

Sulfate reduction and sulfur isotopic fractionation in marine sediments

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Abstract

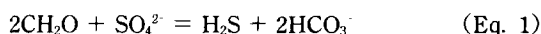
Concentrations of sulfate and δ -values of sulfate, $(\delta^{34}\text{SO}_4)_{\text{pw}}$, dissolved in pore waters were measured from the sediment cores of the two different marine environments: deep northeast Pacific (ST-1) and coastal Kyunggi Bay of Yellow Sea (ST-2). Sulfate concentration in pore waters decreases with depth at both cores, reflecting sulfate reduction in the sediment columns. However, much higher gradient of pore water sulfate at ST-2 than ST-1 indicates more rapid sulfate reduction at ST-2, because of high sedimentation rate at the coastal area compared to the deep-sea.

The measured δ -values, $(\delta^{34}\text{SO}_4)_{\text{pw}}$, follow extremely well the predicted trend of the Rayleigh fractionation equation. The range of 26.7‰ to 61.3‰ at the coastal core ST-2 is not so great as that of 32.4‰ to 97.8‰ at the deep-sea core ST-1. Despite greater gradient of pore water sulfate at ST-2, the δ -values become lower than those of the deep-sea core ST-1. This inverse relation between the δ -values and the gradients of pore water sulfate could be explained by the combination of the two subsequent factors: the kinetic effect by which the residual pore water sulfate becomes progressively enriched with respect to the heavy isotope of ^{34}S as sulfate reduction proceeds, and the intrinsic formulation effect of the Rayleigh fractionation equation in which the greater becomes the fractionation factor, the more diminished values of $(\delta^{34}\text{SO}_4)_{\text{pw}}$ are predicted.

Key words : sulfate reduction, δ -value of pore water sulfate, isotopic fractionation

1. INTRODUCTION

Sulfate reduction is a common process by which organic matters undergo decomposition in marine sediments (Goldhaber et al., 1977; Berner, 1980; Martens and Klump, 1984). Sulfate reduction can be schematically represented as:



During this process pore water sulfate is used as an energy source by sulfate-reducing bacteria which reduce sulfate to H_2S and at the same time decompose sedimentary organic matter represented here as CH_2O (Bender and Heggie, 1984;

Westrich and Berner, 1984; Middelburg, 1989). Because of this sulfate reduction process, concentrations of pore water sulfate in marine sediments decrease subsequently with depth from that of bottom water at the top of sediment core and are either completely exhausted or remain constant at any subsurface depths (Boudreau and Westrich, 1984).

If the concentration gradients of porewater sulfate are great, rates of sulfate reduction are regarded to be rapid, and vice versa (Goldhaber and Kaplan, 1975; Westrich, 1983). The rate of sulfate reduction is likely to be correlated with the rate of sedimentation (Berner, 1978). A distinct positive correlation was found to exist between

the sedimentation rates and the rates of sulfate reduction (Goldhaber and Kaplan, 1975); rapid decrease in pore water sulfate, i. e., rapid sulfate reduction rate, is due to rapid rate of sedimentation (Berner, 1978).

The sulfur-isotopic compositions of pore water sulfate have not been considered in its relation to the rate of sulfate reduction, though it is known that as sulfate reduction proceeds the residual pore water sulfate becomes progressively enriched with respect to the heavy isotope of ^{34}S thereby giving greater sulfur isotopic enrichment of pore water sulfate (Kaplan et al., 1963; Kaplan and Rittenberg, 1964).

In this paper the patterns of the sulfur isotopic enrichment of pore water sulfate have been investigated in terms of their relation to sulfate reduction.

2. METHODS

Two marine sediments were used for this study: a sediment core, ST-1, from the northeast Pacific with water depth of about 2000 m, and a coastal sediment core, ST-2, from Kyunggi Bay of Yellow Sea.

Pore waters were extracted from the sediment cores by pressure filtration through a $0.45\mu\text{m}$ membrane filter with nitrogen gas at in situ temperatures immediately after core sampling to avoid temperature effects on extractions (Mangelsdorf et al., 1969). Each aliquot of 25ml pore water sample was treated with 30% BaCl_2 . Precipitate of barium sulfate was filtered and ignited at 800°C for two hours, and then weighed to determine gravimetrically sulfate concentrations in pore water.

Stable isotopic ratios ($^{34}\text{S}/^{32}\text{S}$) were measured on the SO_4 -sulfur, which remains after bacterial reduction of pore water sulfate, only for 3 samples per each core using Finnigan MAT Gas-Inlet

Isotope Ratio Mass Spectrometer at a commercial laboratory, Global Geochemistry, Canoga Park, California after the samples being treated by the following procedures. Pore water sulfate was precipitated to barium sulfate, and then the precipitates were cleaned up using a Ag_3PO_4 trap. After the cleaning, an excess of graphite is mixed with barium sulfate and heated to 1100°C for 10 minutes in a stream of nitrogen (Hoefs, 1980).

The unit of stable isotopic measurement is the δ -value (δ), given in per mil (‰). The δ -value is defined as

$$\delta \text{ in } \text{‰} = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000 \quad (\text{Eq. 2})$$

where R represents the isotopic ratio. Therefore, sulfur isotopic value of pore water sulfate can be written as

$$(\delta^{34}\text{SO}_4)_{\text{pw}} = (R_{\text{pw}}/R_{\text{std}} - 1) \times 1000 \quad (\text{Eq. 3})$$

where $R_{\text{pw}} = (^{34}\text{SO}_4/^{32}\text{SO}_4)_{\text{pore water}}$ (i. e. the ratio of ^{34}S to light ^{32}S in pore water sulfate); and R_{std} is the sulfur isotopic ratio of the standard for which sulfur from troilite of the Canon Diablo iron meteorite (CDT) is commonly used (Holser and Kaplan, 1966).

3. RESULTS

In two sediment samples concentrations of pore water sulfate decrease with depth because of sulfate reduction (Fig. 1 and Table 1). However, the magnitude of decrease in pore water sulfate shows a substantial difference between the cores: at ST-2 pore water sulfate very rapidly decreases with depth and is almost completely exhausted at depth of 200 cm, meanwhile at ST-1 it decreases moderately and is not exhausted even at depth of 420 cm.

δ -value of pore water sulfate, $(\delta^{34}\text{SO}_4)_{\text{pw}}$, becomes greater with depth at both cores (Fig. 2 and Table 2). This is well documented from the

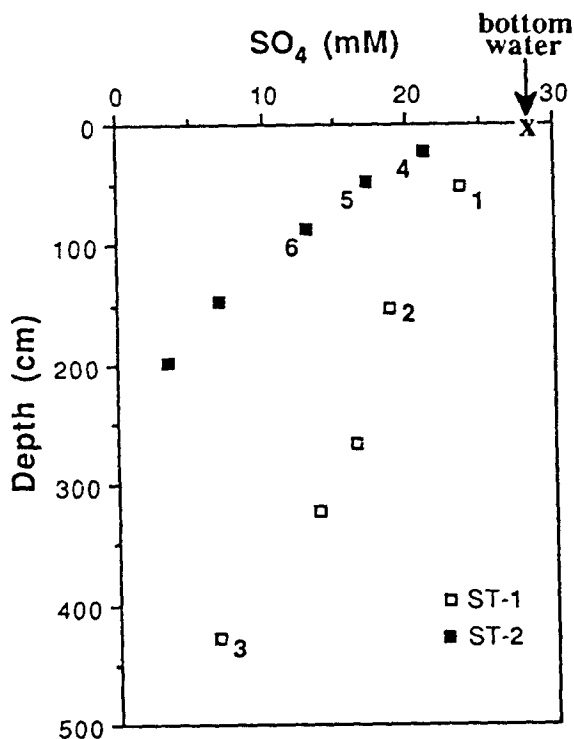


Fig. 1. Concentration profiles of pore water sulfate with depth. Note rapid decrease in sulfate at ST-2.

sulfur isotopic fractionation during the process of sulfate reduction, because as sulfate reduction proceeds the residual pore water sulfate becomes progressively enriched with respect to the heavy isotope of ^{34}S (Hoefs, 1980).

An apparent alignment of the sulfur isotopic data in Fig. 2 is purely fortuitous. In fact, this apparent alignment implies a problem; it implies a direct contradiction to what is stated in the preceding paragraph. Independently for each core the increasing trend of the data dispersal with depth invites no problem (Fig. 2). Relating the two cores, however, one can find a contradiction to the relation between the depth profiles of $(\delta^{34}\text{SO}_4)_{\text{pw}}$, and sulfate concentration. Datum point 1 of ST-1 shows greater $(\delta^{34}\text{SO}_4)_{\text{pw}}$ than that of datum point 4 of ST-2 despite the point 1 has greater amount of the residual pore water sulfate than the point 4; the same contradiction between the points 2 and 5. This apparent contradiction is explained in the discussion section below.

Table 1. Concentration and isotope data of pore water sulfate. The column * denotes sample numbers for which sulfur isotope data on pore water sulfate are available. These numbers correspond to those in Figs. 2 and 3. The predicted δ -values were calculated from the Rayleigh equation, Eq. 4. Parameters given for the predicted: α for ST-1 was 0.952; α for ST-2 was 0.987; $(\text{SO}_4)_{\text{sw}} = 28.25 \text{ mM}$; $(\delta^{34}\text{SO}_4)_{\text{sw}} = 20.0$

*	Depth(cm)	$\text{SO}_4(\text{mM})$	measured $(\delta^{34}\text{SO}_4)_{\text{pw}}$	predicted $(\delta^{34}\text{SO}_4)_{\text{pw}}$
ST-1				
1	50~ 55	23.51	32.4	37.5
2	150~ 155	18.78	47.9	48.8
	265~ 270	16.30	—	—
	320~ 325	13.71	—	—
3	425~ 430	6.75	97.8	101.3
ST-2				
4	20~ 25	21.22	26.7	32.3
	45~ 50	17.09	—	—
5	85~ 90	13.04	36.2	38.5
	145~ 155	6.99	—	—
6	195~ 200	3.55	61.3	57.1

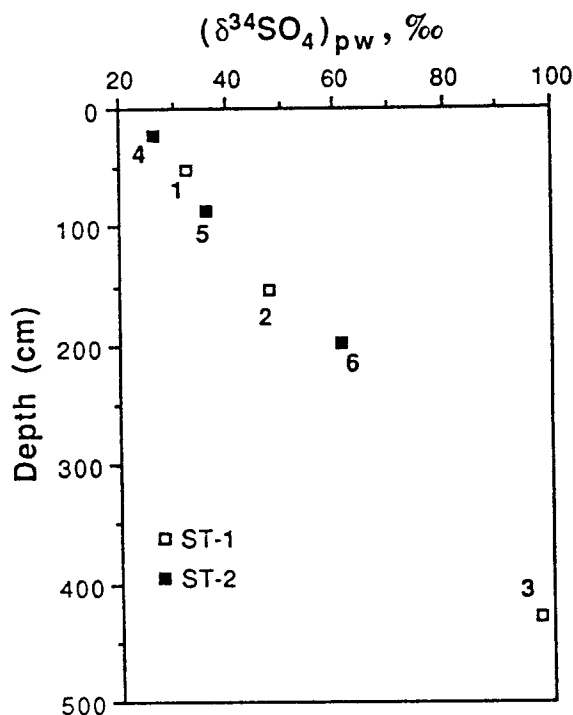


Fig. 2. Depth profiles of the δ -values of sulfur in pore water sulfate, $(\delta^{34}\text{SO}_4)_{pw}$. Note increasing $(\delta^{34}\text{SO}_4)_{sw}$ with depth. Refer to Table 1 for the identification of the total six data points.

4. DISCUSSION

Isotopic fractionation during unidirectional chemical reactions always show a preferential enrichment of the light isotope in the reaction products (Hoefs, 1980). Therefore, during bacterial reduction of pore water sulfate, the product H_2S is enriched with ^{32}S (light sulfur) and the residual pore water SO_4 enriched with ^{34}S (heavy sulfur) (Kaplan et al., 1963; Kaplan and Rittenberg, 1964). As microbes being continually reducing pore water sulfate until its exhaustion the δ value of residual pore water sulfate, $(\delta^{34}\text{SO}_4)_{pw}$, continually increases against decreasing sulfate concentration (Fig. 1 and Fig. 2). Therefore, an extremely

heavy sulfur in sulfate may be found at the final stage of sulfate reduction as observed at ST-1 (Fig. 2).

To explain the contradiction afore-mentioned, the sulfur isotopic data were applied to Rayleigh equation (Rayleigh, 1896):

$$(\delta^{34}\text{SO}_4)_{pw} = [(\delta^{34}\text{SO}_4)_{sw} + 1000] \left[(\text{SO}_4)_{pw} / (\text{SO}_4)_{sw} \right]^{\alpha-1} - 1000 \quad (\text{Eq. 4})$$

and

$$\alpha = R_{pw} / R_{sw} \quad (\text{Eq. 5})$$

where the 'sw' stands for seawater, i. e., initial pore water at the top of core.

With no exception the measured values of $(\delta^{34}\text{SO}_4)_{pw}$ at both ST-1 and ST-2 follow extremely well the predicted trend by the Rayleigh equation which assumes bacterial sulfate reduction in a closed system. This is an extraordinarily good fit considering the general assumption.

The predicted curves are based on $(\delta^{34}\text{SO}_4)_{sw} = 20$ ‰ CDT for ambient seawater (Claypool et al., 1980; Francois and Gerard, 1986). For ST-1 a fractionation factor between the residual pore water SO_4 and the initial SO_4 is $\alpha = 0.952$ and for ST-2 $\alpha = 0.987$ (Table 1). Greater fractionation factor for ST-2 than ST-1 is reasonable since pore water sulfate reduces much faster at ST-2. These factors of both cores correspond fairly well to $\alpha = 0.978$ for the more commonly used fractionation factor (Faure, 1977).

Regardless of these good fits, however, Fig. 3 reveals the contradiction in a more distinctive manner than Fig. 2 does. Fig. 3 shows that at a constant value of pore water sulfate, ST-1 has the values of $(\delta^{34}\text{SO}_4)_{pw}$ systematically greater than ST-2, despite ST-2 ought to have greater values of $(\delta^{34}\text{SO}_4)_{pw}$ as it shows greater sulfate reduction.

This apparent contradiction is considered to be due to the impact of the two subsequent factors

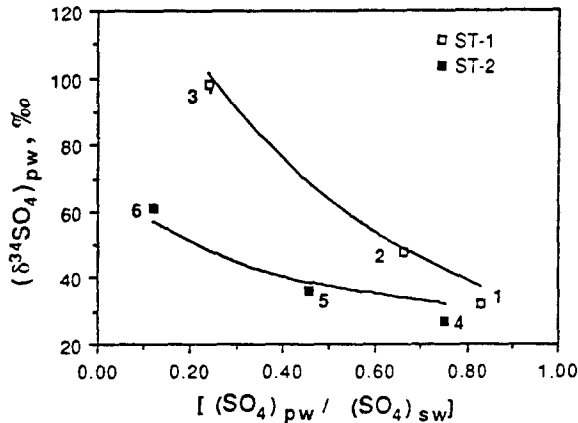


Fig. 3. Plot of $(\delta^{34}SO_4)_{pw}$ versus the fraction of pore water sulfate residual after sulfate reduction to initial pore water sulfate, $(SO_4)_{pw}/(SO_4)_{sw}$. The lines indicate trends predicted by the Rayleigh equation, Eq. 4. Parameters given to the equation include α for ST-1 as 0.952; α for ST-2 as 0.987; $(SO_4)_{sw} = 28.25$ mM; $(\delta^{34}SO_4)_{sw} = 20.0$

on the final values of $(\delta^{34}SO_4)_{pw}$: the fractionation factor in Eq. 5 and the formulation effect of Rayleigh equation, Eq. 4. Rapid decrease in pore water sulfate at ST-2 (Fig. 1) resulted in a greater fractionation factor of residual pore water $^{34}SO_4$ relative to the initial pore water (sea water) (refer to Eq. 5). However, this result is only for the fractionation factor and not for the final value of $(\delta^{34}SO_4)_{pw}$ that is derived from the Rayleigh equation, Eq. 4. The Rayleigh equation gives a lower value of $(\delta^{34}SO_4)_{pw}$ when a greater fractionation factor is applied. This is because the base of the exponential $\alpha-1$ in Eq. 4, $[(SO_4)_{pw}/(SO_4)_{sw}]$, intrinsically has the values ranging from zero to one in the case of sulfate reduction in pore water.

Unless otherwise either sulfide phases dissolve in sediment columns or a bottom water rich in sulfate infiltrates to a great extent, pore water sulfate can not be greater than the bottom water

sulfate which represents sea water sulfate at the top of sediments. Depth profiles of pore water sulfate in Fig. 1 suggest these possibilities very unlikely as the concentrations all decrease with depth. Therefore, the ratio of residual pore water sulfate to the initial, $[(SO_4)_{pw}/(SO_4)_{sw}]$, is always less than one.

This tricky generation of the $(\delta^{34}SO_4)_{pw}$ values by the Rayleigh equation leads to an explanation of the apparent contradiction between the gradients of pore water sulfate and the $(\delta^{34}SO_4)_{pw}$ values. Rapid reduction of pore water sulfate (large concentration gradient) gives greater value of the fractionation factor, but ultimately results in a weakened increment of the values of $(\delta^{34}SO_4)_{pw}$ compared to the case of slow sulfate reduction (small concentration gradient).

Finally, changes in pore water sulfate with depth have been found to be directly proportional to the rate of sedimentation (Goldhaber and Kaplan, 1975; Berner, 1978): the greater the rate of sedimentation, the greater becomes the gradient of pore water sulfate (i.e., greater decrease in pore water sulfate with depth). The reason for rapid decrease in pore water sulfate in rapidly depositing sediments is because more readily metabolizable organic matter are available. The refractory organic matter could also be used for sulfate reduction once the more readily metabolizable organic matter is exhausted. But this is not likely to occur because pore water sulfate is very likely to be exhausted by the time when the refractory organic matter is about to be decomposed, and as a result sulfate reduction ceases. For slowly depositing sediments, decomposable organic matter is limited. A limited amount of refractory organic matter is forcefully utilized for sulfate reduction. Therefore, sulfate reduction is slowly progressed and thus pore water sulfate decreases slowly.

Depth profiles of pore water sulfate in Fig. 1

lend themselves to self-explanatory about their relation to rates of sedimentation. Sedimentation at ST-2 would be much more rapid than at ST-1. This is obvious when one considers the fact that ST-2 is from a coastal environment and ST-1 from a deep-sea area. Rapid sedimentation followed by rapid sulfate reduction results in a less intense increase in $\delta^{34}\text{S}$ of pore water sulfate than that of slow sulfate reduction.

5. CONCLUSION

Rapid decrease in pore water sulfate resulting from rapid sulfate reduction in rapidly depositing sediment gives a greater sulfur isotopic fractionation in pore water sulfate, but the degree of increment of the δ -values of pore water sulfate, ($\delta^{34}\text{SO}_4$)_{pw}, becomes in opposite weakened. An exactly converse logic can be applied to slowly depositing sediments. Therefore, increasing trend of the final δ -values of pore water sulfate with depth will be proportionally weakened as sulfate reduction becomes stronger.

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해양퇴적물내에서의 황산염 환원과 황의 안정동위원소 분화

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두개의 서로 다른 해양환경에서 수거된 퇴적물의 공극수로부터 황산염 농도와 황산염의 황 안정 동위원소값 ($\delta^{34}\text{SO}_4$)_{pw}이 측정되었다. 한지역은 북동태평양 심해(ST-1)이었고, 다른 한 지역은 황해 경기만의 연안역(ST-2)이었다. 두 개의 시추 코아 공히 공극수 황산염의 농도가 깊이에 따라 감소하는 것을 보였는데, 이것은 황산염 환원작용이 두 지역 퇴적환경에서 모두 일어나고 있음을 시사한다. 정점 ST-2에서 공극수 황산염의 감소가 더욱 현저한 것은 이곳에서 황산염 환원이 더욱 빠르게 일어나고 있음을 나타내는 것이며, 이것은 심해환경에 비해 연안환경에서 퇴적속도가 훨씬 빠르다는 사실을 고려할 때 예측된 결과이다.

공극수 황산염의 황 안정동위원소 측정값 ($\delta^{34}\text{SO}_4$)_{pw}들은 Rayleigh 동위원소 분화방정식이 예측한 값들과 매우 잘 일치하고 있다. 측정값들은 정점 ST-2에서 26.7%~61.3%의 범위를 보이는데 이것은 32.4%~97.8%의 분포를 보인 정점 ST-1에 비하면 적은 값들이다. 정점 ST-2에서 공극수 황산염의 농도변화가 훨씬 더 컸음에도 불구하고 동위원소값은 적은 규모로 증가하였다. 황산염 농도변화와 동위원소값의 변화 사이에 이와같은 역비례 관계는 다음과 같은 두가지 연속적인 요인들에 의해 설명될 수 있다. 황산염 환원이 진행됨에 따라 공극수에 남아있는 황산염내 황에는 무거운 ^{34}S 가 점차 농축되는 반응효과가 첫째 요인이며, 이러한 반응효과가 커지면 커질수록 최종값인 ($\delta^{34}\text{SO}_4$)_{pw}는 오히려 줄어들게 하는 Rayleigh 방정식 자체의 구조효과가 둘째 요인이다.