APPROACH TO THE SULPHUR ISOTOPE AGE CURVE

The examples mentioned above give an idea of the difficulties encountered in the construction of a new age curve. Therefore any new attempt in this direction should be regarded merely as an impetus to promote further discussion of the problem and should not claim to be 'better' than the previously published curves. In any case the large number of published and unpublished S isotope data arising since the appearance of the curve of Claypool et al. in 1980 makes it reasonable to risk this. The result is shown in Holser et al. (this volume, Figure 2.2). (In order to facilitate the
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comparison with the previous curves, two of them are inserted in the diagram.)

The new curve is composed of many minor oscillations which had been smoothed out in the previous constructions. The 'oceanic' nature of these oscillations remains debatable, but in my opinion they have the same quality as the strong increase in $^{34}$S at the Permian/Triassic boundary. And this renders it necessary to consider their local or global nature in all the future sulphur cycle models.

The new curve omits isotopic evolution during the Precambrian, because this is the most speculative section of the entire age curve. Some Precambrian data support the decision of Claypool et al. (1980) to draw their curve for the Precambrian at a range slightly above +15‰ (for example Figure 2.2, Chapter 2, this volume), but there are many samples with much higher values. Examples are the values from the Krol, the Vindhyan and the Grenville (Nielsen, 1978) and a new series of barites with $\delta^{34}$S values in the range from +20 to +35‰ and an age somewhere between 1.3 and 2 Ga in the Aggeneys-Gamsberg area, South Africa (Gehlen et al., 1983). If it turns out that these values have a bearing on the age curve this will certainly be a crucial point in any further attempts to model the early biogenic sulphur cycle, but this question must be held open for further discussion.

REFERENCES


