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Dedicated to Professor Lisa Heller-Kallai on the occasion of her 65th birthday

THERMOCHEMICAL SULFATE REDUCTION
A Review

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Abstract

The high concentrations of hydrogen sulfide found in many oil and gas fields is thought to arise from the oxidation of petroleum hydrocarbons by sulfate - a reaction that reduces the value of the resource. This review, undertaken in order to better understand the geochemistry of TSR reaction in oil field sediments, covers the relevant information on thermochemical sulfate reduction (TSR) to 1991. The theoretical and experimental aspects of TSR reactions (including sulfur and carbon isotope studies) are reviewed and their significance to the geochemical system discussed. The present review agrees with previous suggestions that biochemical reduction of sulfate dominates in sedimentary environments below 120°C, and supports the possibility that reactive sulfur species will oxidize certain organic molecules at meaningful rates in geochemically reasonable reaction periods at temperatures above 175°C. We conclude that under typical petroleum reservoir reaction conditions, both elemental sulfur and polysulfides are capable of oxidizing some organic molecules under basic conditions. But that sulfate alone will not react unless lower oxidation state sulfur is present. The possible interaction of low-valence-state sulfur with sulfate to form TSR active oxidants is examined. both H_2S and SO_4^{2-} are required for the formation of active polysulfide reductants (e.g. thiosulfate or polythionates) in TSR systems. Such intermediates can serve to lower the overall activation energy of the oxidation of hydrocarbons by sulfate via thermal generation of sulfur radicals that can function as TSR active oxidants in many oil field sediments. We suggest that some proposed chemical mechanisms for TSR need to be experimentally verified and the results re-interpreted with respect to TSR reactions in geologic systems.

Keywords: thermochemical sulfate reduction (TSR)

Introduction

The high concentrations of hydrogen sulfide found in many oil and gas fields is thought to arise from the oxidation of petroleum hydrocarbons by sulfate. Such reactions are known to occur by microbial processes (e.g. Bacterial Sul-

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fate Reduction or BSR), but it is generally accepted that thermochemical sulfate reduction (TSR) is responsible for the bulk of these reactions, especially in deep or hot reservoirs. The ultimate products of the sulfate reduction/hydrocarbon oxidation reactions are carbon dioxide and hydrogen sulfide. Such reactions serve to reduce the value of the resource by the formation of the inorganic gases at the expense of the petroleum hydrocarbons. Because predictive geochemical information regarding TSR can aid in E & P decision making, we have been examining the chemical features of thermochemical sulfate reduction reactions. This review was undertaken to provide an update on the literature of TSR reactions as it relates to the chemistry and geochemistry of petroleum deposits.

The reduction of sulfate by carbon compounds is a process that is well known to both chemists and biochemists. For example, one of the early methods for manufacturing pure metal sulfides involved heating a mixture of the metal sulfate and carbon at high temperatures (> 900°C). In this way, metal sulfates were reduced to the metal sulfide and the carbon was oxidized to carbon dioxide. The use of other organics, including hydrocarbons, as the reductant in similar redox reactions has also been reported. Similarly, the ability of many microorganisms to utilize sulfate in oxidative processes has been studied in great detail. When deprived of other sources of oxygen, sulfate reducing bacteria can derive energy by 'burning' organic metabolites with sulfate ion, to form carbon dioxide and sulfide ion as the ultimate respiratory end products. However, unlike the thermal reactions, the enzyme-catalyzed microbial transformations proceed rapidly at ambient temperatures.

In this review we are primarily interested in the reduction of sulfate accompanied by the oxidation of sedimentary organic matter as it occurs in the geosphere. Of particular interest to us is the thermochemical reduction of sulfate by hydrocarbons that is reported to take place in many oilfield sediments. The reaction temperatures in such geologic settings are intermediate between the low temperature regime of biochemical transformations, and the very high temperature of synthetic chemical processes. As will be discussed, these intermediate temperatures are high enough to inhibit or kill microorganisms, and yet are too low to provide observable 'thermochemical' reductions in laboratory time. On the other hand, even very slow reactions may give significant conversions in reaction periods measured on a geologic time scale. In order to estimate the importance of such reactions in 'geologic time', we shall consider both the geochemical evidence for their occurrence in sediments, and chemical evidence from model reactions at higher temperatures in laboratory experiments.

The geologic setting

Following the change from a reductive- to an oxidative-atmosphere about the earth, the most abundant form of sulfur in the geosphere has been sulfate. Sulfate, with sulfur in the plus six oxidation state is very stable, but several lower oxidation states, namely the S^{4+}, S^0 or S^{2-} forms, are also stable. In the geosphere, sulfur as sulfate can be reduced to lower stable oxidation states under the anoxic, reducing conditions that exist in many geochemical environments.

The most common geologic conditions for the formation of such reducing environments occur in connection with the deposition of organic matter in aquatic systems. In such systems, oxygen from the air is depleted in bottom waters and sediments by reactions with organic matter, with the result that the sediments are effectively insulated from the oxidative atmosphere. Thus, there is often a connection between the carbon cycle and the sulfur cycle in the geosphere, since organic matter can prevent the re-oxidation of reduced sulfur species to sulfate.

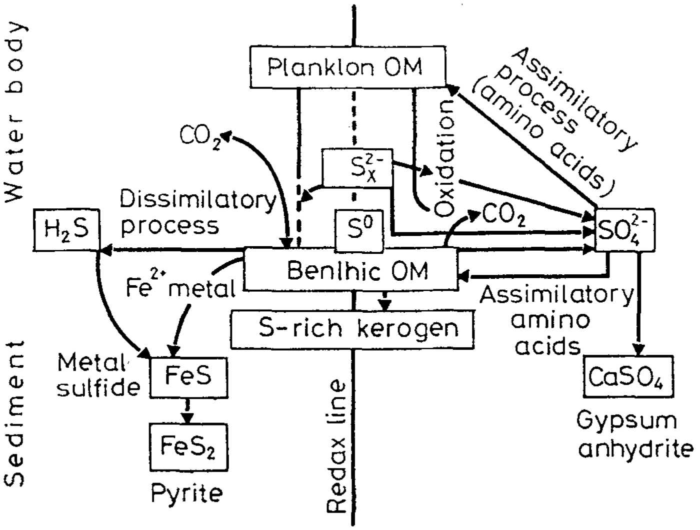


Fig. 1 Schematic changes in sulfur redox cycle at the water sediment interface

At temperatures below about 120°C, the intimate connection between the carbon and sulfur cycles in the geosphere is dominated by biochemically controlled reactions, which in turn reflect depositional environments. As oxygen in sediments is depleted by aerobic microbial oxidation of organic matter, certain anaerobic microorganisms carry out metabolic processes using sulfate as the oxidant to oxidize organics. The ultimate reaction products of bacterial sulfate reduction (CO_2 and H_2S) can both affect the acidity of their environment and interact with the surronding mineral matrix. These microbial processes are also marked by characteristic changes in the stable isotopes distribution of the reaction products. A schematic diagram of the sulfur cycle at the water (ocean) column-sediment interface is shown in Fig. 1. The microbial controlling factors of this scheme were described by Aizenshtat *et al.* [1, 2]. It is obvious that in many sediments the carbon cycle is interwoven with the sulfur cycle by processes controlling both *pH* and *Eh* (the oxidation potential).

As temperatures in sediments increase to about 120°C, it is now generally accepted that the importance of biochemical processes will be diminished due to denaturation of proteins or deactivation of enzymes. Thus, at temperatures in excess of about 120°C, the reduction of sulfate (or other oxidized sulfur species) by organic matter will proceed only by abiogenic thermal processes. In order to determine the relative importance of biological and thermochemical sulfate reductions in sediments, it is important to know at what stage of sedimentation the biochemical processes are 'taken over' by chemically controlled reactions, and if the nonbiological reactions also include direct sulfate reduction (Aizenshtat [3]).

Although the focus of the review is centered on the abiogenic reduction of sulfate by organic matter, it is important to understand the role of the early changes in *pH* and *Eh* imposed on the depositional environment by microbial activity. It is also important to recognize that sulfate can be utilized in the geosphere without change in its oxidative stage (e.g., by precipitation of sulfate-containing minerals such as gypsum or anhydrite). The thermochemical reduction of sulfate by hydrocarbons is illustrated in the equation below which depicts the reduction of sulfate by organic matter (methane in this example) to form carbon dioxide, hydrogen sulfide, and hydroxide ion.

$$CH_4 + SO_4^{2-} \rightarrow CO_2 + H_2S + 2OH^- \qquad (1)$$

Orr [4] has given considerable attention to the question as to whether or not thermochemical sulfate reduction reactions in sediments can occur to any significant extent, at temperatures below about 130°C. As will be discussed later, Orr [5] explained how some relatively high-temperature sulfate reduction reactions might occur in geologic environments based on model chemical reactions. He has recently reexamined and extended some of his earlier concepts on thermochemical sulfate reduction using additional field data and a reevaluation of his earlier experiments. A number of field observations were cited to support the idea that TSR reactions do occur at these intermediate temperatures in oil field settings. These include: (i) abundance of H_2S in natural gas, (ii) changes in sulfur isotope ratios in oil and gas with depth and reservoir temperature, and

(iii) very low concentration of sulfate in waters that are in direct contact with petroleum.

A comprehensive and comparative review of the literature on thermochemical sulfate reduction (that included a report of additional experimental findings) was published in 1985 by Trudinger *et al.* [6]. Based on studies on thermophillic bacteria, the authors concluded that the upper temperature limit for biological reduction could be as high as 120°C. The direct conversion of sulfate by non-biological reactions was considered to be unlikely in sediments below this temperature. On the other hand, the authors stated that thermochemical sulfate reduction reactions could occur in sediments with temperatures higher than about 200°C, and that this process could be important in geological time.

Whereas Orr is somewhat cautious in predicting the source of H_2S and its abundance in petroleum reservoirs (because of the greater diversity of reactants and reaction conditions in the natural systems compared with laboratory experiments), Kiyosu *et al.* [7] state that 'it has long been recognized that the high concentrations of H_2S in sour gas associated with deep carbonate reservoir rock arise from thermochemical sulfate reduction (TSR)'. This decisive statement is based, in part, on the work reported by Orr, but it may not be based on completely verified data.

In summary, we note that sulfate, derived from sea water, is a common constituent of many sediments. On burial, sulfate can undergo redox reactions with organic matter to ultimately form CO_2 and H_2O. Anaerobic microorganisms can utilize sulfate as an oxidant in metabolic processes, and organic matter in sediments can thus be oxidized by biological sulfate reduction (BSR) reactions. These reactions essentially cease as the sediment temperature rises above about 110°C, at which point the biological catalysts (enzymes) denature. At higher temperatures, it has been proposed that sedimentary organic matter can reduce sulfate by abiologic processes called 'thermochemical sulfate reduction'. Although such reactions are known at very high temperatures, there is only limited detailed information on TSR reactions at temperatures encountered in many oil field sediments (e.g. at temperatures of about 120–160°C). Orr [4] has explained how TSR reactions can occur under these conditions, and has discussed their significance for petroleum exploration and production activites.

Kiyosu *et al.* [7] are of the opinion that the remaining problems in understanding thermochemical sulfate reduction under geological conditions involve determining the key chemical steps in the reaction and in elucidating the nature of the reducing agents. We agree, and the present review is aimed at examining these questions. There is, by far, more knowledge about the biochemical mechanisms employed by sulfate reducing bacteria than there is about thermochemical sulfate reduction. However, we think that a critical examination of the literature dealing with the thermodynamics, kinetics, and isotope chemistry of

TSR reactions can provide information relative to both reactions and reactants in this geologic redox system.

Thermodynamics

Thermodynamic aspects of TSR reactions have been addresses by several authors. Anisimov [8] has calculated Gibbs free energy values (ΔG) for a number of sulfate reduction reactions, and gives estimates of energy barriers for the stepwise reduction of SO_4^{2-} to S^{2-} . Values of ΔG for the reduction of sulfate by sugars have been calculated by Kaiser [9]. Using an electrochemical approach, Morris and Stumm [10] have estimated the energetics of sulfate reduction by organic matter in aqueous systems. Studies of the thermodynamics of reactions of reduced sulfur species with sulfate, and related inorganic sulfur reactions, have also been reported. Inorganic intermediates of some of these reactions may be required for abiogenic TSR reactions at temperatures encountered in most oil field sediments.

The reduction of sulfate by hydrocarbons and many other organic compounds is thermodynamically favorable at the temperatures that exist in most geologic settings. For example, the direct reduction of sulfate by methane to form carbon dioxide and hydrogen sulfide is energetically favorable at temperatures well below 20°C. However, although these reactions are thermodynamically favorable, the non catalyzed, direct reduction of sulfate by hydrocarbons under laboratory conditions has never been observed at temperatures below about 800°C. On the other hand, the low-temperature reduction of sulfate by microorganisms has been thoroughly studied and described.

Although the reduction of sulfate by organic matter is a thermodynamically favorable reaction in most sediments, the uncatalyzed reaction is reported to have a high activation energy (Bostrom [11]). In the absence of sulfate-reducing bacteria, the rate of reduction is considered to be immeasurably slow in diagenetic stage sediments (below about 50°C). At the higher temperatures that are encountered in sediments at the catagenic stage, or in some reservoirs or very hot brines, the rate of the thermochemical reaction is estimated to be high enough to give significant conversions of sulfate (Toland [12], Kaplan *et al.* [13] and Goldhaber *et al.* [14]).

Reduction of sulfate

The reduction of sulfate to sulfide involves an eight electron change in the oxidation state of sulfur as sulfate (SO_4^{2-}) goes to sulfide (S^{2-}). Morris and Stumm [10] estimated the energetics of this transformation from electrochemical analysis of the redox potentials of reactions in the stepwise reduction of S^{6+}

to S^{2-}. The potential for the overall reduction was then derived from values for the various half cell reactions. Electrochemical data for a number of half cell reactions pertaining to TSR reactions were complied by Morris and Stumm, and are reproduced in Table 1.

From the data given in Table 1 and the equilibrium distribution profile *pE* at *pH* 7 (given in Fig. 2), it is possible to estimate the redox potentials and stability of sulfur species in various redox states in comparison to other dissolved species. For example, inspection of Table 1 and Fig. 2 will show that at *pH* 7, reduction of SO_4^{2-} to H_2S or HS^-, requires a *pE* (negative log of relative electron activity) of less than −3.

Table 1 Potentials of redox processes for aquatic conditions [after: Morris and Stumm (1967)]

	Reaction	*pE°*/W
1	$1/4O_2(g) + H^+(W) + e - 1/2H_2O$	+13.75
2	$1/5NO_3^- + 6/5H^+(W) + e - 1/10N_2(g) - 3/5H_2O$	12.65
3	$1/2MnO_2(s) + 1/2HCO_3^-(10^{-3}) + 3/2H^+(W) + e - 1/2MnO_3(s) - 3/8H_2O$	8.5)
4	$1/2NO_3^- + H^+(W) + e - 1/2NO_2^- - 1/2H_2O$	7.15
5	$1/8NO_3^- + 5/4H^+(W) + e - 1/8NH_4 - 3/8H_2O$	6.15
6	$1/6NO_2^- + 4/3H^+(W) + e - 1/6NH_4 - 1/3H_2O$	5.82
7	$1/2CH_3OH + H^+(W) + e - 1/2CH_4(g) - 1/2H_2O$	2.88
8	$1/4CH_2O + H^+(W) + e - 1/4CH_4(g) - 1/4H_2O$	− 0.06
9	$FeOOH(s) + HCO_3^-(10^{-3}) + 2H^+(W) + e - FeCO_3(s) - 2H_2O$	(− 1.67)
10	$1/2CH_2O + H^+(W) + e - 1/2CH_3OH$	− 3.01
11	$1/6SO_4^{2-} + 4/3H^+(W) + e - 1/6S(s) - 2/3H_2O$	− 3.30
12	$1/8SO_4^{2-} + 5/4H^+(W) + e - 1/8H_2S(g) - 1/2H_2O$	− 3.50
13	$1/8SO_4^{2-} + 9/8H^+(W) + e - 1/8HS^- - 1/2H_2O$	− 3.75
14	$1/2S(s) + H^+(W) + e - 1/2H_2S(g)$	− 4.11
15	$1/8CO_2(g) + H^+(W) + e - 1/8CH_4(g) - 1/4H_2O$	−4.13
16	$1/6N_2(g) + 4/3H^+(W) + e - 1/3NH_4$	− 4.68
17	$1/2(NADP) + 1/2H^+(W) + e - 1/2(NADPH)$	− 5.5
18	$H^+(W) + e - 1/2H_2(g)$	− 7.00
19	Oxid. Ferredoxin + e − Red. Ferredoxin	− 7.1
20	$1/4CO_2(g) + H^+(W) + e - 1/24$(glucose) $- 1/4H_2O$	− 7.20
21	$1/2HCOO^- + 3/2H^+(W) + e - 1/2CH_2O - 1/2H_2O$	− 7.68
22	$1/4CO_2(g) + H^+(W) + e - 1/4CH_2O - 1/4H_2O$	− 8.20
23	$1/2CO_2(g) + 1/2H^+(W) + e - 1/2HCOO^-$	− 8.73

These data correspond to $(HCO_3^-) = 10^{-3}$ rather than unity and so are not exactly *pE°*/W; they represent more nearly typical aquatic conditions than *pE°*/W values do.

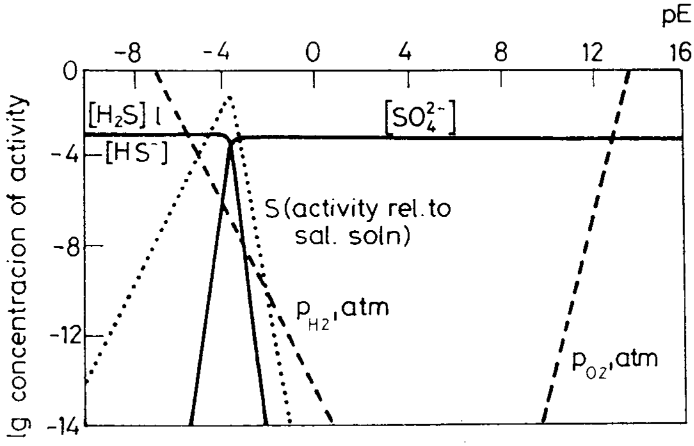


Fig. 2 Equilibrium distribution of sulfur compounds as a function of *pE* at *pH* 7 and 25°C. Total concentration of compounds is 10^{-3}M. P_{H_2S} in atm. is about 50 times ($[H_2S]$ + [HS])

Using such data, Morris and Stumm estimated thermodynamic values for the reduction of sulfate by a variety of organic compounds of a type that might exist in sediments. One such reaction, illustrated in the equation below, is the reduction of sulfate by formaldehyde.

$$SO_4^{2-} + 2CH_2O + 2H^+(W) \rightarrow H_2S(g) + 2CO_2(g) + 2H_2O \tag{2}$$

Lg *K* for this reaction can be calculated from the data presented in Table 1 (Morris and Stumm [10]). Since lg *K* (= 37.6) and ΔpE^o(w) are both positive, the reaction was judged to be thermodynamically favorable. Similar calculations showed that the formation of elemental sulfur by this reaction was also favorable at *pH* 7 under standard conditions.

The possibility that TSR reactions could occur in oil field deposits has also been addressed by Bostrom [11]. Bostrom predicted that the reduction of sulfate by oxidation of organic matter was possible in sediments, and estimated the boundary *pH* and *Eh* ranges for the reaction in relation to the stability of iron- or manganese-oxides. However, these estimates apply more to the reaction conditions encountered in sediments at the diagenetic stage, rather than to those where the temperatures are higher than about 120°C.

One of the major drawbacks in attempting to predict whether or not thermochemical sulfate reduction reactions will occur in sediments is the lack of appropriate thermodynamic data for redox reactions of organic compounds. In sediments, for example, some originally deposited organic molecules can undergo structural alteration without change in oxidation state. However, with increasing sediment age and temperature, both the thermodynamic properties and the rate at which these altered structures react can change. For example, structural alterations leading to the conversion of primary to tertiary hydrogens will lead to increased rates of oxidation of hydrocarbons. Thus, reactions of sulfate with organic matter that might be very slow at low temperatures can be accelerated by temperature increase due to changes in the redox potential of the organic matter, in addition to the usual increase in reaction rate with increasing temperature.

The mineral matrix and other components in sediments can also have a major effect on the course of thermochemical sulfate reduction reactions. For example, Machel [15] reports that minerals such as clays will catalyze the reaction of hydrogen sulfide with organics to form elemental sulfur and 'altered hydrocarbons'. Although this reaction is not sulfate reduction, it does point out that the mineral matrix can interact with and alter TSR reaction products. Similarly, Bostrom [11] examined some of the controlling factors of *pH* in oxidizing-reducing depositional environments. The potential influence of iron-oxides and -sulfides on the in situ *pH* in sedimentary environments and in laboratory experiments is discussed in this publication. However, it should be noted that the reported values are highly dependent on the pH and other ions in the solution. For geologic systems, equilibrium models are available and are valuable for interpreting the stability relation of pertinent redox compounds in natural waters. Non-equilibrium conditions are common in many natural systems, and the equilibrium models must be used judiciously. This can be illustrated by recognizing that because many redox reactions are slow, the concentration of oxidizable or reducible species in the geosphere may be far from those predicted thermodynamically. For this reason, transformations under non-equilibrium conditions may also have to be considered. Moreover, in many real solutions, quantitative electrochemical conditions often cannot be obtained because electrochemical reversibility is usually not achieved.

It has been suggested that sulfate reduction by organic matter in TSR reactions requires the participation of low oxidation state sulfur species. For this reason, the following two reactions (Eq. 3) which involve the reduction of sulfate by sulfide, are of interest. The thermodynamic parameters can be estimated from values listed in Table 1.

$$1/6SO_4^{2-} + 1/3H^+ + 1/2H_2S = 2/3S + 2/3H_2O;\ \Delta pE = 0.81 \qquad (3)$$

or

$$SO_4^{2-} + 2H^+(w) + 3H_2S = 4S^\circ(s) + 4H_2O;\ \lg K = 4.86$$

Table 2 Thermodynamic parameters of sulfate reduction reactions [after: Anisimov (1978)]

Stage		Reaction path	ΔG_{202}	ΔG_{298}	$\Delta G_{500}^{(a)}$
I	1	$2H + CaSO_4 = Ca(OH)_2 + SO_2$	–67.70	–67.45	–67.18
	2	$2H + SO_2 = SO + H_2O$	–69.26	–65.69	–64.02
	3	$2H + SO = S + H_2O$	–166.01	159.00	–153.51
	4	$2H + S = H_2S$	–105.03	–103.63	–102.29
		$8H + CaSO_4 = Ca(OH)_2 + H_2S + 2H_2O$	–408.60	–395.69	–396.99
II	1	$H_2 + CaSO_4 = Ca(OH)_2 + SO_2$	29.44	27.31	25.22
	2	$H_2 + SO_2 = SO + H_2O$	27.88	29.16	28.40
	3	$H_2 + SO = S + H_2O$	–69.47	–64.28	–61.14
	4	$H_2 + S = H_2S$	–7.89	–8.87	–9.69
		$4H_2 + CaSO_4 = Ca(OH)_2 + H_2S + 2H_2O$	–20.04	–16.68	–17.40
III	1	$1/4CH_4 + CaSO_4 = CaSO_2 + 1/4CO_2 + 1/2H_2O$	5.97	0.57	–1.80
	2	$1/4CH_4 + CaSO_3 + 1/4CO_2 = SO + 1/2CaCO_3 + 1/2Ca(OH)_2$	58.02	59.57	57.14
	3	$1/4CH_4 + SO + 1/4Ca(OH)_2 = S + 3/4H_2O + 1/4CaCO_3$	–66.10	–62.44	–60.29
	4	$1/4CH_4 + S + 1/4H_2O + 1/4Ca(OH)_2 = H_2S + 1/4CaCO_3$	–4.55	–7.03	–9.03
		$CH_4 + CaSO_4 = CaCO_3 + H_2S + H_2O$	6.66	–9.34	–13.88

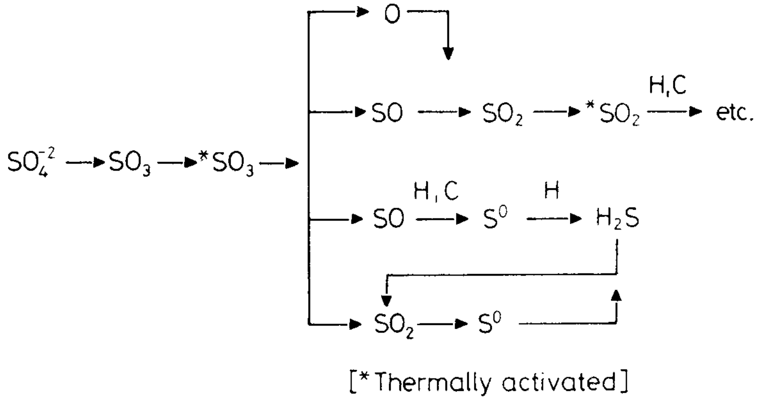
Table 2 Continued

Stage		Reaction path	ΔG_{202}	ΔG_{298}	ΔG_{500}(a)
IV	1	$1/18C_6H_{12} + CaSO_4 = 1/3CaCO_3 + 2/3CaSO_3 + 1/3SO_2 + 1/3H_2O$	8.57	3.59	0.65
	2	$1/18C_6H_{12} + 2/3CaSO_3 + 1/3SO_2 = SO + 1/3CaCO_3 + 1/3Ca(OH)_2$	48.73	48.74	46.13
	3	$1/18C_6H_{12} + SO + 1/3Ca(OH)_2 = S + CaCO_3 + 2/3H_2O$	–69.47	–66.35	–64.67
	4	$1/18C_6H_{12} + S + 2/3H_2O = H_2S + 1/3CO_2$	–1.94	–5.76	–8.20
		$4/18C_6H_{12} + CaSO_4 = CaCO_3 + H_2S + 1/3CO_2 + 1/3H_2O$	–14.11	–19.78	–25.99
V	1	$1/2C + CaSO_4 = 1/2CaCO_3 + 1/2CaSO_3 + 1/2SO_2$	14.415	9.67	6.95
	2	$1/2\ C + 1/2CaSO_3 + 1/2SO_2 = SO + 1/2CaCO_3$	44.145	43.99	41.86
	3	$1/2C + SO = 1/2CO_2 + S$	–59.91	–57.88	–55.84
	4	$1/2C + 1/2CO_2 + S = COS$	6.68	5.68	3.55
		$2C + CaSO_4 = CaCO_3 + COS$	5.33	1.45	–3.48
VI	1	$H_2S + CaSO_4 = CaSO_3 + S + H_2O$	6.04	3.71	3.38
	2	$H_2S + CaSO_2 + CO_2 = CaCO_3 + SO + S + H_2O$	49.18	54.87	54.57
	3	$H_2S + SO = 2S + H_2O$	–61.58	–55.41	–51.25
		$3H_2S + CaSO_4 + CO_2 = CaCO_3 + 4S + 3H_2O$	–6.36	3.17	6.70

(a) All ΔG values are given on the basis of principle of the minimal possible free energy for the end product of each stage.

The calculations show that the formation of elemental sulfur by reaction of product hydrogen sulfide with sulfate is also thermodynamically favorable at *pH* 7 and under standard reaction conditions. As we will discuss further, the conversion of sulfate to lower valence sulfur species may be important for non-microbial sulfate reduction reactions in most sedimentary environments.

For various reasons, Anisimov chose $CaSO_4$ as a representative material for studies of the thermodynamics of sulfate reduction in sediments. Table 2 (from Anisimov [8]) lists the chemical reactions and the thermodynamic parameters for the various stages in the conversion of sulfate to sulfide as depicted in the reaction sequence shown below in Scheme 1.



[*Thermally activated]

Scheme 1

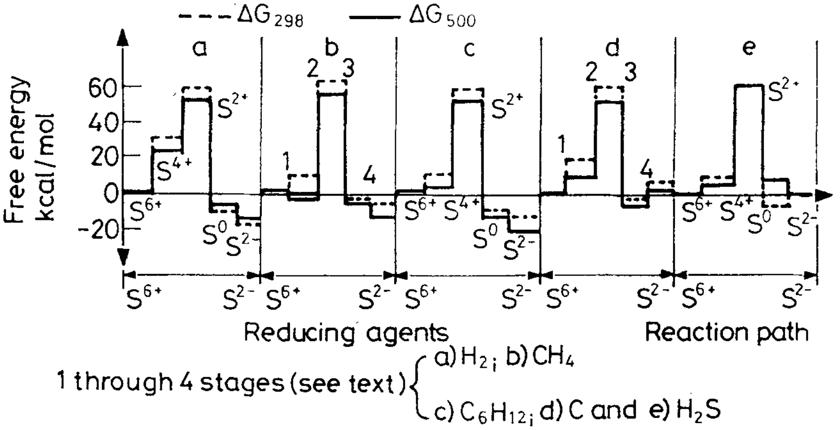
The Gibbs free energies for each of the four stages of sulfate reduction by elemental carbon, H_2, CH_4, C_6H_{12} and H_2S as the reducing agents were calculated at 298, 400 and 500 K. Calculations were made at the listed temperature because similar temperatures would be reasonable in sediments undergoing sulfate reduction reactions. Based on these calculations, Fig. 3 diagramatically illustrates the change in free energy as S^{6+} is reduced to S^{2-}. Inspection of the figure will show that the 'energy barrier' to the overall reduction of sulfate to sulfide is the step to form S^{2+}.

In order to be able to calculate thermodynamic values at various stages of sulfate reduction, Anisimov [8] suggested the following overall scheme for the thermal reduction of sulfate by carbon, hydrogen, or hydrocarbons:

Thermodynamically, the hydrolysis of sulfur to form hydrogen sulfide and sulfuric acid ($4S + 4H_2O \rightarrow 3H_2S + H_2SO_4$) only becomes favorable at temperatures above 150°C.

However because this is a multistep reaction, it further complicates the sulfate reduction scheme shown above. Anisimov [8] stresses the importance of the

$SO_2 \rightarrow SO$ transformation in the overall sulfate reduction scheme. This essential $S^{4+} \rightarrow S^{2+}$ transformation in the chain of sulfate reduction reactions is the key step which governs the chemical stability of sulfates at lower temperatures. Table 2 (Anisimov [8]) lists a series of chemical reactions and their thermodynamic parameters for the reduction of sulfate to sulfide as depicted in the above scheme. Inspection of the table will show that thermochemical reduction of sulfate by the hydrocarbons is thermodynamically favorable at the lowest temperatures expected to be encountered in most sediments.



Redrafted after anisimov (1978)

Fig. 3 Energy profiles of $CaSO_4$ to form S^{2-} sulfide

Using data listed in Table 2 and shown graphically in Fig. 3, Anisimov states that the energy thresholds for thermochemical sulfate reduction by various reducing agents range between +231 and 268 kJ/mol. The reaction of sulfate with elemental carbon only becomes favorable at elevated temperatures (reaction V in Table 2), and neither this reaction nor reductions involving hydrogen gas (reaction I), are considered important in natural environments. For this reason, only the energy profiles for reaction paths II–VI of Table 2 are given in Fig. 3 (reproduced from Anisimov [8]).

Thermodynamic properties of other sulfur reductants

Because the thermodynamic properties of catanated sulfur species (–S–{Sn}–S) are not well known, the whole issue of using thermodynamic parameters that have been calculated for redox reactions of sulfur while ignoring these additional species becomes problematic. For example, at ambient temperatures hydrogen sulfide reacts exothermally with sulfate, but at higher temperatures the reaction becomes endothermic. The interactions of the various sulfur species 'under real chemical reaction conditions' makes the experimental determination of thermodynamic parameters virtually impossible. These 'secondary' reactions and reactions with the reducing agents (not simple electron transfer) complicate the issue of formation of activated intermediates. The marked diversity of intermediates and end products in sulfate reduction reactions makes calculation of equilibrium constants for these complex reactions particularly difficult.

Williamson and Rimstid [16], in their analysis of studies on the oxidation of aqueous sulfide, also provide information on the thermodynamics of sulfate reduction. These authors showed that sulfane monosulfonic acids ($S_nSO_3^{3-}$, where $n = 1, 2, 3, 4, 5, ...$)were intermediate metastable oxidation states in sulfide oxidation. The existence of sulfane sulfonic acids in the oxidation of sulfide raises the possibility that polysulfide species (e.g., HS_n^{1-} may be an intermediate in both sulfide oxidation and in sulfate reduction. This study suggests that sulfane sulfonic acids, or related species, may function as bridging intermediates in the reduction of sulfates.

The relative aquatic stability of the polysulfides indicate these species may function as intermediates in reduction of sulfate to sulfide (Figs 4a, b, c). Based on the values given in Fig. 4, the pathway of lowest energy for sulfate reduction is thought to proceed through the following metastable intermediates: polysulfi-

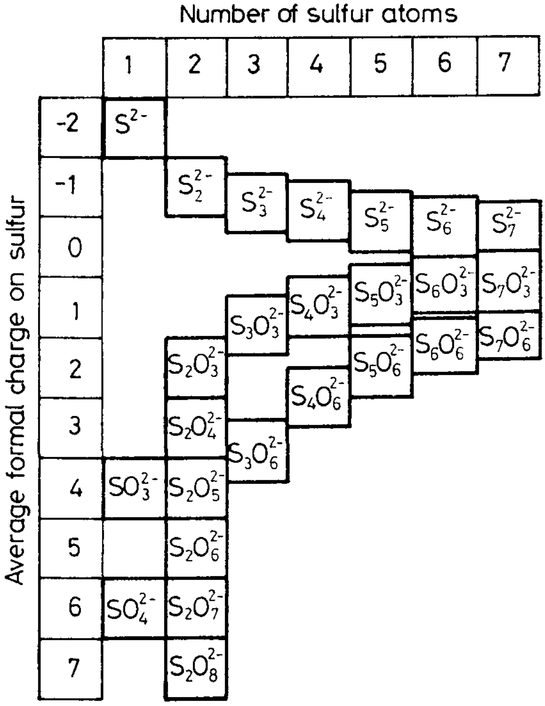


Fig. 4a Sulfur species stable in solution

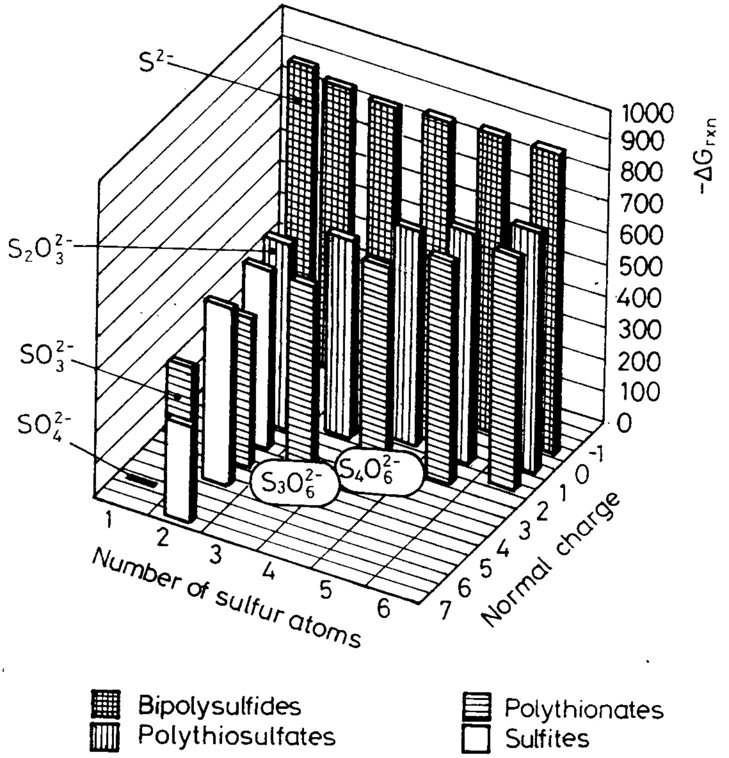


Fig. 4b Thermodynamic stability of sulfur species relative to sulfate

des → thiosulfate → sulfite. This analysis, however, does not predict the products of the reaction of sulfate and polysulfides.

The oxidation of dextrose and other sugars by sulfuric acid has been studied by several workers, and the kinetic and mechanistic aspects of several of these studies will be considered further. According to Kaiser [9], the reduction of sulfuric acid by dextrose (illustrated in Eq. (4) below) is thermodynamically favorable at 250°C with ΔG^0 = 3200 kJ/mol.

$$C_6H_{12}O_6 + HSO_4 + 3H^+ \rightarrow 3H_2S + 6CO_2 + 6H_2O \qquad (4)$$

Experiments

Direct reactions of SO_4^{2-} *with organics*

As was mentioned earlier, there are a number of examples of non-catalytic thermochemical sulfate reductions in which sulfate is directly reduced by carbon or by hydrocarbons to lower valent sulfur species, but these reactions are

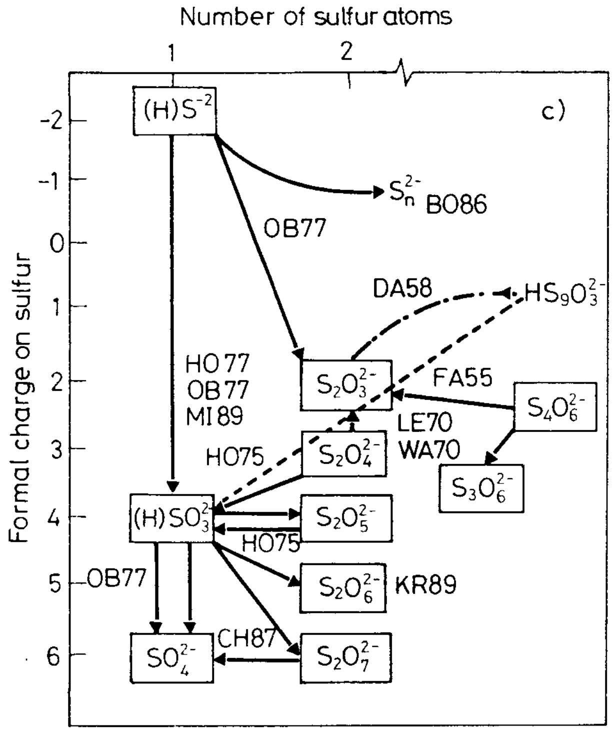


Fig. 4c Reactions among aqueous sulfur species for which rate data are available

only known to occur at elevated temperatures (generally > 800°C). It is also noteworthy to mention that according to Spitsyn and Meyerov [17], temperatures in excess of 300°C are required to initiate sulfate reduction in uncatalyzed reactions using H_2 as the reducing agent.

Smith and Batts [18] suggested that in the absence of oxygen, coals might undergo a direct geochemical reaction with sulfate. This suggestion was based on the fact that reduced sulfur in coals was isotopically close to sea water sulfate. However, in subsequent publications, this possibility has been largely discounted (Trudinger *et al.* [6]).

Anisimov [8] reported the results of kinetic experiments on the high temperature (> 700°C) thermochemical reduction of $CaSO_4$ to CaS by elemental carbon. Based on the results of these experiments he calculated the time required to form about 1% CaS ('alpha' in the rate expression given below).

$$\lg k = 5.95 - 10^{2-}\alpha - 7.55 \times 10^{3}/K$$

The results of these experiments are given in Table 3, it is estimated that at 100°C it would require 3.7×10^9 years to convert 1% of the sulfate to sulfide, and 1.6×10^7 years at 150°C. It should be noted that these estimates are based on results from reactions in the solid state ($CaSO_4$ and coke) and that these reactions proceed with an apparent activation energy of 144 kJ/mol. The reaction was reported to proceed with lower activation energy and higher rate if catalyzed by iron oxides (Fe_2O_3, $FeSO_4$), or if kerosene or olefins were employed as the reductant. The nature and composition of the organic matter can have a controlling effect on the rate of thermochemical sulfate reduction, as will be discussed further.

Although it was not necessary for Anisimov [8] to consider *pH* effects on the gas phase reaction of $CaSO_4$, it is clear that in solution, the *pH* of the medium will have a decisive influence on the rate of sulfate reduction. Furthermore, it is understood that the reaction mechanism for sulfate reduction may also be dependent on the nature of the reducing agent. For example, a change in mechanism could result from a 'activation' of the various sulfur intermediates through bonding to the reducing agents during the course of the multi-step 2-electron reactions.

Anisimov also examined the kinetics of hydrothermal sulfate reduction by organic matter, using Na_2SO_4, $NaHSO_4$, H_2S and NaHS under varying conditions of *pH* and temperature. From these studies, and from Arrhenius plots (Fig. 5), he calculated that the activation energies for the reactions at *pH* 2, 5, and 8.5–9 were 18.4, 29.6 and 41–197 kJ/mol, respectively.

A related inorganic reaction in which sulfates can be reduced involves heating metal sulfates at very high temperatures. The decomposition of metal sulfate salts (MSO_4) to MO, SO_2 and SO_3, occurs at measurable rates only at temperatures higher than 800°C. One of the most studied such reaction is the thermal decomposition of $BaSO_4$ (at 1075–1100°C) because of its use to produce 'clean' SO_2 for $\delta^{34}S$ isotope measurements.

In somewhat similar reactions, sulfate reduction by natural reducing agents was shown to be efficient at 500–700°C in several processes for producing metal sulfides or carbonates from Na or Ca sulfates. The reducing agents for these processes were H_2, C, CO, CH_4 and several higher molecular weight hydrocarbon gases.

Although SO_2 (which we do not consider to be an intermediate in TSR reactions) can be reduced with hydrocarbons, the reaction has a high energy of activation and only takes place at high temperatures. Industrial processes to reduce SO_2 by natural gas have been conducted without catalysts at 1250–1300°C but the use of Ca, Ba, Mg, Mn of Fe sulfides as catalysts dropped the needed temperature to about 900°C. These reactions are conducted at short residence time in flow – through reactor systems.

Table 3 Calculation of the time of formation of 1% of CaS with respect to $CaSO_4$ in relation to temperature [after: Anisimov (1978)]

T/K°	300	343	373	400	423	448	473	500	600	700	800
T/°C	27	70	100	127	150	175	200	227	327	427	527
ln$K$	–19.23	–16.07	–14.03	–12.94	–11.91	–10.91	–10.02	–9.16	–6.64	–4.85	–3.50
K	5.9×10^{-20}	8.6×10^{-17}	5.1×10^{-16}	1.2×10^{-13}	1.2×10^{-12}	1.2×10^{-11}	9.6×10^{-11}	6.9×10^{-10}	2.3×10^{-7}	1.4×10^{-5}	3.2×10^{-4}
τ/years	3.2×10^{14}	2.2×10^{11}	3.7×10^{9}	1.6×10^{8}	1.6×10^{7}	1.6×10^{6}	2.0×10^{5}	2.8×10^{4}	8.26	0.136	0.007

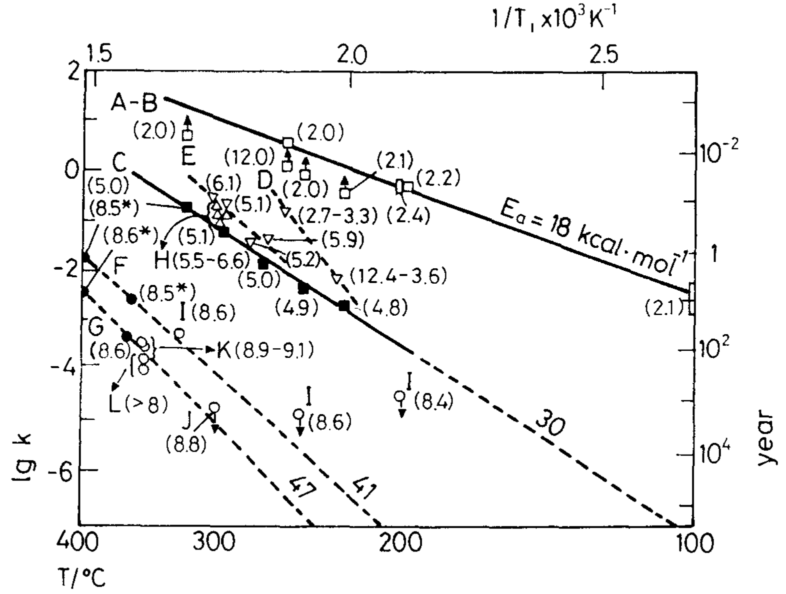


Fig. 5 Arrhenius plot of lg k_1 *vs.* $1/T$ k_1 in units of kg/mol/h. Numbers in parentheses are calculated in situ *pH* values. Symbols: series A–B; series C; series D–E; series F–G; series H; series I–L. The letters A–L refer to experimental grouping of samples in the study. Arrows indicate minimum or maximum *k* values. Scale on right gives the time in years to achieve $F = 0.9$ if $\Sigma S = 10^{-2}$ molar; $^{*}pH$ computed at 350°C

In a series of experiments conducted under mild reaction conditions, Bastin [19] investigated the possibility that organic matter in sediments might act to reduce sulfate in abiogenic reactions. Because he was aware of the thermodynamic feasibility of the reduction of $CaSO_4$ by carbon, and the (high temperature) experiments of Hoffman and Mostowitch [20], Bastin undertook an experimental program to determine if the reaction might also occur under geologically reasonable reaction conditions. However, in reactions over a year in length, but at ambient temperature, he was unable to find evidence for sulfate reduction when calcium sulfate ($CaSO_4$) was reacted with coal, crude petroleum or oil shales. In month long experiments at ambient temperature, Bastin [19] again found no evidence for sulfate reduction in reactions using either hydrogen, methane, or acetylene to reduce the Zn-, Cu-, or Na-sulfates.

Based on these studies, Bastin reported that while high temperature reactions do take place 'no experimental evidence has been obtained ...[for]...reduction of sulfates at ordinary temperatures by dead organic matter'. A similar conclusion was reached by Ginter [21] who reported that thermochemical sulfate reduction reactions were unlikely to occur in oil field waters. It must be noted, however, that both Bastin and Ginter thought that these reactions would have to take place in petroleum reservoirs at temperatures less than 80°C, and in most cases lower than 50°C.

Oxidation of organics with reduced sulfur species

The ability of elemental sulfur (S^0) to abstract hydrogen from organic molecules is a synthetic procedure that has long been utilized by synthetic chemists. Generally, these reactions were used to produce unsaturated organic compounds such as aromatics from alicyclic saturated hydrocarbons. In other cases, dimeric compounds, thiophenes, mercaptans, sulfides and polysulfides were the reaction products. The course of these reactions depends on the nature of the organic substrate and other reagents as well as the reaction conditions. In all cases, however, the minimal reaction temperature was determined to be about 175°C. It is at this temperature that sulfur, in the cyclic S_8 form, opens to give the highly reactive polysulfide di-radical which is the active species in hydrogen abstraction from organic compounds (Pryor [22]). The significance of reaction conditions and other controlling factors in the synthetic reactions as they pertain to the sulfate reduction in geochemical systems will be discussed further.

In studies on oxidation reactions in organic chemistry, Toland *et al.* [23] examined the reaction of sulfur with a variety of organic compounds (Table 4). These workers reported that terephthalic acid and hydrogen sulfide were produced by reacting p-toluic acid and sulfur in the presence of water. The reaction yield was improved by the addition of base (NaOH) to the system. Excellent yields of oxidized products were obtained from a variety of methyl- substituted aromatics under these conditions (e.g., toluene, xylenes). Toland reported that under his reaction conditions, the sulfur disproportionated to give a reactive sulfur species such as thiosulfate, and suggested that the same species might have formed in experiments conducted by Pryor [24] where polysulfides were used rather than elemental sulfur.

The possibility that a variety of sulfur species might form by disproportionation reactions under basic conditions was raised as early as 1924 by Tartar and Graves [25]. They found that thiosulfate was formed in reactions using alkaline solutions of sulfur to oxidize organic compounds. Furthermore, if all of the oxidized sulfur species can exist at temperatures greater than 200°C, it is possible that thiosulfate might function as an active homogeneous oxidant in the basic system.

In a continuation of his earlier work, Toland [12] studied the oxidation of various organic compounds at 315–350°C, using aqueous sulfate containing variable amounts of H_2S as the oxidant. these experiments were conducted in stainless steel autoclaves using reaction times that ranged from 0.5 to 6 h. In

Table 4 Sulfur compounds of intermediate valences as oxidants [after: Toland (1960)]

Run	Oxidant	Compound oxidized	Other[a]	Water[a]	Temp./ °C	Time/ min	Conversion/ %	Yield of acid/%	
								Toluic	Phthalic
1	4.0 S	Sodium toluate[b]	None	56	288	360	100	–	87.1[c]
2	3.0 S		1.0 NaOH	53	293	270	72	–	92.0
3	6.0 S		3.0 NaOH	56	288	230	100	–	90.5
4	2.7 S		5.5 NaOH	56	282	240	7.5	–	95
5	1.0 Na_2SO_4	Sodium *p*-toluate	0.7 H_2S	100	315	60	13.6	–	87.1
6	1.0 Na_2SO_4		2.0 AcOH 0.7 H_2S	100	315	60	23.3	–	80+
7	2.2 $(NH_4)_2SO_4$	Xylene[d]	2.2 NH_4SH	56	315	60	96.7	4.2	87.2
8	2.0 NH_4HSO_3		2.4 NH_4SH	56	315	60	96.1	5.9	76.4
9	2.0 $(NH_4)_2SO_3$		0.4 NH_4OH	70	315	60	69.5	38.5	25.9
10	1.0 $Na_2S_2O_3$	Sodium *p*-toluate	None	100	315	60	40.6	–	93.2
11	1.5 $Na_2S_2O_3$	*m*-Xylene	None	53	315	90	34.0	42.2	37.9
12	1.5 $(NH_4)_2S_2O_3$		None	53	315	90	100	0	94.8

[a] Moles/mole compounds to be oxidized.
[b] 85% *m*-toluate, 15% *p*-toluate.
[c] Also found 10.3% yield benzoic acid.
[d] 85% *m*-xylene, 15% *p*-xylene.

some experiments $(NH_4)_2SO_4$ was the oxidant and in others various metal sulfates were employed (Li, Na, K, Al and Fe); however, in all experiments, sulfide, H_2S,$(NH_4)_2S$,$(NH_4)SH$ or elemental sulfur was added to the reaction (Table 5).

Toland [12] reported that organics were not oxidized in experiments using sulfate alone as the oxidant. He found, however, that the addition of as little as 0.1 mol of sulfide (e.g. H_2S) to the reaction system was sufficient to activate 1 mol of $(HN_4)_2SO_4$ as an oxidant for his reactions.

Because these early observations provided the basis for some of the later geochemical studies on thermochemical sulfate reduction (e.g., Orr [4, 26]), it is instructive to discuss Toland's experiments in some detail. Toland [12] oxidized a variety of organic compounds, using solutions of SO_4^{2-} containing sulfides, to give the products given in Table 5. Among the organic compounds reacted, Toland reported that methane underwent a partial (ca 0.1%) conversion to CO, CO_2 and H_2O. Considering the relative stability of methane, even the low conversion reported under Toland's reaction conditions is surprising. However, much higher conversions were observed if alkenes or methyl-substituted aromatics were oxidized under the same reaction conditions (Toland [12]; Anisimov [8]).

Inspection of Table 5 will show that in these reactions, cyclohexane forms phenol and methylcyclohexane yields benzoic acid, and prompted Toland to suggest that a 'more active species of sulfur or polysulfides (e.g., 'nascent sulfur') was involved in the reaction. It was hypothesized that sulfur in this form might not only transfer oxygen atoms from sulfate to carbon, but might also aromatize the products. Toland concluded that sulfate itself does not initially attack hydrocarbon, and postulated that the thiosulfate is the active form, which under acid conditions is unstable and yields free sulfur and sulfite.

Reactions of sulfate with sugars and sugar derivatives

In a series of isotope exchange experiments carried out in sealed tube reactions, Kiyosu [27] heated dextrose with mixtures of equimolar solutions of dilute sulfuric acid and sodium sulfate adjusted to give *pH* values from 0.9 to 7.0. Hydrogen sulfide from the reaction was collected and converted to Ag_2S for isotope analysis, and the residual sulfate was analyzed as $BaSO_4$. Gases formed in the reaction (e.g. CO_2, CH_4, and H_2) were analyzed by gas chromatography. At 250°C the reduction of sulfuric acid was slow whereas at temperatures greater than 280°C it was much faster. Kiyosu suggests that temperature dependence may result from the formation of molecular hydrogen which reduces H_2SO_4 to yield H_2S. However, at a sulfate conversion of about 40% (at 280°C), the gain in H_2S was much lower and this result may be explained by the formation of elemental sulfur in the reaction system. The black polymeric material was found to contain some hydrolyzable sulfur, but much organically bonded sulfur was also found (released only upon total oxidation by HNO_3/Br_2 treatment).

Kiyosu [27] found that dextrose can reduce sulfuric acid at temperatures above 250°C, and sodium-sulfate and bisulfate at temperatures above 300°C. Chemical aspects of the reaction of sugars with sulfur species will be discussed further, but is should be noted that sugars can also condense to form melanoid in these systems (Rubinsztain *et al.* [28]). Furthermore, sugars can undergo 'caramelization' (dehydration) reactions at temperatures greater than 250°C, forming structures susceptible to acidic attack and subsequent addition of sulfate or sulfide yielding sulfur-rich polymers. Aspects of the sulfur isotope chemistry of these reactions will be discussed further.

Kaiser [9] carried out a series of experiments similar to those of Kiyosu, and showed that more than 50% of the reduced sulfur winds up in an 'organic char'. This 'char' (or residual polymer) was reported to contain as much as 14% sulfur. Kaiser suggested that the hydrogen sulfide formed in the reaction might be derived from the organically bound sulfur in a pseudo first order reaction. It is possible that hydrogen sulfide could also arise from other processes, but it is noteworthy that even at temperatures of 200–300°C, only sulfur in the form of sulfate, sulfide, and organic-sulfur compounds could be found in these reactions.

Kaiser [9] used a similar experimental approach in his study of the kinetics of sulfuric acid reduction by formaldehyde, methanol, ethanol and acetic acid. The change in isotope $\delta^{34}S$ distribution was also examined. Organic sulfur compounds were among the products formed in these reactions, a result also reported by Kiyosu [27]. Most of the reactions Kaiser describes in detail were carried out with an initial *pH* in the 0.3–0.5 range. He looked for the presence of other sulfur oxyanions (such as sulfite or thiosulfate) in the reaction mixtures. Charring of the dextrose under his reaction conditions occurred after a few hours, and the 'char' was found to contain about 50% of the initial carbon in the system.

The experiments with the oxygen-containing molecules listed above did not produce sulfide, but did show intermediate color changes in the organic matter. The oxidation of dextrose and other sugars have been studied in the past; however, in the absence of oxidizing agents, dehydration and polymerization leading to charring at > 200°C have also been reported (under both acidic and basic conditions). Hence, the simplified equation for the overall reaction as depicted in Eq. (4) might be misleading.

Table 5 Sulfate oxidation of organic compounds [after: Toland (1960)]

Compounds oxidized with aqueous ammonium sulfate

Compound	mol	$(NH_4)_2SO_4$/ mol	H_2S/ mol	Water/ mol	Temp./ °C	Pressure/ atm	Time/ min	Feed conversion/%	Major products	Yield mol/%
Methane[a]	3.00	3.03	1.0	83	325-350	23.1	70	(partial)	CO	8.0
									CO_2	92.0
Cyclohexane[a]	3.00	2.00	1.0	90	315	19.5	120	51.3	Phenol	–
Methylcyclohexane[a]	3.00	2.00	1.0	90	315	19.1	60	36.7	Benzoic acid	–
									Phenol	–
Ethylene[a]	4.00	2.00	7.0	90	325	24.7	15	100.0	Acetic acid	63.5
Propylene[b]	3.30	1.51	3.9	60	315	26.8	60	81.8	Propionic acid	–
Isobutene[b]	2.90	1.67	3.9	60	315	32.2	45	83.0	Isobutyric acid	–
Cyclooctatetrane[b]	0.50	0.80	0.2	50	330	16.1	90	100.0	Benzoic acid	–
Tetrahydrofurfuryl	1.00	1.00	0.6	90	315	15.8	90	100.0	Glutaric acid	–
alcohol[a]									Acetic acid	–
m-Xylene[b]	2.12	3.50	1.0d	53	325	19.7	60	100.0	Isophthalic acid	89.0
p-Xylene[a]	1.50	2.30	4.6	100	315	20.7	60	56.8	*p*-Toluic acid	42.4
									Terephthalic acid	37.6
p-Xylene[a]	1.50	2.30	4.6	10	315	20.7	360	100.0	Terephthalic acid	96.2

Table 5 Continued

Compounds oxidized with aqueous ammonium sulfate										
Compound	mol	$(NH_4)_2SO_4$/ mol	H_2S/ mol	Water/ mol	Temp./ °C	Pressure/ atm	Time/ min	Feed conversion/%	Major products	Yield mol/%
o-Xylene^{b}	1.86	3.50	1.0	50	325	20.4	40	90	Benzoic acid	27.2
									o-Toluic acid	6.0
									o-Phthalic acid	35.1
m-*p*-Toluic acid^{b} (85/15)	2.12	1.73	1.1	53	325	18.0	30	100	Isophthalic acid	99.7
									Terephthalic acid	
p-Toluenesulfonic acid^{bf}	1.00	0.76	1.0	60	332	18.2	90	100	*p*-Sulfobenzoic acid	59.3

a: In 4.5-liter autoclave; b: In 2.5-liter autoclave; c: Ag $(NH_4)_2S$ was used in place of H_2S
d: Sulfur was used in place of H_2S; e: Ag NH_4HS used in place of H_2S; f: As NH_4 salt

Table 5 Continued

Oxidations with various sulfates								
Oxidant	Compound oxidized	Initiator[a]	Water[a]	Temp./ °C	Time/ min	Conver-sion/%	Acid product	Yield/ %
1.53 $(NH_4)_2SO_4$	*p*-Xylene	3.1NH_4SH	80	315	360	100.0	Terephthalic	96.2
0.67 $Al_2(SO_4)_3$	*p*-Xylene	1.0 H_2S	50	335	60	100.0	Benzoic	13.1
							p-Toluic	12.3
							Terephthalic	27.5
0.5 K_2SO_4	*p*-Xylene	0.66 H_2S	100	329	60	98.6	Benzoic	1.0
1.5 $KHSO_4$							Terephthalic	73.0
0.29 $Al_2(SO_4)_3$	Toluic acids[b]	0.2 S	40	327	30	61.9	Isoterephthalic	63.8
1.65 $FeSO_4$	Xylene[c]	1.0 H_2S	53	327	60	59.6	Benzoic/Toluic	7.0
1.65 Li_2SO_4	Xylene[c]	1.0 H_2S	53	329	60	15.3	Toluic	26.2
3.1 Na_2SO_4	*p*-Xylene	2.2$(NH_4)_2S$	74	315	60	6.9	*p*-Toluic	34.8
							Terephthalic	14.6
1.0 K_2SO_4	Toulene	0.5 H_2S	50	343	120	45.0	Benzoic	24.5

a: Moles/mole compound to be oxidized; b: 85% *m*-, 15% *p*-toluic acid; c: 85% *m*-, 15% *p*-xylene

Chemical models for TSR

Wilson Orr recognized the implications of Toland's work as it relates to both the genesis of H_2S, and possible thermochemical sulfate reduction/hydrocarbon oxidation reactions in petroleum reservoirs. In a series of laboratory experiments, Orr [4] showed that thermochemical sulfate reduction reactions previously carried out by Toland at higher temperatures (> 300°C) would also occur at temperatures as low as 175°C. Based on kinetic studies, the oxidation of toluene in these experiments was estimated to have an activation energy (E_a) of about 96 kJ/mol. These findings led Orr to propose the thermochemical sulfate reduction reactions might easily occur in rocks at the lower temperatures (e.g. the 80–130°C range) that exist in many hydrogen sulfide-rich petroleum reservoirs.

Orr's reactions were conducted in 500 cm^3 stainless steel autoclaves with 100 cm^3 of 0.05 to 0.48 moles of $(NH_4)_2SO_4$ solution and 20 cm^3 of toluene (large molar excess relative to sulfate). Gaseous H_2S was added to the reactors to provide H_2S partial pressures of 10–225 psi. All reactors were pressurized with nitrogen to provide a total pressure of 300 –1000 psi, and the reactions were held at constant temperatures over times ranging from 92 to 618 h. The extent of thermochemical oxidation by sulfate in these reactions was estimated by analysis of residual sulfate (after acid removal of H_2S).

Orr [5] recognized the complexity of the reaction and stated that other reactions may occur parallel to the oxidation of the toluene (LaLonde [29]; Pryor [22]). However, since the kinetic parameters derived from the data in Table 6

Table 6 Experiments with variable hydrogen sulfide at 250°C [after: Orr (1991 report)]

Time/	Initial H_2S/	Initial SO_4^{2-}/	Final SO_4^{2-}/	% SO_4^{2-}	Rate constants	
h	psi	mM	mM	Reduction	K/h^{-1}	Half-life/h
128	0	48.22	48.78	<1	–	–
120	10	48.12	40.75	15	1.39×10^{-3}	500
120	25	48.12	36.94	23	2.20×10^{-3}	315
120	50	48.22	22.13	54	6.49×10^{-3}	106
120	100	48.12	24.67	49	5.57×10^{-3}	124
141	100	46.88	19.42	59	6.25×10^{-3}	111
240	200	48.22	12.08	75	5.77×10^{-3}	120
240	200	24.85	4.51	82	7.11×10^{-3}	98
92	200	24.35	11.50	53	8.16×10^{-3}	85
120	200	48.22	15.64	58	9.38×10^{-3}	74
168	(~225)?	5.13	(0.54)?	89	–	–

apply to sulfate disappearance (but not necessarily to sulfate reduction) it is tempting to compare this reaction to the H_2S + SO_4^{2-} kinetics studied by Ohmoto and Lasaga [30]. If the *pH* of the system is proportional to the amount of H_2S pressured into the reactor (and if it is between *pH* 4–5), the activation energy for the formation of $S_2O_3^{2-}$ will be about 117 kJ/mol. Toland [12] reported that one gets elemental sulfur and/or polysulfide (S_x) species under these reaction conditions. Ohmoto and Lasaga [30] tend to stress that S^0 and S_x^{2-} species will become more important than thiosulfates only if they afford new kinetic pathways, which are different from and faster than the one proposed by them.

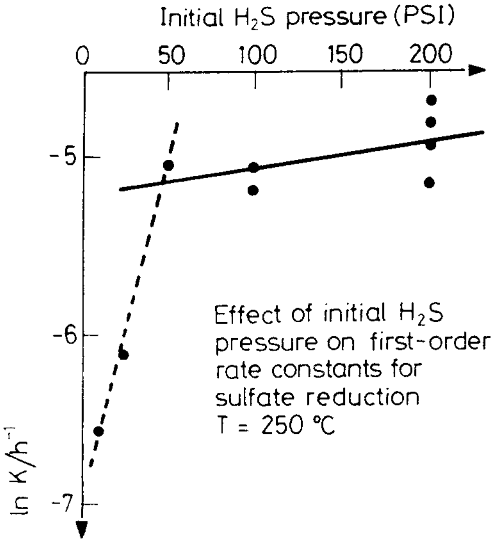


Fig. 6 Effect of initial H_2S pressure on first-order rate constant for sulfate reduction T = 250°C

Inspection of Fig. 6 will show that an increase in the H_2S pressure from 10 psi to 50 psi results in a greater acceleration of the reaction rate than does an increase in pressure of 50 to 200 psi. In these experiments, elemental sulfur was not formed in reactions containing excess toluene. On the other hand, under comparable reaction conditions, large amounts of elemental sulfur were formed in reactions of hydrogen sulfide and sulfate either without or with only small amounts of toluene. Orr [5] offers the explanation that the partial pressure of H_2S, which determines its concentration in the reaction, causes the non-linear response of the reaction rate, due to either a change in reaction order or the fact that the kinetic order might be between 2–3. At pressures above 50 psi, hydrogen sulfide is in excess, and under these conditions the rate is first order with respect to sulfate.

According to Orr, hydrogen sulfide acts autocatalytically in the TSR reaction. However, the initial concentration of hydrogen sulfide in the system has an important effect on the overall reaction rate. Similarly, changes in *pH* during the course of the reaction will also have an effect on the overall TSR rate, with low concentrations of H_2S and/or high *pH* values leading to decreased reaction rates. The implication of Orr's experiments to geological conditions will be discussed further, taking into account the reaction half-lives calculated from the data in Table 7 and shown in Fig. 6.

Table 7 Variation of sulfate half-life with temperature at constant hydrogen sulfide pressure$^{(A)}$ [ibid: (Orr 1991 report)]

Temperature/°C	Number of runs	Half-life/h
250	4	94 ± 20
225	1	313 ± ?
200	2	1150 ± 360
175	1	1740 ± ?

$^{(A)}$ initial load pressure of 200 psi.

We will just note here that Drean [31] was unable to detect the formation of hydrogen sulfide in reactions using methane as the substrate under Orr's [4, 26] reaction conditions (300°C, *pH* 2.3–5.3, 240 h). It may be that small amounts of H_2S were formed in the reaction, but that it reacted with the iron metal of the reactor. This possibility was investigated using ^{35}S labeled sulfate by the Trudinger group [6].

In the 1985 review, Trudinger *et al.* [6] re-examined their earlier sealed tube experiments (Trudinger [32]). In these experiments, organic matter and radioactive sulfate were heated under nitrogen or hydrogen sulfide pressure at temperatures up to 140°C for different lengths of time. At the end to the reaction, hydrogen sulfide was analyzed by reaction with 5,5-dithio-bis 2-nitrobenzoic acid (DTBB). In some experiments, H_2S was converted to Ag_2S for ^{35}S isotopic measurements. Table 8 summarizes the reaction conditions and results, all of which indicated that sulfate was not reduced (within their analytical capability). However, in a 220°C reaction of coal, sulfur and ^{35}S labeled ammonium sulfate, labeled hydrogen sulfide was detected after 10 days. The results of this study were difficult to rationalize, and it is questionable if sulfate was reduced in the majority of the experiments. For this reason, the authors suggested that the isotopic exchange of sulfur might result from the hydrolysis of elemental sulfur (Eq. (5)).

$$4S^0 + 4H_2O \rightarrow 3H_2S + H_2SO_4 \qquad (5)$$

Ohmoto and Lasaga [30] have questioned whether or not sulfur hydrolysis reactions might be important at temperatures of 140–220°C. However, considering the possibility that this reaction does occur and using Drean's [31] values of the stability fields for sulfur species, Trudinger *et al.* [6] attempted to reconcile the above results with those reported by Orr [5]. From the data in Fig. 7 (Drean [31]), it can be seen that (at the same temperature) with an increase in polysulfide sulfur chain length, there is an increase in the range of stable *pH* for

Table 8 Reaction mixtures with ^{35}S-labelled sulphate (these mixtures gave negative results) [after: Trudinger (1985)]

Reaction mixture		Temperature/°C	Time
			(days)
Expt.1	Naphthenic - aromatic oil, NaCl·$Na_2SO_4^b$		
	+H_2S	80	39
	+H_2S + S°	80	39
	+ Na_2S + S°	80	10
Expt.2	Paraffinic oil, NaCl·$Na_2SO_4^b$		
	+ Na_2S	80	10
	+ H_2S + S° + $FeCl_3$	80	42
	+ Na_2S + S° + $FeCl_3$	80	84
	+ H_2S + S°	120–190	10–14
			(months)
Expt.3	Metals, calcite, NaCl·Cu-porphyrin		
	+ kerogen ± pyrite	140	5
	+ cyanobacterial org. C ± pyrite	140	5
	+ coal ± pyrite	140	5
Expt.4	Clucose, clay, Na_2SO_4 or $NaHSO_3^4$ or Na_2SO_4		
	+ N_2	140	4
	+ H_2S	140	4
Expt.5	Light crude oil, clay, H_2SO_4 or $NaHSO_4$ or Na_2SO_4		
	+ N_2	140	4
	+ H_2S	140	4

[a] The amounts of reaction mixtures components were as follows: EXPERIMENTS 1–2: oil. 1 ml: NaCl, 3 M: Na_2SO_4 (^{35}S labelled) 0.4 mM; S°, 0.1 g; H_2S, 1 atm (101.325 kPa) (at room temp.); Na_2S, 0.1 M: $FeCl_3$, 0.45 mM. Final volume of aqueous phase, 4 ml. EXPERIMENT 3: calcite, 0.5 g; NaCl, 3 M; Cu-porphyrin, 10 mg; Na_2SO_4 (^{35}S labelled), 0.1 M; kerogen (tasmanite), 0.5 g; cyanobacterial organic matter, 0.5 g; coal, 0.5 g; pyrite, 0.1 g; trace metals-$FeCl_3$, 7.5 μM, $MnCl_2$, 0.5 μM; $CoCl_2$ 0.5μM; $NiCl_2$,0.1 μM, $CuCl_2$, 0.1 μM; $ZnCl_2$, 0. 5 μM. Final volume of aqueous phase, 1 ml. EXPERIMENTS 4–5: as for Table 5. In all experiments the gas phase was N_2 unless otherwise specified.

[b] From Trudinger (1981)

the zero valent sulfur compounds. However, the possible formation of polysulfides, even at *pH* greater than 6, was not addressed by Trudinger *et al.* [6].

In discussing results of his experiments, Toland cites both his earlier experiments and very early reports of the uses of sulfur as an oxidant (e.g., Priestley in 1775 as quoted by Lewis *et al.* [33]). In experiments conducted in aqueous base and at temperatures above 150°C, SO_2 was found to disproportionate to form modest amounts of S^0 and SO_4^{2-}. These reactions are favored at temperatures higher than about 250°C, leading to the following possible reactions:

$$4S + 8NaOH \rightarrow Na_2SO_4 + 3Na_2S + 4H_2O \tag{6}$$

$$4Na_2SO_3 \rightarrow 3Na_2SO_4 + NaS \tag{7}$$

$$Na_2S_2O_3 \rightarrow Na_2SO_3 + S \tag{8}$$

We should point out that recent work raises some question as to whether or not the above steps are of key importance for thermochemical sulfate reduction reactions. However, the experimental data presented in Fig. 3 and Table 4 clearly show that, depending on the nature of the sulfate species, there can be differences in both the oxidative yields and products form a given organic substrate. Therefore, it is suggested that instead of the disproportionation reaction depicted formally in equation 5, the reaction is *pH* dependent with the rate constant obeying the relationship: $k = [H_2S]^3[SO_4^{2-}][H^+]$.

Actually, we wonder if the disproportionation reaction is reversible, and under which conditions. To the best of out knowledge, the reaction of elemental sulfur with water to yield hydrogen sulfide and sulfuric acid has never been thoroughly investigated.

The experimental studies on the oxidation of aqueous sulfide by Williamson and Rimstid [16] also provides information on the thermodynamics of sulfate reduction. As was mentioned earlier, these authors showed that sulfane monosulfonic acids ($S_nSO_3^{2-}$) were intermediate metastable oxidation states in sulfide oxidation. The existence of sulfane sulfonic acids in the oxidation of sulfide raises the possibility that polysulfide species (e.g. HS_n^- where $n = 1,2,3,4,5, \ldots$) may be intermediates (as a possible bridging step in the reduction of SO_4^{2-}) in both sulfide oxidation and in sulfate reduction. The relative aqueous stability of polysulfides suggest that the reverse sequence of reaction is also possible (Figs 4a, b, c).

From these calculations it would appear that the pathway of lowest energy for sulfate reduction would then proceed via metastable states of: polysulfides, to thiosulfate, to sulfite. If true, the reduction of sulfate in the pressure of hydrogen sulfide may involve similar (or the same) polysulfide intermediates.

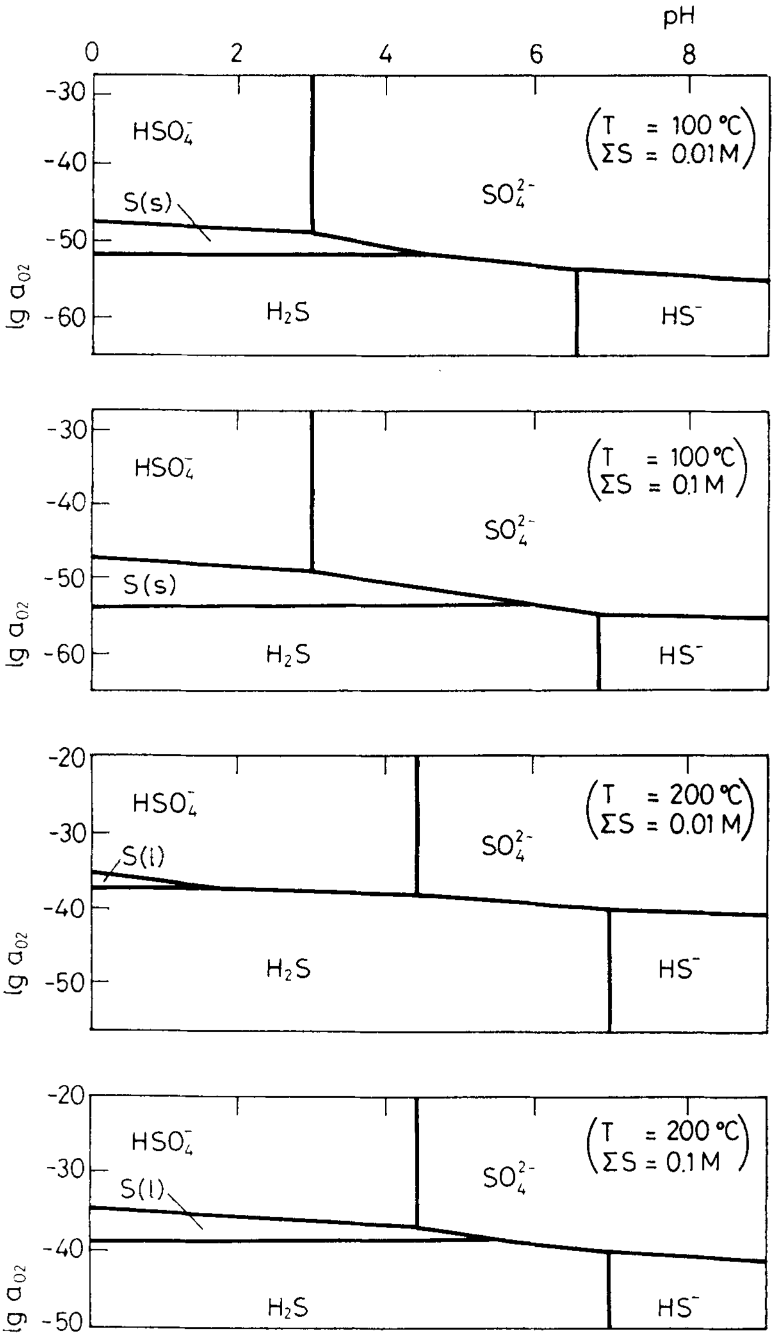


Fig. 7 Stability fields of aqueous sulfur species at 100 and 200°C and total sulfur (ΣS) of 0.01 and 0.1 M. Adapted from Drean (1978), Note: 200°C and 0.5 M Σ S liquid sulfur stability extends to ca. pH 6.0 (not shown)

Sulfur interchange reactions

Ohmoto and Lasaga [30] investigated reactions between aqueous sulfates and sulfides under hydrothermal conditions. The reaction was followed by monitoring the isotopic exchange rate between sulfate and sulfide during the course of the reaction. In this study, the rates of exchange of stable sulfur isotopes (^{32}S and ^{34}S) were used to show that both the chemical and isotopic reactions involve simultaneous oxidation of sulfide-sulfur, and reduction of sulfate-sulfur. In addition to providing kinetic and mechanistic information concerning the reaction, the study also yielded valuable data relating to possible isotope mixing effects during thermal reduction of sulfate. The exchange reaction was found to obey the following second order rate expression: rate = $k[SO_4^{2-}][S^{2-}]$. Mechanistic considerations of this reaction are discussed further in connection with sulfur isotope studies of TSR reactions.

Ohmoto and Lasaga [30] showed that the reduction of $NaHSO_4$ and Na_2SO_4 is very slow even at temperatures above 300°C. The rate of exchange of S^0 between H_2S and SO_4^{2-} as shown in Fig. 5 is very slow at *pH*'s near 7 and at temperatures below 350°C. For example, it is estimated that a 90% sulfur isotope exchange would require a reaction period of 10 000 years at 200°C. Figure 5 shows the different conversion rates for these species. Care must be taken to consider the sulfur mass balance in interpretation of the results of these reactions.

Igumnov [34] was one of the first to point out that the rate constants in the reaction of sulfide with sulfate are dependent on temperature and *pH*, but that the *pH* dependence was complex. For example, in reactions at 200–400°C, the sulfur exchange rate decreased one order of magnitude for each unit increase in *pH* up to *pH* 6. The rate was found to be almost constant at *pH* 4–7, but decreases at higher *pH*. The activation energy for these reactions also was found to depend on *pH*. At *pH* = 2, E_a was found to be 77 kJ/mol, while at *pH* 4–7, the activation energy (E_a) was 167 kJ/mol, and at *pH* 9, E_a was about 197 kJ/mol. This finding is consistent with the generally accepted observation that reduction of sulfate is easier under acidic rather that alkaline conditions. It should be noted that Ohmoto and Lasaga [30] reported that at the same *pH*, the reaction rate was also somewhat dependent on the nature of the sulfide or sulfate counter ion.

In summary, it is generally accepted that thermochemical sulfate reduction/hydrocarbon oxidation reactions are common in many oil field deposits that have a source of sulfate and at least some hydrogen sulfide. These non-biological reactions are thought to have occurred in reservoirs and similar geologic settings at temperatures as low as 120°C. There are many examples of the direct reduction of sulfate by carbon compounds, but unless catalyzed, these reactions only proceed at significant rates at elevated temperatures (generally above 800°C). Based on both theory and experiment, it would appear unlikely that sulfate is directly reduced by organic matter in most sedimentary environments. On the other hand, synthetic organic chemical studies have shown that several lower oxidation state sulfur species are capable of oxidizing a variety of hydrocarbons and other organic compounds at much lower temperatures (about 300°C). In these so called Willgerodt reactions, a variety of organic compounds (e.g. alkyl-aromatics, olefins, cycloalkanes) are oxidized by sulfate derived catanated sulfur compounds (e.g. polysulfides). It should be noted however, that this reaction is highly dependent on the type and structure of the organic component being oxidized. A review of the chemical literature on Willgerodt reactions indicates that while the yields of oxidized products from functionalized organic compounds, olefins, and alkyl aromatics are relatively high, there is a paucity of information on oxidation of acyclic paraffinic compounds.

Several chemical and geochemical studies have concluded that hydrocarbon oxidations in sediments might occur by Willgerodt type reactions employing low oxidation state sulfur species derived from sulfate as the oxidant. The credit for recognizing the analogy of the preparative organic reactions to thermochemical sulfate reduction in the geosphere clearly belongs to Wilson Orr.

Orr explained how TSR active sulfur species could form in oil field sediments by the reaction of H_2S with sulfate and, based on a kinetic study of the oxidation of toluene, suggested that TSR reactions could easily occur at the temperatures found in many petroleum reservoirs. We agree that reactions of this type best account for sulfate oxidation of hydrocarbons under the reaction conditions commonly found in sedimentary systems. However, to best model thermochemical sulfate oxidation in petroleum reservoirs, it will also be necessary to establish the kinetic parameters of TSR reactions of representative hydrocarbon types.

A number of related studies indicate that TSR active oxidants can arise via a dynamic network of inorganic reactions in oil field sediments. Such a network of reactions could provide a low energy pathway for the reduction of sulfate via a sequence of low oxidation state metastable sulfur species. We believe that in oil field sediments, virtually all oxidation of hydrocarbons by sulfate proceed by a low energy pathway of this type, and not by direct reaction with sulfate. Studies involving the oxidation of sugars by sulfuric acid or acid sulfates have extended the study TSR type reactions to temperatures as low as 200°C. Examination of sulfur isotope exchange in such model systems has provided insight into mechanistic details of these reactions and, by analogy, to TSR reactions of hydrocarbons. But the results of these reactions are sometimes difficult to interpret, perhaps because sugars often undergo complex reactions with acids. This is particularly true for reactions of sugars with strong oxidizing acids such as sulfuric. For this reason we believe that caution must be exercised in extrapolating the results of these experimental studies to TSR reactions in the geosphere.

Sulfur and carbon isotopes in TSR

General

The thermal release of CO_2 from sedimentary organic matter in open systems is found to yield CO_2 enriched in ^{13}C relative to the bulk of the organic matter. During photosynthesis and in subsequent enzymatic steps, the alkyl chains of fatty acids become enriched in ^{12}C compared to the carbon of the carboxyl group. Therefore, the decarboxylation of fatty acids will form hydrocarbons with carbons that are isotopic light, and CO_2 that is enriched in ^{13}C. On the other hand the thermal formation of CO_2 from a carbonate ($CaCO_3 \rightarrow CaO + CO_2$) will lead to the formation of ^{12}C-enriched CO_2 and ^{13}C-enriched residual CO_3^{2-} (at low conversion levels). The biogenic, diagenic and catagenic influence of various processes on $\delta^{13}C$ values recorded for organic matter in the geosphere were reviewed extensively in the past (Stahl [35, 36]; Galimov [37]; Schidlowski [38]).

While the biochemical incorporation of sulfur into organic compounds is found to have small isotopic fractionation in relation to the sulfate from which it was derived, the dissimilatory process is found to produce as much as a −40‰ change in $\delta^{34}S\ SO_4 - \delta^{34}S\ H_2S$. There is little information on the sulfur isotopic effects of analogous non-biological processes. Since sulfur appears in multiple valence states, its isotopic chemical behavior is difficult to study. It has been suggested that there is very little isotopic discrimination in either chemical or biochemical processes of incorporation of sulfate sulfur into the organic matter. This is true as long as the sulfatic moiety in not undergoing reduction. However, if such redox changes do occur the variability of $\delta^{34}S$ values of the various reduced sulfur species is very large (Goldhaber and Kaplan [39]; Nielsen [40]; Dinur *et al.* [41]; Aizenshtat *et al.* [1]; Kaplan [42]; Orr, [43]).

The various pathways of the sulfur cycle referred to in the above citations are shown schematically in Fig. 1 (see introduction). This scheme describes the possible main sulfur cycle changes: horizontally divided by the sediment water column interface and vertically from sulfate (S^{6+}) to the sulfide (S^{2-}). Since the temperature of the depositional environment is generally low, all $\delta^{34}S$ changes are a result of bacterial activity or low temperature chemical mixing (Aizenshtat *et al.* [1]). These early diagenetic changes in both carbon and sulfur cycles are reflected in the carbon and sulfur isotope distribution and are important to later considerations of thermochemically controlled reactions at the catagenetic- or methanogenic- states.

Thermochemical sulfate reduction and its influence on $\delta^{34}S$ and $\delta^{13}C$ values

Early experiments on high-temperature (>500°C) reduction of sulfate by organic matter did not include sulfur or carbon isotope studies. However, during the reduction of the sulfate, multistep changes in the oxidative state of sulfur can have an influence on the isotopic distribution for each sulfur species, and could influence the final $\delta^{34}S$ values by equilibration of the various intermediate redox species. We are unaware of any experimental verification of this possibility, but it has been suggested that isotopic mixing of SO_4^{2-} and H_2S might help explain how elemental sulfur forms in these reactions (see Dinur *et al.* [41] and Orr [15], and the following equation).

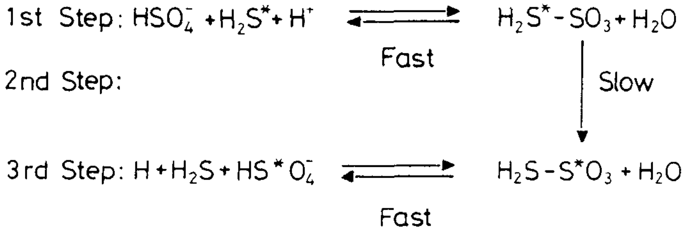
$$3H_2S + SO_4^{2-} \rightarrow 4S^{\circ} + 2H_2O + OH^- \qquad (9)$$

However, at temperatures less than about 200°C, there was essentially no isotopic fractionation of the zero valent sulfur species derived from sulfate and sulfide mixtures of known sulfur isotope composition.

Lower temperature isotope mixing of sulfur was studied and reported by Fossing *et al.* [44] for H_2S and SO_4^{2-} only in the presence of elemental sulfur. If polysulfides are formed, then the sulfur isotope mixing occurs between the HS^- and S_8, and this may react via the sequence of reactions we previously illustrated for reactions of sulfate. This 'diagenetic' isotope mixing process is very important in forming the pool of TSR active sulfur, which in turn can react with organic matter if present in the system. This overall process would facilitate the early isotope variability of $\delta^{34}S$ values (Fig. 1).

Ohmoto and Lasaga [30] [proposed the following schematic three-stage mechanism to account for isotopic mixing in the reaction of ^{34}S enriched sulfate with ^{32}S sulfur of hydrogen sulfide.

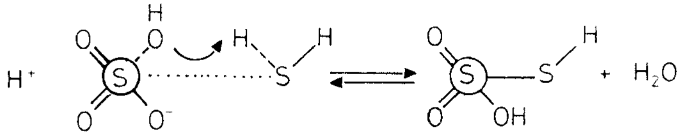
In this scheme the actual exchange of sulfur atoms would occur in an intramolecular reaction of the $H_2S_2O_3$ species shown above. The stage at formation



Where*S represents ^{34}S enriched sulfur

Scheme 2

of the thiosulfate requires breaking of bonds in the bisulfate (HSO_4^-) and in hydrogen sulfide (H_2S), as depicted by Ohmoto and Lasaga [30] in Scheme 3.



Scheme 3

Pryor [45] studied the kinetics of disproportionation of thiosulfate to yield sulfide and sulfate. This reaction is the 3rd step of the scheme of Ohmoto *et al.* (Scheme 2). Pryor reported that the reaction (at 250–280°C) was pseudo first order, and dependent on the concentration of both thiosulfate and hydrogen ion (i.e., $[S_2O_3^{2-}]$ and $[H^+]$. While Pryor reported and an activation energy (E_a) of 238 kJ/mol for the disproportionation reaction, Seibert [46] calculated an activation energy of only 113 kJ/mol for the intramolecular exchange. These differences support the argument that the rate-determining transformation will be the 2nd step in the above scheme by Ohmoto *et al.*

This leads to the assumption that the active form is the thiosulfate, which under acid conditions is unstable yielding free sulfur and sulfite. This mechanism, in broad terms, is now generally accepted. The mixing of HS^- and S^0 (both at high and low temperatures) may lead to the formation of the very active polysulfides (S_x^{2-}), which in turn can react with organic matter. Therefore, we suggest that the formation of the polythionates is the stage allowing isotope exchange, and not thiosulfate as suggested by Ohmoto and Lasaga [30] and others.

An estimate of the equilibrium fractionation factor between SO_4^{2-} and H_2S was calculated by Sakai [47] and re-evaluated by Ohmoto and Rye [48]. Their data show that there can be a 2‰ spread in ΔSO_4^{2-} in the reaction to form H_2S. However, as was discussed previously, if this reaction proceeds through thiosulfate intermediates, it will be highly *pH* dependent and will have a high activation energy.

It is commonly accepted that during redox reactions, the variation in sulfur isotope distribution in the various reduced sulfur species is greatly influenced by microorganisms. It has also been suggested that chemical reduction of sulfate to sulfide will have little or no influence on the isotope composition (Dinur *et al.* [41]). Although it has been proposed that some isotopic discrimination may occur during the hydrothermal disproportionation or reduction of sulfate, we are unaware of experimental verification of such an effect. In experiments on the reduction of dextrose at temperatures between 200 and 250°C, Kiyosu [27] found that the first order reaction for the 'reduction' of sulfate results in an enrichment of ^{32}S in the H_2S formed. This in turn produced a residual sulfate enriched in ^{34}S. The fractionation factor (a) in the reduction was reported to be independent of temperature and is reported to be about 1.007 to 1.009. This observation seems to be in agreement with kinetic calculations on isotope effects in the high temperature reduction of sulfate (Harrison and Thode [49]; Grimenko *et al.* [50]). A separation factor of 8–9‰ was found in the 300°C experiments (Kiyosu [27]).

The range of changes for S-isotope composition in these experiments is somewhat surprising. The sulfur isotope composition of the sulfate (original value of –4.4‰) becomes considerably heavier (+11.0‰) while the sulfur isotopic composition of the H_2S produced in the early part of the reaction was –14.2‰, and declined to about –5‰ at the end of the reaction. The effect of temperature on the sulfur isotope composition is probably connected to conversion, but it is not possible from the published data to estimate mass- or isotopic balances for Kiyosu's experiments. Furthermore, during these reactions, other species of sulfur are created and Kiyosu speculates that these may be sulfur-containing organics.

As was discussed earlier, Kaiser [9] showed that more than half of the reduced sulfur in the reaction appears as an 'organic char', and that this residual polymer contained up to 14% of the total sulfur of the reaction. Kaiser claims that 'although sulfate reduction by dextrose to sulfide is a complex reaction, isotopic mass balance considerations suggest that isotope transfer may be approximated as a single-step reduction'. Isotopically the $\delta^{13}S$ values observed for the sulfur-containing organics are much closer to those of the H_2S than to the original SO_4^{2-} or the residual sulfate (which becomes even heavier).

In these 200–250°C experiments on the reduction of sulfuric acid, sodium bisulfate, and sodium sulfate by dextrose, Kiyosu [27] found that the 'reduction' of sulfate results in an enrichment of ^{32}S in the hydrogen sulfide formed. This in turn leaves the residual sulfate enriched in ^{34}S. The isotopic fractionation factor (a) in the reduction was found to be independent of temperature.

The spread in sulfur isotope ratios in products from these experiments is somewhat surprising. The sulfate value (–4.4‰ at the start of the reaction) increases to +11.0‰, while the initially produced H_2S has a value of –14.2‰, which decreases to –6 to –4.7‰ at the end of the reaction. The effect of temperature on the sulfur isotope compositions is probably related to conversion, but because it is not possible to determine mass- and isotopic-balances for Kiyosu's experiments from the published data, the detailed nature of the effect cannot be determined unambiguously. Kiyosu [27] also notes that organic sulfur compounds are also formed in these experiments.

Another attempt to follow $\delta^{34}S$ in a thermochemical sulfate reduction reaction with acetic acid was undertaken by Kiyosu *et al.* [51]. These authors followed the course of the reaction by monitoring sulfate depletion. In this study a temperature-dependent kinetic isotope effect was observed for the reaction. For the 240°C experiment, the fractionation factor (*a*) was found to be 1.0084 and, at 340°C, $a = 1.0046$. The authors claim that kinetic isotopic effects recorded in this set of experiments coincide well with previous results obtained under very different reducing conditions. Therefore, it was suggested that during abiogenic reduction of sulfate under hydrothermal conditions, the sulfur kinetic-isotopic effect is independent of the reducing agent. It was further suggested that the sulfate-to-sulfite transformation is the reaction step that determines the sulfur isotopic fraction in the overall reaction. It should be noted, that even under steady-stage TSR reaction conditions, it was not possible to detect sulfite in either the dextrose or in the acetic acid experiments.

Because there are many processes that can result in the release of CO_2 from organic compounds, the influence of sulfate reduction by organic matter on the isotope distribution of the carbon ($\delta^{13}C$) is very complex. This problem becomes even more difficult to solve if actual geological conditions are considered. For example, changes in *pH* of the water in contact with some sediments can release CO_2 from carbonates or cause precipitation. Moreover, under depositional conditions and even during early diagenesis sulfate-reducing bacteria can form CO_2 by oxidation of organic matter, while other bacteria may utilize the CO_2 in the further synthesis of metabolic organic compounds.

Despite all of these conflicting processes Kiyosu *et al.* [7] investigated the possibility of carbon isotope fractionation during the thermochemical reduction of sulfate. It was suggested that sulfate reduction by light hydrocarbon gases (C_1–C_4) in reservoirs might show such carbon isotope fractionation. Only sulfate reduction was monitored in experiments conducted at high temperature (>600°C) and under flow-through conditions in open systems. The 600–800°C experiments were carried out using a $CaSO_4/Fe_2O_3$ mixture, and the 800–930°C experiments using $CaSO_4$. However, the data given for the oxidation of C_1–C_3 gases to CO_2 are from experiments carried out at 280–450°C, using CuO as oxidant under closed vessel conditions. It is noteworthy that at about 300°C and after 48 h, 12.2‰ of the initial methane ($\delta^{13}C = -34.5\%$) was oxidized to CO_2, with a −52% isotope ratio, leaving the 87.8% methane with −32.6‰. At higher temperatures and at higher conversions, the $\Delta CH_4 \rightarrow CO_2$ isotopic discrimination is much smaller. The same sort of isotopic discrimination was observed in reactions of ethane and propane, but to a lesser extent.

In conclusion, Kiyosu *et al.* [7] agree that 'in situ reaction may not be simply sulfate reduction by organic matter, since reduction by H_2S may play a dominant role'. However, the formation of ^{12}C-enriched carbon dioxide and residual heavier C_1–C_3 hydrocarbon gases is obtained by oxidation at temperatures below 400°C. This consideration is important for $\delta^{13}C$ analysis of gases by mass spectrometry.

Compared to the filed of carbon isotope geochemistry of petroleum generation, the carbon and sulfur isotope chemistry of TSR reactions is both complex and poorly understood at present. The operation of sulfur isotope exchange reactions between sulfate and lower oxidation state sulfur species is unquestionably a major contribution factor to the complexity of the system. Such exchange reactions are expected to readily occur within the dynamic network of inorganic catanated sulfur compounds that can exist in sediments. Microbiological processes may also alter the isotopic composition of the sulfur catanated species. For these reasons, we believe further research regarding sulfur and carbon isotope geochemistry in TSR reactions is needed. Such research could lead to improvements in predictive geochemistry based on isotope analysis.

Geochemical considerations

The relative importance of bacterial, compared to chemical sulfate reduction in the geosphere has been debated in the literature for almost 100 years. Hunt [52] discussed the potential involvement of these processes in the formation of the major deposits of elemental sulfur in Sicily, and Rogers [53] studied the depletion of sulfate with depth in waters in contact with petroleum. These studies, and early publications on the microbiology of sulfate-reducing bacteria (e.g., Beijerinck [54]) were discussed by Ginter [21].

Peck *et al.* [55] have discussed the biochemistry of microbial sulfate reduction, and the bioenergetics of dissimilatory sulfate reduction in Desulfovibrio vulgaris is shown schematically in Fig. 8. There in no doubt that under 'normal' deposition environments and during diagenesis, where bacterial activity might compete with the possible chemical reduction of sulfate (less than Ca. 100°C), the microbial processes dominate. However, there is no clear geochemical evidence for the existence of a higher-temperature chemical reduction by organic matter under oil field reaction conditions.

Barton [56] suggested that the chemical reduction of sulfate to H_2S by methane or other associated organic matter might account for the formation of Mississippi Valley type lead-zinc ores. The inorganic reduction of sulfate from sea waters under hydrothermal conditions at 250–350°C was shown to provide a possible mechanism for the formation of metal sulfides (Shanks *et al.* [57] and Mottl *et al.* [58]). The possible role of thiosulfate in the formation of barite in these deposits has been discussed by Spirakis [59]. Leventhal [60] recently reinvestigated the possible role of organic matter in the formation of the Mississippi Valley type Pb-Zn deposits. The fact that 'petroleum-like' material is commonly associated with these Pb-Zn deposits suggested that oil-derived organic matter might serve as the reducing agent for these ores, but no direct proof for this idea was offered. Leventhal [60] has reviewed the literature deal-

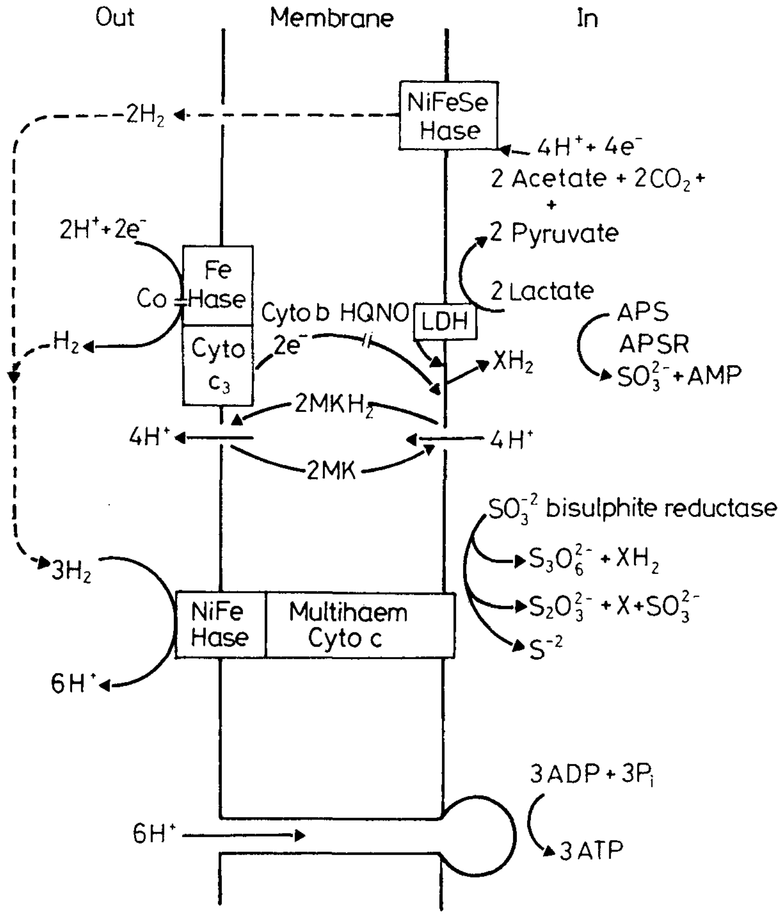


Fig. 8 Proposed bioenergetics of dissimilatory sulfate reduction in Desulfovibrio vulgaris

ing with the origin of these ores and ores at other locations where the organic matter was considered to be the reductant of sulfate to provide hydrogen sulfide for the concentration of heavy metal-sulfides.

Sassen [61] studied the Smackover Formation crude oils as well as the lower section source faces using various oil source rock correlation parameters. He concluded that thermochemical sulfate reduction and crude oil destruction occurred over a long span of geologic time at temperatures in the 120–150°C range, based on studies of maturation trends and of the occurrence of H_2S and hydrocarbon gases. A slow thermal cracking of petroleum in reservoirs was said to form both gas-condensate and pyrobitumen. The end products of this process, pyrobitumen, methane, H_2S and other non-hydrocarbon gases, persist in the deepest Smackover reservoirs. Examination of the carbon isotopes of the asphaltenes and NSO-compounds, as well as the hydrocarbons in the thermally altered bitumen, shows that great differences appear at higher levels of maturation that correspond to oil destruction. The overall picture of the ^{13}C values presented in this paper is somewhat confusing. There is no marked Stahl-Galimov relation for these samples that should exhibit an increase in ^{12}C in the progression: asphaltenes, NSO compounds, aromatics, saturates. Moreover, a lighter carbon isotope signature was found for organic matter extracted from sediments at the same maturation level as the associated oils (Sassen [61]). The fact that, in addition to the H_2S, many of the samples had elemental sulfur associated with the pyrobitumen and anhydrite, prompted Sassen to suggest that sulfur might have reacted with the crude oil. The generalized diagram (Fig. 9) for these transformations suggests that bitumen converts to pyrobitumen and CH_4 at a vitrinite reflectance (Ro) value of about 1.7%, while the sulfate reduction stage begins at a vitrinite reflectance value of about 1%.

Based on the flux of H_2S from the reservoirs, Wade *et al.* [62] cite the probability that thermochemical sulfate reduction occurred in the Eastern Smackover Trend. These authors estimated the rate of methane destruction in the reservoirs from their H_2S concentration. From the economic stand-point, information relating to the possible occurrence of TSR derive H_2S can be important in *E & P* considerations for deep carbonate reservoirs similar to those of the Smackover.

Heydari and Moore [63] also adopt the sulfate reduction mechanism for the Smackover Formation. The 'burial diagenesis' is divided into two stages: pre-hydrocarbons migration and post-hydrocarbon migration. These two stages are marked by oxygen isotope change. The sulfur isotope $\delta^{34}S$ values for the late anhydrite is +18 to +19‰ and reflects 'normal' sea water sulfate. On the other hand the $\delta^{34}S$ values for the elemental sulfur appears to be +16 to +0.3‰, and the carbonates replacing anhydrite exhibit a $\delta^{13}C$ range of −3 to −4‰. These data are interpreted as resulting from a rapid thermochemical reduction of solid sulfates by the organic matter at temperatures less than 150°C.

Orr [4] was the first to examine the geochemical implications of sulfur content and sulfur-isotope ratios in a study of the Big Horn Basin (Wyoming USA). In this study, sets of oils and related gases were examined. Based on some assumptions, Orr concluded that at temperatures of 80–120°C sulfate in the reservoir water was reduced to form hydrogen sulfide, and that this reaction occurred without isotopic fractionation. The fact that the ^{34}S values found in the oil, H_2S, and in dissolved sulfate were observed to converge with increasing maturation, was said to result from thermal equilibration. The mechanisms proposed for these reactions are discussed elsewhere above.

Krouse *et al.* [64] claim to have chemical and isotopic evidence of thermochemical sulfate reduction (TSR) by light hydrocarbon gases in deep carbonate

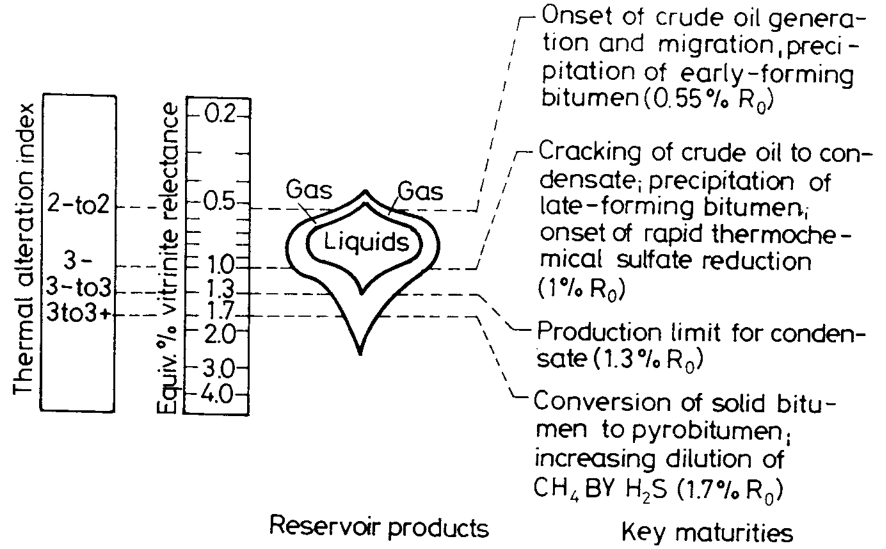


Fig. 9 Generalized relationship of thermal maturity to phases of crude oil generation, crude oil destruction, and thermochemical sulfate reduction in the Smackover Formation

reservoirs. They discuss the fact that gas and oil fields exhibit H_2S as free gas or as gas dissolved in the formation waters in concentrations from traces up to 90% of the total gases. The very high concentrations usually occur in deep carbonate reservoirs. Krouse *et al.* [64] argue the point that they found subsurface environments where chemical evidence and carbon isotopes indicate TSR below 200°C where the substrate are light hydrocarbon gases. They argue that if sulfate is reduced by the C_1–C_5 gases by forming CO_2 and H_2S, then the number of moles of hydrocarbons oxidized should correspond to the amount of CO_2 and H_2S formed. However, other sources and sinks of CO_2 must also be considered. In most of the cases studied, with increasing mole % H_2S and CO_2 in the gas phase there is an increasing domination of methane in the C_1–C_4 gases (> 96%).

Two remarks should be made here: 1) biogenic processes would have yielded the same overall results, and 2) the formation of H_2S by any other process would cause a change in *pH* leading to removal of CO_2 from carbonates. However, $\delta^{34}S$ and $\delta^{18}O$ of the anhydrite close to the section said to have undergone thermochemical sulfate reduction are found to have values similar to those of anhydrite formed by 'normal precipitation' from sea water, while the H_2S is isotopically light ($\delta^{34}S = -7‰$). This result is interpreted as being due to a kinetic isotope effect during thermochemical sulfate reduction.

Krouse *et al.* [64] considered the $\delta^{13}C$ values of the residual gases and CO_2 to be the most compelling evidence for the operation of thermochemical sulfate reduction. While the observed $\delta^{13}C$ values for methane are about –40 to –38‰, the values for ethane and propane appear to become heavier with increased CO_2 production, while CO_2 becomes ^{12}C-enriched (Fig. 10). However, examination of Fig. 10 will show that there is no evidence for a well defined trend in $\delta^{13}C$ values with depth. On the other hand, it is obvious that while all of the dolomitic carbon is derived from 'normal' sea water CO_2, some of the carbon in calcite samples shows $\delta^{13}C$ values of −29‰ (which could come from the oxidation of organic matter).

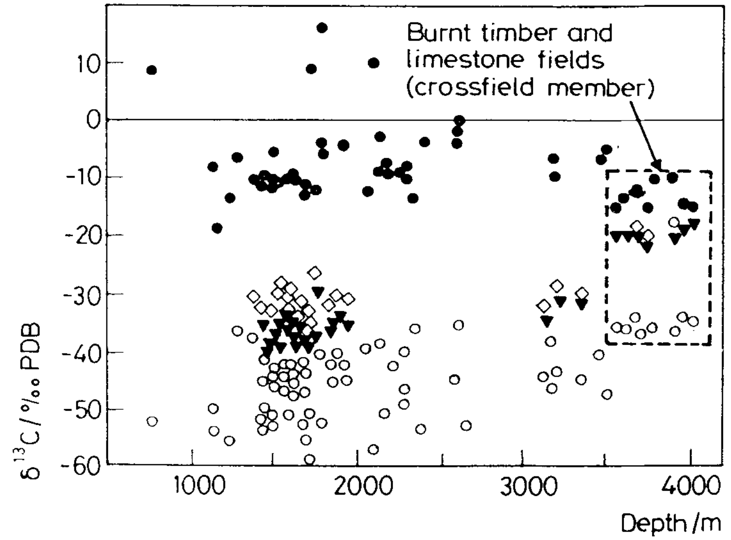


Fig. 10a Values of $\delta^{13}C$ for methane (open circles), ethane (filled triangles), propane (diamonds) and carbon dioxide (filled circles) gases produced from ten different Devonian stratigraphic unites in the Alberta Basin are plotted against depth. Values for samples from the Crossfield Member at Limestone and Burnt Timber Fields are in the box outlined on the right-hand side (depth greater than 3.500 m). Ethane and propane values are anomalously heavy by ~10‰, as compared with other Devonian gases reflecting their participation in TSR. Methane values are in the upper range of Devonian values, whereas carbon dioxide values are among the most negative values encountered in the Devonian. The data at depths < 3500 m are from Krouse

In many sedimentary environments, the oxidation of organic matter can occur by both bacterial and thermochemical sulfate reduction. There is abundant evidence to show that only the enzyme catalyzed biochemical reaction is important at temperatures below about 100°C, and that these reactions essentially cease at temperatures above 115°C. As we have pointed out, the existence in sediments of a low energy pathway for thermochemical sulfate reduction can account for TSR reactions under geologic reaction conditions that were difficult to account for by the energetically demanding direct reduction of sulfate. But further research is necessary to better define the kinetic and thermodynamic features of these reactions in order to extend our knowledge to thermochemical sulfate reduction processes in oil field sediments at temperatures of economic importance (e.g. 120–250°C).

The ability to better predict the occurrence of TSR reactions in petroleum deposits can be of considerable significance for *E & P* decision making. The operation of such reactions in petroleum reservoirs acts ultimately to produce H_2S and CO_2 at the expense of valuable hydrocarbons.Some 'NSO' type compounds may also be formed from hydrocarbons in the process, further reducing the value of the resource. On a more positive note however, it is believed that acidic products form the reaction (e.g. organic acids, H_2S or CO_2) should act to solubilize minerals or otherwise improve reservoir porosity in some sedimentary settings.

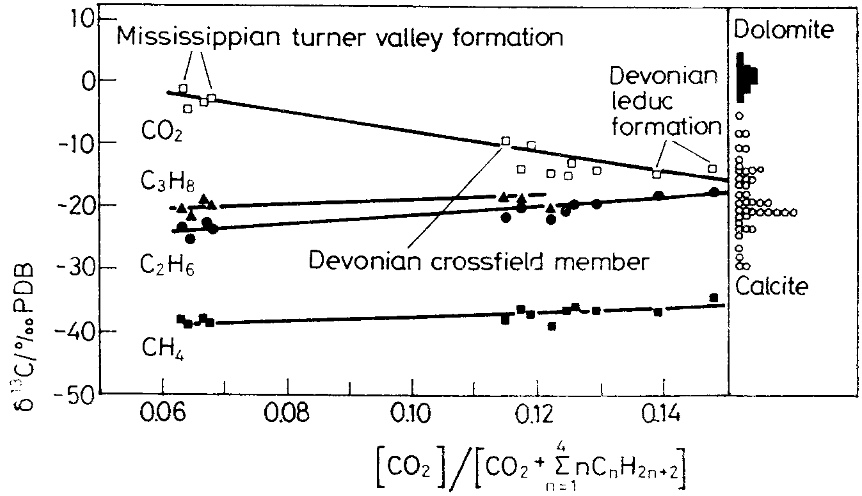


Fig. 10b Values of $\delta^{13}C$ for methane, propane and carbon dioxide gases from the Mississippian Turner Valley Formation, Devonian Crossfield Member and Devonian Leduc Formation plotted against the extent of (TSR) reaction parameter. The diagram shows the inverse relation between $\delta^{13}C$ of CO_2 and that of other gases, particularly ethane and propane. This is interpreted, along with the anomalous composition of these gases with respect to other Devonian gases (shown in Fig. 5), as evidence that natural gases presently in the reservoirs have served as reactants in the thermochemical reduction of sulphate. Values of $\delta^{13}C$ for reservoir dolomite and calcite are shown on the right-hand side. The negative values for calcite reflect substantial incorporation of organic carbon from the isotopically light gas, whereas the more positive values reflect various mixtures of organic carbon and carbon (with near 0‰ composition) released by the dissolution of dolomite

Both bacterial and thermochemical sulfate reduction reactions have been considered as the major source of hydrogen sulfide responsible for the formation of some types of ore deposits (e.g. Mississippi Valley type lead – zinc ores and some Texas and Canadian uranium ores).

Additionally, TSR derived hydrogen sulfide (from underlying oil or gas deposits) is thought to reduce water soluble uranium salts to insoluble minerals in some sediments. Thus, information concerning TSR activity might provide exploration clues for the location of novel ore deposits. The ability to distinguish clearly between a bacterial and thermochemical source of hydrogen sulfide, would greatly aid in exploration considerations for such deposits.

Summary and conclusions

The present review covers relevant information on TSR through 1991. Information on bacterial sulfate reduction (BSR) that is relevant to TSR reactions in oil field sediments is also covered. The authors sought, not only to report and survey the previously published data, but to achieve a better understanding of the temperatures range in which TSR can be geochemically considered as significant. An attempt was made to design a better mechanistic approach to the correlation between type of organic matter, which is proposed to be oxidized, it's oxidation products and reduction steps from S^{6+} to S^{2-}. Thermodynamic considerations show that direct reduction of sulfate by most organic molecules is favorable at temperatures above 20°C. However, this reaction is not considered to be kinetically important in most oil field sediments because of the very high activation energy of the one-step reduction process. Under laboratory conditions the direct reduction of sulfate by hydrocarbons, particularly methane, does not proceed at measurable rates below 500°C. On the other hand, a number of 'activated' organic model compounds have been shown to reduce sulfur species with valence states intermediate between sulfate (S^{6+}) and sulfide (S^{2-}), at temperatures above about 175°C. The nature of the active sulfur species responsible for the oxidation of organic matter in TSR reactions has been the subject of much speculation. We review the various approaches: e.g. elemental (S_8), $S_2O_3^{2-}$,H_2S, H_2S-SO_4^{2-} mixtures, polysulfides, etc. Our conclusion, based on various parameters, is that polysulfides are the most active species for TSR.

Prior to the present review a four step mechanism for the reduction of S^{6+} to S^{2-}, involving 2-electron reactions for each stage, was stipulated. This was proposed as an alternative, low activation energy pathway to the kinetically – improbable one step reaction. In this review we prefer a multi-step mechanism of the type proposed for the oxidation of polysulfides to sulfate (e.g. Williamson and Rimsted [15]). This mechanism involves sulfur species of redox state intermediate between sulfate and sulfide that can be formed via a network of reactions that initially involve the reaction of hydrogen sulfide with sulfate. Polysulfides ($^-S-S_x-S^-$), thiosulfates ($^-S-SO_3^-$), dithionites ($^-O_2S-SO_2^-$), and dithionates ($^-O_3S-SO_3^-$) are some of the possible species that might exist in this network of reaction intermediates. Polythiosulfates ($^-S-S_x-SO_3^-$), and polythionates ($^-S-S_x-SO_2^-$) can also be formed from intermediates in this reaction network. These various catanated sulfur compounds possess nominal oxidation states intermediate between sulfate and sulfide, hence, redox transformations between these species have low activation energies. Since the energy required to cleave a sulfur-sulfur bond decreases as the number of sulfur atoms in the polysulfide chain increases, the formation of thiyl radicals from polysulfides will occur under milder reaction conditions than that required for the formation of radicals from thiol, sulfide, or disulfide bonds. Thus, the oxidation of hydrocarbons by abstraction of hydrogen by thiyl radicals derived from polysulfides will proceed with lower activation energy than hydrogen abstraction by radicals that must be formed from disulfides or thiols. Likewise, the 'stepwise conversion' of sulfate to polysulfides could provide a TSR-active oxidant capable of reacting with organic compounds under relatively mild conditions that exist in many oil field sediments. The fact that isotope exchange between HS^- and SO_4^{2-} is H dependent, and that at much lower temperatures the formation of polysulfides facilitates the same exchange with much lower activation energy, supports the concept that thermochemical sulfate reduction could start at lower temperatures than 175°C. However, suitable (i.e. reactive) organic substrates must be available for TSR reactions to proceed at meaningful rates at the lower temperatures. Future work on TSR-active sulfur species and on TSR susceptible organic molecules is needed to define in which geochemical conditions TSR will dominate.

* * *

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References

1 Z. Aizenshtat, A. Stoler, Y. Cohen and H. Nielsen, The geochemical sulfur enrichment of recent organic matter by polysulfides in the Solar Lake (Sinai). Advances in Organic Geochemistry, Ed. Byoroy *et al.* J. Wiley & Sons. 1983, pp. 279–289.

2 Z. Aizenshtat, G. Lipiner and Y. Cohen, Biogeochemistry of carbon and sulfur cycles in the microbial mats of the Solar Lake (Sinai), Microbial Mats: Stromatolites, Eds. Cohen, Y., Castenholts, R. W. and Halvorson, H. O.; R. Alan Liss Inc., New York 1984, pp. 281–312.

3 Z. Aizenshtat, Microbial Mats: Chemical post mortem, in: Microbial Mats, Chp. 37, section IV. Biogeochemistry of microbial mats. Eds. Y. Cohen and E. Rosenberg, Byrd Am. Soc., Microbiology Books, Washington D. C., 1989, pp. 303–336.

4 W. L. Orr, Am. Assoc. Petrol. Geol. Bull., 50 (1974) 2295.

5 W. L. Orr, Rate and mechanism of non-microbial sulfate reduction. 95th GSA Annual Meeting Abst. New Orleans, October, paper 213, 1982, p. 580.

6 P. A. Trudinger, L. A. Chambers and J. W. Smith, Can. J. Earth Sci., 22 (1985) 1910.

7 K. Kiyosu, H. R. Krouse and C. A. Viau, (1990) Am. Chem. Soc., (1990) 633.

8 L. A. Anisimov, Conditions of abiogenic reduction of sulfate in oil-an-gas bearing basins. Trans. from geokhimiya No 11, 1692–1702 Geochemistry International, 1978, pp. 15, 63–71.

9 C. J. Kaiser, Chemical and isotopic kinetics of sulfate reduction by organic matter under hydrothermal conditions. Ph. D. Thesis 1988, Pennsylvania State University.

10 J. C. Morris and W. Stumm, Redox equilibria and measurements of potentials in the aquatic environment. In: Equilibrium concepts in natural Water Systems. Advances in Chemistry Series #67. American Chemical Society, Washington D. C. 1967, pp. 270–285.

11 K. Bostrom, Some *pH*-controlling redox reactions in natural waters. ibid 1967, pp. 286–311.

12 W. G. Toland, J. Am. Chem. Soc., 82 (1960) 1911.

13 I. R. Kaplan, R. E. Sweeney and A. Nissenbaum, Sulfur Isotope Studies on Red Sea Geothermal Brines and Sediments. Hot Brines and Geothermal Brines and Sediments. Eds E. T. Degens and D. A. Ross, Springer, New York 1969, pp. 474–498.

14 M. B. Goldhaber and I. R. Kaplan, Marine Chem., 9 (1980) 97.

15 H. G. Machel, Geological Society Special Publication, 36 (1987) 15.

16 M. A. Williamson and J. D. Rimstidt, Thermodynamic and kinetic controls on the aqueous oxidation of sulfide minerals, V. M. Goldschmidt International Conference for the Advancement of Geochemistry, Programs with Abstract 1990, p. 91.

17 V. I. Spitsyn and M. A. Meyerov, Zh. Obshch. Khim., 22 (1952).

18 J. W. Smith and B. D. Batts, Geochim. Cosmochim. Acta, 38 (1974) 121.

19 E. S. Bastin, Am. Assoc. Petrol. Geol. Bull., 10 (1926) 1270.

20 H. O. Hoffman and W. Mostowitch, Trans. A. I. E. M. Vol. XLI (1910) 763.

21 R. L. Ginter, Am. Assoc. Petrol. Geol. Bull., 14 (1930) 139.

22 W. A. Pryor, Oxidation by polysulfides to form aldehydes carboxylic acids or carboxyamides, Mechanisms of Sulfur Reactions, Chap. 7 McGraw-Hill, 1962, pp. 127–138.

23 W. G. Toland, D. L. Hagmann, J. B. Wilkes and F. J. Brutschy, J. Am. Chem. Soc., 80 (1958) 5423.

24 W. A. Pryor, J. Am. Chem. Soc., 80 (1958) 6481.

25 H. V. Tartar and C. Z. Draves, J. Am. Chem. Soc., 46 (1924) 574.

26 W. L. Orr, Geologic and Geochemical Controls on the Distribution of Hydrogen Sulfide in Natural Gas, Advances in Organic Geochemistry (Ed. R. Campos and J. Goni) Enadimsa Madrid, Spain, 1977, pp. 571–579.

27 Y. Kiyosu, Chem. Geol., 30 (1980) 47.

28 Y. Rubinsztain, P. Ioselis, R. Ikan and Z. Aizenshtat, Investigation on Structural Units of Melanoidins in: Advances in Organic Geochemistry (1983) Eds. P. A. Schenk, J. W. de Leeuw and G. W. M. Lumbach, Vol. 6, Org. Geochem., 1984, pp. 791–804.

29 R. T. LaLonde, Am. Chem. Soc., (1990) 68.

30 H. Ohmoto and A. C. Lasaga, Geochim. Cosmochim. Acta, 46 (1982) 1727.

31 T. A. Drean, Reduction of sulfate by Methane, Xylene and Iron at Temperatures of 175 to 350°C. M. Sc. Thesis, Pennsylvania State University, University Park, PA 90p, 1978.

32 P. A. Trudinger, J. Bacteriology, 104 (1970) 158.

33 G. N. Lewis, M. Randall and F. R. V. Bichowsky, J. Am. Chem. Soc., 40 (1918) 356.

34 S. A. Igumnov, Geokhimiya, 4 (1976) 497.

35 W. J. Stahl, Chem. Geol., 20 (1977) 121.

36 W. J. Stahl, Geochem. Cosmochim. Acta, 42 (1978) 1573.

37 E. M. Galimov, The Biological Fractionation of Isotopes, Academic Press, Orlando FL, 1985.

38 M. Schidlowski, Nature, 333 (1988) 313.

39 M. B. Goldhaber and I. R. Kaplan, The sulfur cycle in: The Sea (ed. E. D. Goldberg), Vol. 5 Wiley Chichester, 1974, pp. 569–655.

40 H. Nielsen, Isotopes in Nature (sulfur) in Handbook of Geochemistry (ed. K. H. Wedepohl) Vol. II–I, sec 16-B Springer-Verlag, 1978.

41 D. Dinur, B. Spiro and Z. Aizenshtat, Chem. Geol., 31 (1980) 37.

42 I. R. Kaplan, Stable isotope of sulfur, nitrogen and deuterium in recent marine environments. in: Stable Isotopes in Sedimentary Geology, 1983.

43 W. L. Orr, Org. Geochem., 10 (1986) 499.

44 H. Fossing, S. Thode-Andersen and B. Jørgensen, Marine Chem., 38 (1992) 117.

45 W. A. Pryor, J. Am. Chem. Soc., 82 (1960) 4794.

46 A. Seibert, Z. Phys. Chem. Neue Folge, 97 (1975) 11.

47 H. Sakai, Geochem J., 2 (1968) 29.

48 H. Ohmoto and R. O. Rye, Isotopes of sulfur and carbon. in: Geochemistry of Hydrothermal Ore Deposites (second Edition) (Ed. H. L. Barnes). Wiley & Sons, New York, 1970, CH. 10, pp. 509–567.

49 A. G. Harrison and H. G. Thode, Trans. Faraday Soc., 53 (1957) 1648.

50 V. A. Grimenko, L. N. Grimenko and G. D. Zagryazhskaya, Geokhimya, 4 (1969) 484.

51 Y. Kiyosu and H. R. Krouse, Geochemical J., 24 (1990) 21.

52 W. F. Hunt, Economic Geology, 10 (1915) 543.

53 G. S. Rogers, U.S. Geol. Survey Bull., 653 (1917) 6.

54 M. W. Beijerinck, - 'Über Spirillum desulfuricans als Ursache von Sulfate - reduktion. Central blatt für Bakteriologie, Parasitenkunde, Infektionskrankheiten und Hygiene, Abteilung I Originale 1, 1895, pp. 1–9, 49–59, 104–114.

55 H. D. Peck, Jr., and T. Lissolo, Symposium of the Society for General Microbiology 42nd. (Nitrogen Sulphur Cycles) Cambridge Univ. Press. Assimilatory and dissimilatory sulfate reduction; Enzymology and Bioenergetics in: Biochemistry of Sulfate Reduction, 1988, pp. 99–132.

56 P. B. Barton, Possible role of organic matter in the precipitation of the Mississippi Valley Ores In: Genesis of stratiform lead-zinc-barite-fluorite deposits (Ed. J. S. Brown). The Economic Geology Publishing Co., Lancaster, PA. 1967, pp. 371–378.

57 W. C. Shanks III, J. L. Bischoff and R. J. Rosenbauer, Geochim. Cosmochim., Acta, 45 (1981) 1977.

58 M. J. Mottl, H. D. Holland and R. F. Corr, Geochem. Cosmochim. Acta, 43 (1979) 869.

59 C. S. Spirakis, Mineral. Depos., 26 (1991) 60.

60 J. S. Leventhal, Economic Geology, 85 (1990) 622.

61 R. Sassen, Org. Geochem., 12 (1988) 351.

62 J. W. Wade, J. S. Hanor and R. Sassen, Trans. Gulf Coast Assoc. Geol. XXXIX (1989) 309.

63 E. Heydari and C. H. Moore, Geology, 17 (1989) 1080.
64 H. R. Krouse, C. A. Viau, L. S. Flink, A. Ueda and S. Halas, Nature, 333 (1988) 415.

Zusammenfassung — Die hohe Konzentration von Schwefelwasserstoff, die man in zahlreichen Öl- und Gasfeldern findet, wird der Oxidation von Petrol-Kohlenwasserstoffen durch Sulfat zugeschrieben, einer Reaktion, die den Wert der Vorkommen reduziert. Vorliegender Rückblick, der einem besseren Verständnis der Geochemie von TSR-Reaktionen in Ölfeldsedimenten dienen soll, umfaßt die relevanten Informationen von thermochemischen Sulfatreduktionen (TSR) bis zum Jahre 1991. Es wird ein Überblick über theoretische und praktische Aspekte von TSR-Reaktionen (einschließlich der Untersuchungen von Schwefel- und Kohlenstoffisotope) gegeben und ihre Bedeutung für geochemische Systeme diskutiert. Dieser Überblick stimmt mit vorangehenden Überlegungen dahingehend überein, daß die biochemische Reduktion von Sulfaten in sedimentärer Umgebung unter 120°C dominiert und die Möglichkeit unterstützt, daß reaktionsfreudige Schwefelverbindungen bestimmte organische Moleküle oberhalb 175°C in geochemisch sinnvollen Reaktionszeiten in beträchtlichem Ausmaße oxidieren. Es wurde geschlußfolgert, daß sowohl elementarer Schwefel als auch Polysulfide unter typischen Petrollagerstättenbedingungen in der Lage sind, einige organische Moleküle zu oxidieren, daß aber Sulfat allein nicht reagiert, solange kein Schwefel mit niedrigerer Oxidationsstufe vorhanden ist. Es wird die Möglichkeit einer Wechselwirkung zwischen niedervalentem Schwefel und Sulfat geprüft, die zur Bildung TSR-aktiver Oxidantien führt. In TSR-Systemen ist sowohl die Gegenwart von H_2S als auch von SO_4^{2-} ist für die Bildung aktiver Polysulfid-Reduktionsmittel (z.B. Thiosulfat oder Polythionat) erforderlich. Derartige Zwischenprodukte können über die thermische Generierung von Schwefelradikalen, die in zahlreichen Ölfeldsedimenten als TSR-aktive Oxidantien fungieren können, zu einer Herabsetzung der resultierenden Aktivierungsenergie der Oxidation von Kohlenwasserstoffen durch Sulfat führen. Es wird darauf hingedeutet, daß einige für TSR vorgeschlagene chemische Mechanismen experimentell überprüft und die Ergebnisse im Hinblick auf TSR-Reaktionen in geologischen Systemen neu interpretiert werden sollten.